Preface

This book is the culmination of about ten years of studying sulfuric acid plants. Its objectives are to introduce readers to sulfuric acid manufacture and to show how acid production may be controlled and optimized.

One of the authors (MJK) operated an acid plant while writing this book. His Ph.D. work also centered on analyzing sulfuric acid manufacture. He is now a sulfuric acid and smelter specialist with Hatch.

The other author (WGD) has been interested in sulfuric acid plants since his 1957 student internship at Cominco's lead/zinc smelter in Trail, British Columbia. Cominco was making sulfuric acid from lead and zinc roaster offgases at that time. It was also making ammonium sulfate fertilizer.

In the book, we consider SO₂(g) to be the raw material for sulfuric acid manufacture. Industrially it comes from:

(a) burning elemental sulfur with air
(b) smelting and roasting metal sulfide minerals
(c) decomposing spent acid from organic catalysis.

These sources are detailed in the book, but our main subject is production of sulfuric acid from SO₂(g). Readers interested in smelting and roasting offgases might enjoy our other books Extractive Metallurgy of Copper (2002) and Flash Smelting (2003).

The book begins with a 9 chapter description of sulfuric acid manufacture. These chapters introduce the reader to industrial acidmaking and give reasons for each process step. They also present considerable industrial acid plant operating data. We thank our industrial colleagues profusely for so graciously providing this information.

The book follows with a mathematical analysis of sulfuric acid manufacture. It concentrates on catalytic SO₂(g) + ½O₂(g) → SO₃ oxidation. It also examines temperature control and production of H₂SO₄(ℓ) from SO₃(g).

We have tried to make our analysis completely transparent so that readers can adapt it to their own purposes. We have used this approach quite successfully in our examinations of several metallurgical processes. We hope that we have also succeeded here.
We have used Microsoft Excel for all our calculations. We have found it especially useful for matrix calculations. We also like its Goal Seek, Visual Basic and Chart Wizard features. All the Excel techniques used in this book are detailed in our forthcoming book *Excel for Freshmen*. Please note that, consistent with Excel, we use * for multiply throughout the book.

A note on units – we have used SI-based units throughout. The only controversial choice is the use of K for temperature. We use it because it greatly simplifies thermodynamic calculations. We use bar as our pressure unit for the same reason. Lastly we use Nm$^3$ as our gas volume unit. It is 1 m$^3$ of gas at 273 K and 1 atmosphere (1.01325 bar) pressure. 22.4 Nm$^3$ contain 1 kg-mole of ideal gas.

We were helped enormously by our industrial colleagues during preparation of this book. We thank them all most deeply.

As with all our publications, Margaret Davenport read every word of our typescript. While she may not be an expert on sulfuric acid, she is an expert on logic and the English language. We know that if she gives her approval to a typescript, it is ready for the publisher. We also wish to thank George Davenport for his technical assistance and Vijala Kiruvanayagam of Elsevier Science Ltd. for her unflagging support during our preparation of this and other books.

Lastly, we hope that our book *Sulfuric Acid Manufacture* brings us as much joy and insight as Professor Dr von Igelfeld’s masterpiece *Portuguese Irregular Verbs* has brought him.

William G. Davenport
Tucson, Arizona

Matthew J. King
Perth, Western Australia

# See, for example, *At the Villa of Reduced Circumstances*, Anchor Books, a Division of Random House, Inc., New York (2005), p63.
CHAPTER 1

Overview

Sulfuric acid is a dense clear liquid. It is used for making fertilizers, leaching metallic ores, refining petroleum and for manufacturing a myriad of chemicals and materials. Worldwide, about 180 million tonnes of sulfuric acid are consumed per year (Kitto, 2004).

The raw material for sulfuric acid is SO\textsubscript{2} gas. It is obtained by:

(a) burning elemental sulfur with air
(b) smelting and roasting metal sulfide minerals
(c) decomposing contaminated (spent) sulfuric acid catalyst.

Elemental sulfur is far and away the largest source.

Table 1.1 describes three sulfuric acid plant feed gases. It shows that acid plant SO\textsubscript{2} feed is always mixed with other gases.

Table 1.1. Compositions of acid plant feed gases entering SO\textsubscript{2} oxidation 'converters', 2005. The gases may also contain small amounts of CO\textsubscript{2} or SO\textsubscript{3}. The data are from the industrial tables in Chapters 3 through 9.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Sulfur burning furnace</th>
<th>Sulfide mineral smelters and roasters</th>
<th>Spent acid decomposition furnace</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO\textsubscript{2}</td>
<td>11</td>
<td>10</td>
<td>9</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>10</td>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td>79</td>
<td>79</td>
<td>76</td>
</tr>
</tbody>
</table>

Sulfuric acid is made from these gases by:

(a) catalytically reacting their SO\textsubscript{2} and O\textsubscript{2} to form SO\textsubscript{3}(g)
(b) reacting (a)'s product SO\textsubscript{3}(g) with the H\textsubscript{2}O(\ell) in 98.5 mass% H\textsubscript{2}SO\textsubscript{4}, 1.5 mass% H\textsubscript{2}O sulfuric acid.

Industrially, both processes are carried out rapidly and continuously, Fig. 1.1.
1.1 Catalytic Oxidation of \( \text{SO}_2 \) to \( \text{SO}_3 \)

\( \text{O}_2 \) does not oxidize \( \text{SO}_2 \) to \( \text{SO}_3 \) without a catalyst. All industrial \( \text{SO}_2 \) oxidation is done by sending \( \text{SO}_2 \) bearing gas down through 'beds' of catalyst, Fig. 1.2. The reaction is:

\[
\begin{align*}
\text{SO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) & \rightarrow \text{SO}_3(\text{g}) \\
\text{in dry SO}_2, \text{O}_2, \text{N}_2 \text{ feed gas} & \quad \text{in feed gas} & \quad \text{catalyst} & \quad \text{in SO}_3, \text{SO}_2, \text{O}_2, \text{N}_2 \text{ gas}
\end{align*}
\]

(1.1).

It is strongly exothermic \( (\Delta H^0 \approx -100 \text{ MJ per kg-mole of SO}_3) \). Its heat of reaction provides considerable energy for operating the acid plant.
Fig. 1.2. Catalyst pieces in a catalytic SO₂ oxidation 'converter'. Converters are ~15 m high and 12 m in diameter. They typically contain four, ½-1 m thick catalyst beds. SO₂-bearing gas descends the bed at ~3000 Nm³ per minute. Individual pieces of catalyst are shown in Fig. 8.1. They are ~0.01 m in diameter and length.

1.1.1 Catalyst

At its operating temperature, 700-900 K, SO₂ oxidation catalyst consists of a molten film of V, K, Na, (Cs) pyrosulfate salt on a solid porous SiO₂ substrate. The molten film rapidly absorbs SO₂(g) and O₂(g) – and rapidly produces and desorbs SO₃(g), Chapters 7 and 8.

1.1.2 Feed gas drying

Eqn. (1.1) indicates that catalytic oxidation feed gas is always dry#. This dryness avoids:

(a) accidental formation of H₂SO₄ by reaction of H₂O(g) with the SO₃(g) product of catalytic SO₂ oxidation

(b) condensation of the H₂SO₄ in cool flues and heat exchangers

(c) corrosion.

The H₂O(g) is removed by cooling/condensation (Chapter 4) and by dehydration with H₂SO₄(ℓ), Chapter 6.

# A small amount of sulfuric acid is made by wet catalysis. This is discussed in Section 1.9 and Chapter 25.
1.2 H₂SO₄ Production

Catalytic oxidation's SO₃(g) product is made into H₂SO₄ by contacting catalytic oxidation's exit gas with strong sulfuric acid, Fig. 1.3. The reaction is:

\[ \text{SO}_3(g) + \text{H}_2\text{O}(\ell) \rightarrow \text{H}_2\text{SO}_4(\ell) \]

\[ \begin{array}{c}
\text{in SO}_3, \text{SO}_2, \\
\text{O}_2, \text{N}_2 \text{ gas}
\end{array} \quad \begin{array}{c}
\text{in 98.5\% H}_2\text{SO}_4, \\
1.5\% \text{H}_2\text{O}
\end{array} \quad \begin{array}{c}
\text{in strengthened} \\
\text{sulfuric acid}
\end{array} \quad 350-380 \text{ K} \]

\[ \Delta H^\circ \approx -130 \text{ MJ per kg mole of SO}_3. \]

Reaction (1.2) produces strengthened sulfuric acid because it consumes H₂O(ℓ) and makes H₂SO₄(ℓ).

H₂SO₄(ℓ) is not made by reacting SO₃(g) with water. This is because Reaction (1.2) is so exothermic that the product of the SO₃(g) + H₂O(ℓ) → H₂SO₄ reaction would be hot H₂SO₄ vapor – which is difficult and expensive to condense.

The small amount of H₂O(ℓ) and the massive amount of H₂SO₄(ℓ) in Reaction (1.2)'s input acid avoids this problem. The small amount of H₂O(ℓ) limits the extent of the reaction. The large amount of H₂SO₄(ℓ) warms only 25 K while it absorbs Eqn. (1.2)'s heat of reaction.

Fig. 1.3. Top of H₂SO₄-making ('absorption') tower, courtesy Monsanto Enviro-Chem Systems, Inc. www.enviro-chem.com The tower is packed with ceramic saddles. 98.5 mass\% H₂SO₄, 1.5 mass\% H₂O sulfuric acid is distributed uniformly across this packed bed. Distributor headers and 'downcomer' pipes are shown. The acid flows through slots in the downcomers down across the bed (see buried downcomers below the right distributor). It descends around the saddles while SO₃-rich gas ascends, giving excellent gas-liquid contact. The result is efficient H₂SO₄ production by Reaction (1.2). A tower is ~7 m diameter. Its packed bed is ~4 m deep. About 25 m³ of acid descends per minute while 3000 Nm³ of gas ascends per minute.
1.3 Industrial Flowsheet

Fig. 1.4 is a sulfuric acid manufacture flowsheet. It shows:

(a) the three sources of SO₂ for acid manufacture (metallurgical, sulfur burning and spent acid decomposition gas)

(b) acid manufacture from SO₂ by Reactions (1.1) and (1.2).

(b) is the same for all three sources of SO₂. The next three sections describe (a)'s three SO₂ sources.

1.4 Sulfur Burning

About 70% of sulfuric acid is made from elemental sulfur. All the sulfur is obtained as a byproduct from refining natural gas and petroleum.

The sulfur is made into SO₂ acid plant feed by:

- melting the sulfur
- spraying it into a hot furnace
- burning the droplets with dried air.

The reaction is:

\[ S(\ell) + \frac{3}{2} O_2(g) \xrightarrow{1400 \text{ K \ in \ air}} \ SO_2(g) \]

\[ \text{in SO}_2, \ O_2, \ N_2 \text{ gas} \]

\[ \Delta H^\circ \approx -300 \text{ MJ per kg-mole of } S(\ell). \]

Very little SO₃(g) forms at the 1400 K flame temperature of this reaction, Fig. 7.4. This explains Fig. 1.4's two-step oxidation, i.e.:

(a) burning of sulfur to SO₂

then:

(b) catalytic oxidation of SO₂ to SO₃, 700 K.

The product of sulfur burning is hot, dry SO₂, O₂, N₂ gas. After cooling to ~700 K, it is ready for catalytic SO₂ oxidation and subsequent H₂SO₄-making.

1.5 Metallurgical Offgas

SO₂ in smelting and roasting gas accounts for about 20% of sulfuric acid production. The SO₂ is ready for sulfuric acid manufacture, but the gas is dusty. If left in the gas,
Fig. 1.4. Double contact sulfuric acid manufacture flowsheet. The three main SO₂ sources are at the top. Sulfur burning is by far the biggest source. The acid product leaves from two H₂SO₄ making towers at the bottom. Barren tail gas leaves the final H₂SO₄ making tower, right arrow.
the dust would plug the downstream catalyst layers and block gas flow. It must be removed before the gas goes to catalytic SO₂ oxidation.

It is removed by combinations of:

(a) settling in waste heat boilers
(b) electrostatic precipitation
(c) scrubbing with water (which also removes impurity vapors).

After treatment, the gas contains ~1 milligram of dust per Nm³ of gas. It is ready for drying, catalytic SO₂ oxidation and H₂SO₄ making.

1.6 Spent Acid Regeneration

A major use of sulfuric acid is as catalyst for petroleum refining and polymer manufacture, Chapter 5. The acid becomes contaminated with water, hydrocarbons and other compounds during this use. It is regenerated by:

(a) spraying the acid into a hot (~1300 K) furnace – where the acid decomposes to SO₂, O₂ and H₂O(g)
(b) cleaning and drying the furnace offgas
(c) catalytically oxidizing the offgas's SO₂ to SO₃
(d) making the resulting SO₃(g) into new H₂SO₄(ℓ) by contact with strong sulfuric acid, Fig. 1.4.

About 10% of sulfuric acid is made this way. Virtually all is re-used for petroleum refining and polymer manufacture.

1.7 Sulfuric Acid Product

Most industrial acid plants have three flows of sulfuric acid – one gas-dehydration flow and two H₂SO₄-making flows. These flows are connected through automatic control valves to:

(a) maintain proper flows and H₂SO₄ concentrations in the three acid circuits
(b) draw off newly made acid.

Water is added where necessary to give prescribed acid strengths.

Sulfuric acid is sold in grades of 93 to 99 mass% H₂SO₄ according to market demand. The main product in cold climates is ~94% H₂SO₄ because of its low (238 K) freezing
point (Gable et al., 1950). A small amount of oleum (H₂SO₄ with dissolved SO₃) is also made and sold (BASF, 2005).

Sulfuric acid is mainly shipped in stainless steel trucks, steel rail tank cars (DuPont, 2003) and double-hulled steel barges and ships (Barge, 1998; Bulk, 2003). Great care is taken to avoid spillage.

1.8 Recent Developments

The three main recent developments in sulfuric acidmaking have been:

(a) improved materials of construction, specifically more corrosion resistant materials (Salehi and Hopp, 2001, 2004; Sulphur, 2004)

(b) improved SO₂(g) + ½O₂(g) → SO₃(g) catalyst, specifically V, Cs, K, Na, S, O, SiO₂ catalyst with low activation temperatures (Hansen, 2004)

(c) improved techniques for recovering the heat from Reactions (1.1), (1.2) and (1.3) (Puricelli et al., 1998).

All of these improve H₂SO₄ and energy recovery.

1.9 Alternative Process

An alternative to the conventional acidmaking described here is Wet Sulfuric Acidmaking (Laursen, 2005; Topsoe, 2005; WSA, 2005).

This process:

(a) catalytically oxidizes the SO₂ in H₂O(g), SO₂, O₂, N₂ gas

(b) condenses H₂SO₄(ℓ) directly from the gas.

It is described in Chapter 25.

In 2005, it is mainly used for low flow, low% SO₂ gases. It accounts for 1 or 2% of world H₂SO₄ production. Development of a large, rapid-heat-removal condenser will likely widen its use.

1.10 Summary

About 180 million tonnes of sulfuric acid are produced/consumed per year. The acid is used for making fertilizer, leaching metal ores, refining petroleum and for manufacturing a myriad of products.

Sulfuric acid is made from dry SO₂, O₂, N₂ gas. The gas comes from:
burning molten elemental sulfur with dry air, Chapter 3
smelting and roasting metal sulfide minerals, Chapter 4
decomposing contaminated (spent) sulfuric acid catalyst, Chapter 5.

Sulfur burning is far and away the largest source.

The SO₂ in the gas is made into sulfuric acid by:

(a) catalytically oxidizing it to SO₃(g), Chapters 7 and 8

(b) reacting this SO₃(g) with the H₂O(ℓ) in 98.5 mass% H₂SO₄, 1.5 mass% H₂O sulfuric acid, Chapter 9.

Suggested Reading


References


WSA (2005) WSA applications in refineries www.haldortopsoe.com
CHAPTER 2

Production and Consumption

Sulfuric acid was first produced around the 10th century AD (Al Hassan and Hill, 1986; Islam, 2004). It was made by (i) decomposing natural hydrated sulfate minerals and (ii) condensing the resulting gas. Example reactions are:

\[
\begin{align*}
\text{heat} & \quad \text{CuSO}_4 \cdot 5\text{H}_2\text{O}(s) \rightarrow \text{CuO}(s) + \text{SO}_3(g) + 5\text{H}_2\text{O}(g) \\
\text{condensation} & \quad 5\text{H}_2\text{O}(g) \rightarrow 5\text{H}_2\text{O}(\ell) \\
\text{acidmaking} & \quad \text{SO}_3(g) + 5\text{H}_2\text{O}(\ell) \rightarrow \text{H}_2\text{SO}_4(\ell) + 4\text{H}_2\text{O}(\ell)
\end{align*}
\] (2.1)

The process was carried out in a ceramic retort (inside a furnace) and 'bird-beak' condenser (outside the furnace). Acid composition was adjusted by adding or evaporating water.

The earliest uses for sulfuric and other mineral acids were as solvents for:

- (a) separating gold and silver
- (b) decorative etching of metals, e.g. Damascus Steel

(Killick, 2005).

Thermal decomposition of sulfates was still being used in the 19th century – to make 90+% $\text{H}_2\text{SO}_4$ sulfuric acid. The process entailed (Wikipedia, 2005):

- (a) making $\text{Fe}_2(\text{SO}_4)_3$ by oxidizing pyrite ($\text{FeS}_2$) with air
- (b) thermally decomposing the $\text{Fe}_2(\text{SO}_4)_3$ in a retort to make $\text{SO}_3$ and $\text{Fe}_2\text{O}_3$, i.e:
750 K
\[ \text{Fe}_2(\text{SO}_4)_3(s) \rightarrow \text{Fe}_2\text{O}_3(s) + 3\text{SO}_3(g) \quad (2.4) \]

(c) bubbling the SO₃ through water to make H₂SO₄, i.e:

\[ \text{SO}_3(g) + \text{H}_2\text{O}(\ell) \rightarrow \text{H}_2\text{SO}_4(\ell) \quad (2.5). \]

The process was slow and costly, but it was the only way to make pure 90+% H₂SO₄ sulfuric acid – until catalytic SO₂ oxidation was invented. Pure, high strength acid was needed for making dyes and other chemicals.

Industrial sulfuric acid production began in the 18th century with the burning of sulfur in the presence of natural niter (KNO₃) and steam. This developed into the lead chamber and tower processes – which used nitrogen oxides to form an aqueous SO₂ oxidation catalyst. The overall acidmaking reaction with this catalyst is:

\[
\begin{align*}
\text{in aqueous solution} \\
\text{SO}_2 + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{SO}_4 \\
\text{NOHSO}_4 \text{catalyst}
\end{align*}
\quad (2.6)
\]

(Sander et al., 1984).

The lead chamber and tower processes were used into the 20th century. Unfortunately their H₂SO₄ strength was limited to below about 70 mass% H₂SO₄. Above 70% H₂SO₄, the product acid contained stable nitrosyl hydrogen sulfate which made it unsuitable for many purposes.

The 20th century saw the nitrogen oxide processes gradually but completely replaced by the catalytic SO₂ oxidation/SO₃-sulfuric acid contact process, Chapter 1. This process economically produces sulfuric acid of all H₂SO₄ concentrations. Platinum was the dominant catalyst until the 1930's. V, K, Na, (Cs), S, O, SiO₂ catalyst (Chapters 7 and 8) has dominated since.

World production of sulfuric acid since 1950 is shown in Fig. 2.1. Sources of SO₂ for this production are given in Table 2.1.

<table>
<thead>
<tr>
<th>Source</th>
<th>% of total supply</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elemental sulfur from natural gas purification and petroleum refining, Chapter 3</td>
<td>70</td>
</tr>
<tr>
<td>SO₂ from smelting and roasting non-ferrous minerals, Chapter 4</td>
<td>20</td>
</tr>
<tr>
<td>SO₂ from decomposing spent petroleum/polymer sulfuric acid catalyst, Chapter 5</td>
<td>10</td>
</tr>
</tbody>
</table>
2.1 Uses

Sulfuric acid is mostly used for making phosphate fertilizers, Table 2.2. The most common process is:

(a) production of phosphoric acid by reacting phosphate rock with sulfuric acid, i.e.:

\[
\text{phosphate rock} + 3\text{H}_2\text{SO}_4(\ell) + 6\text{H}_2\text{O}(\ell) \rightarrow 2\text{H}_3\text{PO}_4(\ell) + 3\text{CaSO}_4\cdot 2\text{H}_2\text{O}(s)
\]  

(2.7)

followed by:

(b) reaction of the phosphoric acid with ammonia to make ammonium phosphates, e.g. \(\text{NH}_4\text{H}_2\text{PO}_4\) and \((\text{NH}_4)\text{H}_2\text{PO}_4\).

Sulfuric acid is also used extensively as a solvent for ores and as catalyst for petroleum refining and polymer manufacture.
Fig. 2.2. World production of sulfuric acid, percent by region (Sulphur, 2004). Total 2003 world production was 180 million tonnes contained H₂SO₄.
Table 2.2. World uses of sulfuric acid by percentage, 2003. The data are mainly from Kitto, 2004a.

<table>
<thead>
<tr>
<th>Use</th>
<th>% of total consumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphoric acid production</td>
<td>48</td>
</tr>
<tr>
<td>Single superphosphate fertilizer production</td>
<td>8</td>
</tr>
<tr>
<td>Ammonium sulfate fertilizer production</td>
<td>7</td>
</tr>
<tr>
<td>Petroleum refining catalyst</td>
<td>5</td>
</tr>
<tr>
<td>Copper ore leaching</td>
<td>4</td>
</tr>
<tr>
<td>Titanium dioxide pigment production</td>
<td>3</td>
</tr>
<tr>
<td>Pulp and paper production</td>
<td>2</td>
</tr>
<tr>
<td>Methyl methacrylate catalyst</td>
<td>2</td>
</tr>
<tr>
<td>Nickel concentrate leaching</td>
<td>1</td>
</tr>
<tr>
<td>Other</td>
<td>20</td>
</tr>
</tbody>
</table>

2.2 Acid Plant Locations and Costs

Sulfuric acid plants are located throughout the industrialized world, Fig. 2.2. Most are located near their product acid's point of use, i.e. near phosphate fertilizer plants, nickel ore leach plants and petroleum refineries. This is because elemental sulfur is cheaper to transport than sulfuric acid. Examples of long distance sulfur shipment are from natural gas purification plants in Alberta, Canada to acid plants near phosphate rock based fertilizer plants in Florida and Australia. A new sulfur-burning sulfuric acid plant (4400 tonnes of acid per day) is costing ~75 million U.S. dollars (Sulfuric 2005).

Smelter acid, on the other hand, must be made from byproduct SO$_2$(g) at the smelter and transported to its point of use. An example of this is production of acid at the Cu-Ni smelters in Sudbury, Canada and rail transport of the product acid to fertilizer plants in Florida. A new metallurgical sulfuric acid plant (3760 tonnes of acid per day) is costing ~59 million U.S. dollars (Sulfuric 2005).

Production of pure sulfuric acid from contaminated 'spent' sulfuric acid catalyst is almost always done near the source of the spent acid – to minimize forward and return acid shipping distance.

2.3 Price

Fig. 2.3 plots sulfuric acid price (actual U.S.$) as function of calendar year. The most notable features of the graph are:

(a) the volatility in price year to year
(b) a slightly downward price trend between 1980 and 2001
(c) the rapid increase in price from 2001 to 2003.

The volatility of year to year price is due to (i) small imbalances between acid demand and supply and (ii) the difficulty of storing large quantities of acid. The large increase in price after 2001 is due to China's increasing demand for fertilizer, hence sulfuric acid.
Fig. 2.3. Northwest Europe sulfuric acid price trends, 1980-2003. Actual prices are negotiated between buyer and seller. Data sources:
1980-1982 Sander et al., 1984, p 415
1983-1987 Kitto, 2004b

2.4 Summary

Worldwide, about 180 million tonnes of sulfuric acid are produced per year. 70% comes from burning elemental sulfur. The remainder comes from SO$_2$ in smelter, roaster and spent acid regeneration furnace offgases.

By far the largest use of sulfuric acid is in the production of phosphate fertilizers, e.g. ammonium phosphate. Other large uses are as solvent for copper and nickel minerals and as catalyst for petroleum refining and polymer manufacture.

Sulfuric acid price averaged about 33 ± 20 U.S.$ per tonne between 1980 and 2003. It varies widely year to year due to small imbalances between acid demand and supply.

Suggested Reading


References


Killick, D. (2005) Personal communication, Department of Materials Science and Engineering, University of Arizona.  www.arizona.edu


Kitto, M (2004b) Personal communication.  www.britishsulphur.com


Fig. 3.0. View of spinning cup sulfur burner from inside sulfur burning furnace – burning capacity 870 tonnes of molten sulfur per day. The thermocouple at top and central blue sulfur-rich flame are notable. Photograph courtesy of Outokumpu OYJ. www.outokumpu.com
CHAPTER 3

Sulfur Burning

70% of sulfuric acid is made from elemental sulfur. The elemental sulfur is:

(a) received molten or melted with pressurized steam (sulfur melting point ~390 K)
(b) atomized in a hot (1400 K) furnace
(c) burnt in the furnace with excess dry air to form hot SO₂, O₂, N₂ gas.

Sulfuric acid is then made from step (c)'s gas by:

(d) cooling the gas in a boiler and steam superheater
(e) catalytically reacting its SO₂(g) and O₂(g) to form SO₃(g)
(f) contacting step (e)'s product gas with strong sulfuric acid to make H₂SO₄ by the reaction SO₃(g) + H₂O(ℓ)_{in acid} → H₂SO₄(ℓ)_{in strengthened acid}.

Steps (b) to (f) are continuous.

This chapter describes steps (a) to (d), Fig. 3.1. Steps (e) and (f) are described in Chapters 7, 8 and 9.

3.1 Objectives

The objectives of this chapter are to describe:

(a) the physical and chemical properties of elemental sulfur
(b) transportation of elemental sulfur to the sulfur burning plant
(c) preparation of elemental sulfur for combustion
(d) sulfur burners and sulfur burning furnaces
(e) control of sulfur burning offgas composition, temperature and volume.
molten sulfur (410 K) delivered molten or delivered solid and steam-melted on site

sulfur burning furnace

1400 K

boiler & steam superheater

11 volume% SO₂, 10 volume% O₂, 79 volume% N₂ gas (700 K) to catalytic SO₂ oxidation and H₂SO₄ making

Fig. 3.1. Sulfur burning flowsheet – molten sulfur to clean dry 700 K SO₂, O₂, N₂ gas. The furnace is supplied with excess air to provide the O₂ needed for subsequent catalytic oxidation of SO₂ to SO₃. Table 3.1 gives industrial sulfur burning data.

3.2 Sulfur

The elemental sulfur used for making sulfuric acid is virtually all a byproduct of natural gas and petroleum refining. It contains 99.9+% S. Its main impurity is carbon from natural gas or petroleum.

Its melting point is 388 – 393 K, depending on its crystal structure. It is easily melted with pressurized steam pipes.

3.2.1 Viscosity

The viscosity of molten sulfur is described in Fig. 3.2. Its key features are a viscosity minimum at 430 K and a ten thousand-fold viscosity increase just above 430 K.

Sulfur burners are fed with ~410 K molten sulfur, near the viscosity minimum but safely below the steep viscosity increase. Sulfur temperature is maintained by circulating 420 K steam through sulfur storage tank steam pipes just ahead of sulfur burning. Below ground or insulated above ground storage tanks are used.

Sulfur's huge increase in viscosity just above 430 K is due to a transition from S₈ ring molecules to long interwoven S chain molecules (Dunlavy, 1998).

3.3 Molten Sulfur Delivery

Elemental sulfur is produced molten. It is also burnt molten.
Fig. 3.2. Molten sulfur viscosity as a function of temperature (Tuller, 1954). The viscosity minimum at 430 K and the enormous viscosity increase just above 430 K are notable.

Where possible, therefore, sulfur is transported molten from sulfur making to sulfur burning. It is mainly shipped in double walled, steam heatable barges and railway tank cars. This gives easy handling at both ends of the journey. Even if the sulfur solidifies during the journey, it is easily melted out with 420 K steam to give a clean, atomizable raw material. Short distance deliveries are sometimes made in single walled tanker trucks.

Sulfur that is shipped this way is ready for burning. Sulfur that is shipped as solidified pellets or flakes picks up dirt during shipping and storage. This sulfur is melted and filtered before being burnt (Sander et al., 1984, p 174, Sparkler, 2004).

Sulfur is shipped solid when there are several intermediate unloading-loading steps during its journey, e.g. train-ship-train. An example of this is shipment of solid sulfur from interior Canada to interior Australia.

3.3.1 Sulfur pumps and pipes

Molten sulfur has a viscosity (~0.01 kg m$^{-1}$ s$^{-1}$, 400-420 K, Fig. 3.2) about ten times that of water (~0.001 kg m$^{-1}$ s$^{-1}$, 293 K). Its density is ~1.8 kg/m$^3$. It is easily moved in steam jacketed steel pipes (Jondle and Hornbaker, 2004). Steam heated pumps much like that in Fig. 9.2 are used. Molten sulfur is an excellent lubricant at 410 K. Sulfur pump impellers need no additional lubrication.
3.4 Sulfur Atomizers and Sulfur Burning Furnaces

Sulfur burning consists of:

(a) atomizing molten sulfur and spraying the droplets into a hot furnace, Fig. 3.3
(b) blowing clean, dry 390 K air into the furnace.

The tiny droplets and warm air give:

(c) rapid vaporization of sulfur in the hot furnace
(d) rapid and complete oxidation of the sulfur vapor by O₂ in the air.

Representative reactions are:

\[
S(\ell) \rightarrow S(g) \quad \text{(3.1)}
\]

S(g) + O₂(g) → SO₂(g) + heat \quad \text{in air in SO₂, O₂, N₂ gas} \quad \text{(3.2)}.

The combined heat of reaction for Reactions (3.1) and (3.2) is ~300 MJ per kg-mole of S(\ell).

**Fig. 3.3.** Burner end of sulfur burning furnace. Atomized molten sulfur droplets are injected into the furnace through steam-cooled lances. Dry combustion air is blown in through the circular openings behind. The sulfur is oxidized to SO₂ by Reactions (3.1) and (3.2). Atomization is done by spiral or right angle flow just inside the burner tip.
3.4.1 Sulfur atomizers

Molten sulfur spraying is done with:

(a) a stationary spray nozzle at the end of a horizontal lance, Fig. 3.3

(b) a spinning cup sulfur atomizer, Fig. 3.0 (Outokumpu, 2005)

In both cases, molten sulfur is pumped into the atomizers by steam jacketed pumps.

The stationary spray nozzle has the advantage of simplicity and no moving parts. The spinning cup atomizer has the advantage of lower input pressure, smaller droplets, more flexible downturn and a shorter furnace.

Fig. 3.4. Entrance to fire tube boiler tubes after Fig. 3.3’s sulfur burning furnace. 1400 K gas (~11 volume% SO2, 10 volume% O2, 79 volume% N2) leaves the furnace and enters the boiler. It turns 90° in the boiler and flows into the tubes. The tubes are surrounded by water. Heat is transferred from the hot gas to the water – cooling the gas and making (useful) steam. The tubes are typically 0.05 m diameter. Table 3.1 gives industrial furnace data. Sulfur furnace boilers are discussed by Roensch (2005).

3.4.2 Dried air supply

Air for sulfur burning is filtered through fabric and dried. It is then blown into the sulfur burning furnace. It is blown in behind the sulfur spray to maximize droplet-air contact.

The drying is done by contacting the air with strong sulfuric acid, Chapter 6. This removes H2O(g) down to ~0.05 grams per Nm³ of air. Drying to this level prevents accidental H2SO4(ℓ) formation and corrosion after catalytic SO3(g) production.
## Table 3.1. Details of S1

<table>
<thead>
<tr>
<th>Plant Details</th>
<th>S1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Startup date</td>
<td></td>
</tr>
<tr>
<td>Acid production, tonnes $\text{H}_2\text{SO}_4$/day</td>
<td>4400</td>
</tr>
</tbody>
</table>

### Sulfur
- Source: imported pastel
- Impurities, parts per million by mass:
  - Carbon
  - Inorganic oxides
  - Other
- Sulfur filtration method: three 35 leaf pressure leach filters, 2 online

### Sulfur burning furnace data
- Number of furnaces: 1
- Shell length x diameter, m: $18.36 \times 6.0$
- Refractory types:
  - 0.23 m HB fire brick &
  - 0.115 m insulting brick
- Sulfur burners:
  - Spinning cup or spray guns: spray guns
  - Number of burners per furnace: 7
  - Sulfur burning rate, tonnes/hour: 60.1
- Temperatures, K:
  - Dry air into furnace: 416
  - Molten sulfur into furnace: 405
  - Gas out of furnace: 1445

### Boiler
- Type: fire tube
- Number: 2
- Length x diameter, m: $7.85 \times 3.505$ (each)
- Number of tubes: 1550 each
- Tube diameter, m: 0.046 ID
- Tube material: SA-178-A
- Number of superheaters: 2
- Number of economizers: 3
- Gas temperatures, K:
  - Into boiler: 1444
  - Out of economizer: 696
- Steam production, tonnes of steam per tonne of sulfur:
  - Pressure, bar: 63.8
  - Temperature, K: 554 (753 after superheaters)

### Product gas
- Flowrate, thousand Nm$^3$/hour: 356
- Composition, volume%:
  - $\text{SO}_3$: 0.184
  - $\text{SO}_2$: 11.6
  - $\text{O}_2$: 9.06
  - $\text{N}_2$: 79.1
sulfur burning furnace operations.

<table>
<thead>
<tr>
<th></th>
<th>M1</th>
<th>S2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1974</td>
<td>1965</td>
</tr>
<tr>
<td></td>
<td>270</td>
<td>1800</td>
</tr>
<tr>
<td>including from molybdenum</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sulfide roaster gas</td>
<td>liquid</td>
<td>&lt;1000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&lt;200</td>
</tr>
<tr>
<td>none</td>
<td>none</td>
<td></td>
</tr>
</tbody>
</table>

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>10.4 x 3.2</td>
</tr>
<tr>
<td></td>
<td>&lt;1000</td>
</tr>
<tr>
<td></td>
<td>&lt;200</td>
</tr>
</tbody>
</table>

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>18.3 x 5.5 inside shell</td>
</tr>
<tr>
<td></td>
<td>0.23 m hard (high T) brick</td>
</tr>
<tr>
<td></td>
<td>0.11 m insulating brick</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>spray gun</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2.0 max</td>
</tr>
<tr>
<td></td>
<td>714</td>
</tr>
<tr>
<td></td>
<td>408</td>
</tr>
<tr>
<td></td>
<td>870-1260</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>spray guns</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>24.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>fire tube</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>6.4 x 2.2</td>
</tr>
<tr>
<td></td>
<td>600</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>carbon steel</td>
</tr>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>870-1280</td>
</tr>
<tr>
<td></td>
<td>810-950</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>fire tube</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>5 x 3.5; 2.9 x 2.7</td>
</tr>
<tr>
<td></td>
<td>1860; 1210</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>carbon steel</td>
</tr>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1362</td>
</tr>
<tr>
<td></td>
<td>700</td>
</tr>
<tr>
<td></td>
<td>1.64</td>
</tr>
</tbody>
</table>

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>517</td>
</tr>
</tbody>
</table>

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>210</td>
</tr>
</tbody>
</table>

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.7-5.6</td>
</tr>
<tr>
<td></td>
<td>8.38</td>
</tr>
<tr>
<td></td>
<td>13.6</td>
</tr>
<tr>
<td></td>
<td>12.6</td>
</tr>
<tr>
<td></td>
<td>79.02</td>
</tr>
</tbody>
</table>
3.4.3 Main blower

The dried air is blown into the sulfur burning furnace by the acid plant's main blower.

The blower is a steam or electricity driven centrifugal blower (Jacoby, 2004). It blows air into the sulfur burning furnace and the furnace's offgas through the remainder of the acid plant. 0.3 to 0.5 bar pressure is required.

A 2000 tonnes of H_2SO_4 per day sulfur burning acid plant typically requires a 4000 to 4500 kW main blower.

3.4.4 Furnace

Sulfur burning furnaces are 2 cm thick cylindrical steel shells lined internally with 30 to 40 cm of insulating refractory, Fig. 3.3. Air and atomized molten sulfur enter at one end. Hot SO_2, O_2, N_2 gas departs the other into a boiler and steam superheater (Fig. 3.4). Some furnaces are provided with internal baffles. The baffles create a tortuous path for the sulfur and air, promoting complete sulfur combustion. Complete sulfur combustion is essential to prevent elemental sulfur condensation in downstream equipment.

3.5 Product Gas

Sulfur burning is operated to produce 1400 K gas containing:

- ~11 volume% SO_2
- ~10 volume% O_2
- 79 volume% N_2

This product has enough SO_2 and a high enough O_2/SO_2 ratio for subsequent catalytic SO_2 + 1/2O_2 → SO_3 oxidation. It is also cool enough for its heat to be recovered as steam in a simple fire-tube boiler (Thermal Ceramics, 2005) and steam superheater.

The gas contains only 0.1 or 0.2 volume% SO_3 despite its high O_2 content. This is because the equilibrium constant for SO_2 + 1/2O_2 → SO_3 oxidation is small (0.06) at 1400 K, Fig. 7.3.

3.5.1 Gas destination

Product gas departs the sulfur burning furnace/boiler/superheater into:

(a) a catalytic SO_2 oxidation 'converter'

then to:

(b) SO_3(g) +H_2O(l)_{in sulfuric acid} → H_2SO_4(l)_{in strengthened acid acidmaking}. 
The boiler and superheater cool the gas to ~700 K, the usual temperature for catalytic 
SO₂ oxidation. They also produce steam for the acid plant main blower and for making 
electricity.

3.5.2 Composition and temperature control

The composition and temperature of sulfur burning's product gas are controlled by 
adjusting the sulfur burning furnace's:

\[
\frac{\text{input air}}{\text{input sulfur}}
\]

ratio, Figs. 3.5 and 3.6.

As the figures show, raising a furnace's air/sulfur ratio:

(a) increases product gas O₂ concentration, Fig. 3.5
(b) decreases product gas SO₂ concentration, Fig. 3.5
(c) decreases product gas temperature, Fig. 3.6.

These relationships allow simple automatic control of product gas composition and 
temperature. Note, however, that composition and temperature are not independent 
variables.

Replacement of some of the sulfur burner's input air with oxygen can be used to give 
independent temperature control (Miller and Parekh, 2004). Raising the oxygen/air 
ratio increases offgas temperature because less N₂ has to be heated by the S(ℓ) + O₂ → 
SO₂ reaction. Lowering the oxygen/air ratio has the opposite effect.

3.5.3 Target gas composition

The Section 3.5 gas (11 volume% SO₂, 10 volume% O₂, 79 volume% N₂) is chosen to 
give efficient downstream catalytic SO₂ + ½O₂ → SO₃ oxidation. A requirement for 
this is a volume% O₂/volume% SO₂ ratio around one.

In recent years there has been a tendency to increase volume% SO₂ in sulfur burning 
gas by lowering the input air/sulfur ratio, Fig. 3.5. An increase in SO₂ concentration 
lowers the volume of gas that must be blown through the acid plant per tonne of product 
H₂SO₄. It thereby lowers:

(a) blowing energy cost
(b) equipment size requirements, hence capital cost.
Fig. 3.5. Volume% SO₂ and O₂ in gas produced by burning S with excess dry air (calculated by means of S, O and N molar balances). N₂ concentration is 79 volume% at all ratios, not shown. This is because consumption of one kg-mole of O₂ produces one kg-mole of SO₂. (# For example, 7 kg of input air for every 1 kg of input sulfur.)

Unfortunately, decreasing the input air/input sulfur ratio also decreases the O₂/SO₂ ratio of the gas (Fig. 3.5), potentially lowering catalytic oxidation efficiency.

An alternative way to increase SO₂ concentration (and decrease furnace exit gas volume) is to feed less N₂ to the sulfur burning furnace – by replacing some air with oxygen (Miller and Parekh, 2004).

3.5.4 Target gas temperature

Decreasing sulfur burning's air/sulfur ratio raises product gas temperature, Fig. 3.6. If carried too far (i.e. to raise % SO₂-in-gas), this may damage the sulfur burning furnace or boiler.

11-12 volume% SO₂, 1400 K sulfur burning gas seems optimum.

3.6 Summary

70% of the world's sulfuric acid is made from elemental sulfur. Virtually all of this sulfur is the byproduct of natural gas and petroleum refining.

Elemental sulfur melts at ~390 K. It is easily melted with pressurized steam pipes and pumped molten around the sulfur burning plant.
Sulfur burning is the first step in making sulfuric acid from elemental sulfur. It entails:

(a) atomizing molten sulfur in a hot furnace and burning it with excess dried air

(b) cooling the product gas in a boiler and steam superheater.

The product is ~11 volume% SO₂, 10 volume% O₂, 79 volume% N₂ gas (700 K), perfect for subsequent catalytic SO₂ + ½O₂ → SO₃(g) oxidation and H₂SO₄ manufacture.

Sulfur burning's product gas composition and temperature are readily controlled by adjusting the sulfur furnace's input air/input sulfur ratio. Replacement of some of the input air with oxygen gives the process independent O₂/SO₂, temperature and volume control.

References


CHAPTER 4

Metallurgical Offgas Cooling and Cleaning

About 20% of the world's sulfuric acid is made from SO₂ in smelter and roaster offgases. The gases contain 10 to 75 volume% SO₂, Table 4.1. They are hot and dusty. They may also contain impurity vapors, e.g. chlorine and gaseous arsenic compounds.

The SO₂ is suitable for sulfuric acid manufacture, but the gases must be:

(a) cooled

(b) cleaned

(c) diluted with weak SO₂ process gas and/or air

and:

(d) dried

before they go to acidmaking, Fig. 4.1.

This chapter describes gas cooling, cleaning, dilution and H₂O(g) condensation. Final dehydration by contact with strong sulfuric acid is described in Chapter 6.

4.1 Initial and Final SO₂ Concentrations

Continuous smelting and converting gases contain 20-75 volume% SO₂ as they leave the furnace. This is too strong for downstream catalytic SO₂ + ½O₂ → SO₃ oxidation. The heat of oxidation with this strong gas would overheat the catalyst, Chapters 7 and 8.

For this reason, continuous smelting/converting gas is always diluted with weak process gas (e.g. anode furnace gas) and/or air before it is sent to catalytic SO₂ oxidation.

Table 4.1 shows continuous smelting and converting offgas SO₂ strengths. Tables 7.1 and 7.2 show pre-catalytic oxidation SO₂ strengths.
metallurgical offgas
10-75 volume\% SO₂
10 to 200 g dust per Nm³

1500 K

steam

waste heat boiler
dust dust

dry electrostatic precipitator
600 K

clean, cool gas, 310 K, 8-13 volume\% SO₂, 0.001 g dust per Nm³ of gas - to gas dehydration, catalytic SO₂ + 1/2O₂ → SO₃ oxidation and H₂SO₄ making

low-SO₂ gas,
e.g. anode furnace offgas

wet electrostatic precipitator

310 K

sludge

cool water

packed bed direct contact condensation

340 K

dust

H₂O

H₂O

scrubber

water plus condensate

water + dust + condensed vapors

Fig. 4.1. Flowsheet for cooling, diluting and cleaning metallurgical offgas. Gas temperature is lowered from 1500 to 310 K. SO₂ concentration is lowered from 10-75 volume\% SO₂ to 8-13 volume\% SO₂. Dust plus vapor concentration is lowered from 10-200 g per Nm³ of gas to 0.001 g per Nm³ of gas. Efficient gas cleaning minimizes plugging of downstream catalyst and equipment. It also minimizes poisoning of the catalyst. It is the key to efficient, continuous long term metallurgical acid plant operation. Mercury-from-gas removal is described in Section 4.5.3.
Table 4.1. Offgas temperatures and SO$_2$ and dust concentrations leaving metallurgical furnaces (Davenport et al., 2002). The high SO$_2$ concentrations are due to the use of oxygen enriched air for smelting and continuous converting. The furnace offgases are diluted with weak SO$_2$ process gases and air to obtain the <13 volume% SO$_2$ gas required by catalytic SO$_2$ oxidation. SO$_2$ gases are also made by gold, lead, molybdenum and pyrite roasting (not shown).

<table>
<thead>
<tr>
<th>Metallurgical Process</th>
<th>Offgas temperature, K</th>
<th>SO$_2$ in offgas, volume%</th>
<th>Dust in offgas g per Nm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inco flash smelting</td>
<td>1540-1570</td>
<td>50-75</td>
<td>200-250</td>
</tr>
<tr>
<td>Outokumpu flash smelting</td>
<td>1540-1620</td>
<td>30-45</td>
<td>100-250</td>
</tr>
<tr>
<td>Outokumpu flash converting</td>
<td>1560</td>
<td>35-40</td>
<td>200</td>
</tr>
<tr>
<td>Outokumpu flash direct-to-copper smelting</td>
<td>1590-1670</td>
<td>15-45</td>
<td>200</td>
</tr>
<tr>
<td>Mitsubishi smelting</td>
<td>1510-1520</td>
<td>30-35</td>
<td>70</td>
</tr>
<tr>
<td>Mitsubishi converting</td>
<td>1500-1520</td>
<td>25-30</td>
<td>100</td>
</tr>
<tr>
<td>Submerged-tuyere smelting (Noranda &amp; Teniente)</td>
<td>1470-1510</td>
<td>20-25</td>
<td>15-20</td>
</tr>
<tr>
<td>Top-lance smelting (Isasmelt &amp; Ausmelt)</td>
<td>1490-1520</td>
<td>20-25</td>
<td>10</td>
</tr>
<tr>
<td>Batch converting (Peirce-Smith &amp; Hoboken)</td>
<td>1470</td>
<td>8-15</td>
<td>3-5</td>
</tr>
<tr>
<td>ZnS roasting (fluid bed)</td>
<td>623-673*</td>
<td>10*</td>
<td>2*</td>
</tr>
</tbody>
</table>

* After cooling in a waste heat boiler and removing product particulate in a cyclone.

4.2 Initial and Final Dust Concentrations

Metallurgical offgas contains:

10 to 250 grams of dust per Nm$^3$ of gas

as it leaves the furnace, Table 4.1. If not removed, this dust would quickly plug downstream SO$_2$ oxidation catalyst. The dust is removed by:

(a) gas cooling and dust settling in a waste heat boiler (occasionally by quenching with water)

(b) dry electrostatic dust precipitation

(c) scrubbing and cooling with water

(d) wet electrostatic 'mist' precipitation.

These steps lower dust-in-gas levels to

$\sim$0.001 grams of dust per Nm$^3$ of gas.

Downstream catalyst beds can be operated continuously for several years with dust at this level.

The next five sections discuss these cooling and dust removal steps.
4.3 Offgas Cooling and Heat Recovery

The first step in treating metallurgical offgas is cooling in preparation for electrostatic dust precipitation. Electrostatic precipitators operate at about 600 K. Above this temperature, their steel structure weakens. Below this temperature, sulfuric acid forms from small amounts of \( \text{SO}_3 \) and \( \text{H}_2\text{O(g)} \) in the furnace offgas – causing corrosion of the precipitator.

Gas cooling is mostly done in waste heat boilers, Fig. 4.2. These boilers cool the gas and recover its heat in useful form – steam (Abeck, 2003; Peippo et al, 1999).

![Fig. 4.2. Waste heat boiler for a copper smelting flash furnace (Peippo et al, 1999). Note, left to right: (i) flash furnace gas offtake; (ii) boiler radiation section with water tubes in walls; (iii) suspended water tube baffles in radiation section to evenly distribute gas flow; (iv) convection section with hanging water tubes. Steam from the boiler is used to generate electricity, to power the acid plant’s main blower and for general heating and drying.](image)

Most offgas dust falls out in the waste heat boiler. It is collected and recycled to smelting. It falls out due to low gas velocities in the large boiler chambers.

An alternative method of cooling metallurgical offgas is to pass it through sprays of water. Spray cooling avoids investment in waste heat recovery equipment but wastes the heat of the gas. It also generates acidic waste liquid that must be neutralized and treated for solids removal/recycle.
4.4 Electrostatic Collection of Dust

Boiler exit gas is passed through electrostatic precipitators for further dust removal, Figs. 4.3 and 4.4.

The dust particles are caught by:

(a) passing the dusty gas between plate ‘dust collection’ electrodes and around rod ‘corona’ electrodes, Fig. 4.3

(b) applying a large electrical potential (~60 000 V) between the plates and rods.

This arrangement causes:

(a) formation of an ‘avalanche’ of electrons in a corona around the negative rod electrodes (Oglesby and Nichols, 1978)

(b) movement of these electrons towards the positive dust collection plates

Fig. 4.3. Schematic of dry ‘rod and plate’ electrostatic precipitator (after Oglesby and Nichols, 1978). The rods have sharp horizontal protrusions (nails) which promote corona formation. Dusty gas flows between the plates and around the rods. A large electrical potential (60 000 V) is applied between the rods and plates. This negatively charges the dust particles – causing them to approach and adhere to the positive collection plates. The dust is gathered by periodically rapping the plates, causing sheets of dust to fall into dust bins below, Fig. 4.4. Table 4.2 gives industrial precipitation data.
<table>
<thead>
<tr>
<th>Operation</th>
<th>M2</th>
<th>M3</th>
</tr>
</thead>
<tbody>
<tr>
<td>startup date</td>
<td>1998</td>
<td>2003</td>
</tr>
<tr>
<td>acid plant builder</td>
<td>Korea Zinc Engineering</td>
<td>Outokumpu-Lurgi</td>
</tr>
<tr>
<td>acid production,</td>
<td>1150 (2 roasters, 2 gas cleaning plants, 1 acid plant)</td>
<td>2200 (nominal)</td>
</tr>
<tr>
<td>tonnes H₂SO₄ per day</td>
<td>zinc sulfide roaster</td>
<td>Noranda smelting furnace, air dilution and water quenching</td>
</tr>
<tr>
<td>gas source</td>
<td></td>
<td></td>
</tr>
<tr>
<td>total gas through precipitators thousand Nm³ per hour</td>
<td>102</td>
<td>163</td>
</tr>
<tr>
<td>number of precipitators</td>
<td>two 3 field precipitators</td>
<td>2 identical</td>
</tr>
<tr>
<td>series or parallel</td>
<td>parallel</td>
<td>parallel</td>
</tr>
<tr>
<td>Gas composition before precipitation, volume%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₃</td>
<td>0.1</td>
<td>0</td>
</tr>
<tr>
<td>SO₂</td>
<td>10.0</td>
<td>11.5</td>
</tr>
<tr>
<td>O₂</td>
<td>5.0</td>
<td>13.4</td>
</tr>
<tr>
<td>H₂O</td>
<td>10.4</td>
<td>12.6</td>
</tr>
<tr>
<td>CO₂</td>
<td></td>
<td>2.1</td>
</tr>
<tr>
<td>N₂</td>
<td>remainder</td>
<td>remainder</td>
</tr>
<tr>
<td>Precipitator details</td>
<td></td>
<td></td>
</tr>
<tr>
<td>height x length x width, m</td>
<td>7.5 x 10.45 x 4.8</td>
<td>19.2 x 20.1 x 8.5</td>
</tr>
<tr>
<td>collection plates</td>
<td>11</td>
<td>57</td>
</tr>
<tr>
<td>collection plate area, m²</td>
<td></td>
<td>1134</td>
</tr>
<tr>
<td>'corona' electrode type</td>
<td>Variody 15 • 2 mm</td>
<td>stiff rods</td>
</tr>
<tr>
<td>number</td>
<td>792</td>
<td>756</td>
</tr>
<tr>
<td>rod to plate voltage, V</td>
<td>65 000</td>
<td>110 000</td>
</tr>
<tr>
<td>rod to plate current, A</td>
<td>0.8</td>
<td>0.5</td>
</tr>
<tr>
<td>gas temperature, K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>before precipitation</td>
<td>623-673</td>
<td>653-673</td>
</tr>
<tr>
<td>after precipitation</td>
<td>593-643</td>
<td>643-653</td>
</tr>
<tr>
<td>Gas composition after precipitation, volume%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₃</td>
<td>0.1</td>
<td>11</td>
</tr>
<tr>
<td>SO₂</td>
<td>9.5</td>
<td>14</td>
</tr>
<tr>
<td>O₂</td>
<td>5.5</td>
<td>12</td>
</tr>
<tr>
<td>H₂O</td>
<td>10.0</td>
<td>2</td>
</tr>
<tr>
<td>CO₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>remainder</td>
<td>remainder</td>
</tr>
<tr>
<td>Dust-in-gas loading, g/Nm³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>before precipitation</td>
<td>2.0</td>
<td>12</td>
</tr>
<tr>
<td>after precipitation</td>
<td>0.2</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>Asarco Hayden</td>
<td>Phelps Dodge Miami</td>
</tr>
<tr>
<td>----------------------</td>
<td>---------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>M4</td>
<td>1999</td>
<td>1972 to 1998</td>
</tr>
<tr>
<td>Mitsubishi-Lurgi</td>
<td>1983</td>
<td>Lurgi Fleck</td>
</tr>
<tr>
<td>2100-2400</td>
<td>1630</td>
<td>2400</td>
</tr>
<tr>
<td>Mitsubishi continuous</td>
<td></td>
<td></td>
</tr>
<tr>
<td>copper smelter</td>
<td></td>
<td></td>
</tr>
<tr>
<td>148</td>
<td>197</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>INCO flash furnace</td>
<td></td>
<td>Isasmelt furnace</td>
</tr>
<tr>
<td>and</td>
<td></td>
<td>Hoboken</td>
</tr>
<tr>
<td>Peirce-Smith</td>
<td></td>
<td>converters</td>
</tr>
<tr>
<td>converter gas</td>
<td></td>
<td>electric furnace</td>
</tr>
<tr>
<td>8</td>
<td>230</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 identical</td>
<td>2 parallel</td>
<td>1 (3 fields)</td>
</tr>
<tr>
<td>parallel</td>
<td>sets of 4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.48</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>15.2</td>
<td>9.0</td>
<td>14.1</td>
</tr>
<tr>
<td>10.6</td>
<td>11.4</td>
<td>2</td>
</tr>
<tr>
<td>45 g per dry Nm³</td>
<td>8.4</td>
<td>28.9</td>
</tr>
<tr>
<td>3.59</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>remainder</td>
<td>remainder</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>each precipitator</td>
<td>each precipitator</td>
<td>19 × 9.1 × 9.1</td>
</tr>
<tr>
<td>15.9 × 18.7 × 7.4</td>
<td>6.6 × 5.2 × 4.4</td>
<td>558</td>
</tr>
<tr>
<td>57</td>
<td>2426</td>
<td>7294</td>
</tr>
<tr>
<td>stiff rods</td>
<td>rods</td>
<td>steel ribbons</td>
</tr>
<tr>
<td>1134</td>
<td>1408</td>
<td>6480</td>
</tr>
<tr>
<td></td>
<td>623</td>
<td>616</td>
</tr>
<tr>
<td></td>
<td>613</td>
<td>610</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.48</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>15.2</td>
<td>9.0</td>
<td>14.1</td>
</tr>
<tr>
<td>10.6</td>
<td>11.4</td>
<td>2</td>
</tr>
<tr>
<td>45 g per dry Nm³</td>
<td>5.9</td>
<td>28.9</td>
</tr>
<tr>
<td>3.59</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>remainder</td>
<td>remainder</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>4.8 g per wet Nm³</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>0.2 g per wet Nm³</td>
<td></td>
</tr>
</tbody>
</table>
(c) negative charging (ionization) of gas molecules outside the corona by collision and combination of electrons with gas molecules
(d) negative charging of dust by collision and attachment of gas ions to dust particles
(e) electrical attraction of negatively charged dust to the positive collection plates
(f) adhesion of the dust to the collection plates by electrical, mechanical and molecular forces.

About 70% of the dust-in-offgas is removed in the waste heat boiler and about 30% in electrostatic precipitators. The small remainder (~1%) is removed by water scrubbing, next section.

Fig. 4.4. Wire and plate dry electrostatic precipitator, reprinted from Oglesby and Nichols (1978), p 269 by courtesy of Taylor and Francis Group, LLC. The parallel collector plates and bottom dust bins are notable. In this case, wires are hung between the plates – weights for keeping them vertical are just visible. Structural and operating data for a recent precipitator are:

- length × width × height, m: 8 × 7 × 6
- total dust collection plate area, m²: 2200
- gas velocity between plates, m per second: 0.5
- gas residence time in precipitator, s: 15
- 'corona' electrodes: wires and stiff rods
- applied rod to plate voltage, V: 60 000
- rod to plate current, A: 0.4
4.5 Water Scrubbing (Table 4.3)

Gas leaves electrostatic precipitators at ~600 K. It still contains 0.1 to 1 g of dust and unwanted vapors per Nm$^3$ of gas. These are now removed by intimately contacting the gas with water sprays. This contact:

(a) lowers the gas's dust content to ~0.001 g per Nm$^3$ of gas

(b) condenses and absorbs unwanted vapors, e.g. Cl$_2$ and gaseous metal compounds.

The result is clean, vapor free gas.

Venturi, radial flow, packed bed and Dynawave®, Fig. 4.5 (Enviro-chem, 2005) scrubbers are used.

![Diagram of Dynawave® scrubber](image)

**Fig. 4.5.** Dynawave® scrubber for removing particulate and soluble impurities from cooled (600 K), partially cleaned furnace offgas (Puricelli et al., 1998; Enviro-chem, 2005). Note the (i) upward sprays in and (ii) the weir atop the 'downcomer'. The sprays clean the gas. The weir continuously overflows water, which wets and cools the downcomer walls. These scrubbers are used for both metallurgical and spent acid regeneration furnace gases. Large scrubber details are:

- downcomer diameter: 1 m (Hastelloy G30)
- settler diameter: 4 m (Hastelloy G30)
- gas flow: 1 000 000 Nm$^3$ per hour
- spray flow (total): 8000 m$^3$ per hour.

The downcomer often enters through the roof of the settler. Multiple sprays at one level, rather than a single spray at two levels, are also used.
### Table 4.3. Details of 5 industrial gas plants

<table>
<thead>
<tr>
<th>Plant</th>
<th>M2</th>
<th>M3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Scrubber data</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>type of scrubber</td>
<td>radial flow, 2 sets</td>
<td>radial flow</td>
</tr>
<tr>
<td>number of scrubbers</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>height × diameter, m</td>
<td>16 × 2.5</td>
<td>17 × 6</td>
</tr>
<tr>
<td><strong>Gas data</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>gas source</td>
<td>dry precipitator exit gas</td>
<td>precipitator exit gas</td>
</tr>
<tr>
<td>particulate concentration g/Nm³ before scrubber</td>
<td>0.2</td>
<td>0.5</td>
</tr>
<tr>
<td>after scrubber</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>gas flow through scrubber thousand Nm³ per hour</td>
<td>50</td>
<td>175</td>
</tr>
<tr>
<td>gas temperature, K before scrubber</td>
<td>623</td>
<td>643-653</td>
</tr>
<tr>
<td>after scrubber</td>
<td>339</td>
<td>339</td>
</tr>
<tr>
<td>scrubber liquid flow, m³/hour</td>
<td>350 × 2 sets</td>
<td>528</td>
</tr>
<tr>
<td>liquid temperature, K into scrubber</td>
<td>338</td>
<td>339</td>
</tr>
<tr>
<td>out of scrubber</td>
<td>338</td>
<td>339</td>
</tr>
<tr>
<td>mass% H₂SO₄ in scrubber liquid</td>
<td>1 to 5</td>
<td>1 to 10</td>
</tr>
</tbody>
</table>

**Water removal from gas by cooling/condensation**

<table>
<thead>
<tr>
<th>method</th>
<th>direct cooling/water condensation in packed tower</th>
<th>direct cooling/water condensation in packed tower</th>
</tr>
</thead>
<tbody>
<tr>
<td>number of condensers</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>height × diameter, m</td>
<td>15 × 5.2</td>
<td>17 × 6.8</td>
</tr>
<tr>
<td>packing or tubes</td>
<td>polypropylene spheres</td>
<td>polypropylene spheres</td>
</tr>
<tr>
<td>packing height, m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>liquid flow through condenser</td>
<td></td>
<td></td>
</tr>
<tr>
<td>liquid temperature in, K</td>
<td>310</td>
<td></td>
</tr>
<tr>
<td>gas temperature in, K</td>
<td>339</td>
<td>339</td>
</tr>
<tr>
<td>gas temperature out, K</td>
<td>310.5</td>
<td>308</td>
</tr>
</tbody>
</table>

**Wet electrostatic precipitation**

| number of precipitators | 4 | 6 |
| height × diameter, m | 10.7 × 3.7 | 5.2 × 10.6 |
| number of rods and collection tubes per precipitator | 126 | 248 |
| tube length × diameter, m | 4.5 × 0.25 | 5.7 × 0.25 |
| tube area per precipitator, m² | 445 | 28 |
| tube material | polypropylene | ceramic |
| rods | | |
| | lead, 50 mm diameter | 6mm diameter |

**Gas composition (volume%) after scrubbing, condensing and electrostatic precipitation**

<table>
<thead>
<tr>
<th></th>
<th>SO₃</th>
<th>SO₂</th>
<th>O₂</th>
<th>CO₂</th>
<th>H₂O</th>
<th>N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₃</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>9.0</td>
<td>11.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>6.0</td>
<td>14.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.9</td>
</tr>
<tr>
<td>H₂O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>76 g per Nm³ of gas</td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>remainder</td>
<td></td>
</tr>
<tr>
<td>dust concentration g/Nm³ of gas</td>
<td>0.001</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
cleaning and water condensation plants.

<table>
<thead>
<tr>
<th></th>
<th>M4 Asarco Hayden</th>
<th>Phelps Dodge Miami</th>
</tr>
</thead>
<tbody>
<tr>
<td>Venturi scrubber (VS) + washing tower (WT)</td>
<td>open and packed towers</td>
<td>Venturi scrubbers</td>
</tr>
<tr>
<td>1 each</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>25×1.2-5.4 (VS); 22×8.2 (WT)</td>
<td>9.1 × 6.1</td>
<td>20 × (2.4 inlet; 1.8 throat; 3 outlet)</td>
</tr>
<tr>
<td>dry precipitator exit gas</td>
<td>precipitator exit gas</td>
<td>dry precipitator exit gas</td>
</tr>
<tr>
<td>0.5</td>
<td>148</td>
<td>197</td>
</tr>
<tr>
<td>673</td>
<td>337</td>
<td>580 (VS), 1130 (WT)</td>
</tr>
<tr>
<td>469</td>
<td>299</td>
<td>132 to 727</td>
</tr>
<tr>
<td>355 (VS), 340 (WT)</td>
<td>343</td>
<td>950</td>
</tr>
<tr>
<td>340</td>
<td>363</td>
<td></td>
</tr>
<tr>
<td>10-15</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>heat exchanger condenser</td>
<td>direct cooling/water condensation in packed tower</td>
<td>Venturi scrubbers, retention coolers &amp; heat exchanger star coolers</td>
</tr>
<tr>
<td>3 parallel, 2 series</td>
<td>2</td>
<td>649 tubes: 0.076 m dia. ×3 m long</td>
</tr>
<tr>
<td>3.1 × 2.2</td>
<td>9.1 × 6.1</td>
<td></td>
</tr>
<tr>
<td>Pb lined tubes</td>
<td>polypropylene spheres</td>
<td>3.7</td>
</tr>
<tr>
<td>337</td>
<td>343</td>
<td>334</td>
</tr>
<tr>
<td>320</td>
<td>363</td>
<td>309</td>
</tr>
<tr>
<td>3 parallel, 2 series</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>13.3 × 6.6</td>
<td>176</td>
<td>129 or 302</td>
</tr>
<tr>
<td>424</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.4 × 0.25</td>
<td>3.7 × 0.25</td>
<td>7.6 × 0.2 or 4.6 × 0.25</td>
</tr>
<tr>
<td>60</td>
<td></td>
<td>7200 (total)</td>
</tr>
<tr>
<td>PVC</td>
<td>lead</td>
<td>hexagonal PVC</td>
</tr>
<tr>
<td>carbon steel, lead lining</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>14.63</td>
<td>9.0</td>
<td>9.6</td>
</tr>
<tr>
<td>11.02</td>
<td>11.4</td>
<td>9.6</td>
</tr>
<tr>
<td>3.47</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>101 g per dry Nm³ of gas remainder</td>
<td>5.9 (volume%)</td>
<td>8.5 (volume%)</td>
</tr>
<tr>
<td></td>
<td>remainder</td>
<td>71.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.009</td>
</tr>
</tbody>
</table>
4.5.1 Gas temperature after scrubbing

Liquid scrubbing removes dust and vapors. It also cools the gas to ~340 K, mainly by evaporating water.

4.5.2 Impure scrubbing liquid

The Fig. 4.5 scrubbing liquid is acidic and impure. Excessive buildup of H$_2$SO$_4$ (from SO$_3$(g) and H$_2$O) and impurities is avoided by:

(a) continuously bleeding off a small portion of the liquid

(b) replacing the bleed with clean water.

The amount of bleed is controlled to keep the scrubber liquid's acid level to below ~10 mass% H$_2$SO$_4$ – to minimize corrosion. The bleed is neutralized and treated for metal recovery (Newman et al., 1999).

4.5.3 Mercury removal

Mercury vapor is not removed from gas by Fig. 4.1 processing. It can, however, be removed (Hultbom, 2003) by:

(a) contacting the gas with an aqueous solution of HgCl$_2$ – forming solid calomel, Hg$_2$Cl$_2$

(b) passing the gas through a bed of porous Se impregnated ceramic pieces – forming solid HgSe.

These processes are referred to as the Boliden Norzink Mercury Removal Process (Boliden Norzink, 2004) and the selenium filter process (Selenium Filter, 2004). Combined sequentially, they keep Hg-in-sulfuric acid below 0.25 parts per million.

An alternative is to pass Boliden Norzink exit gas through a column of activated PbS coated pumice (Dowa Process). This precipitates solid HgS and keeps Hg-in-sulfuric acid below 0.05 parts per million (Lossin and Windhager, 1999).

4.6 H$_2$O(g) Removal from Scrubber Exit Gas (Table 4.3)

Scrubber exit gas is saturated with H$_2$O(g). This H$_2$O(g) must be removed prior to catalytic SO$_2$ + $\frac{1}{2}$O$_2$ → SO$_3$ oxidation – to avoid accidental downstream H$_2$SO$_4$(ℓ) formation/corrosion after SO$_3$ has formed. The H$_2$O(g) is removed by:

(a) cooling the gas

then:
(b) contacting it with strong sulfuric acid, Chapter 6.

Gas cooling is an inexpensive way to remove most of scrubber exit gas's H₂O(g), Fig. 4.6. It is done by transferring heat to cool water in:

(a) direct contact packed beds

or:

(b) shell and tube heat exchangers.

In a packed bed, the condensing water joins the cool water stream. In a heat exchanger, the condensing water flows down the cool tube walls in a separate stream. In both cases the cooling water is air cooled and recycled to condensation.

The clean, cool, partially dried gas leaves the top of the condenser and passes through electrostatic mist precipitation to final dehydration with strong sulfuric acid, Chapter 6.

![Graph](image)

**Fig. 4.6.** Volume% H₂O(g) in saturated gas as a function of saturation temperature (Perry and Green, 1997). A decrease in gas temperature from 340 K to 310 K is seen to lower volume% H₂O(g)-in-gas from ~27 volume% to 6 volume%, equivalent to about 75% H₂O(g) removal.

### 4.7 Summary

About 20% of the world's sulfuric acid is made from the SO₂ in smelter and roaster offgases. The gases contain 10 to 75 volume% SO₂. Their SO₂ is suitable for making sulfuric acid but the gases must be:
cooled
cleaned of dust and unwanted vapors
diluted with weak SO₂ process gas and/or air
dried

before they are sent to catalytic SO₂ oxidation.

Cooling is usually done in a waste heat boiler – which cools the gas and recovers its heat as steam. Considerable dust also 'falls out' in the waste heat boilers.

Dust and unwanted vapors are removed from the gas by electrostatic precipitation and aqueous scrubbing.

Finally, H₂O(g) is removed by:

gas cooling and water condensation, Section 4.6
then:

dehydration with strong sulfuric acid, Chapter 6.

The gas is now ready for catalytic SO₂ oxidation and subsequent H₂SO₄ making.

Suggested Reading


References


CHAPTER 5

Regeneration of Spent Sulfuric Acid

About 10% of sulfuric acid is used as catalyst in petroleum refining and polymer manufacture. The acid is not consumed during these uses, but its effectiveness is diminished by contamination with water, hydrocarbons and other chemicals.

Excessive contamination is prevented by:

(a) bleeding contaminated 'spent' acid from the catalyst circuit
(b) replacing it with new strong (98+ mass% H$_2$SO$_4$) acid.

The contaminated 'spent' is made into new strong acid by:

(a) decomposing its H$_2$SO$_4$($\ell$) to SO$_2$(g), O$_2$(g) and H$_2$O(g) in a hot (1300 K) furnace, Fig. 5.1
(b) cooling the furnace offgas in a heat recovery system
(c) cleaning ash and soot particles from the gas
(d) condensing H$_2$O(g) from the gas
(e) dehydrating the gas by contact with strong sulfuric acid
(f) oxidizing the gas's SO$_2$ to SO$_3$
(g) making H$_2$SO$_4$($\ell$) by the reaction:

$$\text{SO}_3(\text{g}) + \text{H}_2\text{O}(\ell)_{\text{in strong sulfuric acid}} \rightarrow \text{H}_2\text{SO}_4(\ell)_{\text{in strengthened sulfuric acid}}.$$ 

The steps are all continuous. This chapter describes steps (a) to (d). Steps (e) to (g) are described in Chapter 6 onwards.
Fig. 5.1. Spent sulfuric acid regeneration flowsheet. $\text{H}_2\text{SO}_4(\ell)$ in the contaminated spent acid is decomposed to $\text{SO}_2(\text{g})$, $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ in a mildly oxidizing, 1300 K fuel fired furnace. The furnace offgas (6-14 volume% $\text{SO}_2$, 2 volume% $\text{O}_2$, remainder $\text{N}_2$, $\text{H}_2\text{O}$, $\text{CO}_2$) is cooled, cleaned and dried. It is then sent to catalytic $\text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{SO}_3$ oxidation and $\text{H}_2\text{SO}_4$ making, Eqn. (1.2). Air is added just before dehydration (top right) to provide $\text{O}_2$ for catalytic $\text{SO}_2$ oxidation. Molten sulfur is often burnt as fuel in the decomposition furnace. It provides heat for $\text{H}_2\text{SO}_4$ decomposition and $\text{SO}_2$ for additional $\text{H}_2\text{SO}_4$ production. Tables 5.2 and 5.3 give details of industrial operations.
5.1 Spent Acid Compositions

Table 5.1 shows the compositions of two spent acids. Both are made into new, strong sulfuric acid as described in Fig. 5.1.

Water rich acids (e.g. methyl methacrylate spent acid) often have part of their water evaporated before they are sent to the H₂SO₄ decomposition furnace (Rohm and Haas, 2003). This decreases:

(a) the amount of liquid that must be treated in the furnace per tonne of new H₂SO₄
(b) the decomposition furnace’s fuel requirement per tonne of new H₂SO₄ (because less water has to be heated and evaporated in the furnace).

Table 5.1. Compositions (mass%) of spent sulfuric acids from two chemical processes. Both processes use sulfuric acid as catalyst. The acid becomes contaminated with water, hydrocarbons, and other chemicals during use. It is made into new sulfuric acid as described in Fig. 5.1.

<table>
<thead>
<tr>
<th>Component</th>
<th>Spent sulfuric acid from</th>
<th>petroleum alkylation catalysis</th>
<th>methyl methacrylate catalysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂SO₄, mass%</td>
<td>~90</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>H₂O, mass%</td>
<td>3-5</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>dissolved hydrocarbons, mass%</td>
<td>4-7#</td>
<td>5</td>
<td>5###</td>
</tr>
<tr>
<td>ammonium bisulfate, mass%</td>
<td>45###</td>
<td>5###</td>
<td></td>
</tr>
<tr>
<td>acetone disulfonic acid, mass%</td>
<td>5###</td>
<td>5###</td>
<td></td>
</tr>
<tr>
<td>low fuel value tars, mass%</td>
<td>5</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>particulate (mainly iron)</td>
<td>&lt;100 parts per million##</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

# H/C atomic ratio ~3 ** occasionally higher ### These components are decomposed to CO₂, H₂O(g), N₂ & SO₂.

5.2 Spent Acid Handling

Spent acid is handled very carefully. It is very corrosive. Also, its H₂SO₄ and hydrocarbons may continue to react during storage and transport (Lang, 1998).

The acid is delivered to the spent acid regeneration plant by:

- stainless steel pipe (within a chemical complex)
- dedicated stainless steel (road) trailers
- phenolic lined steel railway cars
- double hulled steel barges.

It is stored in isolated corrosion resistant stainless steel tanks. The spent acids from various sources (e.g. alkylation catalyst, jet fuel catalyst) are stored separately. This avoids unanticipated reactions between their different organic components.
5.3 Decomposition

Spent acid is decomposed by spraying fine droplets of the acid into a mildly oxidizing furnace, Fig. 5.2. The decomposition reaction is:

\[
\text{H}_2\text{SO}_4(\ell) \rightarrow \text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) + \text{H}_2\text{O}(g) \quad \Delta H^\circ \approx +380 \text{ MJ/kg-mole H}_2\text{SO}_4
\]

in spent acid, 300 K in furnace offgas, 1300 K

(5.1). Heat for this reaction is mainly provided by burning molten sulfur and other fuels with preheated air (occasionally oxygen-enriched) and the \( \text{O}_2 \) from Reaction (5.1). A small amount of heat is obtained from oxidizing the spent acid’s hydrocarbons. Sulfur burning has the advantages that it increases \( \text{SO}_2 \) concentration in decomposition furnace offgas and \( \text{H}_2\text{SO}_4 \) production rate.

5.3.1 Other reactions

Other reactions in the decomposition furnace are:

(a) water evaporation, i.e.:

\[
\text{H}_2\text{O}(\ell) \rightarrow \text{H}_2\text{O}(g)
\]

(5.2)

and:

(b) chemical decomposition, e.g. ammonium bisulfate decomposition:

\[
4\text{NH}_4\text{HSO}_4 + \text{O}_2 \rightarrow 2\text{N}_2 + 10\text{H}_2\text{O}(g) + 4\text{SO}_2
\]

(5.3)

all of which:

(a) require heat

(b) produce \( \text{H}_2\text{O}(g) \).

The heat is provided by burning extra fuel, e.g. molten sulfur or natural gas. The \( \text{H}_2\text{O}(g) \) is removed by condensation (Fig. 5.1) and dehydration (Chapter 6).

5.3.2 Spent acid spraying

Spent acid is sprayed into a decomposition furnace in the form of 500-1000 \( \mu \text{m} \) droplets (Dafft and White, 2002). The droplets present a large acid surface to the hot combustion gas, promoting rapid evaporation and decomposition. The droplets are most commonly produced by forcing the acid into the furnace through fine nozzles (Rohm and Haas, 2003; Bete, 2005). Spinning cup atomizers are also used.

The acid is sprayed into the furnace at two to six locations. This multi spray arrangement avoids localized cooling that occurs when all the acid is sprayed in at one location.
### Table 5.2. Operating details of 2 industrial spent acid decomposition furnaces.

<table>
<thead>
<tr>
<th>Plant</th>
<th></th>
<th>composite</th>
</tr>
</thead>
<tbody>
<tr>
<td>acid production, tonnes H₂SO₄/day</td>
<td>SP1</td>
<td>composite</td>
</tr>
<tr>
<td></td>
<td>444</td>
<td></td>
</tr>
<tr>
<td><strong>Spent acid</strong></td>
<td>alkylation catalyst</td>
<td>methyl methacrylate catalyst</td>
</tr>
<tr>
<td>composition, mass%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>88.48</td>
<td>~15</td>
</tr>
<tr>
<td>H₂O</td>
<td>4.99</td>
<td>~25</td>
</tr>
<tr>
<td>hydrocarbons</td>
<td>6.53</td>
<td>~5</td>
</tr>
<tr>
<td>ammonium bisulfate</td>
<td></td>
<td>~45</td>
</tr>
<tr>
<td>acetone disulfonic acid</td>
<td></td>
<td>~5</td>
</tr>
<tr>
<td>tars</td>
<td></td>
<td>~5</td>
</tr>
</tbody>
</table>

**Spent acid decomposition furnace data**

| | number of furnaces | 1 |
| | shell length x diameter, m | 15.3 x 4.9 | 20 x 4 |
| | spent acid injection | spray guns | both |
| | number of sprayers per furnace | 6 | 6 |
| | spent acid input rate, tonnes/hour | 24.6 | 24.6 |

**Combustion details**

| | fuel, e.g. molten sulfur, natural gas | natural gas | molten S and natural gas |
| | rate, MJ per tonne of spent acid | 2200 | 2200 |
| | air rate, kg per tonne of spent acid | 1440 | 1440 |

**Temperatures, K**

| | air into furnace | 678 | 800 |
| | fuel into furnace | ambient | ambient |
| | spent acid into furnace | ambient | ambient |
| | gas out of furnace | 1317 | 1330 |

**Waste heat boiler**

| | type | fire tube | fire tube |
| | length x diameter, m | 5.5 x 2.6 | 5.5 x 2.6 |
| | number of tubes | 1000 | 1000 |
| | tube diameter, m | 0.05 | 0.05 |
| | tube material | carbon steel | carbon steel |
| | number of steam superheaters | | |
| | gas temperatures, K | | |
| | into boiler | 1317 | 1330 |
| | out of steam super heater | 554 | 620 |

**Steam production, tonnes of steam per tonne spent acid**

| | pressure, bar gage | 32 | 40 |
| | temperature, K | 511 | 511 |

**Product gas**

| | flowrate, thousand Nm³/hour | 37 | |
| | composition, volume% | | |
| SO₂ | 14.2 | 6-8 |
| SO₂ | | 6-8 |
| O₂ | 2.75 | 2 |
| H₂O | | 2 |
| CO₂ | 10.2 | |
5.4 Decomposition Furnace Product

Decomposition furnace exit gas typically contains:

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration, volume%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂</td>
<td>6-14</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.1-0.3</td>
</tr>
<tr>
<td>O₂</td>
<td>2-3</td>
</tr>
<tr>
<td>H₂O(g)</td>
<td>25-30</td>
</tr>
<tr>
<td>CO₂</td>
<td>10</td>
</tr>
<tr>
<td>N₂</td>
<td>50</td>
</tr>
<tr>
<td>particulates (mainly ash and soot)</td>
<td>0.1-1 gram per Nm³</td>
</tr>
</tbody>
</table>

Its H₂O and particulates are removed before it is sent to catalytic SO₂ oxidation. Its O₂ content is increased by adding air just before gas dehydration, Fig. 5.1.

5.5 Optimum Decomposition Furnace Operating Conditions

Decomposition furnaces are operated to efficiently decompose their spent acid into SO₂, O₂ and H₂O(g). Fig. 5.3 suggests optimum conditions for achieving this goal. They are:

- furnace temperature: 1250 to 1350 K
- O₂ in product gas: 1.5 to 2.5 volume%.
5.5.1 Temperature effects

Decomposition furnace temperatures below \( \sim 1250 \) K give un-decomposed \( \text{H}_2\text{SO}_4(\text{g}) \) in the furnace gas. This decreases acid recovery and causes downstream corrosion.

Temperatures above \( \sim 1350 \) K tend to damage the furnace structure.

Furnace temperature is measured with thermocouples. It is controlled to \( \sim 1300 \) K by adjusting fuel combustion rate and air preheat temperature. Feed forward control based on scheduled changes in spent acid composition and feed rate is employed to optimize the process (Rohm and Haas, 2003).

5.5.2 \( \text{O}_2 \) content effects

Low \( \text{O}_2 \) levels in the decomposition furnace gas give sulfur vapor in the gas. This sulfur sublimes and plugs downstream cooling and cleaning equipment (Monsanto Enviro-Chem, 2005). It is avoided by keeping \( \text{O}_2 \)-in-decomposition furnace gas at 2 to 2.5 volume\% (Lang, 1998).

Excessive \( \text{O}_2 \)-in-gas levels, on the other hand, give SO\(_3 \) in the product gas. This SO\(_3 \) is inadvertently absorbed during gas scrubbing and cooling – which:

(a) decreases acid regeneration efficiency

(b) increases the amount of acidic scrubbing/cooling liquid that must be neutralized and evaporated.
O₂-in-furnace gas concentrations are measured with zirconium oxide sensors (Ametek, 2005; Weiss and Puricelli, 2004). They are controlled by adjusting air input rate.

5.6 Preparation of Offgas for SO₂ Oxidation and H₂SO₄ Making

Decomposition furnace offgas is:

- hot (~1300 K)
- dusty (~1 g particulate/Nm³ of gas)
- concentrated in H₂O(g) (25+ volume%)
- too weak in O₂ for catalytic SO₂ oxidation.

It must, therefore, be:

(a) cooled
(b) treated for dust and H₂O(g) removal
(c) strengthened with O₂, by adding air.

The gas is cooled by:

(a) passing it through a waste heat boiler and steam superheater (or air heater), Fig. 5.1
(b) scrubbing with cool water.

Its dust is removed by aqueous scrubbing and wet electrostatic precipitation.

Its H₂O(g) is removed by condensation with cool water and dehydration with strong sulfuric acid, Chapter 6.

Its O₂ content is raised by adding air just before dehydration.

Industrial details are given in Table 5.3.

5.6.1 Gas composition

After the above treatments, spent acid regeneration gas typically contains:

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration entering catalytic SO₂ oxidation volume %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂</td>
<td>8-10</td>
</tr>
<tr>
<td>SO₃</td>
<td>0</td>
</tr>
<tr>
<td>O₂</td>
<td>10-12</td>
</tr>
<tr>
<td>H₂O(g)</td>
<td>0</td>
</tr>
<tr>
<td>CO₂</td>
<td>6-10</td>
</tr>
<tr>
<td>N₂</td>
<td>68-76</td>
</tr>
<tr>
<td>particulate</td>
<td>&lt; 0.1 grams per Nm³ of gas</td>
</tr>
</tbody>
</table>
Table 5.3 Details of spent acid decomposition furnace offgas cleaning and water condensation.

<table>
<thead>
<tr>
<th>Plant</th>
<th>SP1 composite</th>
</tr>
</thead>
</table>

**Scrubber data**
- type of scrubber: spray tower
- number of scrubbers: 1
- height x diameter, m: 10.6 x 3.96

**Gas data**
- gas source:
  - waste heat boiler
- particulate concentration, g/Nm³:
  - before scrubber
  - after scrubber
- gas flow through scrubber, thousand Nm³/hour: 37
- gas temperature, K:
  - before scrubber: 566
  - after scrubber: 340
- scrubber liquid flow, m³/hour: 338
- liquid temperature, K:
  - into scrubber
  - out of scrubber
- mass% H₂SO₄ in scrubber liquid

**Water removal from gas by cooling/condensation**
- Method: Karbate heat exchanger
- number of condensers: 4
- height x diameter, m: 4.88 x 1.1
- liquid flow through tower, m³/hour
- liquid temperature in, K: 377
- gas temperature in, K: 312
- gas temperature out, K: 308

**Wet electrostatic precipitation**
- number of precipitators: 2
- height x diameter, m: 9.2 x 4.8
- number of rods and collection tubes per precipitator: 120
- tube diameter, m: round
- tube area per precipitator, m²: 290
- tube material: lead
- rods: star wire
- applied voltage, V: 260-360
- wire-to-tube current, milliamps: 50-160

**Gas composition (volume%)**
- after scrubbing, condensing and precipitation
  - SO₂: 9.9
  - SO₃: 9
  - O₂: 7.9
  - H₂O: 8.2
  - CO₂: 8.5
  - N₂: 60.5
  - mist droplets, g/Nm³ of gas: 0.02-0.1
It is sent to:

(a) catalytic $\text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_3$ oxidation, Chapter 7

(b) $\text{H}_2\text{SO}_4$ making from $\text{SO}_3$ by the reaction $\text{SO}_3(\text{g}) + \text{H}_2\text{O(}\text{in strong sulfuric acid}) \rightarrow \text{H}_2\text{SO}_4(\text{in strengthened sulfuric acid})$ (Chapter 9).

The new acid is then returned for further catalyst service – or sold.

5.7 Summary

Sulfuric acid is used as catalyst in petroleum refining and other industrial organic processes. The sulfuric acid catalyst is not consumed, but it becomes ineffective as it absorbs water, hydrocarbons and other chemicals over time. Its catalytic properties are maintained by bleeding off some of the contaminated 'spent' acid and replacing the bleed with new strong acid.

The spent acid bleed is recycled and made into new acid by:

(a) decomposing its $\text{H}_2\text{SO}_4$ into $\text{SO}_2$, $\text{O}_2$ and $\text{H}_2\text{O}(\text{g})$ in a hot (1300 K), mildly oxidizing furnace

(b) removing dust and condensing water from the furnace’s offgas

(c) adding $\text{O}_2$ (in air)

(d) dehydrating the gas with strong sulfuric acid

(e) catalytically oxidizing the gas’s $\text{SO}_2$ to $\text{SO}_3$

(f) making new, strong sulfuric acid from (e)’s $\text{SO}_3$.

Suggested Reading


References


CHAPTER 6

Dehydrating Air and Gases with Strong Sulfuric Acid

Industrial experience has shown that SO$_2$ bearing gas must be dry before it goes to catalytic:

\[ \text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{SO}_3(g) \]  

(1.1)

otherwise, Reaction (1.1)'s SO$_3(g)$ will react with the gas's H$_2$O(g) to form corrosive liquid H$_2$SO$_4(\ell)$:

(a) in cool flues and heat exchangers during normal operation

and:

(b) in flues, heat exchangers and catalyst during plant shutdowns.

The H$_2$SO$_4(\ell)$ forms by the reaction:

\[ \text{SO}_3(g) + \text{H}_2\text{O}(g) \rightarrow \text{H}_2\text{SO}_4(\ell) \]  

(6.1).

It is avoided by dehydrating:

(a) sulfur combustion air, Fig. 6.1

(b) scrubbed metallurgical offgas

(c) scrubbed spent acid decomposition offgas, Fig. 6.2.

In all three cases the gas is dehydrated by contacting it with strong sulfuric acid.

# A small amount of sulfuric acid is made by wet catalysis, Section 1.9.
Fig. 6.1. Dehydration of sulfur combustion air in a sulfur burning acid plant. The dried air contains ~50 milligrams of H$_2$O(g) per Nm$^3$ of gas.

Fig. 6.2. Dehydration of metallurgical and spent acid decomposition furnace offgas. Dehydration is done after (i) H$_2$O(g) has been condensed by gas cooling and (ii) aqueous mist has been removed by electrostatic precipitation (not shown). The gas leaving dehydration contains ~50 milligrams of H$_2$O(g) per Nm$^3$ of gas. The acid plant’s main blower is situated immediately after dehydration.
6.1 Objectives

The objectives of this chapter are to describe:

(a) the H$_2$O(g) contents of pre-dehydration gases

(b) the dehydration process

(c) H$_2$O(g) contents after dehydration.

6.1.1 H$_2$O(g) before gas dehydration

The H$_2$O(g) contents of pre-dehydration acid plant gases are shown in Table 6.1. They range from 2 to 10 volume% H$_2$O(g).

Table 6.1. H$_2$O(g) contents of pre-dehydration gases. The H$_2$O(g) content of air in cool, dry climates is lower than that shown in the table.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Temperature, K</th>
<th>Volume% H$_2$O(g) in gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>air for sulfur burning#</td>
<td>305-315</td>
<td>2-4</td>
</tr>
<tr>
<td>metallurgical furnace offgas after</td>
<td></td>
<td></td>
</tr>
<tr>
<td>scrubbing, gas cooling and wet</td>
<td></td>
<td></td>
</tr>
<tr>
<td>electrostatic mist precipitation</td>
<td>310-315</td>
<td>6-10</td>
</tr>
<tr>
<td>spent acid decomposition furnace offgas after</td>
<td></td>
<td></td>
</tr>
<tr>
<td>scrubbing, gas cooling and wet</td>
<td></td>
<td></td>
</tr>
<tr>
<td>electrostatic mist precipitation</td>
<td>310-315</td>
<td>6-10</td>
</tr>
</tbody>
</table>

# Often filtered through a cloth pad prior to dehydration.

6.2 Dehydration with Strong Sulfuric Acid (Tables 6.3-6.5)

The industrial method of removing H$_2$O(g) from sulfur burning air and metallurgical/spent acid offgas is to pass the air or gas upwards through descending strong sulfuric acid, Fig. 6.3. Dehydration is represented by the reaction:

\[
\text{H}_2\text{O}(g) + \text{H}_2\text{SO}_4(\ell) \rightarrow \text{H}_2\text{SO}_4(\ell) + \text{H}_2\text{O}(\ell) \tag{6.2}
\]

for which:

\[\Delta H = -80 \text{ MJ per kg-mole H}_2\text{O}(g).\]
Fig. 6.3. Circuit for dehydrating sulfur burning air and scrubbed metallurgical and spent acid furnace offgas. Sulfuric acid descends around ceramic saddles while moist gas ascends. This creates turbulence, a large gas/acid interfacial area and rapid gas dehydration. At the top, small acid droplets are removed from the exit gas by passing it through a Teflon®/stainless steel mesh pad (Ziebold, 2000). With metallurgical and spent acid gas, the departing acid (right) is stripped of inadvertently absorbed SO₂ before it is sent to product storage or H₂SO₄ making. This is most often done by passing the SO₂ bearing acid down a small packed bed (like that above) while blowing air upwards. The resulting SO₂ bearing air is sent back to the main gas stream just before dehydration. Industrial dehydration data are given in Tables 6.3-6.5.

6.2.1 H₂O(g) concentration after gas dehydration

H₂O(g)-in-gas concentrations after dehydration are close to those predicted by equilibrium H₂O(g) pressures over Fig. 6.3's input acid. These pressures are shown in Table 6.2 along with their equivalent volume% H₂O(g) and mg H₂O(g) per Nm³ of gas.
Table 6.2. Equilibrium \( \text{H}_2\text{O(g)} \) pressures over sulfuric acid at temperatures around those of industrial acid plant gas dehydration (Perry and Green, 1997). The pressures are translated into volume\% \( \text{H}_2\text{O(g)} \) in gas and milligrams \( \text{H}_2\text{O(g)} \) per Nm\(^3\) of gas. An industrial dehydration target of \(-50\) milligrams \( \text{H}_2\text{O(g)} \) per Nm\(^3\) of gas is chosen to avoid downstream corrosion.

<table>
<thead>
<tr>
<th>Temp K</th>
<th>Equilibrium ( \text{H}_2\text{O(g)} ) pressure of feed acid, bar</th>
<th>Equivalent volume% ( \text{H}_2\text{O(g)} ) in dehydrated gas</th>
<th>Equivalent mg ( \text{H}_2\text{O(g)} ) per Nm(^3) of dehydrated gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>93.5 mass% ( \text{H}_2\text{SO}_4 ), 6.5 mass% ( \text{H}_2\text{O} ) sulfuric acid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>320</td>
<td>17.2E-06</td>
<td>16.9E-04</td>
<td>14</td>
</tr>
<tr>
<td>330</td>
<td>38.6E-06</td>
<td>38.1E-04</td>
<td>31</td>
</tr>
<tr>
<td>340</td>
<td>82.6E-06</td>
<td>81.5E-04</td>
<td>66</td>
</tr>
<tr>
<td>350</td>
<td>169 E-06</td>
<td>166 E-04</td>
<td>134</td>
</tr>
<tr>
<td>360</td>
<td>329 E-06</td>
<td>324 E-04</td>
<td>261</td>
</tr>
<tr>
<td>98.5 mass% ( \text{H}_2\text{SO}_4 ), 1.5 mass% ( \text{H}_2\text{O} ) sulfuric acid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>320</td>
<td>0.9E-06</td>
<td>0.8E-04</td>
<td>1</td>
</tr>
<tr>
<td>330</td>
<td>2.0E-06</td>
<td>2.0E-04</td>
<td>2</td>
</tr>
<tr>
<td>340</td>
<td>4.5E-06</td>
<td>4.4E-04</td>
<td>4</td>
</tr>
<tr>
<td>350</td>
<td>9.5E-06</td>
<td>9.5E-04</td>
<td>8</td>
</tr>
<tr>
<td>360</td>
<td>19.7E-06</td>
<td>19.4E-04</td>
<td>16</td>
</tr>
<tr>
<td>370</td>
<td>38.5E-06</td>
<td>38.0E-04</td>
<td>31</td>
</tr>
<tr>
<td>380</td>
<td>72.0E-06</td>
<td>71.9E-04</td>
<td>58</td>
</tr>
<tr>
<td>390</td>
<td>134 E-06</td>
<td>132 E-04</td>
<td>106</td>
</tr>
</tbody>
</table>

The table indicates that its:

\[ 50 \text{ mg } \text{H}_2\text{O(g)} \text{ per Nm}^3 \text{ of dried gas} \]

target is achievable with:

93.5 mass\% \( \text{H}_2\text{SO}_4 \) acid below 340 K

and with:

98.5 mass\% \( \text{H}_2\text{SO}_4 \) acid below 380 K.

6.2.2 Choice of dehydration acid strength

Strong acid, \(-98.5\) mass\% \( \text{H}_2\text{SO}_4 \), is an excellent choice for air and gas dehydration. It has a low equilibrium \( \text{H}_2\text{O(g)} \) vapor pressure. It removes \( \text{H}_2\text{O(g)} \) from air/gas very efficiently.

Also it:

(a) is less corrosive than lower strength (e.g. 93 mass\% \( \text{H}_2\text{SO}_4 \)) acid

(b) minimizes the amount of water that has to be pumped around the dehydration circuit.

It is always used for dehydrating sulfur burning air.
Metallurgical and spent acid regeneration acid plants use 93 to 96 mass% H\textsubscript{2}SO\textsubscript{4} acid for dehydrating their gases. The advantage of these low H\textsubscript{2}SO\textsubscript{4} acids is that they are easily controlled to their design H\textsubscript{2}SO\textsubscript{4} concentrations by:

\[
\text{making small changes to the rate at which 99\% H}_2\text{SO}_4 \text{ acid is pumped over from the H}_2\text{SO}_4 \text{ making circuit, Fig. 6.3.}
\]

This is important for smelter gas dehydration towers because their H\textsubscript{2}O(g) input rates vary considerably over time – due to inadvertent variations in smelting rates.

Spent acid dehydration H\textsubscript{2}O(g) input rates also vary – due to changes in feed acid composition.

H\textsubscript{2}SO\textsubscript{4}-in-acid concentrations are most commonly determined by speed-of-sound-through-acid measurements (Mesa Labs, 2005).

### 6.3 Residence Times

The Table 6.3 to 6.5 data indicate that typical industrial tower diameters, packing heights, and residence times are:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>tower diameter</td>
<td>7-9 meters</td>
</tr>
<tr>
<td>packed bed thickness</td>
<td>2-4 meters</td>
</tr>
<tr>
<td>acid residence time in packing</td>
<td>400-700 s</td>
</tr>
<tr>
<td>gas residence time in packing</td>
<td>2-4 s</td>
</tr>
</tbody>
</table>

These conditions are designed to give 50 mg H\textsubscript{2}O(g) per Nm\textsuperscript{3} of dehydrated gas with low acid droplet entrainment.

### 6.4 Recent Advances

The main advances in air/gas dehydration have been in the areas of:

(a) materials of construction

(b) ceramic packing and packing supports.

The tendency in dehydration construction and acid distribution materials is towards increased use of strongly corrosion resistant:

- stainless steels
- ductile iron piping.

Both are simplifying initial construction, decreasing maintenance and extending plant life (Sulphur, 2004).
<table>
<thead>
<tr>
<th><strong>Table 6.3.</strong> Details of two sulfur burning air dehydration plants.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Operation</strong></td>
</tr>
<tr>
<td><strong>Dehydration packed tower data</strong></td>
</tr>
<tr>
<td>number of packed towers</td>
</tr>
<tr>
<td>materials of construction</td>
</tr>
<tr>
<td>tower height x diameter, m</td>
</tr>
<tr>
<td>packing height, m</td>
</tr>
<tr>
<td>type of packing</td>
</tr>
<tr>
<td>acid distributor type</td>
</tr>
<tr>
<td>materials of construction</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>acid mist eliminator type</td>
</tr>
<tr>
<td><strong>Air</strong></td>
</tr>
<tr>
<td>input filtration method</td>
</tr>
<tr>
<td>input rate thousand Nm³/hour</td>
</tr>
<tr>
<td>H₂O(g) in air, volume% before dehydration</td>
</tr>
<tr>
<td>temperature, K into packed tower</td>
</tr>
<tr>
<td>out of packed tower</td>
</tr>
<tr>
<td><strong>Sulfuric acid used for drying</strong></td>
</tr>
<tr>
<td>acid flowrate, m³/hour</td>
</tr>
<tr>
<td>composition, mass% H₂SO₄ into packed tower</td>
</tr>
<tr>
<td>out of packed tower</td>
</tr>
<tr>
<td>temperature, K into packed tower</td>
</tr>
<tr>
<td>out of packed tower</td>
</tr>
<tr>
<td>outlet acid destination</td>
</tr>
<tr>
<td><strong>Acid plant main blower</strong></td>
</tr>
<tr>
<td>number of blowers</td>
</tr>
<tr>
<td>power rating, each blower kW</td>
</tr>
<tr>
<td>steam or electric powered</td>
</tr>
<tr>
<td>gas temperature after blower, K</td>
</tr>
</tbody>
</table>
Table 6.4. Details of 5 copper smelting operation

<table>
<thead>
<tr>
<th>Dehydration packed tower data</th>
<th>Cumerio (Bulgaria)</th>
<th>M3</th>
</tr>
</thead>
<tbody>
<tr>
<td>number of packed towers</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>materials of construction</td>
<td>brick lined carbon steel</td>
<td></td>
</tr>
<tr>
<td>tower height x diameter, m</td>
<td>12 x 7.2</td>
<td>11.92 x 8.3 (OD)</td>
</tr>
<tr>
<td>packing height, m</td>
<td>3.8</td>
<td>4</td>
</tr>
<tr>
<td>type of packing</td>
<td>7.6 &amp; 5.1 cm saddles</td>
<td>5.1 to 7.6 cm saddles</td>
</tr>
<tr>
<td>acid distributor type</td>
<td>Lurgi pipes and tubes</td>
<td>Lurgi pipes and tubes</td>
</tr>
<tr>
<td>acid mist eliminator type</td>
<td>Alloy 20 – Teflon®</td>
<td>Alloy 20 – Teflon®</td>
</tr>
</tbody>
</table>

Feed gas description

<table>
<thead>
<tr>
<th>gas input rate, thousand Nm³/hour</th>
<th>160</th>
<th>190</th>
</tr>
</thead>
<tbody>
<tr>
<td>gas composition, volume%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SO₃</td>
<td>12.11</td>
<td>11.0</td>
</tr>
<tr>
<td>O₂</td>
<td>11.51</td>
<td>14.6</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.40</td>
<td>1.83</td>
</tr>
<tr>
<td>H₂O</td>
<td>5.42</td>
<td>76 g per Nm³ of gas remainder</td>
</tr>
<tr>
<td>N₂</td>
<td>70.56</td>
<td></td>
</tr>
<tr>
<td>gas temperature, K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>into packed tower</td>
<td>313</td>
<td>310</td>
</tr>
<tr>
<td>out of packed tower</td>
<td>335</td>
<td>328</td>
</tr>
</tbody>
</table>

Sulfuric acid used for drying

<table>
<thead>
<tr>
<th>acid flowrate, m³/hour</th>
<th>1053</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>composition, mass% H₂SO₄</td>
<td></td>
<td></td>
</tr>
<tr>
<td>into packed tower</td>
<td>96</td>
<td>96</td>
</tr>
<tr>
<td>out of packed tower</td>
<td>95.43</td>
<td></td>
</tr>
<tr>
<td>temperature, K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>into packed tower</td>
<td>335</td>
<td>328</td>
</tr>
<tr>
<td>out of packed tower</td>
<td>354</td>
<td>343</td>
</tr>
<tr>
<td>outlet acid destination</td>
<td>H₂SO₄ making</td>
<td>product acid, contact acid, drying tower, stripper</td>
</tr>
</tbody>
</table>

is SO₂ stripped from outlet acid?

Gas composition after drying

| SO₂ (volume%) | 11.29 | 11.0 |
| O₂            | 13.23 | 14.6 |
| CO₂           | 0.38  | 1.83 |
| H₂O           | <0.02 |     |
| N₂            | 75.10 |     |

Acid plant main blower

<table>
<thead>
<tr>
<th>number of blowers</th>
<th>1</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>power rating, each blower kW</td>
<td>3950 nominal</td>
<td>6400 (nominal)</td>
</tr>
<tr>
<td>steam or electric powered</td>
<td>electric</td>
<td>electric</td>
</tr>
<tr>
<td>gas temperature after blower, K</td>
<td>363</td>
<td>392</td>
</tr>
</tbody>
</table>

# The feed gases come from wet gas electrostatic precipitation.
gas dehydration plants.

<table>
<thead>
<tr>
<th></th>
<th>Asarco Hayden</th>
<th>Phelps Dodge Miami</th>
</tr>
</thead>
<tbody>
<tr>
<td>M4</td>
<td>brick lined carbon steel, 20.3 x 8.32 OD 6.27, 5.1 &amp; 7.6 cm saddles, submerged distributor pipes, Teflon®</td>
<td>brick lined steel, 17.8 x 7.61D 3.7, 7.6 cm saddles, ZeCor™ Teflon® mesh</td>
</tr>
<tr>
<td>1</td>
<td>208</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>11.29</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>13.29</td>
<td>11.4</td>
</tr>
<tr>
<td></td>
<td>2.68</td>
<td>0.9</td>
</tr>
<tr>
<td>85 g per Nm³ of gas remainder</td>
<td>5.9</td>
<td>remainder</td>
</tr>
<tr>
<td></td>
<td>317</td>
<td></td>
</tr>
<tr>
<td></td>
<td>328</td>
<td></td>
</tr>
<tr>
<td></td>
<td>910</td>
<td>860</td>
</tr>
<tr>
<td></td>
<td>96</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td>94.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>328</td>
<td>305</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>322</td>
</tr>
<tr>
<td></td>
<td>product acid</td>
<td>recy</td>
</tr>
<tr>
<td>no</td>
<td>yes with air</td>
<td></td>
</tr>
<tr>
<td>11.0-13.5</td>
<td>9.0</td>
<td></td>
</tr>
<tr>
<td>13.3</td>
<td>12.4</td>
<td></td>
</tr>
<tr>
<td>2.68</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>remainder</td>
<td>remainder</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>4500</td>
<td>electric</td>
<td></td>
</tr>
<tr>
<td>383</td>
<td>342</td>
<td></td>
</tr>
</tbody>
</table>
Table 6.5. Details of zinc roaster and spent acid regeneration gas dehydration plants.

<table>
<thead>
<tr>
<th>Operation</th>
<th>M2</th>
<th>SP1</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dehydration packed tower data</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>number of packed towers</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>materials of construction</td>
<td>brick lined carbon steel</td>
<td>brick lined steel</td>
</tr>
<tr>
<td>tower height x diameter, m</td>
<td>12.6 x 7.2</td>
<td>4 x 7.6</td>
</tr>
<tr>
<td>packing height, m</td>
<td>4.3</td>
<td>3.8</td>
</tr>
<tr>
<td>type of ceramic packing</td>
<td>ceramic saddles</td>
<td>7.6 cm Intalox®</td>
</tr>
<tr>
<td>acid distributor type</td>
<td>pipe distributor, buried</td>
<td>cast iron troughs and spouts</td>
</tr>
<tr>
<td>acid mist eliminator type</td>
<td>hanging fiber bed</td>
<td>candle</td>
</tr>
<tr>
<td><strong>Feed gas</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>gas input rate, thousand Nm³/hour</td>
<td>101</td>
<td>46</td>
</tr>
<tr>
<td>gas composition, volume%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₃</td>
<td>0</td>
<td>8.5</td>
</tr>
<tr>
<td>SO₂</td>
<td>10.0</td>
<td>11.6</td>
</tr>
<tr>
<td>O₂</td>
<td>5.89</td>
<td>5.5</td>
</tr>
<tr>
<td>CO₂</td>
<td>0</td>
<td>68 g per Nm³ of gas</td>
</tr>
<tr>
<td>H₂O</td>
<td>remainder</td>
<td>74.4</td>
</tr>
<tr>
<td>gas temperature, K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>into packed tower</td>
<td>311</td>
<td>314</td>
</tr>
<tr>
<td>out of packed tower</td>
<td>328</td>
<td>319</td>
</tr>
<tr>
<td><strong>Sulfuric acid used for drying</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>acid flowrate, m³/hour</td>
<td>870</td>
<td>384</td>
</tr>
<tr>
<td>composition, mass% H₂SO₄</td>
<td></td>
<td></td>
</tr>
<tr>
<td>into packed tower</td>
<td>96</td>
<td>93.5</td>
</tr>
<tr>
<td>out of packed tower</td>
<td>96</td>
<td>93.1</td>
</tr>
<tr>
<td>temperature, K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>into packed tower</td>
<td>328</td>
<td>319</td>
</tr>
<tr>
<td>out of packed tower</td>
<td>347</td>
<td>330</td>
</tr>
<tr>
<td>outlet acid destination</td>
<td>absorption tower</td>
<td></td>
</tr>
<tr>
<td>is SO₂ stripped</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>from outlet acid?</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Gas composition after drying</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₂ (volume%)</td>
<td>8.5</td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>8.8</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>remainder</td>
<td></td>
</tr>
<tr>
<td><strong>Acid plant main blower</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>number of blowers</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>power rating, each blower kW</td>
<td>3500</td>
<td>1150</td>
</tr>
<tr>
<td>steam or electric powered</td>
<td>steam &amp; electric</td>
<td>steam</td>
</tr>
<tr>
<td>gas temperature after blower, K</td>
<td>373</td>
<td>349</td>
</tr>
</tbody>
</table>

# The feed gases come from wet electrostatic precipitation
The tendency in ceramic packing is towards high surface area, low gas flow resistance perforated saddles. These saddles give rapid dehydration with low resistance to gas flow.

6.5 Summary

SO$_2$ bearing gas must be dry before it goes to catalytic $\text{SO}_3(g) + \frac{1}{2}\text{O}_2 \rightarrow \text{SO}_2(g)$ oxidation. Otherwise the $\text{SO}_3(g)$ made by catalytic oxidation will react with $\text{H}_2\text{O}(g)$-in-gas to form corrosive liquid sulfuric acid in cool flues and heat exchangers.

This problem is avoided by dehydrating (i) sulfur burning air and (ii) scrubbed metallurgical/spent acid furnace offgas by contacting these gases with strong sulfuric acid. Dehydration is represented by the reaction:

$$\text{H}_2\text{O}(g) + \text{H}_2\text{SO}_4(\ell) \rightarrow \text{H}_2\text{SO}_4(\ell) + \text{H}_2\text{O}(\ell)$$

Individually, the process is carried out in towers packed with ceramic saddles. Acid descends around the saddles where it meets and reacts with rising $\text{H}_2\text{O}(g)$ laden gas.

$\text{H}_2\text{O}(g)$-in-gas is lowered to $\sim$50 mg per Nm$^3$ of dehydrated gas.

Suggested Reading


References


Catalytic Oxidation of SO₂ to

Sulfuric acid manufacture from clean, dry, SO₂ bearing

(a) catalytically oxidizing the gas's SO₂ to SO₃, i.e.:

\[
\text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{SO}_3(g)
\]

700 K-900 K

in SO₂, O₂, N₂ feed gas or added to it in air

catalyst in SO₃, SO₂, O₂, N₂ gas

\[\Delta H^\circ \approx -100 \text{ MJ per kg-mole of SO}_3(g)\]

(b) making H₂SO₄ from Eqn. (1.1)'s SO₃(g) by reacting it with the H₂O(ℓ) in strong sulfuric acid, i.e.:

\[
\text{SO}_3(g) + \text{H}_2\text{O}(\ell) \rightarrow \text{H}_2\text{SO}_4(\ell)
\]

350 K-380 K

in SO₃, SO₂, O₂, N₂ gas

98.5% H₂SO₄ sulfuric acid

1.5% H₂O, strengthened

\[\Delta H^\circ \approx -130 \text{ MJ per kg-mole of H}_2\text{SO}_4(\ell)\]

This chapter and Chapter 8 describe catalytic SO₂ oxidation. H₂SO₄ making is described in Chapter 9.

7.1 Objectives

The objectives of this chapter are to:

(a) show how industrial SO₂ oxidation is carried out, Figs. 1.2 and 7.7.
(b) explain why catalyst is necessary for SO₂ oxidation
(c) show how multi catalyst bed processing maximizes $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$ oxidation
(d) describe industrial operating procedures.

7.2 Industrial SO₂ Oxidation

Industrial SO₂ oxidation consists of blowing:

- warm (~700 K)
- clean
- dry

$SO_2 + O_2$ bearing gas down through a 'bed' of warm V, K, Na, Cs, S, O, silica catalyst, Fig. 7.1.

![Diagram of SO₂ Oxidation Bed](image)

Fig. 7.1. 'Bed' of catalyst pieces for oxidizing SO₂ to SO₃. It is circular, 7 to 17 m diameter. Industrial SO₂ oxidation is done in a 'converter' of 3 to 5 such beds, Figs. 7.6 and 7.7. Downward gas flows are ~25 Nm³/minute per m² of top surface. Active catalyst consists of a molten V, K, Na, Cs, S, O phase supported on a solid porous silica substrate, Chapter 8. A top layer of silica rock holds the catalyst in place. A bottom layer prevents the catalyst from sticking to the stainless steel support grid.

SO₂ oxidation proceeds as the feed gas descends the bed. It:

(a) produces SO₃
(b) consumes SO₂ and O₂
(c) heats the descending gas.
Fig. 7.2 describes these phenomena. It shows that as the gas descends:

(a) SO$_2$ oxidation proceeds (left graph)

(b) gas and catalyst temperatures increase.

Fig. 7.2. Sketch of SO$_2$ oxidation in Fig. 7.1 catalyst bed. SO$_2$ and O$_2$ in the feed gas react to form SO$_3$ as the gas descends the catalyst bed. The heat of reaction warms the gas (left graph).

7.2.1 Source of O$_2$

SO$_2$ oxidation requires O$_2$. Sulfur burning furnace offgas already contains O$_2$, Table 7.1. None needs to be added. Metallurgical and waste acid decomposition furnace offgases often contain little O$_2$, so some must be added before catalytic SO$_2$ oxidation. It is added in air or ventilation gas before gas dehydration.

Volume% O$_2$/volume% SO$_2$ ratios in industrial catalytic oxidation feed gas are in the range of 1 to 2, Table 7.2. This is 2 to 4 times the stoichiometric SO$_2$+$\frac{3}{4}$O$_2$ \(\rightarrow\) SO$_3$ requirement of 0.5 moles O$_2$ per mole of SO$_2$. The excess O$_2$ promotes rapid SO$_2$ oxidation.
Table 7.1. Compositions of furnace offgases and catalyst bed feed gases. Sulfur burning gases don't change. Metallurgical and waste acid decomposition furnace offgases lose SO$_3$ and H$_2$O(g). The SO$_3$ is removed during water scrubbing. The H$_2$O(g) is removed during condensation and dehydration.

<table>
<thead>
<tr>
<th>Offgas leaving furnace</th>
<th>Sulfur burning furnace</th>
<th>Metallurgical furnaces*</th>
<th>Waste acid decomposition furnace</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_3$</td>
<td>0.2</td>
<td>0-0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>8-12</td>
<td>8-15</td>
<td>6-14</td>
</tr>
<tr>
<td>O$_2$</td>
<td>9-12</td>
<td>5-15</td>
<td>2-3</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0</td>
<td>0-5</td>
<td>10</td>
</tr>
<tr>
<td>H$_2$O(g)</td>
<td>0</td>
<td>5-30</td>
<td>25-30</td>
</tr>
<tr>
<td>N$_2$</td>
<td>79</td>
<td>50-70</td>
<td>~50</td>
</tr>
</tbody>
</table>

# after electrostatic precipitation, Chapter 4

Acid plant feed gas entering catalytic SO$_2$ oxidation 'converter'

<table>
<thead>
<tr>
<th>Prior treatment</th>
<th>usually none, O$_2$ is occasionally added in dried air</th>
<th>gas cleaning and cooling; O$_2$ addition in air; dehydration</th>
<th>gas cleaning and cooling; O$_2$ addition in air; dehydration</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_2$</td>
<td>0.2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>8-12</td>
<td>8-13</td>
<td>8-10</td>
</tr>
<tr>
<td>O$_2$</td>
<td>9-12</td>
<td>9-14</td>
<td>10-12</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0</td>
<td>0-7</td>
<td>6-10</td>
</tr>
<tr>
<td>H$_2$O(g)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>N$_2$</td>
<td>79</td>
<td>~75</td>
<td>~70</td>
</tr>
</tbody>
</table>

7.3 Catalyst Necessity

All industrial SO$_2$ oxidation is done in beds of catalyst. Sander et al. (1984) explain the need for catalyst as follows:

"Gas phase oxidation of sulphur dioxide is kinetically inhibited and virtually impossible without a catalyst at any temperature. At ordinary temperatures the reaction is so slow that, in practical terms, it does not occur at all. Increasing the temperature increases the rate of reaction, but simultaneously the position of the equilibrium shifts unfavourably toward sulfur dioxide and oxygen. Without a catalyst, the temperature needed to make the system react at a practical speed is so high that a very poor conversion [i.e. very little SO$_3$ production] is obtained."

7.3.1 Temperature effect

The temperature effect described in the above statement is confirmed by Fig. 7.3, which shows that the equilibrium constant for SO$_2$ oxidation, i.e.:

$$K_E = \frac{P_{SO_3}^E}{P_{SO_2}^E \left( P_{O_2}^E \right)^2}$$

($P^E =$ equilibrium partial pressure, bar)

decreases with increasing temperature.
Fig. 7.3. Equilibrium constant for $\text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{SO}_3$ oxidation as a function of temperature. It decreases nearly 80 000 times between 600 and 1400 K.

This indicates that:

(a) the equilibrium ratio

$$\frac{p_{E}^{\text{SO}_3}}{p_{E}^{\text{SO}_2} \cdot (p_{E}^{\text{O}_2})^2}$$

and

(b) maximum attainable $\text{SO}_3$ production

both decrease significantly with increasing temperature.

(b) is confirmed by Fig. 7.4 – which shows that maximum attainable $\text{SO}_2$ oxidation decreases from:

- nearly 100% at 600 K
- to about 2% at 1400 K.

It can be concluded from this that raising reaction temperature to increase reaction rate decreases maximum attainable (equilibrium) $\text{SO}_3$ production.

This problem is overcome by using catalyst which promotes:

rapid $\text{SO}_2$ oxidation

at cool temperatures (~700 K) where:

equilibrium $\text{SO}_3$ production is efficient.
Fig. 7.4. Maximum attainable (equilibrium) SO$_2$ oxidation as a function of reaction temperature. It decreases markedly with increasing temperature. Calculation and plotting of this curve are described in Chapter 10.

The catalyst is described in Chapter 8. It consists of vanadium oxide; K, Na, Cs pyrosulfates and porous silica substrate. It is in the form of 10-20 mm rings and pellets, Fig. 8.1 (most commonly, 10-12 mm). It begins to speed up SO$_2$ oxidation at 660-690 K when the vanadium oxide and K, Na, Cs pyrosulfates combine to form a molten layer on the substrate. It becomes fully active at 680-700 K.

Feed gas must enter beds of this catalyst at or above the fully active temperature. Otherwise the gas will cool and solidify (deactivate) the catalyst, preventing SO$_2$ oxidation.

**7.4 SO$_2$ Oxidation 'Heatup' Path (Chapter 11)**

Fig. 7.2 indicates that:

$\text{SO}_2$ oxidation

and

gas temperature

increase as SO$_2$, O$_2$, N$_2$ gas descends an active catalyst bed. Fig. 7.5 quantifies this behavior. It confirms that gas temperature rises as % SO$_2$ oxidized increases (due to heat from SO$_2$ oxidation).

Fig. 7.5 also shows that SO$_2$ oxidation and gas heat up end when the heatup path reaches Fig. 7.4's equilibrium % SO$_2$ oxidized curve.
Feed gas:  
10 volume% SO₂  
11 volume% O₂  
79 volume% N₂  

**Fig. 7.5.** 'Heatup' path for gas descending the Fig. 7.1 catalyst bed. It begins at the feed gas's input temperature and 0% SO₂ oxidized. Its temperature rises as SO₂ oxidizes. Maximum attainable SO₂ oxidation is predicted by the 'heatup' path-equilibrium curve intercept, 69% oxidized at 893 K in this case. This low % SO₂ oxidized confirms that efficient SO₂ oxidation cannot be obtained in a single catalyst bed. Multiple catalyst beds with gas cooling between must be used.

### 7.5 Industrial Multi Catalyst Bed SO₂ Oxidation (Table 7.2)

Industrial SO₂ oxidation is done in a sequence of 3 to 5 catalyst beds, Figs. 7.6 and 7.7. This section and Fig. 7.8 describe passage of warm feed gas through three catalyst beds with gas cooling between. The sequence is:

Feed gas (10 volume% SO₂, 11 volume% O₂, 79 volume% N₂, 690 K) enters the 1ˢᵗ catalyst bed, Fig. 7.6. It:

(a) descends the 1ˢᵗ catalyst bed where its SO₂ and O₂ react to form SO₃, heating the gas
(b) departs the bed at near-intercept conditions (69% of feed SO₂ oxidized/893 K) into Fig. 7.6's top (1-2) gas cooler where it is cooled to 700 K without composition change
(c) enters and descends the 2ⁿᵈ catalyst bed, reacting to form more SO₃, re-heating the gas
(d) departs the 2ⁿᵈ bed at near-intercept conditions (94% SO₂ oxidized/773 K) into Fig. 7.6's bottom (2-3) gas cooler – where it is cooled to 710 K without composition change
(e) enters and descends the 3ʳᵈ catalyst bed, forming more SO₃, again re-heating the gas
(f) departs the 3ʳᵈ catalyst bed at near-intercept conditions (98% SO₂/721 K) and proceeds to cooling and H₂SO₄ making, Chapter 9.
**Fig. 7.6.** Schematic of SO₂ oxidation 'converter' in which three Fig. 7.1 catalyst beds (with gas cooling between) are used to oxidize ~98% of feed SO₂ to SO₃. Fig. 1.2 shows the inside of an industrial 'converter' – Fig. 7.7, the outside. Hot gas leaving the catalyst beds is cooled by waste heat boilers, steam superheaters, water heaters, heat exchangers etc.

**Fig. 7.7.** Photograph of catalyst bed converter, courtesy Outokumpu OYJ www.outokumpu.com Gas inlet and outlet flues are shown. Others are hidden behind. Fig. 7.6's gas coolers are also hidden behind. Converter walls and roofs are designed to be strong enough to withstand their acid plant's main blower 'shutoff' pressure without damage (Friedman and Friedman, 2004). Catalyst 'tray' supports are also strong enough to withstand the downward force exerted by the descending feed gas (at the converter's operating temperature).
Fig. 7.8. 'Heatup' paths, intercepts and cooldown paths for Fig. 7.6 'converter'. They are described in Section 7.5. Final % SO₂ oxidation after Fig. 7.6's three catalyst beds is ~98%.

7.5.1 Overall multi catalyst bed results

Fig. 7.8 describes the benefits of multi catalyst bed SO₂ oxidation. SO₂ oxidation is increased in each succeeding bed. The figure shows, however, that the incremental amount of SO₂ oxidation diminishes in each successive bed.

Addition of a fourth bed would probably not be worthwhile from the SO₃ production (hence H₂SO₄ production) point of view. It might, however, be worthwhile from the point of view of minimizing SO₂ escape to the environment (because SO₂ passes untouched through subsequent H₂SO₄ making). These factors are detailed in Chapters 12 to 22.

7.5.2 Double contact acidmaking

This chapter describes SO₂ oxidation in 'single contact' acid plants. These plants:

(a) oxidize SO₂(g) to SO₃(g) as described here then:

(b) make H₂SO₄(ℓ) by 'single contact' of the resulting SO₃(g) bearing gas with strong sulfuric acid, Chapter 9.

'Double contact' acidmaking:

(a) oxidizes SO₂(g) to SO₃(g) as described here
(b) makes $\text{H}_2\text{SO}_4(\ell)$ from the resulting $\text{SO}_3(\text{g})$ by contact with strong sulfuric acid.

(c) oxidizes the $\text{SO}_2(\text{g})$ remaining after (a) and (b) to $\text{SO}_3(\text{g})$ in 1 (occasionally 2) catalyst beds.

(d) makes $\text{H}_2\text{SO}_4$ from the new $\text{SO}_3(\text{g})$ by second contact of the gas with strong sulfuric acid.

Its advantage is more efficient $\text{SO}_2$ oxidation and $\text{H}_2\text{SO}_4$ production. Its disadvantage is more equipment and more heating and cooling.

(d) is discussed in Chapter 9. (c) is discussed in Chapter 19.

### 7.6 Industrial Operation (Table 7.2)

#### 7.6.1 Startup

Catalyst must be at its fully active temperature before it is fed with $\text{SO}_2$ bearing feed gas. Otherwise the $\text{SO}_2$ will pass through unreacted. Industrially, the catalyst is heated by passing hot, dry air through the catalyst beds before the $\text{SO}_2$ producing furnace is started (BASF, 2004). The air is heated by heat exchange with hot fossil fuel combustion gas. Metallurgical and spent acid regeneration plants have a dedicated air heater for this purpose. Sulfur burning plants heat the air in their sulfur burning furnace.

Once the catalyst beds are hot, the $\text{SO}_2$ production furnace is started and hot, clean, dry $\text{SO}_2$ bearing gas is introduced into the catalytic converter.

Sulfur burning offgas is introduced directly into the hot converter because it leaves the sulfur burning furnace/boiler/superheater at its specified feed gas temperature, $\sim 700 \text{ K}$.

Metallurgical and spent acid decomposition gases are initially passed through their fuel-fired startup heat exchanger because they are cool from gas cleaning/dehydration. Once $\text{SO}_2$ oxidation has begun, this gas heating duty is switched to heat exchange from hot catalyst bed exit gas.

#### 7.6.2 Steady operation

Steady ‘converter’ operation entails:

(a) feeding constant composition, constant temperature $\text{SO}_2$ bearing gas at a constant rate.

# The furnace is first heated by fossil fuel combustion. Combustion is then stopped and dry air is passed through the furnace into the catalyst beds (repeated several times). Once the catalyst beds are hot enough to avoid $\text{H}_2\text{O}(\text{g})$ condensation, hot combustion offgas is passed directly through the beds.
(b) continuously monitoring catalyst bed gas input and output temperatures.

7.6.3 Control

The main catalytic converter control objective is maintenance of constant, specified catalyst bed input gas temperatures.

Low input gas temperatures must be avoided because they may cool, solidify and deactivate a bed's catalyst.

High input gas temperatures must be avoided because they:

(a) raise catalyst bed gas output temperature and consequently lower \( \text{SO}_2 \) oxidation efficiency, Fig. 12.2

(b) raise the gas output temperature above the catalyst degradation temperature, Section 8.3

(c) raise the gas output temperature to the point where it weakens the converter's stainless steel structure.

Catalyst bed input gas temperatures are measured with three thermocouples in the top of each bed. They are controlled by adjusting the amount of gas being bypassed around the catalytic converter's gas cooling devices, Fig. 22.2.

Catalyst bed exit gas temperatures are also measured. They are indicative of each bed's \( \text{SO}_2 \) oxidation efficiency. First catalyst bed exit gas temperature is especially important. This bed's catalyst may overheat and degrade near the bottom of the bed.

7.6.4 Shutdown

Catalytic \( \text{SO}_2 \rightarrow \text{SO}_3 \) oxidation is stopped by:

(a) shutting down the \( \text{SO}_2 \) production unit, e.g. the sulfur burning furnace

(b) blowing 700 K dehydrated air through the catalyst beds and their gas coolers (BASF, 2004)

(c) gradually cooling the air flow.

Steps (b) and (c) remove \( \text{SO}_2 \) and \( \text{SO}_3 \) from all the catalytic oxidation equipment (avoiding corrosion). They also cool equipment and catalyst slowly (avoiding thermal stress and catalyst fragmentation).

An important strategy during short interruptions of \( \text{SO}_2 \) supply is to keep the catalyst at its chemically active temperature, 680-700 K. This is accomplished by (i) raising the temperature of the catalyst just before a forecast interruption and by (ii) preventing air leakage into the converter.
Table 7.2. Details of before-$H_2SO_4$ making catalytic

<table>
<thead>
<tr>
<th>Operation</th>
<th>S1</th>
<th>M2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid production, tonnes $H_2SO_4$/day</td>
<td>4400</td>
<td>1150</td>
</tr>
<tr>
<td>Source of $SO_2$</td>
<td>sulfur burning</td>
<td>zinc roasting</td>
</tr>
<tr>
<td>Single or double contact plant</td>
<td>double</td>
<td>double</td>
</tr>
<tr>
<td>Number of catalyst beds</td>
<td>$3 + 1^*$</td>
<td>$3 + 2^*$</td>
</tr>
<tr>
<td>Converter height x diameter, m</td>
<td>$19.23 \times 16.65$</td>
<td>$15 \times 10$</td>
</tr>
<tr>
<td>Construction materials</td>
<td>304 SS; passes 1&amp;2, 321 SS; pass 3&amp;4</td>
<td>304 SS;</td>
</tr>
<tr>
<td>Heat recovery system</td>
<td>2 x HRS boilers</td>
<td>economizer for boiler</td>
</tr>
</tbody>
</table>

**Input gas data**

<table>
<thead>
<tr>
<th></th>
<th>Flowrate, thousand Nm$^3$/hour</th>
<th>Temperature, K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>356</td>
<td>696</td>
</tr>
<tr>
<td>$SO_3$ composition, volume%</td>
<td>0.184</td>
<td>0</td>
</tr>
<tr>
<td>$SO_2$</td>
<td>11.6</td>
<td>8.5</td>
</tr>
<tr>
<td>$O_2$</td>
<td>9.06</td>
<td>8.84</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>79.1</td>
<td>remainder</td>
</tr>
<tr>
<td>$N_2$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Catalyst bed data**

<table>
<thead>
<tr>
<th></th>
<th>Thickness of beds, m</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bed 1</td>
</tr>
<tr>
<td></td>
<td>Bed 2</td>
</tr>
<tr>
<td></td>
<td>Bed 3</td>
</tr>
<tr>
<td></td>
<td>Bed 4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Catalyst type(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bed 1</td>
</tr>
<tr>
<td></td>
<td>Bed 2</td>
</tr>
<tr>
<td></td>
<td>Bed 3</td>
</tr>
<tr>
<td></td>
<td>Bed 4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Catalyst bed temperatures, K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bed 1 in</td>
</tr>
<tr>
<td></td>
<td>Bed 2 in</td>
</tr>
<tr>
<td></td>
<td>Bed 3 in</td>
</tr>
<tr>
<td></td>
<td>Bed 4 in</td>
</tr>
</tbody>
</table>

|                | Bed 1 out                       | 718             |
|                | Bed 2 out                       | 723             |
|                | Bed 3 out                       | 727             |
|                | Bed 4 out                       | 748             |

**Product gas to $H_2SO_4$ making**

<table>
<thead>
<tr>
<th></th>
<th>$SO_3$</th>
<th>11.8</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$SO_2$</td>
<td>0.688</td>
</tr>
<tr>
<td></td>
<td>$O_2$</td>
<td>3.78</td>
</tr>
<tr>
<td></td>
<td>$CO_2$</td>
<td>83.7</td>
</tr>
</tbody>
</table>

|                | $N_2$                           | 8.49            |
|                |                                 | 0.38            |
|                |                                 | 4.88            |

# 3 catalyst beds before intermediate $H_2SO_4$ making, 1 bed after
### SO₂ Oxidation Plants

(SS = Stainless Steel)

<table>
<thead>
<tr>
<th>Cumerio 1 (Bulgaria)</th>
<th>Cumerio 2 (Bulgaria)</th>
<th>M5</th>
</tr>
</thead>
<tbody>
<tr>
<td>1940</td>
<td>1500</td>
<td></td>
</tr>
<tr>
<td>Copper smelting</td>
<td>Copper smelting</td>
<td>Lead zinc smelting/roasting</td>
</tr>
<tr>
<td>Double</td>
<td>Double</td>
<td>Single</td>
</tr>
<tr>
<td>3 + 1&quot;</td>
<td>3 + 1&quot;</td>
<td>4</td>
</tr>
<tr>
<td>19.3 x 11.6</td>
<td>22.3 x 12</td>
<td>12.83 x 8.4 ID</td>
</tr>
<tr>
<td>Stainless steel, gray iron posts and grids</td>
<td>Brick lined carbon steel</td>
<td>none</td>
</tr>
<tr>
<td>None</td>
<td>None</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material</th>
<th>1940</th>
<th>1500</th>
<th>M5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>160</td>
<td>150</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>703</td>
<td>693</td>
<td>698-713</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>11.29</td>
<td>9.5</td>
<td>8.33</td>
<td></td>
</tr>
<tr>
<td>13.23</td>
<td>14.9</td>
<td>10.79</td>
<td></td>
</tr>
<tr>
<td>0.38</td>
<td>0.3</td>
<td>6.65</td>
<td></td>
</tr>
<tr>
<td>75.10</td>
<td>75.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.66</td>
<td>0.70</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td>0.81</td>
<td>0.60</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>0.88</td>
<td>0.80</td>
<td>0.37 combined</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.37 combined</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material</th>
<th>10 x 4 &amp; 11 x 4 mm rings</th>
<th>12 x 6 mm rings</th>
<th>VK38</th>
</tr>
</thead>
<tbody>
<tr>
<td>1940</td>
<td>703</td>
<td>693</td>
<td>698-713</td>
</tr>
<tr>
<td>1500</td>
<td>903</td>
<td>868</td>
<td>803-853</td>
</tr>
<tr>
<td></td>
<td>723</td>
<td>741</td>
<td>703-723</td>
</tr>
<tr>
<td></td>
<td>804</td>
<td>803</td>
<td>763-773</td>
</tr>
<tr>
<td></td>
<td>708</td>
<td>708</td>
<td>703-713</td>
</tr>
<tr>
<td></td>
<td>737</td>
<td>713</td>
<td></td>
</tr>
<tr>
<td></td>
<td>713-733</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material</th>
<th>1940</th>
<th>1500</th>
<th>M5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>11.47</td>
<td>10.08</td>
<td>8.05</td>
</tr>
<tr>
<td></td>
<td>0.51</td>
<td>0.42</td>
<td>0.61</td>
</tr>
<tr>
<td></td>
<td>7.37</td>
<td>5.67</td>
<td>7.20</td>
</tr>
<tr>
<td></td>
<td>0.32</td>
<td>0.28</td>
<td>6.92</td>
</tr>
<tr>
<td></td>
<td>80.33</td>
<td>83.55</td>
<td></td>
</tr>
</tbody>
</table>
Table 7.2 (continued). Details of before-H₂SO₄ making catalytic acid production, tonnes H₂SO₄/day

<table>
<thead>
<tr>
<th>Operation</th>
<th>M6</th>
<th>M3</th>
</tr>
</thead>
<tbody>
<tr>
<td>source of SO₂</td>
<td>nickel</td>
<td>copper</td>
</tr>
<tr>
<td>single or double contact plant</td>
<td>double</td>
<td>single</td>
</tr>
<tr>
<td>number of catalyst beds</td>
<td>3 + 1ₖ</td>
<td>4</td>
</tr>
<tr>
<td>converter height x diameter, m</td>
<td>17.3 x 12.5</td>
<td>14.515 x 11.75 (OD)</td>
</tr>
<tr>
<td>construction materials</td>
<td>304H stainless steel</td>
<td>AISI PT 304H stainless steel</td>
</tr>
<tr>
<td>heat recovery system</td>
<td>none</td>
<td></td>
</tr>
</tbody>
</table>

**Input gas data**

<table>
<thead>
<tr>
<th></th>
<th>M6</th>
<th>M3</th>
</tr>
</thead>
<tbody>
<tr>
<td>flowrate, thousand Nm³/hour</td>
<td>231 (design)</td>
<td>136</td>
</tr>
<tr>
<td>temperature, K</td>
<td>671-703</td>
<td></td>
</tr>
<tr>
<td>composition, volume%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>12</td>
<td>11.0</td>
</tr>
<tr>
<td>O₂</td>
<td>18.22</td>
<td>14.6</td>
</tr>
<tr>
<td>CO₂</td>
<td>2.32</td>
<td>1.83</td>
</tr>
<tr>
<td>N₂</td>
<td>remainder</td>
<td></td>
</tr>
</tbody>
</table>

**Catalyst bed data**

<table>
<thead>
<tr>
<th></th>
<th>bed 1</th>
<th>bed 2</th>
<th>bed 3</th>
<th>bed 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>thickness of beds, m</td>
<td>0.65</td>
<td>0.78</td>
<td>0.78</td>
<td>1.419</td>
</tr>
<tr>
<td>catalyst type(s)</td>
<td>VK59 and VK38</td>
<td>BASF LP111</td>
<td></td>
<td></td>
</tr>
<tr>
<td>bed 1</td>
<td>VK38</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>bed 2</td>
<td>LP110 and VK48</td>
<td>BASF LP110</td>
<td></td>
<td></td>
</tr>
<tr>
<td>bed 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>bed 4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>catalyst bed temperatures, K</td>
<td>673</td>
<td>709</td>
<td>713</td>
<td>683</td>
</tr>
<tr>
<td>bed 1 in</td>
<td>903</td>
<td>771</td>
<td>742</td>
<td>699</td>
</tr>
<tr>
<td>bed 1 out</td>
<td>897</td>
<td>853</td>
<td>764</td>
<td></td>
</tr>
<tr>
<td>bed 2 in</td>
<td>703</td>
<td></td>
<td>703</td>
<td></td>
</tr>
<tr>
<td>bed 2 out</td>
<td>453</td>
<td></td>
<td>764</td>
<td></td>
</tr>
<tr>
<td>bed 3 in</td>
<td>853</td>
<td></td>
<td>764</td>
<td></td>
</tr>
<tr>
<td>bed 3 out</td>
<td>742</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>bed 4 in</td>
<td>699</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>bed 4 out</td>
<td>699</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Product gas to H₂SO₄ making**

<table>
<thead>
<tr>
<th></th>
<th>M6</th>
<th>M3</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₃</td>
<td>12.20</td>
<td>11.44</td>
</tr>
<tr>
<td>SO₂</td>
<td>0.50</td>
<td>0.23</td>
</tr>
<tr>
<td>O₂</td>
<td>12</td>
<td>9.61</td>
</tr>
<tr>
<td>CO₂</td>
<td></td>
<td>1.94</td>
</tr>
<tr>
<td>N₂</td>
<td>remainder</td>
<td></td>
</tr>
</tbody>
</table>

# 3 catalyst beds before intermediate H₂SO₄ making, 1 bed after
### SO₂ Oxidation Plants

<table>
<thead>
<tr>
<th></th>
<th>M4</th>
<th>Asarco Hayden</th>
</tr>
</thead>
<tbody>
<tr>
<td>2100-2400</td>
<td>1630</td>
<td></td>
</tr>
<tr>
<td>Continuous copper smelting</td>
<td>double</td>
<td>double</td>
</tr>
<tr>
<td>3 + 1&quot;</td>
<td>3 + 1&quot;</td>
<td></td>
</tr>
<tr>
<td>22.1 x 12</td>
<td>16.1 x 14.0</td>
<td></td>
</tr>
<tr>
<td>Aluminum coated steel</td>
<td>brick lining</td>
<td>304 stainless steel</td>
</tr>
<tr>
<td>None</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>188</th>
<th>201</th>
</tr>
</thead>
<tbody>
<tr>
<td>663</td>
<td>672</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>11.0-13.5</th>
<th>8.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.29</td>
<td>12.6</td>
<td></td>
</tr>
<tr>
<td>2.68</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Remainder</td>
<td>75.0</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>0.76</th>
<th>0.46</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.85</td>
<td>0.56</td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>0.56</td>
<td></td>
</tr>
</tbody>
</table>

### VK59 and VK 38 Layers

<table>
<thead>
<tr>
<th></th>
<th>LP120/VK38</th>
<th>LP120/VK38</th>
</tr>
</thead>
<tbody>
<tr>
<td>VK38</td>
<td></td>
<td>LP110/VK48</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>663</th>
<th>672</th>
</tr>
</thead>
<tbody>
<tr>
<td>873</td>
<td>894</td>
<td></td>
</tr>
<tr>
<td>713</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td>813</td>
<td>812</td>
<td></td>
</tr>
<tr>
<td>693</td>
<td>711</td>
<td></td>
</tr>
<tr>
<td>723</td>
<td>727</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>10.89-13.3</th>
<th>12.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7-1.1</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>7.5-8.6</td>
<td>7.1</td>
<td></td>
</tr>
<tr>
<td>2.9</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Remainder</td>
<td>79.1</td>
<td></td>
</tr>
</tbody>
</table>
Table 7.2 (continued). Details of before-H₂SO₄ making catalytic acid production, tonnes H₂SO₄/day

<table>
<thead>
<tr>
<th>Operation</th>
<th>Phelps Dodge Miami</th>
<th>M1</th>
</tr>
</thead>
<tbody>
<tr>
<td>acid production, tonnes H₂SO₄/day</td>
<td>2400</td>
<td>270</td>
</tr>
<tr>
<td>source of SO₂</td>
<td>copper smelting</td>
<td>MoS₂ roasting &amp; S burning</td>
</tr>
<tr>
<td>single or double contact plant</td>
<td>double</td>
<td>double</td>
</tr>
<tr>
<td>number of catalyst beds</td>
<td>3 + 1ᵣ</td>
<td>2 + 2ᵣ</td>
</tr>
<tr>
<td>converter height x diameter, m</td>
<td>23.3 x 14.76</td>
<td>9.8 x 6.9</td>
</tr>
<tr>
<td>construction materials</td>
<td>all welded</td>
<td>carbon steel with</td>
</tr>
<tr>
<td>heat recovery system</td>
<td>stainless steel</td>
<td>cast iron grids</td>
</tr>
</tbody>
</table>

Input gas data

<table>
<thead>
<tr>
<th>flowrate, thousand Nm³/hour</th>
<th>233</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>temperature, K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>trace</td>
<td></td>
</tr>
<tr>
<td>SO₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Catalyst bed data

<table>
<thead>
<tr>
<th>thickness of beds, m</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>bed 1</td>
<td>0.49</td>
<td>0.56</td>
</tr>
<tr>
<td>bed 2</td>
<td>0.79</td>
<td>0.48</td>
</tr>
<tr>
<td>bed 3</td>
<td>0.84</td>
<td></td>
</tr>
<tr>
<td>bed 4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>catalyst type(s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>bed 1</td>
<td>13 mm diameter 13 mm long</td>
<td>daisy ring</td>
</tr>
<tr>
<td>bed 2</td>
<td>13 mm diameter 13 mm long</td>
<td>daisy ring</td>
</tr>
<tr>
<td>bed 3</td>
<td>13 mm diameter 13 mm long</td>
<td></td>
</tr>
<tr>
<td>bed 4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>catalyst bed temperatures, K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>bed 1 in</td>
<td>703</td>
<td>700-727</td>
</tr>
<tr>
<td>bed 1 out</td>
<td>891</td>
<td>805-839</td>
</tr>
<tr>
<td>bed 2 in</td>
<td>723</td>
<td>700-727</td>
</tr>
<tr>
<td>bed 2 out</td>
<td>796</td>
<td>708-736</td>
</tr>
<tr>
<td>bed 3 in</td>
<td>723</td>
<td></td>
</tr>
<tr>
<td>bed 3 out</td>
<td>744</td>
<td></td>
</tr>
<tr>
<td>bed 4 in</td>
<td></td>
<td></td>
</tr>
<tr>
<td>bed 4 out</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Product gas to H₂SO₄ making

<table>
<thead>
<tr>
<th></th>
<th>Phelps Dodge Miami</th>
<th>M1</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₃</td>
<td>10.38</td>
<td>11.8</td>
</tr>
<tr>
<td>SO₂</td>
<td>0.66</td>
<td>0.2</td>
</tr>
<tr>
<td>O₂</td>
<td>5.85</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>82.05</td>
<td></td>
</tr>
</tbody>
</table>

# 3 catalyst beds before intermediate H₂SO₄ making, 1 bed after
SO$_2$ oxidation plants.

<table>
<thead>
<tr>
<th></th>
<th>S2</th>
<th>SP1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1800 sulfur burning</td>
<td>444 spent acid regeneration</td>
</tr>
<tr>
<td></td>
<td>single</td>
<td>single</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>13.7 x 12.8 carbon steel, gray iron posts and grids</td>
<td>10.8 x 7.6 carbon steel &amp; mehanite cast iron superheater</td>
</tr>
<tr>
<td></td>
<td>210</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.38</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td>12.6</td>
<td>11.6</td>
</tr>
<tr>
<td></td>
<td>79.02</td>
<td>72.5</td>
</tr>
<tr>
<td></td>
<td>0.51</td>
<td>0.78</td>
</tr>
<tr>
<td></td>
<td>0.62</td>
<td>0.86</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>0.92</td>
<td>1.29</td>
</tr>
<tr>
<td></td>
<td>daisy ring</td>
<td>10 mm ring</td>
</tr>
<tr>
<td></td>
<td>10 mm ring</td>
<td>10 mm ring</td>
</tr>
<tr>
<td></td>
<td>10 mm ring</td>
<td>10 mm ring</td>
</tr>
<tr>
<td></td>
<td>10 mm ring</td>
<td>10 mm ring</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>705</td>
</tr>
<tr>
<td></td>
<td>898</td>
<td>879</td>
</tr>
<tr>
<td></td>
<td>705</td>
<td>709</td>
</tr>
<tr>
<td></td>
<td>789</td>
<td>800</td>
</tr>
<tr>
<td></td>
<td>715</td>
<td>725</td>
</tr>
<tr>
<td></td>
<td>733</td>
<td>744</td>
</tr>
<tr>
<td></td>
<td>700 (after air dilution)</td>
<td>705</td>
</tr>
<tr>
<td></td>
<td>704</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8.18</td>
<td>9.02</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>9.44</td>
<td>7.13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.74</td>
</tr>
<tr>
<td></td>
<td>82.23</td>
<td>75.92</td>
</tr>
</tbody>
</table>
7.7 Recent Advances (Friedman and Friedman, 2004)

Important recent advances in catalytic SO$_2$ oxidation have been:

(a) development of low activation temperature, high reaction rate cesium-based catalyst, Chapter 8

(b) adoption of low gas flow resistance daisy ring catalyst pieces, Fig. 8.1

(c) use of strong, corrosion resistant stainless steel in converter construction.

All contribute to efficient, steady, long term SO$_3$(g) production.

7.8 Summary

Catalytic oxidation of SO$_2$(g) to SO$_3$(g) is a key step in sulfuric acid production. It produces the SO$_3$ required for H$_2$SO$_4$ making, Chapter 9.

SO$_2$+½O$_2$ → SO$_3$ oxidation is always done by passing warm SO$_2$ bearing gas down through horizontal beds of V, K, Na, Cs, S, O, SiO$_2$ catalyst. The catalyst promotes rapid SO$_2$ oxidation at temperatures (700-900 K) where SO$_2$ oxidation is thermodynamically efficient.

Industrially, the oxidation is carried out in a sequence of 3 to 5 catalyst beds with gas cooling between. Removal of heat from the gas between catalyst beds allows it to leave the last bed at a low temperature (~720 K) – where equilibrium SO$_2$+½O$_2$ → SO$_3$ oxidation efficiency is high (98+ percent).

Suggested Reading


References


CHAPTER 8

SO₂ Oxidation Catalyst and Catalyst Beds

Chapter 7 shows that SO₂ + ⅓O₂ → SO₃ oxidation is a key step in sulfuric acid manufacture. The SO₃(g) is essential for H₂SO₄ making, i.e. for the reaction:

\[
\text{SO}_3(g) \text{ in SO}_3, \text{ SO}_2, \text{ O}_2, \text{ N}_2 \text{ gas} \quad + \quad \text{H}_2\text{O}(\ell) \quad \rightarrow \quad \text{H}_2\text{SO}_4(\ell) \quad \text{in strengthened sulfuric acid}
\]

Chapter 7 also shows that V, K, Na, Cs, S, O, SiO₂ catalyst is a key ingredient in ensuring rapid, efficient SO₂ oxidation. Without catalyst, SO₂ oxidation is slow at temperatures where the oxidation is thermodynamically efficient.

This chapter describes SO₂ oxidation catalyst. It does so in terms of:

(a) catalyst physical and chemical characteristics, Fig. 8.1

(b) catalyst reaction mechanisms

(c) choice of catalyst chemical compositions for different industrial tasks, e.g. strong SO₂ gas, weak SO₂ gas

(d) industrial catalyst quantity requirements.

---

Fig. 8.1. Photograph of catalyst pieces, courtesy Haldor Topsoe A/S www.haldortopsoe.com Rings, daisy (star) rings and pellets are shown. The daisy rings maximize catalyst area and minimize resistance to gas flow. In operation (700-900 K), the catalyst consists of a molten vanadium-alkali metal sulfate/pyrosulfate layer on a porous solid silica substrate. The outside diameter of the largest piece (far left) is 20 mm.
8.1 Catalytic Reactions

Active SO$_2$ oxidation catalyst consists of molten vanadium-alkali metal pyrosulfate layer on porous solid silica substrate. Catalytic SO$_2$+½O$_2$ → SO$_3$ oxidation takes place with dissolved V$_2$O$_5$ ionic complexes by reactions like:

\[
(\text{VO})_2\text{O} (\text{SO}_4)_4^{4-} + \text{O}_2 (g) \rightarrow (\text{VO})_2\text{O} (\text{SO}_4)_4^{4-} \quad (8.1)
\]

\[
(\text{VO})_2\text{O} (\text{SO}_4)_4^{4-} + \text{SO}_2 (g) \rightarrow (\text{VO})_2\text{O} (\text{SO}_4)_4^{4-} + \text{SO}_3 (g) \quad (8.2)
\]

\[
(\text{VO})_2\text{O} (\text{SO}_4)_4^{4-} + \text{SO}_2 (g) \rightarrow (\text{VO})_2\text{O} (\text{SO}_4)_4\text{SO}_3^{4-} \quad (8.3)
\]

\[
(\text{VO})_2\text{O} (\text{SO}_4)_4\text{SO}_3^{4-} \rightarrow (\text{VO})_2\text{O} (\text{SO}_4)_4^{4-} + \text{SO}_3 (g) \quad (8.4)
\]

or, overall:

\[
2\text{SO}_2 (g) + \text{O}_2 (g) \rightarrow 2\text{SO}_3 (g) \quad (8.5)
\]

(Lapina et al., 1999). N$_2$ and CO$_2$ don’t react during the SO$_2$ oxidation process.

Reactions (8.1) to (8.4) have smaller activation energies than Reaction (8.5). They give rapid SO$_2$ oxidation at moderate temperatures.

Rapid reaction between gases and ions requires that the vanadium ion salt be molten (Folkmann et al., 1991; Hatem et al., 2002). Melting at moderate temperatures (~650 K) is obtained by combining high melting point:

vanadium pentoxide (melting point, 943 K)

with low melting point:

potassium (692 K), sodium (675 K), cesium (733 K) pyrosulfates, Fig. 8.2.

The resulting low melting point salt also:

(a) dissolves SO$_2$(g) and O$_2$(g)

and:

(b) exsolves SO$_3$(g)

as required by Reactions (8.1) through (8.4).

8.1.1 Deactivation and reactivation

Catalyst deactivates when it is cooled below its solidification temperature. This happens when a catalyst bed is fed with cold gas or when the acid plant is shut down.
Fig. 8.2. $\text{Cs}_2\text{S}_2\text{O}_7 - \text{V}_2\text{O}_5$ phase diagram (after Folkmann et al., 1991). The lowest melting point is 617 K, far below $\text{V}_2\text{O}_5$'s 943 K melting point.

Fortunately, catalyst solidification and melting are reversible so that the catalyst reactivates when it is once again heated and remelted.

8.2 Maximum and Minimum Catalyst Operating Temperatures

Tables 7.2 and 19.3 indicate that industrial catalysts operate between:

$\sim 680$ K (occasionally lower)

and:

$\sim 900$ K.

Operating above $\sim 690$ K ensures that the catalyst is molten and active.

Operating below $\sim 900$ K ensures the presence of Reactions 8.1 to 8.4's active ions in the molten catalyst. Above $\sim 900$ K, these active ions transform to inactive vanadates ($\text{VO}_4^{3-}$) causing $\text{SO}_2$ oxidation to cease (Rasmussen, 2001). Also, above 900 K, the molten catalyst and solid substrate tend to irreversibly form a viscous inactive liquid.

8.3 Composition and Manufacture

Compositions and methods of manufacturing commercial catalysts are proprietary. Roughly, however, commercial catalysts contain (mass%):
4 - 9% V₂O₅
15 - 20% potassium sulfate/pyrosulfate (SO₄/S₂O₇)
2 - 5% sodium sulfate/pyrosulfate
5 - 15% cesium sulfate/pyrosulfate (when present)
55 - 70% porous silica substrate.

8.3.1 Manufacture

The catalyst is made by:

(a) mixing vanadium oxide, alkali metal oxides and diatomaceous earth (SiO₂) powders in specified proportions

(b) forming a paste of these components by mixing them with water and inorganic/organic binding additives

(c) extruding the paste into ring- or pellet-shaped rods

(d) chopping the extrudates into rings or pellets

(e) baking the rings and pellets in an SO₂/SO₃ atmosphere to:

  remove water
  add strength
  form alkali metal sulfates and pyrosulfates.

(e)'s SO₂/SO₃ atmosphere is adjusted to give the manufacturer's specified sulfate/pyrosulfate (SO₄/S₂O₇) ratio.

8.3.2 Installation and plant startup

Purchased rings and pellets are carefully shipped in sealed barrels or in 1 m × 1 m × 1 m fiberglass bags. They are carefully loaded onto the acid plant's catalytic converter 'trays'. The catalytic converter is then closed up and SO₂ oxidation is begun as described in Section 7.6.1.

8.3.3 Chemical change and melting

Flow of ~700 K SO₂/SO₃ bearing gas around the loaded catalyst causes it to form a vanadium oxide-alkali metal pyrosulfate melt on the surfaces of the catalyst's porous silica substrate.

It is in this melt that catalytic SO₂(g) + ½O₂(g) → SO₃(g) occurs, Reactions (8.1) through (8.4).
The steady state *in situ* composition of the catalyst melt is affected by the composition of the gas that is passing around the melt. It varies down the catalyst beds.

### 8.4 Choice of Size and Shape

Catalyst pieces are sold in the form of daisy rings, simple rings and cylindrical pellets, Fig. 8.1.

Daisy rings have the largest surface area and lowest resistance to gas flow. Pellets have the smallest surface area and highest resistance to flow. Simple rings are intermediate.

Industrial data (Table 7.2) suggest that daisy rings and rings are equally favored. Pellets are only used to ensure well distributed gas flow through catalyst beds in low gas velocity converters (Topsoe, 2004).

### 8.5 Choice of Chemical Composition

Manufacturers choose catalyst chemical composition to give:

(a) a low melting point with a high vanadium ion solubility

(b) strong catalytic activity

(c) a high catalyst degradation temperature.

Low melting point and high V$_2$O$_5$ solubility are obtained by choosing a low melting point eutectic mixture of V$_2$O$_5$ and K, Na, Cs pyrosulfates.

Strong catalytic activity is provided by vanadium, Eqns. (8.1) to (8.4). Catalytic activity increases with increasing vanadium ion concentration. Cs also contributes to strong catalytic activity (Rasmussen, 2001, p72).

High degradation temperature is favored by low vanadium ion concentration (Rasmussen, 2005). The low V concentration minimizes inert (VO$_4$)$^{3-}$ formation as temperature rises.

Table 8.1 summarizes these effects.
Table 8.1. Descriptions, advantages and uses of Haldor Topsoe's sulfuric acid catalysts (Hansen, 2004; Topsoe, 2004). Industrial input gas temperatures are somewhat higher than those indicated here, Tables 7.2 and 19.3. Other manufacturers make similar catalysts (BASF, 2004; Monsanto, 2004*).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>VK38</th>
<th>VK48</th>
<th>VK59</th>
<th>VK69</th>
</tr>
</thead>
<tbody>
<tr>
<td>Characteristic</td>
<td>alkali metals</td>
<td>vanadium ion concentration</td>
<td>special characteristics</td>
<td>continuous operating temperature range, K</td>
</tr>
<tr>
<td></td>
<td>K, Na</td>
<td>K, Na</td>
<td>K, Cs, Na</td>
<td>K, Cs, Na</td>
</tr>
<tr>
<td></td>
<td>high</td>
<td></td>
<td>manufactured silica substrate with many uniform, high surface area gas accessible pores</td>
<td>manufactured silica substrate with many uniform, high surface area gas accessible pores</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Advantage</th>
<th>high temperature stability</th>
<th>strong catalytic activity</th>
<th>low continuous gas input temperature</th>
<th>(i) low continuous gas input temperature (ii) highest catalytic activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suggested use</td>
<td>all catalyst beds, especially 1st and 2nd</td>
<td>last bed before H₂SO₄ making</td>
<td>(i) ignition layer in any bed (ii) last bed in single contact acid plant</td>
<td>after H₂SO₄ making oxidation</td>
</tr>
</tbody>
</table>

8.6 Catalyst Bed Thickness and Diameter

Table 7.2 gives measured industrial:

- catalyst bed thicknesses, m
- catalyst bed (converter) diameters, m
- converter input gas rate, Nm³/hour.

This section discusses these values.

8.6.1 Bed thicknesses

Fig. 8.3 shows industrial catalyst bed thicknesses. Average bed thicknesses are:
1\textsuperscript{st} (feed gas) catalyst bed \hspace{1cm} 0.62 m
2\textsuperscript{nd} catalyst bed \hspace{1cm} 0.72 m
3\textsuperscript{rd} catalyst bed \hspace{1cm} 0.84 m

with a scatter of ±0.2 m each.

Fig. 8.3. Industrial 1\textsuperscript{st}, 2\textsuperscript{nd} and 3\textsuperscript{rd} catalyst bed thicknesses. They are from Table 7.2. They increase from bed 1 through bed 3.

Bed 2 is thicker than bed 1 to provide a longer gas residence time, Fig. 8.5. This is necessary because bed 2 input gas contains:

less \( \text{SO}_2 \) and \( \text{O}_2 \)

more \( \text{SO}_3 \)

than bed 1 feed gas. These changes all tend to slow \( \text{SO}_2 \) oxidation. Bed 2’s longer residence time offsets them.

Bed 3 is thicker than bed 2 for the same reason.
8.6.2 Bed diameters

Fig. 8.4 shows industrial catalytic converter (hence catalyst bed) diameters as a function of measured 1st catalyst bed feed gas volumetric flowrates. Bed diameters are between 8 and 16 m. They increase with increasing input gas flowrate. They are quite precisely predicted by the trendline equation on the graph.

![Graph showing bed diameters](image)

**Fig. 8.4.** Measured industrial catalytic converter diameter as a function of measured converter gas input rate. Diameter increases with increasing flowrate. This keeps catalyst bed residence times roughly constant, Fig. 8.5.

8.7 Gas Residence Times

Nominal residence times of gas in a converter's catalyst beds are calculated from measured bed thickness, converter diameter and converter gas input rate. The equation is:

\[
\text{Nominal gas residence time in catalyst bed, s} = \frac{\text{bed thickness, m}}{\frac{\pi}{4} \cdot \text{converter gas input rate, Nm}^3 \cdot s^{-1}}. \quad \frac{\text{Nm}^3}{s}
\]
Fig. 8.5 plots values calculated from Table 7.2's measured data. Residence times are seen to be 1½ or 2 seconds, increasing with bed number.

![Graph showing nominal residence time vs. catalyst bed number]

**Average nominal residence time, s = 0.26*bed number + 1.19**

**Fig. 8.5.** Industrial 1st, 2nd and 3rd catalyst bed gas nominal residence times. They increase with increasing bed number. This is due to the increase in bed thickness with increasing bed number, Fig. 8.3. The points have been calculated from Table 7.2's industrial catalyst bed thicknesses, converter diameters and converter input gas flowrates.

### 8.8 Catalyst Bed Maintenance

Over time, catalyst beds (especially bed 1) become clogged with dust. This gradually increases the pressure that must be applied to push gas through the beds. Eventually this pressure becomes too high and the dust must be screened out of the catalyst.

Screening entails removing the catalyst from its converter tray, passing it across vibrating screens and loading the screened catalyst back into the tray with a small amount of new catalyst makeup. It is done every year or two, most frequently for the 1st catalyst bed. It is done as quickly as possible to minimize acid production loss.

### 8.9 Summary

SO$_3$(g) is a key ingredient in making H$_2$SO$_4$(l). It is produced rapidly and efficiently by oxidizing SO$_2$(g) to SO$_3$(g) in molten V, K, Na, Cs, S, O catalyst, 700-900 K. The molten catalyst is supported on solid, porous silica substrate.

SO$_2$(g) and O$_2$(g) dissolve in the molten catalyst. They then react with V, S, O anions to form and exsolve SO$_3$(g). The reactions are rapid at temperatures (700-900 K) where
SO₂(g) + ½O₂(g) → SO₃(g) oxidation is thermodynamically efficient.

The process is carried out industrially in ½ to 1 m thick beds of 10 to 12 mm catalyst rings or pellets, Fig. 8.1. Reaction times are 1½ to 2 seconds.

Suggested Reading


References


Rasmussen, S.B. (2005) personal communication. sbr@kemi.dtu.dk

CHAPTER 9

Production of \( \text{H}_2\text{SO}_4(\ell) \) from \( \text{SO}_3(\text{g}) \)

The last step in sulfuric acid manufacture is production of liquid \( \text{H}_2\text{SO}_4 \) from \( \text{SO}_3 \) gas. The \( \text{H}_2\text{SO}_4 \) is produced by reacting:

the \( \text{SO}_3 \) bearing gas from catalytic \( \text{SO}_2 \) oxidation

with:

strong sulfuric acid, Fig. 9.1.

The reaction is:

\[
\text{SO}_3(\text{g}) + \text{H}_2\text{O}(\ell) \rightarrow \text{H}_2\text{SO}_4(\ell)
\]

350-380 K

in \( \text{SO}_3, \text{SO}_2 \) in strong in strengthened

\( \text{O}_2, \text{N}_2 \) gas sulfuric acid sulfuric acid

(1.2).

Industrially the process is carried out by:

(a) trickling 98.5 mass\% sulfuric acid down through a packed bed of ceramic 'saddles'

while:

(b) blowing \( \text{SO}_3 \) bearing gas upward through the descending acid, Figs. 6.3 and 9.1.

The product of the process is \( \sim \)99 to 99.5 mass\% \( \text{H}_2\text{SO}_4 \) sulfuric acid. It is diluted with:

(a) the acid product from air or gas dehydration, Chapter 6

and:

(b) water

to give the acid plant's range of products, mostly 93 to 98 mass\% \( \text{H}_2\text{SO}_4 \) acid.
100 warm, dry SO₂, O₂, N₂ gas

Catalyst layers

SO₂+1/2 O₂→SO₃

Gas cooling

SO₂, SO₃, O₂, N₂ gas

480 K

H₂SO₄ MAKING

380 K

Acid cooling

99 to 99.5 mass% H₂SO₄ sulfuric acid to dilution and market

Low SO₃, SO₂ 'tail' gas, 350 K to environment or basic solution scrubbing

98.5 mass% H₂SO₄, 1.5 mass% H₂O sulfuric acid, 350 K
dilution

Fig. 9.1. Single contact H₂SO₄ making flowsheet. SO₃ rich gas from catalytic SO₂ oxidation is reacted with strong sulfuric acid, Reaction (1.2). The reaction consumes H₂O(ℓ) and makes H₂SO₄(ℓ), strengthening the acid. Double contact H₂SO₄ making is described in Fig. 9.6. *A few plants lower the SO₂ content of their 'tail' gas by scrubbing the gas with basic solution (Hay et al., 2003).

9.1 Objectives

The objectives of this chapter are to:

(a) indicate why SO₃ is reacted with strong sulfuric acid rather than water
(b) describe industrial H₂SO₄ making
(c) suggest optimum conditions for efficient H₂SO₄ making.

9.2 Sulfuric Acid Rather than Water

Reaction (1.2) is strongly exothermic. It releases ~130 MJ per kg mole of SO₃. Stoichiometric reaction of 350 K SO₃(g) with 350 K water produces 840 K H₂SO₄ vapor (H₂SO₄ boiling point ≈ 550 K, Perry and Green, 1997).
Condensation of $\text{H}_2\text{SO}_4(\ell)$ from this vapor is slow and expensive, so the $\text{SO}_3(\text{g})$ water process is never used. Instead, the $\text{SO}_3(\text{g})$ is reacted with strong sulfuric acid.

The large amount of $\text{H}_2\text{SO}_4$ in the acid reactant absorbs Reaction (1.2)'s heat of reaction while the acid warms only $\sim 30 \text{ K}$, Table 9.3. This ensures that the product acid is liquid and relatively cool.

Pumping acid around the $\text{H}_2\text{SO}_4$ making system (Fig. 9.2) requires considerable energy. Nevertheless, reacting $\text{SO}_3(\text{g})$ with strong sulfuric acid is the most economic way of producing $\text{H}_2\text{SO}_4$.

![Acid pump](https://www.lewispumps.com)

**Fig. 9.2.** Acid pump, courtesy Lewis Pumps www.lewispumps.com A submerged impeller (right) draws acid in through the bottom mouth and pumps it up the up-leg (left). A pipe extension is bolted to the top of the up-leg to get the acid to its destination. The motor and motor-shaft connection are well above the acid. Details:

- design flowrate: 20 $\text{m}^3$ of acid per minute
- pump speed: 1775 RPM
- suction mouth diameter: 0.3 m
- materials: impeller - Lewmet®, shaft - Alloy 20; suction head and discharge pipe - L14 iron.

- pumping height: 23 m
- motor: 135 kW
- up-leg diameter: 0.3 m
9.3 Industrial H₂SO₄ Making (Table 9.3)

Industrial H₂SO₄ making is similar to the air/gas dehydration process described in Chapter 6. In both cases, gas is passed upwards through descending strong sulfuric acid, Figs. 6.3 and 9.1. The difference is that:

\[
\text{air/gas dehydration reacts } H₂O(\ell) \text{ with } H₂SO₄(\ell) \text{ in descending acid, i.e.}:
\]

\[
\begin{align*}
  H₂O(\ell) + H₂SO₄(\ell) & \rightarrow H₂SO₄(\ell) + H₂O(\ell) \\
  \text{in strong acid} & \rightarrow \text{slightly weakened acid}
\end{align*}
\]

while:

\[
\text{H₂SO₄ making reacts } SO₃(\ell) \text{ with the } H₂O(\ell) \text{ in descending acid, i.e.}:
\]

\[
\begin{align*}
  SO₃(\ell) + H₂O(\ell) & \rightarrow H₂SO₄(\ell) \\
  \text{in strong sulfuric acid} & \rightarrow \text{slightly strengthened acid}
\end{align*}
\]

Gas dehydration dilutes the input acid while H₂SO₄ making strengthens it. Both reactions are exothermic. Both heat up their circulating acid so that it must be cooled before being recycled or sent to storage.

9.3.1 Residence times

Table 9.3 indicates that typical H₂SO₄ making ('absorption') tower diameters, packing heights, and residence times are:

\[
\begin{align*}
  \text{tower diameter, m} & \quad 7-9 \text{ meters} \\
  \text{packing height, m} & \quad 2-4 \text{ meters} \\
  \text{gas residence time in packing} & \quad 2-4 \text{ seconds} \\
  \text{acid residence time in packing} & \quad 300-600 \text{ seconds}
\end{align*}
\]

These residence times give 99+% transformation of SO₃(\ell) to H₂SO₄(\ell).

9.3.2 Acid mist

Air/gas dehydration (Chapter 6) produces fine spray of 10-250 μm diameter acid droplets. The droplets are removed from the dehydrated gas to prevent downstream corrosion. They are usually captured in a knitted Teflon®/stainless steel pad at the gas exit, Fig. 6.3.

H₂SO₄ making also produces this spray. In addition, SO₃(\ell) in ascending gas and H₂O vapor from descending acid react to form very fine (<10μm diameter) acid droplets (mist). This mist must also be prevented from leaving in H₂SO₄ making exit gas.

It is most often removed by 'candle' filters suspended near the gas exit, Fig. 9.3 (Brink, 2005; Friedman and Friedman, 2004). These 'candles' remove 99+ % of spray and mist.
Fig. 9.3. Acid mist removal 'candle' filter being installed atop a stainless steel H₂SO₄ making tower. It is one of many. Exiting gas passes inward through the candle fabric and out the top of the candle — then out of the tower. The acid mist is caught in the candle fabric by impact, diffusion and Brownian forces (Brink, 2005; Friedman and Friedman, 2004; Lee and Byszewski, 2005; Ziebold and Azwell, 2005). The large total area of the candles gives a low gas velocity through the fabric, which allows 99+% capture of the mist. The captured mist trickles down the fabric and drips back into the tower or into collection pipes (Outokumpu 2005).
9.4 Choice of Input and Output Acid Compositions

Industrial input and output acid compositions are typically:

input: 98.5 mass% H$_2$SO$_4$, 1.5 mass% H$_2$O

output: 98.8 to 99.6 mass% H$_2$SO$_4$, remainder H$_2$O, Table 9.3.

These compositions are chosen to avoid excessive:

(a) acid mist formation

(b) SO$_3$(g) and H$_2$SO$_4$(g) evolution.

Acid mist formation is minimized by minimizing H$_2$O vapor pressure. This is done by using high H$_2$SO$_4$, low H$_2$O acid, Fig. 9.4.

SO$_3$(g) and H$_2$SO$_4$(g) evolution is, on the other hand, minimized by using low H$_2$SO$_4$ acid, Fig.9.4.

Section 9.4’s industrial acid compositions strike a balance between these opposing effects.

Fig. 9.4. Equilibrium vapor pressures of H$_2$O, H$_2$SO$_4$ and SO$_3$ over sulfuric acid, 353 K (Perry and Green, 1997). H$_2$O vapor pressure decreases and H$_2$SO$_4$ and SO$_3$ vapor pressures increase with increasing H$_2$SO$_4$-in-acid. All vapor pressures increase with increasing temperature, not shown.
9.5 Acid Temperature

Industrial \( \text{H}_2\text{SO}_4 \) making input and output acid temperatures (Table 9.3) are typically:

\[
\text{input acid temperature} = -350 \text{ K} \\
\text{output acid temperature} = -380 \text{ K}.
\]

They are high enough to give:

rapid \( \text{H}_2\text{SO}_4 \) making, Reaction (1.2)

while avoiding:

excessive \( \text{H}_2\text{O(g)} \), \( \text{SO}_3(g) \) and \( \text{H}_2\text{SO}_4(g) \) formation
(which increases with increasing acid temperature).

9.5.1 Acid temperature control

Input acid temperature is controlled by indirect water cooling in an acid cooler, Figs. 9.5 and 24.6.

Output acid temperature is controlled by adjusting the \( \text{H}_2\text{SO}_4 \) making tower's:

\[
\text{acid input rate} \\
\text{gas input rate}
\]

ratio. Increasing the ratio results in cooler output acid and vice versa.

9.6 Gas Temperatures

Gas enters industrial \( \text{H}_2\text{SO}_4 \) making towers at 450-500 K. This is hot enough to avoid \( \text{H}_2\text{SO}_4(\ell) \) condensation in the flues between catalytic \( \text{SO}_2 \) oxidation and \( \text{H}_2\text{SO}_4 \) making. It is cool enough to avoid excessive acid mist formation.

Gas leaves \( \text{H}_2\text{SO}_4 \) making near the acid input temperature, 350 K. Corrosive \( \text{H}_2\text{SO}_4(\ell) \) may condense from this gas in cool downstream flues. For this reason, the flues are usually made of stainless steel.

9.7 Operation and Control

9.7.1 Startup and shutdown

\( \text{H}_2\text{SO}_4 \) making is started by:

(a) pumping strong acid around the Fig. 9.1 circuit at its design rate

(b) initiating \( \text{SO}_3 \) gas production as described in Section 7.6.1

(c) blowing the \( \text{SO}_3 \) bearing gas into Fig. 9.1's packed bed
Fig. 9.5. Acid cooler, courtesy Chemetics www.chemetics.com Cool water flows through 1610 internal 2 cm diameter tubes while warm acid flows counter currently (and turbulently) between the tubes. The tubes are 316L stainless steel. They are resistant to water-side corrosion. They are electrochemically passivated against acid-side corrosion by continuously applying an electrical potential between the tubes and several electrically isolated metal rods. Details: shell diameter 1.65 m; shell material: 304L stainless steel; acid flow: 2000 m³/hour; water flow: 2900 m³/hour; acid temperature drop: 40 K. (Green pipes = water; metallic pipes = acid.) Fig. 24.6 gives an internal view.

(d) starting acid cooling

(e) adjusting acid and dilution flows to match H₂SO₄ production rate.

It is stopped by:

(a) stopping SO₃ gas production, Section 7.6.4

(b) shutting down (i) acid cooling and (ii) dilution and product acid flows.

Acid circulation through the H₂SO₄ making tower is continued during plant shutdowns. This maintains controlled corrosion conditions in pipes, pumps, coolers and the H₂SO₄ making tower.
9.7.2 Steady Operation and Control

Steady operation of an H₂SO₄ making tower consists of:

(a) steadily producing SO₃ bearing gas at its prescribed rate, composition and temperature, Section 7.6.2
(b) blowing this gas steadily into the Fig. 9.1 H₂SO₄ making tower
(c) steadily circulating strong acid through the tower at its prescribed rate, composition and temperature
(d) adjusting acid circulation rate to give the prescribed output 99 to 99.5 mass% H₂SO₄ acid
(e) cooling the circulating acid and product acid to their prescribed temperatures.

Table 9.1 describes measurements and adjustments that are used to control the process.

Table 9.1. Sensors and adjustments for controlling H₂SO₄ making packed tower. All sensors are placed in ceramic shield tubes to prevent corrosion.

<table>
<thead>
<tr>
<th>Adjustable parameter</th>
<th>On-line sensor</th>
<th>Method of adjustment</th>
</tr>
</thead>
<tbody>
<tr>
<td>input gas temperature</td>
<td>thermocouple</td>
<td>adjust after-catalytic-oxidation gas cooler bypass valve</td>
</tr>
<tr>
<td>input acid composition</td>
<td>'speed of sound through acid' meter (Mesa Labs, 2005)</td>
<td>adjust dilution water input rate</td>
</tr>
<tr>
<td>input acid temperature</td>
<td>thermocouple</td>
<td>adjust acid cooler bypass valve</td>
</tr>
</tbody>
</table>
| output acid composition    | 'speed of sound through acid' meter (Mesa Labs, 2005) | adjust H₂SO₄ making tower acid circulation rate at constant gas input rate
| output acid temperature    | thermocouple                        | adjust H₂SO₄ making tower acid circulation rate at constant gas input rate

# Output acid composition and temperature are not independent variables.

9.8 Double Contact H₂SO₄ Making (Tables 19.3, 23.2)

Fig. 9.6 is a flowsheet for double contact H₂SO₄ making. It shows:

(a) catalytic oxidation of most of the feed gas’s SO₂ to SO₃ in 3 catalyst beds, Reaction (1.1)

then:

(b) intermediate H₂SO₄ making by contact of step (a)’s SO₃ bearing product gas with strong sulfuric acid, Reaction (1.2)

then:

(c) catalytic oxidation of the SO₂ not oxidized by step (a)
Fig. 9.6. Double contact H₂SO₄ making flowsheet. The two H₂SO₄ making packed towers are notable. The left half of the flowsheet oxidizes most of the SO₂-in-feed-gas and makes the product SO₃(g) into strengthened sulfuric acid. It makes about 95% of the plant's new H₂SO₄. The right half of the flowsheet oxidizes almost all the remaining SO₂ and makes its product SO₃(g) into strengthened sulfuric acid. The final exit gas is very dilute in SO₂. Industrially, all the catalyst beds are in the same 'converter', Fig. 7.7. Table 23.2 gives industrial final H₂SO₄ making data.
then:

(d) final H₂SO₄ making by contacting step (c)’s SO₃ bearing gas with strong sulfuric acid in a second H₂SO₄ making tower.

9.8.1 Double contact advantages

Double contact acidmaking oxidizes its SO₂ more completely to SO₃ than single contact acidmaking. For this reason it:

(a) makes H₂SO₄ more efficiently
(b) emits less SO₂ to the environment.

The more efficient SO₂ oxidation is due not only to Fig. 9.6's extra catalyst bed, but also to the fact that:

virtually all of the SO₃ produced in the first three catalyst beds is removed from the gas in the first H₂SO₄ making tower.

The latter causes SO₂ + ½O₂ → SO₃ oxidation to go almost to completion in the after intermediate H₂SO₄ making catalyst bed, Chapter 19.

9.9 Intermediate vs. Final H₂SO₄ Making

Table 9.2 compares intermediate and final H₂SO₄ making. Notably, final contact input gas contains little SO₃ and produces little new H₂SO₄. Also final contact’s output acid gains little strength. Otherwise the processes are quite similar.

Table 9.2. Comparison of Fig. 9.6’s intermediate and final H₂SO₄ making towers. Note that final contact H₂SO₄ making makes only about 5% of the plant’s H₂SO₄.

<table>
<thead>
<tr>
<th>Quantities</th>
<th>Intermediate contact, Table 9.3</th>
<th>Final contact, Table 23.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>tower diameter, m</td>
<td>7-9</td>
<td>7-9</td>
</tr>
<tr>
<td>packed bed height, m</td>
<td>2½-5</td>
<td>2½-6</td>
</tr>
<tr>
<td>input gas</td>
<td></td>
<td></td>
</tr>
<tr>
<td>volume% SO₃</td>
<td>8-12</td>
<td>0.4-0.7</td>
</tr>
<tr>
<td>temperature, K</td>
<td>440-490</td>
<td>410-460</td>
</tr>
<tr>
<td>input acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>mass% H₂SO₄</td>
<td>98.5</td>
<td>98.5 or slightly less</td>
</tr>
<tr>
<td>temperature, K</td>
<td>340-355</td>
<td>330-355</td>
</tr>
<tr>
<td>output gas</td>
<td></td>
<td></td>
</tr>
<tr>
<td>temperature, K</td>
<td>340-355</td>
<td>330-355</td>
</tr>
<tr>
<td>output acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>mass% H₂SO₄</td>
<td>0.6% more than input acid</td>
<td>0.1% more than input acid</td>
</tr>
<tr>
<td>temperature, K</td>
<td>~30 K more than input acid</td>
<td>~20 K more than input acid</td>
</tr>
<tr>
<td>gas input rate, thousand Nm³/hr</td>
<td>100-250</td>
<td>~10% less than intermediate</td>
</tr>
<tr>
<td>acid input rate, m³/hour</td>
<td>800-1700</td>
<td>500-1100</td>
</tr>
<tr>
<td>H₂SO₄ production</td>
<td>~95%</td>
<td>~5%</td>
</tr>
</tbody>
</table>
Table 9.3. Details of packed bed H₂SO₄-from-SO₃ plants. The data are for

<table>
<thead>
<tr>
<th>Plant</th>
<th>S1 (double contact)</th>
<th>M2 (double contact)</th>
</tr>
</thead>
<tbody>
<tr>
<td>acid production, tonnes H₂SO₄/day</td>
<td>4400</td>
<td>1150</td>
</tr>
<tr>
<td>input gas flowrate, thousand Nm³/hour</td>
<td>336</td>
<td>121</td>
</tr>
<tr>
<td>estimated SO₃ utilization efficiency</td>
<td>99.9</td>
<td></td>
</tr>
</tbody>
</table>

**Packed bed details**

<table>
<thead>
<tr>
<th></th>
<th>2</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>number of packed beds</td>
<td></td>
<td></td>
</tr>
<tr>
<td>height × diameter, m</td>
<td>23.0 × 9.5</td>
<td>18.5 × 6.5</td>
</tr>
<tr>
<td>construction material</td>
<td>310/304 stainless steel</td>
<td>brick lined carbon steel</td>
</tr>
<tr>
<td>ceramic packing</td>
<td>7.5 cm saddles</td>
<td>5.1 &amp; 7.6 cm saddles</td>
</tr>
<tr>
<td>packing height, m</td>
<td>2.125</td>
<td>4</td>
</tr>
<tr>
<td>acid distributor type</td>
<td>trough and downcomer</td>
<td>buried pipe distributor</td>
</tr>
<tr>
<td>mist eliminator type</td>
<td>ES mist eliminator candles</td>
<td>hanging fiber bed</td>
</tr>
<tr>
<td>exit gas mist concentration, g/Nm³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>acid flowrate, m³/hour</td>
<td>1349</td>
<td>762</td>
</tr>
</tbody>
</table>

**Temperature data, K**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>inlet gas</td>
<td>439</td>
</tr>
<tr>
<td>outlet gas</td>
<td>344</td>
</tr>
<tr>
<td>inlet acid</td>
<td>339</td>
</tr>
<tr>
<td>outlet acid</td>
<td>485</td>
</tr>
<tr>
<td>acid cooling method</td>
<td>heat recovery system boilers</td>
</tr>
</tbody>
</table>

**Gas composition in, vol.%**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₃</td>
<td>11.8</td>
</tr>
<tr>
<td>SO₂</td>
<td>0.688</td>
</tr>
<tr>
<td>O₂</td>
<td>3.78</td>
</tr>
<tr>
<td>CO₂</td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>83.7</td>
</tr>
</tbody>
</table>

**Gas composition out, vol.%**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₃</td>
<td>0.78</td>
</tr>
<tr>
<td>SO₂</td>
<td>4.28</td>
</tr>
<tr>
<td>O₂</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>94.9</td>
</tr>
</tbody>
</table>

**Acid comp., mass% H₂SO₄**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>into tower</td>
<td>98.5</td>
</tr>
<tr>
<td>out of tower</td>
<td>99.6</td>
</tr>
</tbody>
</table>

**Acid plant products, mass% H₂SO₄**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>98.5</td>
</tr>
</tbody>
</table>
single contact plants or first (intermediate) contact in double contact plants.

<table>
<thead>
<tr>
<th>Cumerio 1 (double contact)</th>
<th>Cumerio 2 (double contact)</th>
<th>M5 (single contact)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1940</td>
<td>1500</td>
<td>52</td>
</tr>
<tr>
<td>160</td>
<td>150</td>
<td>99.98</td>
</tr>
<tr>
<td>99.98</td>
<td>99.98</td>
<td></td>
</tr>
</tbody>
</table>

| 1                       | 1                        | 1                   |
| 19.174 × 7              | 25.13 × 7                | 13 × 6.5            |
| brick lined carbon steel | brick lined carbon steel |                      |
| 7.6 & 5.1 cm saddles    | 5.1 cm saddles           |                     |
| 3.5                     | 8.5                      |                     |
| Lurgi pipes and tubes   | distribution plates      |                     |
| high efficiency candles | candle type              |                     |

| 1093                     | 950                       | 684                 |
| 487                      | 473                       | 540                 |
| 355                      | 343                       | 328                 |
| 355                      | 343                       | 338                 |
| 384                      | 373                       | 358                 |
| shell and tube           | shell and tube            | shell and tube      |

| 11.47                    | 10.08                     | 8.05                |
| 0.51                     | 0.42                      | 0.61                |
| 7.37                     | 5.67                      | 7.2                 |
| 0.32                     | 0.28                      | 6.92                |
| 80.33                    | 83.55                     |                     |

| 0                        | 0                         | 0.13                |
| 0.57                     | 0.45                      | 0.66                |
| 8.33                     | 6.31                      | 7.82                |
| 0.36                     | 0.31                      | 7.52                |
| 90.74                    | 92.93                     |                     |

tail gas scrubbed with ammonia

| 98.5                     | 98.3                      |
| 94-98.5                  | 94-98.5                   |
Table 9.3 (cont.). Details of packed bed H$_2$SO$_4$-from-SO$_3$ plants. The data are for

<table>
<thead>
<tr>
<th>Plant</th>
<th>M6 (double contact)</th>
<th>M3 (single contact)</th>
</tr>
</thead>
<tbody>
<tr>
<td>acid production,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>tonnes H$_2$SO$_4$/day</td>
<td>2200 (nominal)</td>
<td></td>
</tr>
<tr>
<td>input gas flowrate,</td>
<td>150-210</td>
<td>184</td>
</tr>
<tr>
<td>thousand Nm$^3$/hour</td>
<td></td>
<td></td>
</tr>
<tr>
<td>estimated SO$_3$ utilization efficiency</td>
<td>96</td>
<td></td>
</tr>
</tbody>
</table>

**Packed bed details**

| number of packed beds | 1 | 1 |
| height * diameter, m  | 23.3 x 6.8 | 12.2 x 7.8 OD |
| construction material | brick lined carbon steel | ASTM A 283 Grade C |
| ceramic packing packing height, m | 3.7 | 4 |
| acid distributor type | high efficiency candles | Lurgi spray |
| mist eliminator type | suspended candles |                     |
| exit gas mist concentration, g/Nm$^3$ | 0.035 |                     |
| acid flowrate, m$^3$/hour | 1150 top, 517 bottom | 3132 |

**Temperature data, K**

| inlet gas | 505 | 473 |
| outlet gas | 350 | 335 |
| inlet acid | 350 | 335 |
| outlet acid | 383 | 364 |
| acid cooling method | shell and tube | plate coolers |

**Gas composition in, vol.%**

| SO$_3$ | 12.1 | 11.44 |
| SO$_2$ | 0.5  | 0.23  |
| O$_2$  | 12   | 9.61  |
| CO$_2$ | 1.94 | remainder |
| N$_2$  | remainder | remainder |

**Gas composition out, vol.%**

| SO$_3$ | <35mg/Nm$^3$ |
| SO$_2$ | 0.56 <0.4 |
| O$_2$  | 13.6 10.85 |
| CO$_2$ | remainder 2.18 |
| N$_2$  | no tail gas scrubbing |

**Acid comp., mass% H$_2$SO$_4$**

| into tower | 98.5 |
| out of tower | 99.1 |

**Acid plant products, mass% H$_2$SO$_4$**

| 93, 99, 20% oleum$^#$ | 97.98 |

$^#$Liquid H$_2$SO$_4$ with dissolved 20 mass% dissolved SO$_3$, Chapter 19.
single contact plants or first (intermediate) contact in double contact plants.

<table>
<thead>
<tr>
<th></th>
<th>M4 (double contact)</th>
<th>Asarco Hayden (double contact)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2100-2400</td>
<td>1630</td>
</tr>
<tr>
<td></td>
<td>178</td>
<td>192</td>
</tr>
<tr>
<td></td>
<td>99.9</td>
<td>99</td>
</tr>
<tr>
<td>1</td>
<td>20.4 × 7.5 OD</td>
<td>17.8 × 7.0</td>
</tr>
<tr>
<td></td>
<td>brick lined carbon steel</td>
<td>brick lined carbon steel</td>
</tr>
<tr>
<td></td>
<td>5.1 and 7.6 cm saddles</td>
<td>7.6 cm ceramic saddles</td>
</tr>
<tr>
<td></td>
<td>5.66</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>submerged distributor pipes</td>
<td>Z core</td>
</tr>
<tr>
<td></td>
<td>Alloy 66 + Teflon</td>
<td>energy saver candles</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1280</td>
<td>1295</td>
</tr>
<tr>
<td></td>
<td>488</td>
<td>470</td>
</tr>
<tr>
<td></td>
<td>343</td>
<td>355</td>
</tr>
<tr>
<td></td>
<td>343</td>
<td>355</td>
</tr>
<tr>
<td></td>
<td>373</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.9-13.3</td>
<td>12.1</td>
</tr>
<tr>
<td></td>
<td>0.7-1.0</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>7.5-8.6</td>
<td>7.1</td>
</tr>
<tr>
<td></td>
<td>2.9</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>remainder</td>
<td>79.1</td>
</tr>
<tr>
<td></td>
<td>0.8-1.2</td>
<td>0.69</td>
</tr>
<tr>
<td></td>
<td>8.4-9.9</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>3.3</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>remainder</td>
<td>90.0</td>
</tr>
<tr>
<td></td>
<td>98.5</td>
<td>98.5</td>
</tr>
<tr>
<td></td>
<td>98.5</td>
<td>98.8</td>
</tr>
<tr>
<td></td>
<td>98.5</td>
<td>93/98</td>
</tr>
</tbody>
</table>
Table 9.3 (cont.). Details of packed bed H₂SO₄-from-SO₃ plants. The data are for Phelps Dodge (double contact) M1 (double contact) acid production, tonnes H₂SO₄/day input gas flowrate, thousand Nm³/hour estimated SO₃ utilization efficiency

<table>
<thead>
<tr>
<th>Plant</th>
<th>Phelps Dodge (double contact)</th>
<th>M1 (double contact)</th>
</tr>
</thead>
<tbody>
<tr>
<td>酸生产, 吨 H₂SO₄/日</td>
<td>2400</td>
<td>270</td>
</tr>
<tr>
<td>进口气流量, 千立方米/小时</td>
<td>267</td>
<td>46-51</td>
</tr>
<tr>
<td>SO₃利用率</td>
<td>99.9</td>
<td>99.9</td>
</tr>
</tbody>
</table>

### Packed bed details

- **number of packed beds**: 1
- **height * diameter, m**: 22.3 x 9.5 inside brick, 8.5 x 4.0
- **construction material**: brick lined carbon steel, brick lined carbon steel
- **ceramic packing**: 5.1 and 7.6 cm saddles, 7.6 cm saddles
- **acid distributor type**: cast iron header and arms, trough and spouts
- **mist eliminator type**: high efficiency candles, HE candles
- **acid mist concentration, g/Nm³**: 4.6
- **exit gas flowrate, m³/hour**: 1680, 227

### Temperature data, K

<table>
<thead>
<tr>
<th></th>
<th>Phelps Dodge (double contact)</th>
<th>M1 (double contact)</th>
</tr>
</thead>
<tbody>
<tr>
<td>进口气温</td>
<td>483</td>
<td>472-494</td>
</tr>
<tr>
<td>出口气温</td>
<td>353</td>
<td>339-366</td>
</tr>
<tr>
<td>进酸温</td>
<td>353</td>
<td>347-358</td>
</tr>
<tr>
<td>出酸温</td>
<td>389</td>
<td>358-375</td>
</tr>
<tr>
<td>酸冷却方法</td>
<td>acid coolers</td>
<td>shell and tube</td>
</tr>
</tbody>
</table>

### Gas composition in, vol.%

<table>
<thead>
<tr>
<th></th>
<th>Phelps Dodge (double contact)</th>
<th>M1 (double contact)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₃</td>
<td>10.38</td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>0.66</td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>5.85</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>82.05</td>
<td></td>
</tr>
</tbody>
</table>

### Gas composition out, vol.%

<table>
<thead>
<tr>
<th></th>
<th>Phelps Dodge (double contact)</th>
<th>M1 (double contact)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₃</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>0.74</td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>6.53</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>1.17</td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>91.52</td>
<td></td>
</tr>
</tbody>
</table>

### Acid comp., mass% H₂SO₄

<table>
<thead>
<tr>
<th></th>
<th>Phelps Dodge (double contact)</th>
<th>M1 (double contact)</th>
</tr>
</thead>
<tbody>
<tr>
<td>进到塔</td>
<td>98.5</td>
<td>98.5</td>
</tr>
<tr>
<td>出到塔</td>
<td>99.23</td>
<td>99.2</td>
</tr>
</tbody>
</table>

### Acid plant products, mass% H₂SO₄

<table>
<thead>
<tr>
<th></th>
<th>Phelps Dodge (double contact)</th>
<th>M1 (double contact)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>94.5</td>
<td>93.5</td>
</tr>
</tbody>
</table>
single contact plants or first (intermediate) contact in double contact plants.

<table>
<thead>
<tr>
<th>S2 (single contact)</th>
<th>SP1 (single contact)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1800</td>
<td>444</td>
</tr>
<tr>
<td>210</td>
<td></td>
</tr>
<tr>
<td>99.9</td>
<td>&gt;99.99</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>1</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>11 × 7</td>
<td>7.6 × 4</td>
</tr>
<tr>
<td>brick lined carbon steel</td>
<td>brick lined carbon steel</td>
</tr>
<tr>
<td>5.1-7.6 cm saddles</td>
<td>5.1 cm and 7.6 cm intalox</td>
</tr>
<tr>
<td>4</td>
<td>3.8</td>
</tr>
<tr>
<td>cast iron trough and spouts</td>
<td>candles</td>
</tr>
<tr>
<td>high efficiency candles</td>
<td>0.0125 g/Nm³</td>
</tr>
</tbody>
</table>

| 505 | 405 |
| 358 | 356 |
| 358 | 356 |
| 389 | 378 |
| shell and tube |

| 8.18 | 9.02 |
| 0.15 | 0.19 |
| 9.44 | 7.13 |
| 0 | 7.74 |
| 82.23 | 75.92 |

<0.1
0.17
10.27

| 89.56 |
| no tail gas scrubbing |

| 98.5 | 98.29 |
| 99.1 | 98.75 |

93, 98, 99, oleum

#Liquid H₂SO₄ containing dissolved SO₃, Chapter 19.
9.10 Summary

The final step in sulfuric acid manufacture is production of $\text{H}_2\text{SO}_4(\ell)$ from $\text{SO}_3$ bearing gas.

The $\text{H}_2\text{SO}_4$ is made by trickling strong sulfuric acid down between ceramic saddles in a packed bed while blowing $\text{SO}_3$ gas up through the bed.

$\text{SO}_3(\text{g})$ in the ascending gas reacts with $\text{H}_2\text{O}(\ell)$ in the descending acid to produce strengthened sulfuric acid, i.e.:

\[
\text{SO}_3(\text{g}) + \text{H}_2\text{O}(\ell) \rightarrow \text{H}_2\text{SO}_4(\ell)
\]

350-380 K

in $\text{SO}_3$, $\text{SO}_2$, $\text{O}_2$, $\text{N}_2$ gas

$\text{H}_2\text{SO}_4$, 1.5 mass% sulfuric acid

in 98.5 mass% strengthened $\text{H}_2\text{SO}_4$, $\text{H}_2\text{O}$ sulfuric acid

The strengthened acid is mostly diluted and sold.

Most sulfuric acid plants are double contact plants, Fig. 9.6, Tables 9.3, 19.3 and 23.2. They efficiently oxidize their feed $\text{SO}_2(\text{g})$ to $\text{SO}_3(\text{g})$ and efficiently make the resulting $\text{SO}_3(\text{g})$ into $\text{H}_2\text{SO}_4(\ell)$. Single contact plants (Fig. 9.1) are simpler and cheaper – but less efficient.

Suggested Reading


References


This page marks the end of the descriptive section of our book – and the beginning of
the mathematical section.

Most of the mathematical chapters analyze catalytic $\text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{SO}_3$ oxidation in
single and double contact acid plants. The remainder examine temperature control and
$\text{H}_2\text{SO}_4$ making.

Many of the chapters have problems after their chapter summaries. The problems are
not crucial to understanding the concepts in the chapters. They may, however, be useful
for learning how our calculations can be extended to control and optimization of
industrial acidmaking.

Many of the chapters also refer to appendices, which:

(a) derive equations
(b) provide thermodynamic data
(c) give calculation instructions.

The chapters can be understood without reference to these appendices. The appendices
will, however, be useful for readers who wish to derive the book's equations or do its
problems.
CHAPTER 10

Oxidation of SO$_2$ to SO$_3$ – Equilibrium Curves

Catalytic oxidation of SO$_2$ to SO$_3$:

$$\text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{SO}_3(\text{g}) \quad (1.1)$$

is a key step in sulfuric acid production. It makes SO$_3$ for subsequent H$_2$SO$_4$(l) making.

This chapter describes the equilibrium thermodynamics of Reaction (1.1). Its objectives are to:

(a) determine the maximum extent to which SO$_2$ in acid plant feed gas can be oxidized in a catalyst bed

(b) describe the factors which affect this maximum, specifically catalyst bed feed gas composition and equilibrium temperature and pressure.

The chapter concludes that maximum industrial SO$_2$ oxidation is achieved when Reaction (1.1):

(a) proceeds by rapid catalytic oxidation

(b) approaches equilibrium at a low temperature (but warm enough for rapid catalytic oxidation).

This is the basis of all industrial acid plant designs.

10.1 Catalytic oxidation

All industrial SO$_2$ oxidation is done in contact with V, alkali metal, S, O, SiO$_2$ catalyst, Chapters 7 and 8.
Fig. 10.1 shows a catalyst bed and describes SO₂ oxidation in it. SO₂ is oxidized by O₂ as feed gas descends through the catalyst bed. This is indicated by an increasing % SO₂ oxidized on the left graph.

SO₂, O₂ and SO₃ approach equilibrium as the gas descends the catalyst bed (left graph). % SO₂ oxidized at equilibrium is the maximum extent to which the feed SO₂ can be oxidized. As will be seen, this maximum depends on:

(a) equilibrium temperature
(b) equilibrium pressure
(c) feed gas composition, volume% SO₂, O₂, N₂

% SO₂ oxidized anytime anywhere in a catalyst bed is defined as:

\[
\% \text{SO}_2 \text{ oxidized} = \Phi = \frac{\text{kg-mole SO}_2 \text{ in feed gas} - \text{kg-mole SO}_2 \text{ in oxidized gas}}{\text{kg-mole SO}_2 \text{ in feed gas}} \times 100
\]  

(10.1)

where all the quantities are per kg-mole of feed gas.
A special case of this definition is:

\[
\text{Equilibrium } \% \text{SO}_2 \text{ oxidized } = \Phi^E = \frac{\text{kg-mole SO}_2 \text{ in oxidized gas} - \text{kg-mole SO}_2 \text{ in feed gas}}{\text{kg-mole SO}_2 \text{ in feed gas}} \times 100
\]

(10.2).

The Eqn. (10.2) definition is used in all our 1st catalyst bed equilibrium curve calculations.

Fig. 10.2 shows a typical equilibrium % SO\textsubscript{2} oxidized vs. temperature curve for the Fig. 10.1 catalyst bed. This chapter and Appendix D show how it is prepared.

**Fig. 10.2.** Percentage of SO\textsubscript{2}-in-feed-gas that is oxidized when equilibrium is attained in the Fig. 10.1 catalyst bed. The percentage increases with decreasing equilibrium temperature. The curve has been plotted from Eqn. (10.13) as described in Appendix D. It applies only to the specified conditions.

### 10.2 Equilibrium Equation

Fig. 10.1 indicates that maximum SO\textsubscript{2} oxidation is achieved when Reaction (1.1) comes to equilibrium. The next few sections show how this maximum is predicted.

The equilibrium equation for \( \text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{SO}_3 \) oxidation is:
\[ K_E = \frac{P_{SO_3}^E}{P_{SO_2}^E \left( P_{O_2}^E \right)^{1/2}} \]  

(10.3)

where:

\[ K_E = \text{equilibrium constant, dependent only on temperature (Gaskell, 1981),} \bar{p} \]

\[ P_{SO_2}^E, P_{O_2}^E, P_{SO_3}^E = \text{equilibrium partial pressures of SO}_2, \text{O}_2 \text{ and SO}_3, \text{bar.} \]

\[ P_{SO_2}^E, P_{O_2}^E \text{ and } P_{SO_3}^E \text{ in Eqn. (10.3) are related to gas composition by:} \]

\[ P_{SO_2}^E = X_{SO_2}^E \cdot P_t \]

(10.4)

\[ P_{O_2}^E = X_{O_2}^E \cdot P_t \]

(10.5)

\[ P_{SO_3}^E = X_{SO_3}^E \cdot P_t \]

(10.6)

where \( X^E \) is equilibrium mole fraction of each gas and \( P_t \) is total equilibrium gas pressure. Eqns. (10.4) to (10.6) assume ideal gas behavior (based on the low pressure, \(-1 \text{ bar, of industrial SO}_2 \text{ oxidation).} \)

Eqns. (10.3) to (10.6) combine to give:

\[ K_E = \frac{X_{SO_3}^E}{X_{SO_2}^E \cdot \left( X_{O_2}^E \right)^{1/2} \left( P_t \right)^{1/2}} \]

(10.7)

which indicates that equilibrium \( SO_2 \) oxidation (i.e. \( SO_3 \) production) increases with increasing \( K_E \) and \( P_t \).

10.3 \( K_E \) as a Function of Temperature

\( K_E \) in Eqn. (10.7) is related to equilibrium temperature by:

\[ \ln(K_E) = \frac{-\Delta G^o_T}{(R \cdot T_E)} \]

(10.8)

where \( \Delta G^o_T \) is the standard free energy change (MJ/kg-mole \( SO_2 \)) for \( SO_2 \) oxidation at equilibrium temperature \( T_E \).

Appendix C gives published \( \Delta G^o_T \) vs. temperature data. It shows that \( \Delta G^o_T \) may be related to temperature by:

\[ \Delta G^o_T = A \cdot T + B \]

(10.9)

where \( A \) and \( B \) are empirical constants.

Eqns. (10.8) and (10.9) combine to give:
\[
\ln(K_E) = \frac{-(A*T_E + B)}{(R*T_E)}
\]  \hspace{1cm} (10.10)

where:

\(K_E\) = equilibrium constant for Reaction (1.1), bar \(^{-\frac{1}{2}}\)

\(A\) and \(B\) = empirical constants for calculating \(\Delta G^o_T\) from \(T\), Eqn. (10.9) and Appendix C

\[A = 0.09357 \text{ MJ kg-mole SO}_2^{-1} K^{-1}\]
\[B = -98.41 \text{ MJ/kg-mole SO}_2\]

\(R\) = gas constant, 0.008314 MJ kg-mole SO\(_2\) \(K^{-1}\)

\(T_E\) = equilibrium temperature, K

Eqn. (10.10) rearranges to:

\[R*T_E*\ln(K_E) = -A*T_E - B\]

or:

\[A*T_E + R*\ln(K_E) * T_E = -B\]

or:

\[T_E = \frac{-B}{A + R*\ln(K_E)}\] \hspace{1cm} (10.11)

10.4 \(K_E\) in Terms of \%'SO\(_2\) Oxidized\)

Rewritten in terms of:

(a) Fig. 10.1 feed gas composition

(b) equilibrium \%'SO\(_2\) oxidized, \(\Phi^E\)

Eqn. 10.7 becomes (Appendix B):

\[K_E = \frac{\Phi^E}{100 - \Phi^E} * \left(\frac{100 - \frac{1}{2}e*\Phi^E}{100 - \frac{1}{2}f}\right)^{\frac{1}{2}} * P_t^{\frac{1}{2}}\] \hspace{1cm} (10.12)

where:

\(K_E\) = equilibrium constant for Reaction (1.1), bar \(^{-\frac{1}{2}}\)

\(\Phi^E\) = equilibrium \%'SO\(_2\) oxidized, Section 10.1.1

\(e\) = volume\%' SO\(_2\) in feed gas \(f\) remainder 'inerts', i.e. N\(_2\) and CO\(_2\)

\(P_t\) = total equilibrium gas pressure, bar.

\(\#\)The effect of SO\(_3\) in feed gas is described in Appendix P and Chapter 17.
This equation permits equilibrium % \( \text{SO}_2 \) oxidized \( (\Phi^E) \) to be calculated from equilibrium constant \( (K_E) \), input gas composition and equilibrium pressure. It combines (i) equilibrium thermodynamics and (ii) S and O mass balances. It is derived in Appendix B.

### 10.5 Equilibrium % \( \text{SO}_2 \) Oxidized as a Function of Temperature

Equilibrium % \( \text{SO}_2 \) oxidized \( (\Phi^E) \) is related to equilibrium temperature by combining Eqns. (10.11) and (10.12), which gives:

\[
T_E = \frac{-B}{A + R \ln \left( \frac{\Phi^E}{100 - \Phi^E} \right) \left( \frac{100 - \frac{1}{2} e^* \Phi^E}{100} \right)^{\frac{1}{2}} \left( \frac{1}{2} f - \frac{1}{2} e^* \Phi^E \right)^{\frac{1}{2}} p_t^{\frac{1}{2}}} \quad (10.13)
\]

where:

- \( T_E \) = equilibrium temperature
- \( A \) and \( B \) = empirical constants for calculating \( \Delta G^0 \) from \( T \), Eqn. 10.9
  - \( A = 0.09357; B = -98.41 \), Appendix C
- \( R \) = gas constant, 0.008314 MJ kg-mole \( \text{SO}_2^{-1} \) K\(^{-1}\)
- \( \Phi^E \) = equilibrium % \( \text{SO}_2 \) oxidized, Section 10.1.1
- \( e \) = volume% \( \text{SO}_2 \) in feed gas
- \( f \) = volume% \( \text{O}_2 \) in feed gas
- \( P_t \) = total equilibrium gas pressure, bar.

Fig. 10.2 plots this equation as described in Appendix D. The figure emphasizes that equilibrium % \( \text{SO}_2 \) oxidized increases with decreasing equilibrium temperature.

#### 10.5.1 Equilibrium pressure effect

Fig. 10.3 shows the effect of equilibrium pressure on equilibrium % \( \text{SO}_2 \) oxidized. Equilibrium % \( \text{SO}_2 \) oxidized increases slightly with increasing equilibrium pressure.

#### 10.5.2 \( \text{O}_2 \)-in-feed-gas effect

Fig. 10.4 shows the effect of volume% \( \text{O}_2 \) in feed gas on equilibrium % \( \text{SO}_2 \) oxidized.

The curves are for:

- (a) constant 10 volume% \( \text{SO}_2 \)-in-feed-gas
- (b) 8, 11 and 14 volume% \( \text{O}_2 \)-in-feed-gas
- (c) constant equilibrium pressure, \( P_t = 1.2 \) bar.
Equilibrium % $SO_2$ oxidized increases slightly with increasing volume% O$_2$ in feed gas. This is because a high volume% O$_2$•volume% SO$_2$ product pushes SO$_2$ oxidation to the right, Eqn. 10.7.

![Graph showing equilibrium % SO$_2$ oxidized versus equilibrium pressure and temperature.](image)

**Fig. 10.3.** Equilibrium % $SO_2$ oxidized as affected by equilibrium pressure, $P_e$. Equilibrium % $SO_2$ oxidized is seen to increase slightly with increasing pressure, Eqn. (10.7). Industrial catalyst bed pressures are typically 1 to 1.4 bar.

![Graph showing effect of feed gas O$_2$ concentration on equilibrium % SO$_2$ oxidized.](image)

**Fig. 10.4.** Effect of feed gas O$_2$ concentration on equilibrium % $SO_2$ oxidized. High O$_2$ concentration gives high equilibrium % $SO_2$ oxidized and vice versa.
10.5.3 $SO_2$-in-feed-gas effect

Fig. 10.5 shows the effect of volume% $SO_2$ in feed gas on equilibrium % $SO_2$ oxidized. The curves are for:

(a) 7, 10 and 13 volume% $SO_2$-in-feed-gas

(b) constant 1.1 volume% $O_2$/volume% $SO_2$ ratio in feed gas

(c) constant equilibrium pressure, $P_t = 1.2$ bar.

Equilibrium % $SO_2$ oxidized is seen to increase slightly with increasing volume% $SO_2$ in feed gas. This is because a high volume% $O_2$*volume% $SO_2$ product pushes $SO_2$ oxidation to the right, Eqn. 10.7.

![Graph showing the effect of $SO_2$ concentration on equilibrium $SO_2$ oxidized.

Fig. 10.5. Effect of feed gas $SO_2$ concentration on equilibrium % $SO_2$ oxidized. High $SO_2$ concentration gives high % $SO_2$ oxidized.

10.6 Discussion

The curves in Figs. 10.2 to 10.5 combine:

(a) equilibrium thermodynamics

(b) catalyst bed feed gas compositions

(c) S and O balances.
They are not exactly equilibrium curves because their position and shape depend on feed gas composition and equilibrium pressure. Their value is that they show the maximum extent to which SO$_2$ can be oxidized in a catalyst bed. They provide a visual picture of how catalytic SO$_2$ oxidation can be optimized.

This value becomes apparent when the equilibrium curves of this chapter are combined with the approach-to-equilibrium heatup paths of Chapters 11 and 12.

10.7 Summary

Catalytic SO$_2$(g) + $\frac{1}{2}$O$_2$(g) $\rightarrow$ SO$_3$(g) oxidation is a key step in sulfuric acid manufacture. It makes SO$_3$ for subsequent H$_2$SO$_4$ production, Reaction (1.2). Efficient SO$_2$ oxidation contributes to efficient acid production and small emission of SO$_2$.

Maximum SO$_3$ production is attained when SO$_2$ oxidation comes to equilibrium. Near-attainment of equilibrium is favored by sufficient gas residence time in highly reactive catalyst.

Maximum equilibrium SO$_3$ production is favored by a cool equilibrium temperature (but warm enough for rapid catalytic oxidation). Temperature exerts a much greater influence on this maximum than pressure or catalyst bed feed gas composition.

Reference


Problems

10.1 Feed gas containing:

10 volume% SO$_2$

11 volume% O$_2$

79 volume% N$_2$

is fed into the Fig. 10.1 catalyst bed. Its SO$_2$ reacts with its O$_2$ to produce SO$_3$. The SO$_2$, O$_2$ and SO$_3$ come to equilibrium at 1.2 bar total pressure as they leave the catalyst bed.

Chemical analysis of the catalyst bed's exit gas shows that 80% of the feed gas's SO$_2$ has been oxidized to SO$_3$.

At what temperature (K) has the feed gas come to equilibrium? Use Eqn. (10.13).
10.2 Re-do Problem 10.1 by means of an Excel calculation. Use Appendix D. Eqn. (10.13) is used for many calculations in this book. Once it is successfully entered into Excel, it is easily copied into future spreadsheets.

10.3 Problem 10.1's feed gas is fed to the Fig. 10.1 catalyst bed at a slightly cooler temperature. It comes to equilibrium at 840 K.

What percentage of the Problem 10.1 feed SO$_2$ will have been oxidized when equilibrium has been attained at 840 K?

Use the Goal Seek method described in Appendix D, Section D.1. If you wish, check your answer manually by putting your calculated % SO$_2$ oxidized in Eqn (10.13) to back-calculate equilibrium temperature.

10.4 Prepare a table of:

<table>
<thead>
<tr>
<th>equilibrium % SO$_2$ oxidized vs. equilibrium temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>points for 12 volume% SO$_2$, 13.2 volume% O$_2$, 74.8 volume% N$_2$ catalyst bed feed gas (1.2 bar equilibrium pressure).</td>
</tr>
</tbody>
</table>

Use Excel's Chart Wizard function to plot these points, as in Fig. 10.2.
CHAPTER 11

SO₂ Oxidation Heatup Paths

Chapter 10 describes equilibrium:

\[
\text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{SO}_3(g)
\]  

(1.1)

oxidation in a catalyst bed. It shows that maximum SO₂ oxidation is achieved by:

(a) rapid SO₂ oxidation in active V, alkali metal, S, O, SiO₂ catalyst

(b) a cool equilibrium temperature.

It does not, however, show where a feed gas's equilibrium point lies on its equilibrium curve. That is the task of this chapter and Chapter 12.

11.1 Heatup Paths

This chapter discusses catalytic SO₂ oxidation in terms of heatup paths.

Fig. 11.1 presents one such path. It shows the following.

(a) 10 volume% SO₂, 11 volume% O₂, 79 volume% N₂ is fed to a catalyst bed at 690 K. Zero % of its SO₂ is oxidized at this point.

(b) This gas passes down through the catalyst bed where its SO₂(g) is oxidized by its O₂(g) to give SO₃(g) + heat, Reaction (1.1). The heat from the SO₂ oxidation heats the gas above its 690 K input temperature.

(c) This SO₂ oxidation/temperature rise behavior is described by a heatup path, which is a plot of gas temperature vs % of feed SO₂ oxidized.

(d) Eventually, in a deep catalyst bed, the heatup path will meet Chapter 10's equilibrium curve, at which point no more SO₂ oxidation can take place, Chapter 12.
Feed gas
10 volume% SO₂
11 volume% O₂
79 volume% N₂
1.2 bar equilibrium pressure

Fig. 11.1. Heatup path for SO₂, O₂, N₂ gas descending a catalyst bed. The SO₂ and O₂ in feed gas react to form SO₃, Eqn. (1.1). The gas is heated by the exothermic heat of reaction. The result is a path with increasing % SO₂ oxidized and increasing gas temperature. Notice how the feed gas's heatup path approaches its Chapter 10 equilibrium curve.

11.2 Objectives

The objectives of the chapter are to:

(a) show how % SO₂ oxidized/gas temperature heatup paths are prepared

(b) describe the factors affecting heatup path positions and slopes

(c) indicate how heatup paths predict maximum (equilibrium) SO₂ oxidation.

11.3 Preparing a Heatup Path – the First Point

A point on Fig. 11.1’s heatup path is determined by:

(a) specifying feed gas composition and temperature, Fig. 11.2

(b) specifying a measured gas temperature part way down the catalyst bed (after some feed SO₂ has been oxidized and some heating has occurred), Fig. 11.2

(c) calculating the extent of SO₂ oxidation which corresponds to this measured temperature.
11.4 Assumptions

Our heatup path calculations assume that there is no transfer of heat between gas and reactor walls or between gas and catalyst. The result is, therefore, an adiabatic heatup path.

Specification that there is no heat transfer between gas and reactor walls assumes that the reactor is perfectly insulated.

Specification that there is no transfer of heat between gas and catalyst assumes that the process is proceeding at steady state, i.e. that compositions and temperatures at every position in the catalyst bed are constant with time.

11.5 A Specific Example

The following example problem shows how a heatup path point is determined. The problem is:

"10 volume\% \text{SO}_2, 11 \text{ volume}\% \text{O}_2, 79 \text{ volume}\% \text{N}_2 \text{ gas (690 K)} \text{ is being fed to the Fig. 11.2 catalyst bed.}

A thermocouple at level L in the catalyst bed indicates that the gas temperature there is 820 K.

What percent oxidation of Fig. 11.2's feed \text{SO}_2 \text{ gives} 820 \text{ K gas in the catalyst bed}?")
The following six sections show how this problem is solved.

![Diagram of catalyst bed and chemical reaction](image)

**Fig. 11.3.** Vertical segment of Fig. 11.2 catalyst bed over which the Section 11.8 and 11.9 mass and enthalpy balances are applied. Compositions and temperatures are assumed to be uniform horizontally at all levels.

### 11.6 Calculation Strategy

Fig. 11.3 shows the catalyst bed segment from top to level L. Our strategy for solving the Section 11.5 problem is to specify that 1 kg-mole of gas is fed into the top of this segment – and to calculate:

(a) the quantities of SO₂, O₂ and N₂ in this kg-mole of feed gas

(b) the quantities of SO₃, SO₂ and O₂ which correspond to level L’s measured 820 K gas temperature

(c) % SO₂ oxidized at 820 K, where:

\[
\%SO_2 \text{ oxidized} = \Phi = \frac{\text{kg-mole SO}_2 \text{ in feed gas} - \text{kg-mole SO}_2 \text{ in oxidized gas at level L}}{\text{kg-mole SO}_2 \text{ in feed gas}} \times 100
\]

Sulfur, oxygen, nitrogen and enthalpy balances are used. A matrix calculation is employed.

### 11.7 Input SO₂, O₂ and N₂ Quantities

The calculations of this chapter are all based on feeding 1 kg-mole of dry gas into the acid plant's first catalyst bed. The kg-mole of each component (e.g. SO₂) in this feed gas are calculated by equations like:
kg-mole SO₂ in = \frac{\text{mole}\% \text{ SO}_2}{100} \times 1 \text{ kg-mole of feed gas}

or, because \text{mole}\% = \text{volume}\%

\text{kg-mole SO}_2 \text{ in} = \frac{\text{volume}\% \text{ SO}_2}{100} \times 1 \text{ kg-mole of feed gas.}

Equations describing input kg-moles for the Section 11.5 problem (10 volume\% SO₂, 11 volume\% O₂, 79 volume\% N₂ feed gas) are, therefore:

\text{kg-mole SO}_2 \text{ in} = \frac{10 \text{ volume}\% \text{ SO}_2}{100} \times 1 \text{ kg-mole of feed gas} = 0.10 \hspace{1cm} (11.1)

\text{kg-mole O}_2 \text{ in} = \frac{11 \text{ volume}\% \text{ O}_2}{100} \times 1 \text{ kg-mole of feed gas} = 0.11 \hspace{1cm} (11.2)

\text{kg-mole N}_2 \text{ in} = \frac{79 \text{ volume}\% \text{ N}_2}{100} \times 1 \text{ kg-mole of feed gas} = 0.79 \hspace{1cm} (11.3)

11.8 Sulfur, Oxygen and Nitrogen Molar Balances

The next step in calculating a heatup path point is to develop steady state molar S, O and N balances for Fig. 11.3’s feed and level L gases.

11.8.1 Sulfur balance

The steady state sulfur molar balance for Fig. 11.3 is:

\text{kg-mole S in} = \text{kg-mole S out.}

Each mole of SO₂ and SO₃ contains 1 mole of S, so this expands to:

1*kg-mole SO₂ \text{ in} = 1*kg-mole SO₃ \text{ out} + 1*kg-mole SO₂ \text{ out}
or subtracting '1*kg-mole SO\textsubscript{2} in' from both sides:

\[
0 = -1*\text{kg-mole SO}_2 \text{ in} + 1*\text{kg-mole SO}_3 \text{ out} + 1*\text{kg-mole SO}_2 \text{ out} \tag{11.4}
\]

where \text{in} means into the top of the Fig. 11.3 segment and \text{out} means out of the segment at level L.

11.8.2 Oxygen molar balance

The steady state molar oxygen balance for the segment is:

\[
\text{kg-mole O in} = \text{kg-mole O out.}
\]

Each mole of SO\textsubscript{2} and O\textsubscript{2} contains 2 moles of O while each mole of SO\textsubscript{3} contains 3 moles of O, so this equation expands to:

\[
2*\text{kg-mole SO}_2 \text{ in} + 2*\text{kg-mole O}_2 \text{ in} = 3*\text{kg-mole SO}_3 \text{ out} + 2*\text{kg-mole SO}_2 \text{ out} + 2*\text{kg-mole O}_2 \text{ out}
\]

or, subtracting '2*kg-mole SO\textsubscript{2} in + 2*kg-mole O\textsubscript{2} in' from both sides:

\[
0 = -2*\text{kg-mole SO}_2 \text{ in} - 2*\text{kg-mole O}_2 \text{ in} + 3*\text{kg-mole SO}_3 \text{ out} + 2*\text{kg-mole SO}_2 \text{ out} + 2*\text{kg-mole O}_2 \text{ out} \tag{11.5}
\]

11.8.3 Nitrogen molar balance

The segment's steady state molar nitrogen balance is:

\[
\text{kg-mole N in} = \text{kg-mole N out.}
\]

Each mole of N\textsubscript{2} contains 2 moles of N, so this balance becomes:

\[
2*\text{kg-mole N}_2 \text{ in} = 2*\text{kg-mole N}_2 \text{ out}
\]

or, subtracting '2*kg-mole N\textsubscript{2} in' from both sides:

\[
0 = -2*\text{kg-mole N}_2 \text{ in} + 2*\text{kg-mole N}_2 \text{ out} \tag{11.6}
\]
11.9 Enthalpy balance

The steady state enthalpy balance for the Fig. 11.3 catalyst bed segment is:

\[
\text{enthalpy in} = \text{enthalpy out} + \text{conductive, convective plus radiative heat loss from the gas} \quad (11.6A).
\]

*Enthalpy in* for the segment is:

\[
\begin{align*}
\text{kg-mole SO}_2\text{ in} & \times H^o_{690} \\
+ \quad \text{kg-mole O}_2\text{ in} & \times H^o_{690} \\
+ \quad \text{kg-mole N}_2\text{ in} & \times H^o_{690}
\end{align*}
\]

where \(H^o_{690}\) is the enthalpy of \(SO_2\) (MJ/kg-mole) at the segment’s 690 K feed gas temperature (likewise for \(O_2\) and \(N_2\)).

Likewise, *enthalpy out* for the segment is:

\[
\begin{align*}
\text{kg-mole SO}_3\text{ out} & \times H^o_{820} \\
+ \quad \text{kg-mole SO}_2\text{ out} & \times H^o_{820} \\
+ \quad \text{kg-mole O}_2\text{ out} & \times H^o_{820} \\
+ \quad \text{kg-mole N}_2\text{ out} & \times H^o_{820}
\end{align*}
\]

where 820 K is the measured gas temperature at level L.

The final term in Eqn. (11.6A) is conductive, convective plus radiative heat loss from the gas. As discussed in section 11.3, it is assumed here to be zero, i.e.:
conductive, convective
plus radiative heat = 0.
loss from gas

This assumption is discussed further in Section 18.12.

With these three enthalpy components, the segment's enthalpy balance:

\[
\text{enthalpy in} = \text{enthalpy out} + \text{conductive, convective plus radiative heat loss from the gas}
\]

becomes:

\[
\left\{ \begin{array}{l}
\text{kg-mole SO}_2 \text{ in} \times H^\circ_{\text{SO}_2} \\
+ \\
\text{kg-mole O}_2 \text{ in} \times H^\circ_{\text{O}_2} \\
+ \\
\text{kg-mole N}_2 \text{ in} \times H^\circ_{\text{N}_2}
\end{array} \right\} = \left\{ \begin{array}{l}
\text{kg-mole SO}_3 \text{ out} \times H^\circ_{\text{SO}_3} \\
+ \\
\text{kg-mole SO}_2 \text{ out} \times H^\circ_{\text{SO}_2} \\
+ \\
\text{kg-mole O}_2 \text{ out} \times H^\circ_{\text{O}_2} \\
+ \\
\text{kg-mole N}_2 \text{ out} \times H^\circ_{\text{N}_2}
\end{array} \right\} + 0
\]

(11.6B).

11.9.1 Numerical enthalpy values

690 and 820 K SO\textsubscript{2}, O\textsubscript{2}, N\textsubscript{2} and SO\textsubscript{3} enthalpies are shown in Table 11.1.
Table 11.1. SO₂, O₂, N₂ and SO₃ enthalpy values (MJ/kg-mole) at 690 and 820 K. They have been calculated with the enthalpy equations in Appendix G.

<table>
<thead>
<tr>
<th>Compound and temperature</th>
<th>Enthalpy numerical value, MJ per kg-mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁰₆₉₀ SO₂</td>
<td>-278.7</td>
</tr>
<tr>
<td>H⁰₆₉₀ O₂</td>
<td>12.21</td>
</tr>
<tr>
<td>H⁰₆₉₀ N₂</td>
<td>11.66</td>
</tr>
<tr>
<td>H⁰₈₂₀ SO₃</td>
<td>-362.0</td>
</tr>
<tr>
<td>H⁰₈₂₀ SO₂</td>
<td>-272.0</td>
</tr>
<tr>
<td>H⁰₈₂₀ O₂</td>
<td>16.54</td>
</tr>
<tr>
<td>H⁰₈₂₀ N₂</td>
<td>15.71</td>
</tr>
</tbody>
</table>

With the Table 11.1 enthalpies, the Fig. 11.3 segment enthalpy balance becomes:

\[
\begin{align*}
\{ \text{kg-mole SO}_2 \text{ in} \} \cdot -278.7 & + \\
\{ \text{kg-mole O}_2 \text{ in} \} \cdot 12.21 & + \\
\{ \text{kg-mole N}_2 \text{ in} \} \cdot 11.66 & = \\
\{ \text{kg-mole SO}_3 \text{ out} \} \cdot -362.0 & + \\
\{ \text{kg-mole SO}_2 \text{ out} \} \cdot -272.0 & + \\
\{ \text{kg-mole O}_2 \text{ out} \} \cdot 16.54 & + \\
\{ \text{kg-mole N}_2 \text{ out} \} \cdot 15.71 & (11.7)
\end{align*}
\]

or:

\[
0 = - \{ \text{kg-mole SO}_2 \text{ in} \} \cdot -278.7 \\
- \{ \text{kg-mole O}_2 \text{ in} \} \cdot 12.21 \\
- \{ \text{kg-mole N}_2 \text{ in} \} \cdot 11.66 \\
+ \{ \text{kg-mole SO}_3 \text{ out} \} \cdot -362.0 \\
+ \{ \text{kg-mole SO}_2 \text{ out} \} \cdot -272.0 \\
+ \{ \text{kg-mole O}_2 \text{ out} \} \cdot 16.54 \\
+ \{ \text{kg-mole N}_2 \text{ out} \} \cdot 15.71
\]
11.10 Calculating Level L Quantities

The Section 11.5 problem has 7 variables:

\[
\begin{align*}
\text{kg-mole SO}_2 \text{ in} \\
\text{kg-mole O}_2 \text{ in} \\
\text{kg-mole N}_2 \text{ in} \\
\text{kg-mole SO}_3 \text{ out} \\
\text{kg-mole SO}_2 \text{ out} \\
\text{kg-mole O}_2 \text{ out} \\
\text{kg-mole N}_2 \text{ out}.
\end{align*}
\]

Sections 11.7-11.9 provide 7 linear equations (11.1-11.7), which must be satisfied by the values of these 7 variables. Each variable has, therefore, a unique value and the question:

'What percentage of Fig. 11.3's feed SO\textsubscript{2} has been oxidized to SO\textsubscript{3} when the gas has reached 820 K?'

has a unique solution, next section.

11.11 Matrix Calculation

The above question is answered by:

(a) entering Eqns. (11.1) to (11.7) in matrix form into an Excel worksheet, Table 11.2

(b) solving for the seven variables

(c) calculating \% SO\textsubscript{2} oxidized in Table 11.2's cell H17.

Matrix calculation instructions are given in Appendix H.
Table 11.2. Excel worksheet and matrix for determining Fig. 11.3’s 820 K (level L) gas quantities. 'In' refers to feed, 'out' refers to level L. The results are the only quantities that satisfy all the equations in the matrix. Cell H17 contains the equation above and beside it. The matrix has been solved as described in Appendix H. After an initial solving, a change in any matrix cell value causes automatic calculation of a new matrix result.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Equation</td>
<td>Description</td>
<td>numerical term</td>
<td>kg-mole SO₂</td>
<td>kg-mole O₂</td>
<td>kg-mole N₂</td>
<td>kg-mole SO₃</td>
<td>kg-mole SO₂</td>
<td>kg-mole O₂</td>
<td>kg-mole N₂</td>
</tr>
<tr>
<td>2</td>
<td>11.1</td>
<td>feed SO₂ kg-mole</td>
<td>0.10</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>11.2</td>
<td>feed O₂ kg-mole</td>
<td>0.11</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>11.3</td>
<td>feed N₂ kg-mole</td>
<td>0.79</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>11.4</td>
<td>S balance</td>
<td>0</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>11.5</td>
<td>O balance</td>
<td>0</td>
<td>-2</td>
<td>-2</td>
<td>0</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>11.6</td>
<td>N balance</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>11.7</td>
<td>enthalpy balance</td>
<td>0</td>
<td>278.7</td>
<td>-12.21</td>
<td>-11.66</td>
<td>-362.0</td>
<td>-272.0</td>
<td>16.54</td>
<td>15.71</td>
</tr>
</tbody>
</table>

690 K, feed

820 K, level L

11

12 Matrix results per kg-mole of feed gas

| 13 | kg-mole SO₂ in | 0.1000 |
| 14 | kg-mole O₂ in | 0.1100 |
| 15 | kg-mole N₂ in | 0.7900 |

| 16 | kg-mole SO₂ out | 0.0442 |
| 17 | kg-mole SO₂ out | 0.0558 |
| 18 | kg-mole O₂ out | 0.0879 |
| 19 | kg-mole N₂ out | 0.7900 |

\[ \% \text{ SO}_2 \text{ oxidized} = \frac{(\text{kg-mole SO}_2 \text{ in} - \text{kg-mole SO}_2 \text{ out})}{\text{kg-mole SO}_2 \text{ in}} \times 100 \]  

(Eqn. 10.1)

\[ = \frac{(B13-B17)}{B13} \times 100 = 44.2 \]

\[ = \frac{(B13-B17)}{B13} \times 100 = 44.2 \]

Notice that cells D8, E8 and F8 contain \( -H_{SO_2}^{690} \), \( -H_{O_2}^{690} \) and \( -H_{N_2}^{690} \) (Section 11.9.1).
Table 11.2 gives the result. It indicates that an 820 K gas temperature is uniquely produced by 44.2% oxidation of Fig. 11.3’s feed SO₂.

11.12 Preparing a Heatup Path

The heatup path for the Section 11.5 feed gas is prepared by re-doing the above calculation for many different levels and temperatures in the catalyst bed, Fig. 11.4. Only cells G8 to J8 in Table 11.2 are changed.

Fig. 11.4. Segment of catalyst bed showing level L' for calculating % SO₂ oxidized equivalent to 850 K.

The 850 K gas temperature at level L' is, for example, represented by the enthalpy terms:

<table>
<thead>
<tr>
<th>Cell</th>
<th>Contents</th>
<th>Numerical value, MJ/kg-mole&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>G8</td>
<td>H&lt;sub&gt;SO₃&lt;/sub&gt;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>-359.9</td>
</tr>
<tr>
<td>H8</td>
<td>H&lt;sub&gt;SO₂&lt;/sub&gt;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>-270.4</td>
</tr>
<tr>
<td>I8</td>
<td>H&lt;sub&gt;O₂&lt;/sub&gt;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>17.54</td>
</tr>
<tr>
<td>J8</td>
<td>H&lt;sub&gt;N₂&lt;/sub&gt;&lt;sup&gt;0&lt;/sup&gt;</td>
<td>16.64</td>
</tr>
</tbody>
</table>

<sup>a</sup>Calculated with Appendix G’s enthalpy equations.

Inserted into Matrix Table 11.2, these values automatically give the result that 850 K gas is produced by 54.4% SO₂ oxidation.
11.12.1 Enthalpy equations in cells

An efficient method of calculating heatup path points is to put enthalpy equations directly into cells D8 - J8 of Table 11.2. This is detailed in Appendix I.

11.12.2 The heatup path

Table 11.3 summarizes % $SO_2$ oxidized vs gas temperature as calculated by the above described method. The points are equivalent to the heatup path in Fig. 11.1. As expected, high gas temperatures are equivalent to extensive $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$ oxidation and vice versa.

Table 11.3. Heatup path points for 10 volume% $SO_2$, 11 volume% $O_2$, 79 volume% $N_2$, 690 K feed gas. The values are represented graphically in Fig. 11.1.

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>Equivalent % $SO_2$ oxidized</th>
</tr>
</thead>
<tbody>
<tr>
<td>690</td>
<td>0</td>
</tr>
<tr>
<td>710</td>
<td>6.8</td>
</tr>
<tr>
<td>730</td>
<td>13.5</td>
</tr>
<tr>
<td>750</td>
<td>20.3</td>
</tr>
<tr>
<td>770</td>
<td>27.1</td>
</tr>
<tr>
<td>790</td>
<td>33.9</td>
</tr>
<tr>
<td>810</td>
<td>40.8</td>
</tr>
<tr>
<td>830</td>
<td>47.6</td>
</tr>
<tr>
<td>850</td>
<td>54.4</td>
</tr>
</tbody>
</table>

The next two sections describe the effects of:

(a) feed gas composition

and:

(b) feed gas temperature

on heatup paths. The importance of heatup path position and slope is then discussed.

11.13 Feed Gas $SO_2$ Strength Effect

The effect of feed gas $SO_2$ strength on heatup path is determined by inserting different values of:

- volume% $SO_2$
- volume% $O_2$
- volume% $N_2$

into Equations (11.1), (11.2) and (11.3). With 13 volume% $SO_2$, 14.3 volume% $O_2$ and 72.7 volume% $N_2$ (for example), the equations become:
These new equations are put into matrix Table 11.2 by placing new values into cells C2 to C4. The new values are:

- cell C2: 0.13
- cell C3: 0.143
- cell C4: 0.727

With an 820 K measured level L temperature, these values automatically give:

34.7% SO₂ oxidized.

11.13.1 SO₂ strength summary

Fig. 11.5 summarizes the effects of SO₂ feed gas strength on heatup paths. It shows that each % SO₂ oxidized gives a larger temperature increase with:

13 volume% SO₂ in feed gas

than with:

7 volume% SO₂ in feed gas.

This is mainly because, per % SO₂ oxidized:

more SO₂ is oxidized per kg-mole of strong SO₂ feed gas than per kg-mole of weak SO₂ feed gas,

giving more heat evolution and larger temperature increase.
11.14 Feed Gas Temperature Effect

The effect of feed gas temperature on heatup path is determined by inserting new enthalpy values into Eqn. (11.7). With 660 K feed gas (for example), enthalpy Eqn. (11.7) becomes:

\[
0 = \begin{align*}
- \text{kg-mole SO}_2 & \text{ in} \times -280.2 \\
- \text{kg-mole O}_2 & \text{ in} \times 11.21 \\
- \text{kg-mole N}_2 & \text{ in} \times 10.73 \\
+ \text{kg-mole SO}_3 & \text{ out} \times -362.0 \\
+ \text{kg-mole SO}_2 & \text{ out} \times -272.0 \\
+ \text{kg-mole O}_2 & \text{ out} \times 16.54 \\
+ \text{kg-mole N}_2 & \text{ out} \times 15.71
\end{align*}
\] (11.7')

where:

\[
\begin{align*}
-280.2 &= H_{SO_2}^\circ \\
11.21 &= H_{O_2}^\circ \\
10.73 &= H_{N_2}^\circ
\end{align*}
\]

MJ per kg-mole of compound.
These new enthalpy in values are put into cells D8, E8 and F8 of matrix Table 11.2 as:

- D8 = -280.2
- E8 = -11.21
- F8 = -10.73

(because of the negative signs on the first three rows of Eqn. 11.7').

A new heatup path is then calculated as described in Section 11.11. The result is a path nearly parallel to the 690 K path ~30 K cooler at all % SO₂ oxidized values, Fig. 11.6.

**Fig. 11.6.** 660 K and 690 K feed gas heatup paths with 10 volume% SO₂, 11 volume% O₂, 79 volume% N₂ feed gas. The two paths are ~30 K apart throughout their length. They are not exactly straight because: $dH_{SO_3}^o/dT > (dH_{SO_2}^o/dT + \frac{1}{2}dH_{O_2}^o)/dT$, Appendix G.

### 11.15 Significance of Heatup Path Position and Slope

Fig. 11.7 superimposes the Fig. 10.2 % SO₂ oxidized equilibrium curve on Fig. 11.6. It shows that the:

- 660 K feed gas heatup path

will reach the equilibrium % SO₂ oxidized curve:

- at a higher % SO₂ oxidized value

than the 690 K feed gas heatup path.

This predicts high SO₂ oxidation efficiency with low feed gas temperature. This prediction is discussed extensively in Chapter 12 onwards.
Fig. 11.7. Heatup paths and equilibrium curve for 10 volume% SO\(_2\), 11 volume% O\(_2\), 79 volume% N\(_2\) feed gas. Notably, the 660 K heatup path will reach the equilibrium curve at a higher % \(\text{SO}_2\) oxidized value than the 690 K heatup path. 660 K is about the lowest feed gas temperature that will keep V, alkali metal, S, O, SiO\(_2\) catalyst active and \(\text{SO}_2\) oxidation rapid, Table 8.1.

### 11.16 Summary

\(\text{SO}_2\) oxidizes and gas temperature increases as \(\text{SO}_2\), O\(_2\), N\(_2\) gas descends through active V, alkali metal, S, O, SiO\(_2\) catalyst. This behavior is shown by the heatup paths of this chapter.

Chapters 12 onwards combine these heatup paths with Chapter 10's % \(\text{SO}_2\) oxidized equilibrium curves to show how:

(a) \(\text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{SO}_3\) oxidation may be maximized

(b) \(\text{SO}_2\) emission to the environment may be minimized.

They indicate that cool feed gas (but warm enough for rapid catalytic oxidation) gives efficient \(\text{SO}_2\) oxidation and small \(\text{SO}_2\) emission.

### Problems

11.1 12 volume% \(\text{SO}_2\), 13.2 volume% O\(_2\), 74.8 volume% N\(_2\), 690 K gas is fed continuously to the top of a catalyst bed.

A thermocouple is inserted into the catalyst bed part way down the bed. It
indicates that the temperature there is 820 K.

What percentage of the input SO$_2$ has been oxidized at the thermocouple's location?

Use matrix Table 11.2. Only cells C2, C3 and C4 need to be changed (as discussed in Section 11.13).

11.2 Repeat Problem 11.1 with an 850 K thermocouple reading further down the bed. Use your Problem 11.1 matrix with 850 K enthalpy values in cells G8 to J8.

11.3 Repeat Problem 11.2 with 675 K feed gas (and an 850 K thermocouple reading). Use your Problem 11.2 matrix with 675 K enthalpy values in cells D8 to F8.

Remember that these cells contain -H$^\circ$.

11.4 Prepare a heatup path for 12 volume% SO$_2$, 13.2 volume% O$_2$, 74.8 volume% N$_2$, 675 K feed gas – as described in Appendix I. Plot the path with Excel's Chart Wizard function.
CHAPTER 12

Maximum SO₂ Oxidation:
Heatup Path-Equilibrium Curve Intercepts

Chapters 10 and 11 discuss oxidation of SO₂ when warm SO₂, O₂, N₂ feed gas descends a catalyst bed. They do so in terms of:

(a) % SO₂ oxidized-temperature equilibrium curves, Chapter 10

(b) % SO₂ oxidized-temperature heatup paths, Chapter 11.

Together, they indicate that maximum oxidation in a catalyst bed is obtained where a feed gas's:

heatup path

intercepts its:

equilibrium curve, Fig. 11.7.

This chapter:

(a) calculates heatup path-equilibrium curve intercept points

(b) shows how these points are affected by feed gas temperature, feed gas composition and equilibrium pressure

(c) discusses the influence of these points on industrial acid plant practice.

12.1 Initial Specifications

For an intercept calculation to be valid, its heatup path and equilibrium curve must be for the same feed gas. Each intercept calculation must, therefore, specify a feed gas
composition, volume% $\text{SO}_2$, $\text{O}_2$, $\text{N}_2$ etc.

It must also specify:

(a) feed gas temperature, i.e. the temperature at which the heatup path starts

(b) catalyst bed pressure, i.e. the pressure at which $\text{SO}_2$ oxidation Reaction (1.1) comes to equilibrium.

A calculated intercept is valid only for these specified values.

### 12.2 $\% \text{SO}_2$ Oxidized-Temperature Points Near an Intercept

Table 12.1 shows heatup path and equilibrium curve $\% \text{SO}_2$ oxidized-temperature points near a heatup path-equilibrium curve intercept. They are for:

690 K, 10 volume% $\text{SO}_2$, 11 volume% $\text{O}_2$, 79 volume% $\text{N}_2$ feed gas and 1.2 bar equilibrium pressure.

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>Heatup path $% \text{SO}_2$ oxidized, $\Phi$</th>
<th>Equilibrium $% \text{SO}_2$ oxidized, $\Phi^E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>898</td>
<td>70.84</td>
<td>67.85</td>
</tr>
<tr>
<td>897</td>
<td>70.49</td>
<td>68.15</td>
</tr>
<tr>
<td>896</td>
<td>70.15</td>
<td>68.45</td>
</tr>
<tr>
<td>895</td>
<td>69.81</td>
<td>68.75</td>
</tr>
<tr>
<td>894</td>
<td>69.47</td>
<td>69.05</td>
</tr>
<tr>
<td>893</td>
<td>69.12</td>
<td>69.34</td>
</tr>
<tr>
<td>892</td>
<td>68.78</td>
<td>69.64</td>
</tr>
<tr>
<td>891</td>
<td>68.44</td>
<td>69.94</td>
</tr>
<tr>
<td>890</td>
<td>68.09</td>
<td>70.23</td>
</tr>
</tbody>
</table>

The table shows that at 893 K and below:

heatup path $\% \text{SO}_2$ oxidized is less than equilibrium curve $\% \text{SO}_2$ oxidized.

This indicates that at 893 K and below, $\text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{SO}_3$ oxidation can proceed further up the heatup path towards equilibrium, Fig. 12.1.

At 894 K and above, however, heatup path $\% \text{SO}_2$ oxidized is greater than equilibrium $\% \text{SO}_2$ oxidized. This is, of course, impossible because equilibrium $\% \text{SO}_2$ oxidized cannot be exceeded up a heatup path.
Fig. 12.1. Plot of Table 12.1 heatup path points and equilibrium curve, expanded from Fig. 11.7. Below the equilibrium curve, SO₂ is being oxidized, gas temperature is increasing and equilibrium is being approached up the heatup path. Maximum (equilibrium) oxidation is attained where the heatup path meets the equilibrium curve.

Maximum (equilibrium) % SO₂ oxidized occurs, therefore, between 893 K and 894 K. Interpolation shows that it occurs at:

\[
893.3 \text{ K} \\
69.2 \% \text{SO}_2 \text{ oxidized.}
\]

This is confirmed by the Excel Goal Seek calculation in Appendix Table J.2.

The Table J.2 Goal Seek calculation also shows that the intercept gas contains:

\[
\begin{align*}
0.0692 \text{ kg-mole SO}_3 \\
0.0308 \text{ kg-mole SO}_2 \\
0.0754 \text{ kg-mole O}_2 \\
0.7900 \text{ kg-mole N}_2 
\end{align*}
\]

per kg-mole of feed gas. These quantities are used in Chapter 14 and 15's 2nd catalyst bed heatup path and intercept calculations.

12.3 Discussion

The above calculations assume that:

(a) the acid plant's 1st catalyst bed is thick enough

and its:
(b) catalytic SO$_2$ oxidation is rapid enough
for equilibrium to be attained.

Industrial 1st catalyst beds are ½ to 1 m thick, Fig. 8.3. This thickness gives near
equilibrium oxidation under the (i) warm and (ii) strong SO$_2$ + O$_2$ conditions in the 1st
catalyst bed. More catalyst could be added but this isn't often necessary. Non-
attainment of equilibrium is discussed further in Section 18.12.

12.4 Effect of Feed Gas Temperature on Intercept

Fig. 12.2 shows the effect of feed gas temperature on intercept temperature and % SO$_2$
oxidized. It indicates that cool feed gas gives:

(a) a low intercept temperature

(b) a high intercept (equilibrium) % SO$_2$ oxidized.

The high intercept % SO$_2$ oxidized gives efficient SO$_3$ and H$_2$SO$_4$
production. It also
minimizes SO$_2$ emission.

![Fig. 12.2. Near-intercept heatup paths with 660 and 690 K feed gas (same composition). They are expanded from Fig. 11.7. Cool feed gas gives a low intercept temperature and a high intercept % SO$_2$ oxidized. 660 K is about the lowest temperature at which V, alkali metal, S, O, SiO$_2$
catalyst is fully active, Table 8.1.](image-url)
12.5 Inadequate $\% \text{SO}_2$ Oxidized in 1st Catalyst Bed

$\text{SO}_2 + \frac{3}{2}\text{O}_2 \rightarrow \text{SO}_3$ oxidation efficiency in a 1st catalyst bed is always below $\sim 80\%$. This is totally inadequate for efficient, low $\text{SO}_2$ emission $\text{H}_2\text{SO}_4$ production.

This limitation is overcome industrially by passing 1st catalyst bed exit gas through two or more gas cooling/catalytic oxidation steps – bringing $\text{SO}_2$ oxidation efficiency up to 98+ %.

Multi-catalyst bed processing is discussed in Chapter 13 onwards.

12.6 Effect of Feed Gas $\text{SO}_2$ Strength on Intercept

Fig. 12.3 shows the effect of feed gas $\text{SO}_2$ strength on intercept temperature and $\% \text{SO}_2$ oxidized. Increased $\text{SO}_2$ strength is seen to:

(a) increase intercept temperature
(b) decrease intercept $\% \text{SO}_2$ oxidized.

The industrial impact of these effects is discussed in Section 12.10.

![Fig. 12.3. Heatup paths, equilibrium curves and intercepts for 7, 10, and 13 volume% $\text{SO}_2$ feed gas. Volume% $\text{O}_2$/volume% $\text{SO}_2$ ratio = 1.1. Intercept temperature increases with increasing $\text{SO}_2$ strength. Intercept $\% \text{SO}_2$ oxidized decreases with increasing $\text{SO}_2$ strength. The intercepts have been calculated as described in Appendix J.](image-url)
12.7 Minor Influence – Equilibrium Gas Pressure

Industrial catalyst bed gas pressure varies slightly between acid plants depending on altitude. It also tends to increase slightly over time as catalyst beds become clogged with dust and catalyst fragments.

These pressure differences have no effect on heatup paths, Fig. 12.4 – and little effect on equilibrium curves and intercepts. Intercept temperature and \% SO\textsubscript{2} oxidized both increase slightly with increasing pressure.

![Diagram](image)

Fig. 12.4. Effect of pressure on equilibrium curves and heatup path-equilibrium curve intercepts. Equilibrium curves and intercepts are affected by pressure. Heatup paths are not. Intercept temperature and \% SO\textsubscript{2} oxidized both increase slightly with increasing pressure. The intercepts have been calculated as described in Appendix J.

12.8 Minor Influence – O\textsubscript{2} Strength in Feed Gas

Industrial 1\textsuperscript{st} catalyst bed feed gas typically contains O\textsubscript{2} and SO\textsubscript{2} in the ratio:

$$\text{volume}\% \text{O}_2/\text{volume}\% \text{SO}_2 \approx 1 \text{ to } 2, \text{ Table 7.2.}$$

This is 2 to 4 times the SO\textsubscript{2} + \(\frac{1}{2}\text{O}_2 \rightarrow \text{SO}_3\) stoichiometric O\textsubscript{2}/SO\textsubscript{2} = 0.5 requirement. It gives rapid oxidation.
Fig. 12.5 shows that O\(_2\) strength has a negligible effect on heatup paths and a small effect on equilibrium curves and intercepts. Intercept temperature and \(\% \text{ } SO_2 \text{ oxidized}\) both increase slightly with increasing O\(_2\) strength.

**Fig. 12.5.** Effect of feed gas O\(_2\) strength on constant SO\(_2\) strength heatup paths, equilibrium curves and intercepts. Intercept temperature and \(\% \text{ } SO_2 \text{ oxidized}\) increase slightly with increasing O\(_2\)-in-feed-gas. Heatup path is barely affected by O\(_2\) strength – 3 paths are superimposed on this graph. The effect is small because:

(a) O\(_2\) and N\(_2\) substitute for each other at constant SO\(_2\) strength

(b) the heat capacities of O\(_2\) and N\(_2\) are almost the same, Appendix G.

### 12.9 Minor Influence – CO\(_2\) in Feed Gas\(^\#\)

Metallurgical and spent acid regeneration gases contain CO\(_2\) from fossil fuel and spent acid impurities. CO\(_2\) concentrations in 1\(^{\text{st}}\) catalyst bed feed gas are typically:

- metallurgical: 0 to 7 volume\% CO\(_2\)
- acid regeneration: 6 to 10 volume\% CO\(_2\).

CO\(_2\) has no effect on \(SO_2 + \frac{1}{2}O_2 \rightarrow SO_3\) equilibrium curves, Appendix F. It does, however, have a small effect on heatup paths and intercepts, Fig. 12.6.

Intercept temperature decreases slightly with increasing CO\(_2\)-in-feed-gas. Intercept % \(SO_2 \text{ oxidized}\) increases slightly.

\(^\#\)Effects of SO\(_3\) in feed gas are described in Chapter 17 and Appendices P and Q.
Feed gas
10 volume% SO₂
11 volume% O₂
specified volume% CO₂
remainder N₂
1.2 bar equilibrium pressure

0 volume% CO₂
5 volume% CO₂

10 volume% CO₂

Fig. 12.6. Effect of CO₂ on intercept temperature and % SO₂ oxidized. Heatup path slope increases slightly with increasing CO₂ in gas – because CO₂ heat capacity is greater than N₂ heat capacity, Appendix G. This decreases intercept temperature and increases % SO₂ oxidized. CO₂ calculations are described in Chapter 17.

12.10 Catalyst Degradation, SO₂ Strength, Feed Gas Temperature

V, alkali metal, S, O, SiO₂ catalyst begins to degrade when continuously operated above ~900 K, Table 8.1. This can be a problem with high SO₂ strength feed gas.

Fig. 12.7 shows, for example, that the intercept temperature with:

12 volume% SO₂, 690 K feed gas

is 915 K, which may cause catalyst degradation.

Fig. 12.7 also shows, however, that this problem can be overcome by feeding the gas at 660 K. This explains industrial use of low gas input temperature cesium-enhanced catalyst in 1st catalyst beds, Table 8.1. This catalyst can be fed with ~660 K gas without falling below its de-activation temperature.

12.10.1 Two catalyst layers

A number of acid plants use two layers of catalyst in their 1st catalyst beds:

(a) V, Cs, K, Na, S, O, SiO₂ catalyst at the gas input surface for SO₂ oxidation with cool feed gas
Fig. 12.7. Equilibrium curves, heatup paths and intercepts for 12 volume% SO$_2$ feed gas. 690 K feed gas gives a 915 K intercept temperature, in the catalyst degradation range. 660 K feed gas gives a 900 K intercept temperature, avoiding degradation.

(b) V, K, Na, S, O, SiO$_2$ catalyst at the gas exit surface to prevent high temperature catalyst degradation.

About 1/3 of the bed is Cs enhanced catalyst; 2/3 is K, Na catalyst.

12.11 Maximum Feed Gas SO$_2$ Strength

Fig. 12.8 shows that 13 volume% SO$_2$ gas gives an intercept temperature of ~910 K even when fed at 660 K. This may cause catalyst degradation.

Gases stronger than 13 volume% SO$_2$ will always give intercept temperatures in the catalyst degradation range. They must be diluted with air before they are catalytically oxidized.

Dilution is not a problem, but it requires more equipment and gas blowing power.

12.12 Exit Gas Composition = Intercept Gas Composition

This chapter assumes that equilibrium is attained in an acid plant's 1st catalyst bed, i.e. that a feed gas's heatup path always intercepts its equilibrium curve.
We now add the specification that there is no oxidation or reduction once equilibrium is attained, i.e. that:

\[
\text{catalyst bed exit gas composition} = \text{catalyst bed intercept gas composition, Fig. 12.9.}
\]

This exit gas composition \( \equiv \) intercept gas assumption is important because it links catalyst beds in multi-bed \( \text{SO}_2 \) oxidation calculations, Chapter 14 onwards.

### 12.13 Summary

Catalyst bed \( \text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{SO}_3 \) oxidation is represented by heatup paths and equilibrium curves. Maximum \( \text{SO}_2 \) oxidation occurs where a feed gas's heatup path intercepts its equilibrium curve.

High intercept \( \% \text{SO}_2 \) oxidized values are equivalent to efficient \( \text{SO}_3 \) production. They give efficient \( \text{H}_2\text{SO}_4 \) production and low \( \text{SO}_2 \) emission. They are obtained by using cool feed gas - but warm enough (>660 K) for rapid catalytic oxidation.
Fig. 12.9. Sketch of catalyst bed indicating that exit gas composition and temperature = intercept gas composition and temperature. It assumes that there is no transfer of heat from gas to surroundings, Section 11.3. So once equilibrium is attained, temperature remains constant and the gas remains at its intercept composition. This is discussed further in Section 18.12.

Strong SO₂ feed gas gives high intercept temperatures. Above about 12 volume% SO₂, intercept temperatures begin to exceed V, alkali metal, S, O, SiO₂ catalyst's 900 K degradation temperature.

Gas stronger than ~13 volume% SO₂ must be diluted with air before catalytic oxidation. This is not a problem, but it increases cost.

Problems

12.1 In Problem 10.4, you prepared an equilibrium curve for 12 volume% SO₂, 13.2 volume% O₂, 74.8 volume% N₂ gas (1.2 bar equilibrium pressure).

In Problem 11.4 you prepared a heatup path for the same gas (fed into the catalyst bed at 675 K).

Now determine the %SO₂ oxidized - temperature point at which the Problem 11.4 heatup path intercepts the Problem 10.4 equilibrium curve.
Use the technique described in Table 12.1 as follows.

(a) You can see from Fig. 12.7 that the intercept temperature will be \(-908\) K. This suggests that you should calculate your equilibrium curve and heatup path points at \(-904, 905, \ldots, 911\) K.

(b) Use the technique you used in Problem 10.3 to calculate your equilibrium curve points. This gives integer temperatures and simplifies interpolation, Table 12.1.

(c) Use the technique you used in Problem 11.4 to calculate the heatup path points.

12.2 Plot your Problem 12.1 points as in Fig. 12.1. Use Excel's Chart Wizard.

12.3 Repeat Problem 12.1 using the technique described in Appendix J. Familiarity with this technique is essential for later multi-catalyst bed calculations.

Include in your answer:

(a) intercept temperature and \(\% SO_2\) oxidized

(b) kg-mole \(SO_3, SO_2, O_2\) and \(N_2\) in intercept gas, per kg-mole of 1st catalyst bed feed gas.

The problem in Chapter 13 requires the answer to (a).

The problems in Chapters 14 and 15 require the answer to (b).
CHAPTER 13

Cooling 1\textsuperscript{st} Catalyst Bed Exit Gas

Chapter 12 shows that a 1\textsuperscript{st} catalyst bed oxidizes less than 80\% of its input SO\textsubscript{2}. It also indicates that this SO\textsubscript{2} oxidation efficiency is increased to 98\% by passing 1\textsuperscript{st} catalyst bed exit gas through a series of gas cooling/catalytic oxidation steps.

This chapter describes gas cooling between 1\textsuperscript{st} and 2\textsuperscript{nd} catalyst beds, Fig. 13.1. It sets the stage for Chapter 14's examination of 2\textsuperscript{nd} catalyst bed SO\textsubscript{2} oxidation.

Fig. 13.1. Schematic of 1\textsuperscript{st} and 2\textsuperscript{nd} catalyst beds with gas cooling between. The cooling system cools 1\textsuperscript{st} catalyst bed exit gas in preparation for more catalytic SO\textsubscript{2} oxidation in a 2\textsuperscript{nd} catalyst bed. Industrial catalyst bed arrangements are discussed in Chapters 7 and 8. Gas cooling is discussed in Chapter 21.
The objectives of this chapter are to:

(a) show how gas cooling is represented on % $SO_2$ oxidized/temperature graphs
(b) indicate how gas cooling makes more $SO_2$ oxidation possible.

### 13.1 1st Catalyst Bed Summary

Fig. 13.2 summarizes 1st catalyst bed $SO_2$ oxidation. It is for:

- 10 volume% $SO_2$
- 11 volume% $O_2$
- 79 volume% $N_2$
- 690 K

feed gas and 1.2 bar bed pressure.

It confirms that intercept temperature and % $SO_2$ oxidized under these conditions are:

- 893.3 K
- 69.2 % $SO_2$ oxidized.

![Fig. 13.2](image-url)  
*Fig. 13.2. 1st catalyst bed heatup path, equilibrium curve and intercept point, from Fig. 12.1. The 1st catalyst bed's exit gas is its intercept gas, Section 12.12. It is cooled and fed to a 2nd catalyst bed for more $SO_2$ oxidation.*
13.1.1 Inefficient $SO_2$ oxidation explained

Fig. 13.2's $SO_2$ oxidation efficiency is less than 70%. This low efficiency arises because:

(a) feed gas enters the 1\textsuperscript{st} catalyst bed at 690 K, warm enough for rapid catalytic oxidation

(b) heat from $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$ oxidation raises gas temperature even further

(c) the resulting heatup path reaches the equilibrium curve at a high temperature where equilibrium $SO_2$ oxidation is inefficient.

13.2 Cooldown Path

This section adds a cooldown path to Fig. 13.2. It does so by preparing a data table which specifies that:

(a) a 1\textsuperscript{st} catalyst bed's exit gas is its intercept gas, Section 12.12

(b) exit gas composition doesn't change during gas cooling – because the cooling equipment doesn't contain catalyst

(c) the cooldown target temperature is 700 K.

These specifications give the following two cooldown path points. They are plotted in Fig. 13.3 with a straight cooldown path between.

<table>
<thead>
<tr>
<th>Description</th>
<th>gas temperature, K</th>
<th>% $SO_2$ oxidized</th>
</tr>
</thead>
<tbody>
<tr>
<td>1\textsuperscript{st} catalyst bed exit gas = 1\textsuperscript{st} catalyst bed intercept gas</td>
<td>893.3 (Fig. 13.2)</td>
<td>69.2 (Fig. 13.2)</td>
</tr>
<tr>
<td>Cooldown target temperature = specified 2\textsuperscript{nd} catalyst bed gas input temperature</td>
<td>700</td>
<td>69.2 (unchanged during catalyst free cooling)</td>
</tr>
</tbody>
</table>
Fig. 13.3. Cooldown path added to Fig. 13.2. It is a horizontal line at the 1st catalyst bed intercept % SO₂ oxidized level – between the 1st catalyst bed intercept temperature and the specified 2nd catalyst bed gas input temperature. Gas composition and % SO₂ oxidized don’t change in the gas cooling equipment.

13.2.1 2nd catalyst bed gas input temperature

SO₂ and O₂ concentrations in 2nd catalyst bed input gas are lower than in 1st catalyst bed feed gas, Section 12.2. SO₃ concentration is higher. Both of these tend to slow SO₂ oxidation in the 2nd catalyst bed.

This slowing effect is offset industrially by using slightly warmer input gas in the 2nd catalyst bed, Fig. 13.1. ~700 K is quite common, Table 7.2.

13.2.2 Industrial gas cooling (Chapter 21)

Catalyst bed exit gas is cooled by:

(a) making steam from water in a boiler
(b) superheating this steam
(c) heating water for the boiler in an economizer
(d) transferring heat to another gas in a gas-to-gas heat exchanger.

The steam is mainly used to make electricity.
The transferred heat is usually used to heat 1st catalyst bed feed gas to its specified input temperature (in metallurgical and waste acid regeneration plants).

13.3 Gas Composition Below Equilibrium Curve

Fig. 13.3 shows that gas cooling without composition change:

moves \( \% \text{SO}_2 \text{ oxidized} \) from its 893.3 K position on the equilibrium curve
to:

a position below the equilibrium curve, i.e. to a position where more \( \text{SO}_2 \) oxidation is possible.

It prepares the gas for more \( \text{SO}_2 \) oxidation.

13.4 Summary

A 1st catalyst bed oxidizes less than 80\% of its feed \( \text{SO}_2 \) to \( \text{SO}_3 \). This percentage is increased by passing its exit gas through a series of gas cooling/catalytic oxidation steps.

Gas cooling between catalyst beds is done in water-to-steam boilers, superheaters, economizers and gas-to-gas heat exchangers. Gas composition doesn't change in these cooling devices because they don't contain catalyst.

Gas cooling between 1st and 2nd catalyst beds is represented graphically by a horizontal line at:

the 1st catalyst bed intercept \( \% \text{SO}_2 \text{ oxidized} \) level

between:

(a) the 1st catalyst bed intercept temperature
and:

(b) the specified 2nd catalyst bed gas input temperature.

Problem

13.1 Prepare a graph like Fig. 13.3 for:

675 K, 12 volume\% \( \text{SO}_2 \), 13.2 volume\% \( \text{O}_2 \),
74.8 volume\% \( \text{N}_2 \) 1st catalyst bed feed gas.
Assume that this gas:

(a) attains equilibrium (1.2 bar) in a 1st catalyst bed at Problem 12.3's intercept temperature and % $SO_2$ oxidized

(b) is cooled to 685 K without any reaction in preparation for input to a 2nd catalyst bed.

Hints:

(a) You calculated the equilibrium curve for this gas in Problem 10.4.

(b) You calculated most of this gas's 1st catalyst bed heatup path in Problem 11.4. Now add your Problem 12.3 intercept point to the heatup path. This will join it to the equilibrium curve.

(c) Add a cooldown path to 685 K as described in Section 13.2.
CHAPTER 14

2nd Catalyst Bed Heatup Path

Chapter 12 indicates that a 1st catalyst bed oxidizes less than 80% of its feed gas's SO₂. Most of the remaining SO₂ is oxidized to SO₃ in a sequence of gas cooling/catalytic oxidation steps. The oxidant is unused O₂ in 1st catalyst bed exit gas. The reaction is:

\[
\text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{SO}_3(g)
\]

This chapter examines oxidation of the SO₂ in cooled 1st catalyst bed exit gas – in a 2nd catalyst bed.

14.1 Objectives

The objectives of the chapter are to:

(a) define \(\% \text{SO}_2 \text{ oxidized}\) as it applies to a 2nd catalyst bed
(b) prepare a 2nd catalyst bed heatup path – starting with cooled 1st catalyst bed exit gas
(c) show how 2nd catalyst bed oxidation increases overall SO₂ oxidation efficiency.

14.2 \% \text{SO}_2 \text{ Oxidized Re-defined}

Chapter 10 defines catalyst bed \(\% \text{SO}_2 \text{ oxidized}\) anywhere in a 1st catalyst bed as:

\[
\% \text{SO}_2 \text{ oxidized} = \Phi = \frac{\text{kg-mole SO}_2 \text{ in oxidized gas} - \text{kg-mole SO}_2 \text{ in feed gas}}{\text{kg-mole SO}_2 \text{ in feed gas}} \times 100
\]

where all quantities are per kg-mole of 1st catalyst bed feed gas.
This chapter expands that definition to cover all acid plant catalyst beds. The expanded definition is:

$$
\% \text{SO}_2 \text{ oxidized} = \Phi = \frac{\text{kg-mole SO}_2 \text{ in 1st catalyst bed feed gas} - \text{kg-mole SO}_2 \text{in any catalyst bed's oxidized gas}}{\text{kg-mole SO}_2 \text{ in 1st catalyst bed feed gas}} \times 100
$$

(14.1)

where all quantities are per kg-mole of 1st catalyst bed feed gas.

This definition is used throughout the rest of this book.

### 14.3 2nd Catalyst Bed Heatup Path

Fig. 14.3 shows a 2nd catalyst bed heatup path. It is similar to a 1st catalyst bed heatup path but it starts at Fig. 13.3's:

(a) 1st catalyst bed intercept % \text{SO}_2 \text{ oxidized}

(b) specified 2nd catalyst bed input gas temperature.

#### 14.3.1 A heatup path point

2nd catalyst bed heatup path points are calculated much like 1st catalyst bed heatup points. The steps are:

(a) 2nd catalyst bed input temperature and input gas kg-mole are specified

(b) a gas temperature partway down the 2nd bed (after some \text{SO}_2 oxidation has occurred) is specified

(c) % \text{SO}_2 \text{ oxidized} equivalent to (b)'s gas temperature is calculated.

Figs. 14.1 and 14.2 are used.

#### 14.3.2 2nd catalyst bed difference

A significant difference between 2nd catalyst bed input gas and 1st catalyst bed feed gas is that:

2nd catalyst bed input gas always contains SO\text{3} as well as SO\text{2}, O\text{2} and N\text{2}.

This adds:

(a) a new variable (kg-mole SO\text{3} in)
and an equivalent:

(b) new equation (SO$_3$ input quantity)

to our calculations, Table 14.2.

It also alters our heatup path $S$, $O$ and enthalpy balances, Sections 14.6 and 14.7.

![Diagram](image)

**Fig. 14.1.** Sketch of 2$^{nd}$ catalyst bed showing a temperature measured part way down the bed. Compositions and temperatures are assumed to be uniform horizontally at all levels.

### 14.4 A Specific Heatup Path Question

The problem solved in this chapter is:

"Fig. 13.3’s cooled 1$^{st}$ catalyst bed exit gas is fed to a 2$^{nd}$ catalyst bed, Fig. 14.1.

A thermocouple at level L in the bed indicates that the temperature there is 760 K.

What percentage of 1$^{st}$ catalyst bed feed SO$_2$ has been oxidized to SO$_3$ where the 2$^{nd}$ catalyst bed gas is 760 K?"

Fig. 14.2 defines the problem and specifies 2$^{nd}$ catalyst bed gas input temperature and input SO$_3$, SO$_2$, O$_2$ and N$_2$ kg-mole.
1 kg-mole 1st catalyst bed feed gas
10 volume% SO₂ (0.1 kg-mole)
11 volume% O₂
79 volume% N₂
690 K

1st catalyst bed
SO₂ + ½O₂ → SO₃
1.2 bar pressure

cooled 1st catalyst bed exit gas
= cooled 1st catalyst bed intercept gas
0.0692 kg-mole SO₃, Section 12.2
0.0308 kg-mole SO₂
0.0754 kg-mole O₂
0.7900 kg-mole N₂
700 K

2nd catalyst bed
SO₂ + ½O₂ → SO₃
1.2 bar pressure

760 K
SO₃, SO₂, O₂, N₂ gas

Fig. 14.2. Sketch defining Section 14.4's 2nd catalyst bed heatup path problem.

14.5 2nd Catalyst Bed Input Gas Quantities

2nd catalyst bed input gas quantities are specified to be:

1st catalyst bed intercept gas quantities.

This specification is based on the assumptions that:

(a) equilibrium is attained in the 1st catalyst bed, Fig. 12.1
(b) 1st catalyst bed exit gas composition = 1st catalyst bed intercept (equilibrium) gas composition, Section 12.12
(c) 2\textsuperscript{nd} catalyst bed input gas composition = 1\textsuperscript{st} catalyst bed exit gas composition, Section 13.2.

These assumptions link the two catalyst beds.

14.5.1 Input $SO_3$, $SO_2$, $O_2$ and $N_2$ equations

Fig. 14.2's 2\textsuperscript{nd} catalyst bed input gas quantities are represented by the equations:

\begin{align*}
  \text{kg-mole } SO_3 \text{ in} & = 0.0692 \quad \text{(14.2)} \\
  \text{kg-mole } SO_2 \text{ in} & = 0.0308 \quad \text{(14.3)} \\
  \text{kg-mole } O_2 \text{ in} & = 0.0754 \quad \text{(14.4)} \\
  \text{kg-mole } N_2 \text{ in} & = 0.7900 \quad \text{(14.5)}
\end{align*}

where the numerical values are those in Fig. 14.2.

These equations will, of course, be different for different 2\textsuperscript{nd} catalyst bed input gases.

14.6 S, O and N Molar Balances

$SO_3$ in 2\textsuperscript{nd} catalyst bed input gas alters molar balance Eqns. (11.4) to (11.6) as follows.

(a) Sulfur balance Eqn. (11.4) becomes:

\[ 0 = -\text{kg-mole } SO_3 \text{ in} - \text{kg-mole } SO_2 \text{ in} + \text{kg-mole } SO_3 \text{ out} + \text{kg-mole } SO_2 \text{ out} \quad \text{(14.6)} \]

where \text{in} means into the top of Fig. 14.2's 2\textsuperscript{nd} catalyst bed segment and \text{out} means out of the segment at level L.

(b) Oxygen balance Eqn. (11.5) becomes:

\[ 0 = -3\times\text{kg-mole } SO_3 \text{ in} - 2\times\text{kg-mole } SO_2 \text{ in} - 2\times\text{kg-mole } O_2 \text{ in} \\
  + 3\times\text{kg-mole } SO_3 \text{ out} + 2\times\text{kg-mole } SO_2 \text{ out} + 2\times\text{kg-mole } O_2 \text{ out} \quad \text{(14.7)} \]

(c) Nitrogen balance Eqn. (11.6) is unchanged:

\[ 0 = -2\times\text{kg-mole } N_2 \text{ in} + 2\times\text{kg-mole } N_2 \text{ out} \quad \text{(14.8)} \]
14.7 Enthalpy Balance

SO₃ in 2nd catalyst bed feed gas changes Section 11.9's enthalpy balance to:

\[
0 = -\text{kg-mole SO}_3 \text{ in} \times H^\circ_{SO_3}^{700} \\
- \text{kg-mole SO}_2 \text{ in} \times H^\circ_{SO_2}^{700} \\
- \text{kg-mole O}_2 \text{ in} \times H^\circ_{O_2}^{700} \\
- \text{kg-mole N}_2 \text{ in} \times H^\circ_{N_2}^{700} \\
+ \text{kg-mole SO}_3 \text{ out} \times H^\circ_{SO_3}^{760} \\
+ \text{kg-mole SO}_2 \text{ out} \times H^\circ_{SO_2}^{760} \\
+ \text{kg-mole O}_2 \text{ out} \times H^\circ_{O_2}^{760} \\
+ \text{kg-mole N}_2 \text{ out} \times H^\circ_{N_2}^{760}
\] (14.8A)

where 700 K and 760 K are Fig. 14.2's 2nd catalyst bed input and level L temperatures.

With the enthalpy values in Table 14.1, this enthalpy balance is:

\[
0 = -\text{kg-mole SO}_3 \text{ in} \times (-370.6) \\
- \text{kg-mole SO}_2 \text{ in} \times (-278.2) \\
- \text{kg-mole O}_2 \text{ in} \times 12.54 \\
- \text{kg-mole N}_2 \text{ in} \times 11.97 \\
+ \text{kg-mole SO}_3 \text{ out} \times (-366.3) \\
+ \text{kg-mole SO}_2 \text{ out} \times (-275.1) \\
+ \text{kg-mole O}_2 \text{ out} \times 14.54 \\
+ \text{kg-mole N}_2 \text{ out} \times 13.84
\] (14.9).
Table 14.1. 700 K and 760 K enthalpies for Section 14.4 problem. They have been calculated with the enthalpy equations in Appendix G.

<table>
<thead>
<tr>
<th>Compound and temperature</th>
<th>enthalpy numerical value, MJ/kg-mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_{\text{SO}_3}^{\circ}$</td>
<td>-370.6</td>
</tr>
<tr>
<td>$H_{\text{SO}_2}^{\circ}$</td>
<td>-278.2</td>
</tr>
<tr>
<td>$H_{\text{O}_2}^{\circ}$</td>
<td>12.54</td>
</tr>
<tr>
<td>$H_{\text{N}_2}^{\circ}$</td>
<td>11.97</td>
</tr>
<tr>
<td>$H_{\text{SO}_3}^{\circ}$</td>
<td>-366.3</td>
</tr>
<tr>
<td>$H_{\text{SO}_2}^{\circ}$</td>
<td>-275.1</td>
</tr>
<tr>
<td>$H_{\text{O}_2}^{\circ}$</td>
<td>14.54</td>
</tr>
<tr>
<td>$H_{\text{N}_2}^{\circ}$</td>
<td>13.84</td>
</tr>
</tbody>
</table>

14.8 Calculating 760 K (level L) Quantities

The Section 14.4 problem has 8 variables:

- kg-mole $\text{SO}_3$ in
- kg-mole $\text{SO}_2$ in
- kg-mole $\text{O}_2$ in
- kg-mole $\text{N}_2$ in
- kg-mole $\text{SO}_3$ out
- kg-mole $\text{SO}_2$ out
- kg-mole $\text{O}_2$ out
- kg-mole $\text{N}_2$ out
It also has 8 linear equations (14.2 to 14.9) which must be satisfied by the values of the above 8 variables. Each variable has, therefore, a unique value and the question:

"What percentage of 1st catalyst bed feed SO₂ has been oxidized to SO₃ where the 2nd catalyst bed input gas has reached 760 K?"

has a unique answer.

14.9 Matrix Calculation and Result

The answer is obtained by:

(a) entering Eqns. (14.2) to (14.9) in matrix form into an Excel worksheet, Table 14.2
(b) solving for the 8 variables
(c) entering 1st catalyst bed feed kg-mole SO₂ in cell D2 (0.1 kg-mole from Fig. 14.2)
(d) calculating % SO₂ oxidized in cell H25 by Eqn. (14.1).

The results are shown in Table 14.2. They indicate that a 2nd bed temperature increase from 700 K to 760 K is equivalent to raising % SO₂ oxidized from 69.2% after the 1st catalyst bed to 89.7% at level L in the 2nd catalyst bed.

14.10 Preparing a Heatup Path

The 2nd catalyst bed heatup path is prepared by re-doing Section 14.9's calculation for many different temperatures in the bed. Only cells H15 to K15 are changed (most easily with enthalpy equations in cells, Appendix K). The results are tabulated in Table 14.3 and plotted in Fig. 14.3.

<table>
<thead>
<tr>
<th>Gas temperature, K</th>
<th>Equivalent % SO₂ oxidized</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>69.2</td>
</tr>
<tr>
<td>710</td>
<td>72.6</td>
</tr>
<tr>
<td>720</td>
<td>76.0</td>
</tr>
<tr>
<td>730</td>
<td>79.4</td>
</tr>
<tr>
<td>740</td>
<td>82.8</td>
</tr>
<tr>
<td>750</td>
<td>86.3</td>
</tr>
<tr>
<td>760</td>
<td>89.7</td>
</tr>
</tbody>
</table>
Table 14.2. Worksheet for calculating $\% SO_2$ oxidized value equivalent to 760 K gas in a 2nd catalyst bed. The 2nd bed input gas temperature and SO$_3$, SO$_2$, O$_2$ and N$_2$ quantities are from Fig. 14.2. The 1st catalyst bed feed kg-mole SO$_2$ (cell D2) is 0.1, also from Fig. 14.2. It is required for Eqn. (14.1) as shown. An increase in gas temperature from 700 to 760 K is seen to be equivalent to an increase from 69.2% SO$_2$ oxidized after the 1st catalyst bed to 89.7% SO$_2$ oxidized at level L in the 2nd catalyst bed. The matrix has been solved as described in Appendix H.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>All calculations are based on 1 kg-mole of 1st catalyst bed feed gas.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>kg-mole SO$_2$ in 1 kg-mole of 1st catalyst bed feed gas</td>
<td>0.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>2nd catalyst bed matrix</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Equation</td>
<td>description</td>
<td>numerical term</td>
<td>kg-mole SO$_2$ in</td>
<td>kg-mole SO$_2$ out</td>
<td>kg-mole O$_2$ in</td>
<td>kg-mole O$_2$ out</td>
<td>kg-mole N$_2$ in</td>
<td>kg-mole N$_2$ out</td>
<td>kg-mole SO$_2$ in</td>
</tr>
<tr>
<td>8</td>
<td>14.3</td>
<td>input SO$_2$ kg-mole</td>
<td>0.0692</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>14.4</td>
<td>input SO$_2$ kg-mole</td>
<td>0.0308</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>14.5</td>
<td>input O$_2$ kg-mole</td>
<td>0.0754</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>14.6</td>
<td>input N$_2$ kg-mole</td>
<td>0.7900</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>14.7</td>
<td>S balance</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>13</td>
<td>14.7</td>
<td>O balance</td>
<td>0</td>
<td>-3</td>
<td>-2</td>
<td>-2</td>
<td>0</td>
<td>3</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>14</td>
<td>14.8</td>
<td>N balance</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>14.9</td>
<td>enthalpy balance</td>
<td>0</td>
<td>370.6</td>
<td>278.2</td>
<td>-12.54</td>
<td>-11.97</td>
<td>-366.3</td>
<td>-275.1</td>
<td>14.54</td>
</tr>
<tr>
<td>16</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^*$Cells D15 to G15 contain $-H^0_{700}$ values, Section 14.7. Cells H15 to K15 contain $+H^0_{760}$ values.
14.11 Discussion

Table 14.3 and Fig. 14.3 show that:

(a) cooling of 1st catalyst bed exit gas

and

(b) passing of this cooled gas through a 2nd catalyst bed

increases SO2 oxidation efficiency from ~70% to ~90%.

This explains the success of industrial multi-catalyst bed SO2 oxidation.

14.12 Summary

Cooling 1st catalyst bed exit gas to 700 K and passing the cooled gas through a 2nd catalyst bed raises SO2 oxidation efficiency from ~70% to ~90%, Fig. 14.3.

The next chapter shows that attainment of equilibrium in the 2nd catalyst bed increases SO2 oxidation efficiency even further – to almost 95%

Problem

14.1 Prepare a graph like Fig. 14.3 for the following.
(a) 12 volume% SO$_2$, 13.2 volume% O$_2$, 74.8 volume% N$_2$ 1$^{st}$ catalyst bed feed gas.

(b) This gas enters the 1$^{st}$ catalyst bed at 675 K and reacts to equilibrium (1.2 bar) at the gas's heatup path-equilibrium curve intercept.

(c) The intercept gas exits the catalyst bed and is cooled to 685 K with no chemical reaction during cooling.

(d) The cooled exit gas is fed into a 2$^{nd}$ catalyst bed where SO$_2$ oxidation (by O$_2$ in the gas) and gas warming occur.

Hints:

(a) Your answer to Problem 13.1 already contains most of the required graph.

(b) Calculate the 2$^{nd}$ catalyst bed heatup path as described in Sections 14.4 to 14.10. Use 770 K as your top temperature. The 2$^{nd}$ bed's input gas quantities are those in your Problem 12.3(b) answer.

(c) Prepare a matrix like Table K.1 for this purpose. Note the new input SO$_3$ column and row. Note also the changed S, O and enthalpy balance equations.

(d) Remember that the 2$^{nd}$ catalyst bed input gas temperature is 685 K. Your input enthalpies must be for that temperature.

(e) Note that cell D2 must contain 0.12. This is because 1 kg-mole of 12 volume% SO$_2$ 1$^{st}$ catalyst bed feed gas contains 0.12 kg-mole of SO$_2$. This value is needed for Eqn. (14.1)'s \% SO$_2$ oxidized calculation.
CHAPTER 15

Maximum SO₂ Oxidation in a 2nd Catalyst Bed

Chapter 14 describes 2nd catalyst bed heatup paths. This chapter describes 2nd catalyst bed:

- equilibrium curves
- heatup path-equilibrium curve intercepts.

The objectives of the chapter are to:

(a) show that equilibrium curve Eqn. (10.13) applies to 2nd catalyst beds as well as to 1st catalyst beds
(b) determine a 2nd catalyst bed heatup path-equilibrium curve intercept
(c) quantify two bed SO₂ oxidation efficiency.

15.1 2nd Catalyst Bed Equilibrium Curve Equation

Fig. 14.3's 1st catalyst bed equilibrium curve is described by Equation (10.13), i.e.:

\[
T_E = \frac{-B}{A + R \cdot \ln \left( \frac{\Phi^E}{100 - \Phi^E} \right) \cdot \left( \frac{100 - \frac{1}{2} e^* \Phi^E}{100} \right) \cdot \left( \frac{1}{2} p_i \right)^{\frac{1}{2}}} 
\]

where:

\( T_E \) = equilibrium temperature

\( A \), \( B \), \( R \), \( e^* \), \( \Phi^E \), \( p_i \)
A and B = empirical constants relating $\Delta G^\circ$ for $\text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{SO}_3(\text{g})$ oxidation to temperature, Eqn. (10.9) and Appendix C

\[ A = 0.09357 \text{ MJ kg-mole SO}_2^{-1} \text{ K}^{-1} \]

\[ B = -98.41 \text{ MJ/kg-mole SO}_2 \]

$R =$ gas constant, $0.008314 \text{ MJ kg-mole SO}_2^{-1} \text{ K}^{-1}$

$\Phi^E =$ 1st catalyst bed equilibrium $\% \text{SO}_2$ oxidized, Eqn. (10.2)

e = volume$\%$ SO$_2$ in 1st catalyst bed feed gas, 10% in Fig. 14.3

f = volume$\%$ O$_2$ in 1st catalyst bed feed gas, 11% in Fig. 14.3

$P_1 =$ 1st catalyst bed pressure, 1.2 bar in Fig. 14.3.

Re-written with the above numerical e, f and $P_1$ values, Eqn. (10.13) becomes:

\[
T_E = \frac{-B}{A + R \cdot \ln \left( \frac{\Phi^E}{100 - \Phi^E} \right) \cdot \left( \frac{100 - \frac{1}{2} \cdot 10^* \cdot \frac{\Phi^E}{100}}{11 - \frac{1}{2} \cdot 10^* \cdot \frac{\Phi^E}{100}} \right)} \cdot 1.2^{\frac{1}{2}}
\]

(15.1).

So far, this equation has been shown to apply to Fig. 14.3's 1st catalyst bed. This section indicates that it also applies to Fig. 14.3's 2nd catalyst bed – with, however, a slightly different definition of equilibrium $\% \text{SO}_2$ oxidized.

The new, more general, definition of equilibrium $\% \text{SO}_2$ oxidized is:

Equilibrium $\% \text{SO}_2$ oxidized = $\Phi^E$

\[
\frac{\text{kg-mole SO}_2 \text{ in 1st catalyst bed feed gas}}{\text{kg-mole SO}_2 \text{ in oxidized gas in any catalyst bed where equilibrium has been attained}} \cdot \frac{\text{kg-mole SO}_2 \text{ in 1st catalyst bed feed gas}}{100}
\]

(15.2)

where all quantities are per kg-mole of 1st catalyst bed feed gas.
15.1.1 Proof of 2\textsuperscript{nd} catalyst bed applicability

All equations used in deriving Eqn. (15.1) for Fig. 14.2's 1\textsuperscript{st} catalyst bed also apply to Fig. 14.2's 2\textsuperscript{nd} catalyst bed, Appendix L. So Eqn. (15.1) is also applicable to both beds.

In fact, equilibrium Eqn. (15.1) applies to all before-H\textsubscript{2}SO\textsubscript{4}-making catalyst beds where:

(a) the feed to the 1\textsuperscript{st} catalyst bed contains 10 volume\% SO\textsubscript{2}, 11 volume\% O\textsubscript{2} and 79 volume\% N\textsubscript{2}

(b) bed pressure is 1.2 bar pressure.

Industrial bed pressures are discussed in Section 18.7.

15.2 2\textsuperscript{nd} Catalyst Bed Intercept Calculation

Table 15.1 presents:

\begin{itemize}
  \item heatup path
  \item equilibrium curve
\end{itemize}

% SO\textsubscript{2} oxidized/temperature points near Fig. 14.3's expected 2\textsuperscript{nd} catalyst bed intercept point.

The points are for the conditions in Fig. 14.2, i.e.:

(a) 690 K, 10 volume\% SO\textsubscript{2}, 11 volume\% O\textsubscript{2}, 79 volume\% N\textsubscript{2} 1\textsuperscript{st} catalyst bed feed gas

(b) attainment of intercept (equilibrium) conditions in the 1\textsuperscript{st} catalyst bed at 1.2 bar pressure

(c) assumption that 1\textsuperscript{st} catalyst bed exit gas = 1\textsuperscript{st} catalyst bed intercept gas, Section 12.12

(d) cooldown of 1\textsuperscript{st} catalyst bed exit gas to 700 K with no change in gas composition

(e) feeding of this cooled gas to the 2\textsuperscript{nd} catalyst bed

(f) 1.2 bar pressure in the 2\textsuperscript{nd} catalyst bed.
Table 15.1. 2\textsuperscript{nd} catalyst bed % $SO_2$ oxidized/temperature points near heatup path-equilibrium curve intercept. They have been calculated as described in Appendices K and D.

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>Heatup path % $SO_2$ oxidized, $\Phi$</th>
<th>Equilibrium % $SO_2$ oxidized, $\Phi^E$ from Eqn. (15.1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>777</td>
<td>95.49</td>
<td>93.78</td>
</tr>
<tr>
<td>776</td>
<td>95.15</td>
<td>93.89</td>
</tr>
<tr>
<td>775</td>
<td>94.81</td>
<td>94.00</td>
</tr>
<tr>
<td>774</td>
<td>94.47</td>
<td>94.11</td>
</tr>
<tr>
<td>773</td>
<td>94.12</td>
<td>94.21</td>
</tr>
<tr>
<td>772</td>
<td>93.78</td>
<td>94.32</td>
</tr>
<tr>
<td>771</td>
<td>93.44</td>
<td>94.42</td>
</tr>
<tr>
<td>770</td>
<td>93.10</td>
<td>94.53</td>
</tr>
</tbody>
</table>

15.2.1 Intercept

Table 15.1 shows that at 773 K and below:

heatup path % $SO_2$ oxidized is below equilibrium % $SO_2$ oxidized.

This indicates that $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$ oxidation can proceed further up the heatup path towards equilibrium.

At 774 K and above, however:

heatup path % $SO_2$ oxidized is greater than equilibrium % $SO_2$ oxidized

which is impossible because equilibrium % $SO_2$ oxidized cannot be exceeded up a heatup path.

Interpolation suggests that Table 15.1's heatup path intercepts its equilibrium curve at:

773.2 K
94.2 % $SO_2$ oxidized, Fig. 15.1.

This is confirmed by a Goal Seek calculation in Table M.2.

15.2.2 Intercept gas composition

Intercept gas quantities are needed for Chapter 16's 3\textsuperscript{rd} catalyst bed calculations. They are obtained from the intercept results in Table M.2. They are:

0.0942 kg-mole $SO_3$
0.0058 kg-mole $SO_2$
0.0629 kg-mole $O_2$
0.7900 kg-mole $N_2$

per kg-mole of 1\textsuperscript{st} catalyst bed feed gas.
15.3 Two Bed SO$_2$ Oxidation Efficiency

Fig. 15.1 extends Fig. 14.3's 2$^{\text{nd}}$ catalyst bed heatup path to the Section 15.2.1 intercept. It shows that:

(a) cooling Fig. 14.2's 1$^{\text{st}}$ catalyst bed exit gas to 700 K

(b) passing the cooled gas through a 2$^{\text{nd}}$ catalyst bed

increases SO$_2$ oxidation efficiency from:

- 69.2% after the 1$^{\text{st}}$ catalyst bed
- 94.2% after the 2$^{\text{nd}}$ catalyst bed.

This confirms the efficacy of multi-bed catalytic oxidation with gas cooling between beds.

Fig. 15.1. SO$_2$ oxidation efficiency in two catalyst beds with gas cooling between beds. The 1$^{\text{st}}$ bed oxidizes 69.2% of 1$^{\text{st}}$ catalyst bed feed SO$_2$ - the 2$^{\text{nd}}$ bed an additional 25%. Note that the equilibrium curve is exactly the same for both catalyst beds, Section 15.1.1.

15.4 Summary

Cooling 1$^{\text{st}}$ catalyst bed exit gas and passing the cooled gas through a 2$^{\text{nd}}$ catalyst bed increases SO$_2$ oxidation efficiency from:

$\sim$70% to $\sim$95%.
SO₂ oxidation efficiency can be increased even further by:

(a) cooling the 2nd catalyst bed exit gas
(b) passing the cooled gas through a 3rd catalyst bed, next chapter.

Problems

15.1 Prepare a graph like Fig. 15.1 for the following.

(a) 12 volume% SO₂, 13.2 volume% O₂, 74.8 volume% N₂ 1st catalyst bed feed gas
(b) This gas enters the 1st catalyst bed at 675 K and reacts to equilibrium (1.2 bar) at the gas's heatup path-equilibrium curve intercept.
(c) The intercept gas exits the catalyst bed and is cooled to 685 K with no chemical reaction during cooling.
(d) The cooled gas is fed into a 2nd catalyst bed where SO₂ oxidation (by O₂ in the gas) and gas warming occur.
(e) The gas in (d) reacts until its heatup path intercepts its equilibrium curve.

Hints:

(a) Your answer to Problem 14.1 already contains most of the required graph. You only need to calculate the intercept point.
(b) The equilibrium equation for catalyst bed 2 is the same as for catalyst bed 1 because no gas has been added or removed between beds and because 1st and 2nd bed equilibrium pressures are the same (1.2 bar).
(c) Calculate the 2nd catalyst bed intercept point as described in Appendix M. Make sure that you use 685 K for the 2nd catalyst bed gas input temperature.
(d) The 2nd catalyst bed gas input quantities are those in your Problem 12.3(b) answer.
(e) Add your intercept point to Problem 14.1's heatup path and re-plot the path. This completes your graph.

15.2 Tabulate Problem 15.1's intercept kg-mole SO₃, SO₂, O₂ and N₂. They are needed for Problem 16.1.
CHAPTER 16

3rd Catalyst Bed SO₂ Oxidation

Simplest industrial sulfuric acidmaking consists of:

SO₂ oxidation in three catalyst beds with gas cooling between beds

then:

H₂SO₄ making by contact of cooled 3rd catalyst bed exit gas with strong sulfuric acid, Fig. 16.1.

---

**Fig. 16.1.** Schematic of single contact, 3 catalyst bed sulfuric acid plant. It is a single contact plant because it has only one H₂SO₄ making step. Note gas cooling between catalyst beds. It permits additional SO₂ oxidation in the next catalyst bed.
The SO₂ oxidation reaction is:

\[
\text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) \xrightarrow{\text{catalyst}} \text{SO}_3(g)
\]

in catalyst bed input gas 700-900 K

The H₂SO₄ making reaction is:

\[
\text{SO}_3(g) + \text{H}_2\text{O}(\ell) \rightarrow \text{H}_2\text{SO}_4(\ell)
\]

in cooled 3rd catalyst bed exit gas 350-380 K

in strong sulfuric acid in strengthened sulfuric acid

This chapter describes cooling of 2nd catalyst bed exit gas and oxidation of the cooled gas's SO₂ in a 3rd catalyst bed. Its objectives are to:

(a) prepare a 2-3 cooldown path

(b) prepare a 3rd catalyst bed heatup path

(c) calculate a 3rd bed heatup path-equilibrium curve intercept.

Specifications for the calculations are shown in Fig. 16.2. Calculation results are summarized in Figs. 16.3 and 16.4.

### 16.1 2-3 Cooldown Path

This chapter's 2-3 cooldown path is prepared like Fig. 13.3's 1-2 cooldown path. It is a horizontal line at:

94.2% SO₂ oxidized (2nd catalyst bed intercept % SO₂ oxidized)

between:

773.2 K (2nd catalyst bed intercept temperature)

and:

710 K (specified 3rd catalyst bed input gas temperature).

It is shown in Figs. 16.3 and 16.4.

### 16.2 Heatup Path

This chapter's 3rd catalyst bed heatup path is calculated much like Chapter 14's 2nd catalyst bed heatup path. Differences are:
Fig. 16.2. Specifications for (i) 2-3 cooldown and (ii) 3rd catalyst bed heatup path and intercept calculations. The 1st and 2nd catalyst bed exit gas quantities are equivalent to:

69.2% SO₂ oxidized after the 1st catalyst bed

94.2% SO₂ oxidized after the 2nd catalyst bed. Fig. 15.1.
(a) the input gas temperature is 710 K rather than 700 K

(b) the input gas quantities are different, Fig. 16.2.

The latter are represented by the equations:

\[
\text{kg-mole SO}_3 \text{ in} = 0.0942 \quad (16.1)
\]
\[
\text{kg-mole SO}_2 \text{ in} = 0.0058 \quad (16.2)
\]
\[
\text{kg-mole O}_2 \text{ in} = 0.0629 \quad (16.3)
\]
\[
\text{kg-mole N}_2 \text{ in} = 0.7900 \quad (16.4).
\]

Appendix N shows a 3\textsuperscript{rd} catalyst bed heatup path matrix with these equations. It also shows several heatup path points. Figs. 16.3 and 16.4 show the entire heatup path.

16.3 Heatup Path-Equilibrium Curve Intercept

Appendix O describes a 3\textsuperscript{rd} catalyst bed intercept calculation – with the Fig. 16.2 specifications. The 3\textsuperscript{rd} bed intercept with these specifications is:

721.1 K

98.0 \% \textit{SO}_2 \text{ oxidized}.

Its gas quantities are:

- 0.098 kg-mole \text{SO}_3
- 0.002 kg-mole \text{SO}_2
- 0.061 kg-mole \text{O}_2
- 0.790 kg-mole \text{N}_2

per kg-mole of 1\textsuperscript{st} catalyst bed feed gas. These quantities go forward to the next acidmaking step – almost always to \textit{H}_2\text{SO}_4 making but occasionally to a 4\textsuperscript{th} catalyst bed.

16.4 Graphical Representation

Figs. 16.3 and 16.4 describe 3-bed \text{SO}_2 oxidation with Fig. 16.2's specifications. They indicate that the percentages of \text{SO}_2 oxidized in each bed are:

- 69.2\% in the 1\textsuperscript{st} catalyst bed
- 25.0\% in the 2\textsuperscript{nd} catalyst bed
- 3.8\% in the 3\textsuperscript{rd} catalyst bed

for a total of 98.0\%
Fig. 16.3. 3 catalyst bed SO$_2$ oxidation with gas cooling between beds. The equilibrium curve is the same for all beds (Section 15.1.1) because:
(a) no component gas (e.g. SO$_3$) is selectively removed from the Fig. 16.2 gas stream (Appendix L)
(b) no air is added to the Fig. 16.2 gas stream
(c) all beds are at the same pressure.

Fig. 16.4. Blowup of top portion of Fig. 16.3. Overall SO$_2$ oxidation efficiency increases with each bed but the gain diminishes.
16.5 Summary

2nd and 3rd catalyst bed heatup path and intercept calculations are very similar.

Their differences are:

(a) different SO3, SO2, O2 and N2 input quantities
(b) different gas input temperatures.

3 catalyst bed SO2 oxidation efficiency is about ~98%. Beds 1, 2 and 3 contribute ~69%, 25% and 4%.

Chapter 17 examines the effects of SO3 and CO2 in feed gas on these catalytic oxidation efficiencies.

Problems

16.1 Prepare a graph like Fig. 16.3 for:

(a) 12 volume% SO2, 13.2 volume% O2, 74.8 volume% N2 1st catalyst bed feed gas
(b) the following gas input temperatures

1st catalyst bed 675 K
2nd catalyst bed 685 K
3rd catalyst bed 695 K.

(c) 1.2 bar gas pressure in all beds.

(d) attainment of intercept % SO2 oxidized in all beds.

Hints:

(a) Your answer to Problem 15.1 contains most of the required graph. You only need to prepare:

(i) a 2-3 cooldown path
(ii) a 3rd catalyst bed heatup path
(iii) a 3rd catalyst bed intercept point (which you can join to the heatup path).

(b) The 3rd catalyst bed’s input gas quantities are those in your Problem 15.2 answer.

16.2 Tabulate the intercept kg-mole of SO3, SO2, O2 and N2 equivalent to Prob. 16.1’s 3rd catalyst bed intercept point (all per kg-mole of 1st catalyst bed feed gas).
CHAPTER 17

SO₃ and CO₂ in Feed Gas

Industrial sulfur-burning exit gas contains ~0.2 volume% SO₃ when it reaches an acid plant's 1ˢᵗ catalyst bed, Chapter 3. The SO₃ slightly affects catalyst bed:

- equilibrium curves
- heatup paths
- heatup path-equilibrium curve intercepts.

Industrial metallurgical and waste acid regeneration gases don't contain SO₃ when they reach an acid plant's 1ˢᵗ catalyst bed. SO₃ is water scrubbed from these gases during gas cooling and cleaning, Chapters 4 and 5. They do, however, contain up to 8 volume% CO₂ when they reach the acid plant's 1ˢᵗ catalyst bed. The CO₂ comes from fossil fuel and waste acid hydrocarbons. The CO₂ slightly affects:

- heatup paths
- heatup path-equilibrium curve intercepts.

This chapter describes 1ˢᵗ catalyst bed calculations with SO₃ and CO₂ in feed gas. Its objectives are to show how:

(a) feed gas SO₃ and CO₂ are included in our 1ˢᵗ catalyst bed equilibrium curve, heatup path and intercept calculations

(b) these gases affect 1ˢᵗ catalyst bed SO₂ oxidation efficiency.

The effects are shown to be quite small.

17.1 SO₃

17.1.1 SO₃ effect on equilibrium curve equation

SO₃-in-feed-gas changes SO₂ + ½O₂ → SO₃ equilibrium curve Eqn. (10.13) to:
\[
T_E = \frac{A + R \ln \left( \frac{d + e \Phi^E}{100} \right) - B}{A + R \ln \left( \frac{d + e \Phi^E}{100} \right) + \left( \frac{100 - 1}{2} e \Phi^E \right) \left( \frac{100 - 1}{2} f \Phi^E \right)^{1/2} P_i^{-1/2}}
\]

(17.1).

where:

\( T_E \) = equilibrium temperature, K

\( A \) and \( B \) = empirical constants for calculating \( \Delta G_T^{\circ} \) \( \text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{SO}_3(\text{g}) \) from temperature, Eqn. (10.9) and Appendix C

\( A = 0.09357 \text{ MJ kg-mole SO}_2^{-1}K^{-1} \)

\( B = -98.41 \text{ MJ/kg-mole SO}_2 \)

\( R \) = gas constant, 0.008314 MJ kg-mole \( \text{SO}_2 \) \( ^{-1} \) K\(^{-1} \)

\( d \) = volume\% \( \text{SO}_3 \) in 1\(^{st} \) catalyst bed feed gas

\( e \) = volume\% \( \text{SO}_2 \) " " " remainder \( \text{N}_2 \) and \( \text{CO}_2 \)

\( f \) = volume\% \( \text{O}_2 \) " " "

\( \Phi^E \) = equilibrium \% \( \text{SO}_2 \) oxidized, Section 15.1

\( P_i \) = total gas pressure, bar.

Eqn. (17.1) is developed in Appendix P. Notice that a zero value of 'd' reduces it to Eqn. (10.13).

17.1.2 Effect of \( \text{SO}_3 \) on heatup path matrix

\( \text{SO}_3 \)-in-feed-gas changes Chapter 11's heatup path matrix by introducing a new input variable:

\[ \text{kg-mole SO}_2 \text{ in} \]

and a new \( \text{SO}_3 \) input equation:

\[ \text{kg-mole SO}_3 \text{ in} = \frac{\text{mole\% SO}_3 \text{ in feed gas}}{100} \]

which, for 0.2 volume\% \( \text{SO}_3 \), is:

\[ \text{kg-mole SO}_3 \text{ in} = \frac{0.2\% \text{ SO}_3}{100} = 0.002 \]  

(17.2)

per kg-mole of 1\(^{st} \) catalyst bed feed gas.
17.1.3 \( \text{SO}_2 \) input equation changed by \( \text{SO}_3 \)

Assuming a 0.2 volume\% \( \text{SO}_3 \), 9.8 volume\% \( \text{SO}_2 \), 11 volume\% \( \text{O}_2 \), 79 volume\% \( \text{N}_2 \) feed gas, 0.2\% \( \text{SO}_3 \) changes \( \text{SO}_2 \) input Equation (11.7) to:

\[
\text{kg-mole SO}_2 \text{ in} = 9.8\% \text{ SO}_2 = 0.098 \tag{17.3}
\]

17.1.4 Balances changed by \( \text{SO}_3 \)

\( \text{SO}_3 \)-in-feed-gas changes 1st catalyst bed:

(a) \( S \) balance Eqn. (11.4) to:

\[
0 = -\text{kg-mole SO}_3 \text{ in} - \text{kg-mole SO}_2 \text{ in} + \text{kg-mole SO}_3 \text{ out} + \text{kg-mole SO}_2 \text{ out} \tag{14.6}
\]

(b) \( O \) balance Eqn. (11.5) to:

\[
0 = -3\times \text{kg-mole SO}_3 \text{ in} - 2\times \text{kg-mole SO}_2 \text{ in} - 2\times \text{kg-mole O}_2 \text{ in} \\
+ 3\times \text{kg-mole SO}_3 \text{ out} + 2\times \text{kg-mole SO}_2 \text{ out} + 2\times \text{kg-mole O}_2 \text{ out} \tag{14.7}
\]

(c) enthalpy balance Eqn. (11.6B) to:

\[
0 = -\text{kg-mole SO}_2 \text{ in} \times H_{\text{T feed}}^{\circ} \text{SO}_3 \\
- \text{kg-mole SO}_2 \text{ in} \times H_{\text{T feed}}^{\circ} \text{SO}_2 \\
- \text{kg-mole O}_2 \text{ in} \times H_{\text{T feed}}^{\circ} \text{O}_2 \\
- \text{kg-mole N}_2 \text{ in} \times H_{\text{T feed}}^{\circ} \text{N}_2 \\
+ \text{kg-mole SO}_3 \text{ out} \times H_{\text{T bed}}^{\circ} \text{SO}_3 \\
+ \text{kg-mole SO}_2 \text{ out} \times H_{\text{T bed}}^{\circ} \text{SO}_2 \\
+ \text{kg-mole O}_2 \text{ out} \times H_{\text{T bed}}^{\circ} \text{O}_2 \\
+ \text{kg-mole N}_2 \text{ out} \times H_{\text{T bed}}^{\circ} \text{N}_2 \tag{14.8A}
\]

where:

\( H_{\text{T feed}}^{\circ} \) = enthalpy at the 1st catalyst bed feed gas temperature

\( H_{\text{T bed}}^{\circ} \) = enthalpy at a temperature part way down the catalyst bed.

The result of the Section 17.1.2-17.1.4 changes is heatup path matrix Table 17.1.
Table 17.1. 1st catalyst bed heatup path worksheet with 0.2 volume% SO\textsubscript{3} and 9.8 volume% SO\textsubscript{2} in feed gas.\textsuperscript{a} It is similar to Table 14.2's 2nd catalyst bed worksheet. Cells D15 to G15 contain $H_{k_{90}}^r$ values. Cells H15 to K15 contain $H_{k_{80}}^r$ values. All are calculated with Appendix G's enthalpy equations. 820 K part way down the catalyst bed is shown to be equivalent to oxidation of 45.2% of the feed gas's SO\textsubscript{2}.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>All calculations are based on 1 kg-mole of 1st catalyst bed feed gas.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>volume% SO\textsubscript{2} in 1st catalyst bed feed gas = 9.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>kg-mole SO\textsubscript{2} in 1 kg-mole of 1st catalyst bed feed gas = volume% SO\textsubscript{2}/100% = 0.098</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>=D2/100 (11.1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6 1st catalyst bed matrix

<table>
<thead>
<tr>
<th></th>
<th>Equation</th>
<th>Description</th>
<th>Numerical Term</th>
<th>kg-mole SO\textsubscript{2} in</th>
<th>kg-mole SO\textsubscript{2} in</th>
<th>kg-mole O\textsubscript{2} in</th>
<th>kg-mole N\textsubscript{2} in</th>
<th>kg-mole SO\textsubscript{2} out</th>
<th>kg-mole SO\textsubscript{2} out</th>
<th>kg-mole O\textsubscript{2} out</th>
<th>kg-mole N\textsubscript{2} out</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>17.2</td>
<td>input SO\textsubscript{2} kg-mole</td>
<td>0.0020</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>17.3</td>
<td>input SO\textsubscript{2} kg-mole</td>
<td>0.0980</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>11.2</td>
<td>input O\textsubscript{2} kg-mole</td>
<td>0.1100</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>11.3</td>
<td>input N\textsubscript{2} kg-mole</td>
<td>0.7900</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>14.6</td>
<td>S balance</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>14.7</td>
<td>O balance</td>
<td>0</td>
<td>-3</td>
<td>-2</td>
<td>0</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>14.8</td>
<td>N balance</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Enthalpy balance</td>
<td>0</td>
<td>371.3</td>
<td>278.7</td>
<td>-12.21</td>
<td>-11.66</td>
<td>-362.0</td>
<td>-272.0</td>
<td>16.54</td>
<td>15.71</td>
<td></td>
</tr>
</tbody>
</table>

16 690 K feed

18 820 K part way down bed

19 Matrix results per kg-mole of 1st catalyst bed feed gas

20 kg-mole SO\textsubscript{2} in | 0.0020 |
| 21 kg-mole SO\textsubscript{2} in | 0.0980 |
| 22 kg-mole O\textsubscript{2} in | 0.1100 |
| 23 kg-mole N\textsubscript{2} in | 0.7900 |
| 24 kg-mole SO\textsubscript{2} out | 0.0463 | % SO\textsubscript{2} oxidized equivalent to 820 K = (kg-mole SO\textsubscript{2} in - kg-mole SO\textsubscript{2} out)/kg-mole SO\textsubscript{2} in*100 (Eqn. 10.1) |
| 25 kg-mole SO\textsubscript{2} out | 0.0537 | = (F3-B25)/F3*100 |
| 26 kg-mole O\textsubscript{2} out | 0.0879 | 45.2 % SO\textsubscript{2} oxidized |
| 27 kg-mole N\textsubscript{2} out | 0.7900 |

\textsuperscript{a}Feed gas: 0.2 volume% SO\textsubscript{3}, 9.8 volume% SO\textsubscript{2}, 11 volume% O\textsubscript{2}, 79 volume% N\textsubscript{2}; 690 K.
17.1.5 Effect of SO$_3$ on heatup path-equilibrium curve intercepts

Appendix Q shows how:

new equilibrium Eqn. (17.1)

and:

new matrix Table 17.1

are combined to calculate an SO$_3$-in-feed gas heatup path-equilibrium curve intercept.

The results are given in the next section.

17.2 SO$_3$ Effects

Table 17.2 shows 1$^{st}$ catalyst bed intercept temperature-% SO$_2$ oxidized points with and without 0.2 volume% SO$_3$ in feed gas. The presence of 0.2% SO$_3$ is shown to have little effect on intercept % SO$_2$ oxidized.

<table>
<thead>
<tr>
<th>Feed gas type</th>
<th>Intercepts</th>
<th>SO$_2$ oxidized %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metallurgical or spent acid regeneration feed gas $^a$</td>
<td>690; 0</td>
<td>69.9</td>
</tr>
<tr>
<td>Sulfur-burning feed gas $^a$</td>
<td>891.4, 69.9</td>
<td>890.3; 69.7</td>
</tr>
</tbody>
</table>

$^a$11 volume% O$_2$, remainder N$_2$; 1.2 bar

17.3 CO$_2$

CO$_2$-in-feed-gas affects catalyst bed heatup paths and intercepts (but not equilibrium curves, Appendix F). The remainder of this chapter indicates how CO$_2$-in-feed-gas affects:

(a) the Table 17.1 heatup path matrix

(b) 1$^{st}$ catalyst bed intercepts.

It considers 10 volume% CO$_2$ in feed gas (plus 0 volume% SO$_3$, 10 volume% SO$_2$, 11 volume% O$_2$, 69 volume% N$_2$).
17.3.1 CO₂ effect on heatup path matrix

CO₂ in feed gas introduces two new variables into the Table 17.1 heatup path matrix:

\[ \text{kg-mole CO}_2 \text{ in} \]
\[ \text{kg-mole CO}_2 \text{ out}. \]

Of course, their numerical values are the same because CO₂ doesn't react during SO₂ oxidation or H₂SO₄ making.

It also provides two new equations:

(a) A CO₂ input quantity equation:

\[ \text{kg-mole CO}_2 \text{ in} = \frac{\text{mole}\% \text{ CO}_2 \text{ in feed gas}}{100} \]

or, with 10 volume\% CO₂ in feed gas:

\[ \text{kg-mole CO}_2 \text{ in} = \frac{10\% \text{ CO}_2 \text{ in feed gas}}{100} = 0.1 \quad (17.4) \]

(b) A carbon balance equation:

\[ \text{kg-mole C in} = \text{kg-mole C out}. \]

or:

\[ 1 \times \text{kg-mole CO}_2 \text{ in} = 1 \times \text{kg-mole CO}_2 \text{ out} \]

or:

\[ 0 = -1 \times \text{kg-mole CO}_2 \text{ in} + 1 \times \text{kg-mole CO}_2 \text{ out} \quad (17.5). \]

Changed equations

CO₂-in-feed-gas also changes:

(a) Oxygen balance Eqn. (14.7) to:

\[ 0 = -3 \times \text{kg-mole SO}_3 \text{ in} - 2 \times \text{kg-mole SO}_2 \text{ in} - 2 \times \text{kg-mole O}_2 \text{ in} - 2 \times \text{kg-mole CO}_2 \text{ in} \\
+ 3 \times \text{kg-mole SO}_3 \text{ out} + 2 \times \text{kg-mole SO}_2 \text{ out} + 2 \times \text{kg-mole O}_2 \text{ out} + 2 \times \text{kg-mole CO}_2 \text{ out} \]

\[ (17.6) \]
(b) enthalpy balance Eqn. (14.8A) to:

\[
0 = -\text{kg-mole } \text{SO}_3 \text{ in} \cdot H^0_{\text{T feed SO}_3} - \text{kg-mole } \text{SO}_2 \text{ in} \cdot H^0_{\text{T feed SO}_2} - \text{kg-mole } \text{O}_2 \text{ in} \cdot H^0_{\text{T feed O}_2} - \text{kg-mole } \text{N}_2 \text{ in} \cdot H^0_{\text{T feed N}_2} - \text{kg-mole } \text{CO}_2 \text{ in} \cdot H^0_{\text{T feed CO}_2} + \text{kg-mole } \text{SO}_3 \text{ out} \cdot H^0_{\text{T bed SO}_3} + \text{kg-mole } \text{SO}_2 \text{ out} \cdot H^0_{\text{T bed SO}_2} + \text{kg-mole } \text{O}_2 \text{ out} \cdot H^0_{\text{T bed O}_2} + \text{kg-mole } \text{N}_2 \text{ out} \cdot H^0_{\text{T bed N}_2} + \text{kg-mole } \text{CO}_2 \text{ out} \cdot H^0_{\text{T bed CO}_2}
\]

(17.7)

where:

\(H^0_{\text{T feed}}\) = enthalpy at the 1st catalyst bed feed gas temperature

\(H^0_{\text{T bed}}\) = enthalpy at a temperature part way down the catalyst bed.

(c) nitrogen input quantity equation Eqn. (11.3) to:

\[
\text{kg-mole N}_2 \text{ in} = \frac{\text{volume}\% \text{ N}_2 \text{ in feed gas}}{100} = \frac{69 \text{ volume}\% \text{ N}_2 \text{ in feed gas}}{100} = 0.69
\]

(17.8)

because the feed gas contains 69 volume\% N\(_2\) rather than the 79 volume\% N\(_2\) in matrix Table 17.1.

All of these changes are summarized in heatup path matrix Table 17.3.
Table 17.3. 1st catalyst bed heatup path matrix with SO₂ and CO₂ in feed gas. Cells D15 to H15 contain -H<sub>₆₀₀K</sub> values. Cells I15 to M15 contain H<sub>₃₀₀K</sub> values. All are calculated with Appendix G's enthalpy equations. 820 K part way down the catalyst bed is shown to be equivalent to oxidation of 46.7% of the feed gas's SO₂.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
<th>K</th>
<th>L</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>All calculations are based on 1 kg-mole of 1st catalyst bed feed gas.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>volume% SO₂ in 1st catalyst bed feed gas =</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>kg-mole SO₂ in 1 kg-mole of 1st catalyst bed feed gas = volume% SO₂/100% + 0.1 = D2/100 (11.1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Equation</td>
<td>description</td>
<td>numerical term</td>
<td>kg-mole SO₂ in</td>
<td>kg-mole SO₂ in</td>
<td>kg-mole O₂ in</td>
<td>kg-mole N₂ in</td>
<td>kg-mole CO₂ in</td>
<td>kg-mole SO₂ out</td>
<td>kg-mole SO₂ out</td>
<td>kg-mole O₂ out</td>
<td>kg-mole N₂ out</td>
<td>kg-mole CO₂ out</td>
</tr>
<tr>
<td>6</td>
<td>11.1</td>
<td>feed SO₂ kg-mole</td>
<td>0.10</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>11.2</td>
<td>feed SO₂ kg-mole</td>
<td>0.11</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>17.8</td>
<td>feed N₂ kg-mole</td>
<td>0.69</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>17.4</td>
<td>feed CO₂ kg-mole</td>
<td>0.10</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>14.6</td>
<td>S balance</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>17.6</td>
<td>O balance</td>
<td>0</td>
<td>-3</td>
<td>-2</td>
<td>-2</td>
<td>0</td>
<td>-2</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>12</td>
<td>14.8</td>
<td>N balance</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>13</td>
<td>17.5</td>
<td>C balance</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>14</td>
<td>enthalpy balance</td>
<td>371.3</td>
<td>278.7</td>
<td>-12.21</td>
<td>-11.66</td>
<td>376.2</td>
<td>-362.0</td>
<td>272.0</td>
<td>16.54</td>
<td>15.71</td>
<td>-396.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>690 K feed*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>820 K part way down catalyst bed</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>Matrix results per kg-mole of 1st catalyst bed feed gas</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>kg-mole SO₂ in</td>
<td>0.0000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>kg-mole SO₂ in</td>
<td>0.1000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>kg-mole N₂ in</td>
<td>0.1100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>kg-mole O₂ in</td>
<td>0.6900</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>kg-mole CO₂ in</td>
<td>0.1000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>kg-mole SO₂ out</td>
<td>0.0467</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>kg-mole O₂ out</td>
<td>0.0333</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>kg-mole N₂ out</td>
<td>0.0866</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>kg-mole CO₂ out</td>
<td>0.1000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

# Feed gas: 0 volume% SO₂, 10 volume% SO₂, 11 volume% O₂, 69 volume% N₂, 10 volume% CO₂, 690 K
17.4 CO₂ Effects

Fig. 17.1 shows the effect of CO₂ on a 1st catalyst bed heatup path and intercept. CO₂ has no effect on equilibrium curves, Appendix F.

The heatup path is slightly steeper with CO₂. This is because:

(a) CO₂ replaces N₂ in Fig. 17.1

(b) CO₂ heat capacity > N₂ heat capacity, Appendix G.

The overall result is a slightly:

- lower temperature
- higher % SO₂ oxidized

intercept, Fig. 17.1.

Fig. 17.1. Effect of CO₂-in-feed-gas on 1st catalyst bed heatup path and heatup path-equilibrium curve intercept. CO₂ increases heatup path slope and slightly increases intercept (equilibrium) % SO₂ oxidized, Section 17.4. Appendix Table R.1 describes the 10 volume% CO₂ intercept calculation.

17.5 Summary

Feed gas SO₃ and CO₂ are readily included in our catalyst bed calculations. SO₃ and CO₂ affect catalyst bed:
heatup paths
heatup-path/equilibrium curve intercepts.

SO₃ also affects SO₂ + ½O₂ → SO₃ equilibrium curves.

All the effects are quite small.

Problems

17.1 A sulfur burning 1st catalyst bed feed gas contains:

0.2 volume% SO₃
10.8 " SO₂
9.9 " O₂
79.1 " N₂

It enters a 1st catalyst bed at 695 K and 1.2 bar bed pressure.

Calculate:

(a) the percentage of the input SO₂ that will be oxidized when the gas's 1st catalyst bed intercept is attained

(b) the total kg-mole of SO₃ in the 1st catalyst bed's exit gas under these conditions (per kg-mole of 1st catalyst bed feed gas).

Use the technique described in Appendix Q.

17.2 A spent acid regeneration 1st catalyst bed feed gas contains:

10.5 volume% SO₂
10.5 " O₂
9.0 " CO₂
70.0 " N₂

It enters the 1st catalyst bed at 705 K. The bed is at 1.2 bar pressure.

Calculate the percentage of this gas's SO₂ that will be oxidized to SO₃ when the 1st catalyst bed intercept is attained. Use the technique described in Appendix R.

Compare this result to that of a:

10.5 volume% SO₂
10.5 " O₂
79.0 " N₂

1st catalyst bed feed gas under the same conditions.
CHAPTER 18

3 Catalyst Bed Acid Plant

Chapters 10 through 17 do separate 1st, 2nd and 3rd catalyst bed calculations. This chapter joins these calculations. Its objectives are to:

(a) combine Chapter 12 to 17’s 1st, 2nd and 3rd catalyst bed intercept calculations in one Excel worksheet
(b) calculate 1st, 2nd and 3rd catalyst bed intercept SO2 oxidation efficiencies for various feed gas compositions, gas input temperatures and bed pressures
(c) use (b)'s calculations to show how 3 catalyst bed SO2 oxidation can be maximized.

18.1 Calculation Specifications

Chapter 12 through 17's intercept calculations are combined by specifying:

1. a 1st catalyst bed feed gas composition
2. 1st, 2nd and 3rd catalyst bed input gas temperatures
3. 1st, 2nd and 3rd catalyst bed equilibrium pressures
4. that equilibrium is attained in each catalyst bed
5. that a catalyst bed's exit gas composition is its intercept (equilibrium) gas composition
6. that gas composition doesn't change during gas cooldown.

Specifications 4 to 6 link the 1st, 2nd and 3rd catalyst bed calculations.

18.2 Example Calculation

Table 18.1 gives numerical specifications for an example 3 catalyst bed calculation. The calculation itself is described in Appendix S. The objective of the calculation is to determine intercept % SO2 oxidized and temperature values for each of the 3 catalyst beds.
Table 18.1. Numerical specifications for Section 18.3 and 18.4 three catalyst bed calculations.

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st catalyst bed:</td>
<td></td>
</tr>
<tr>
<td>feed gas composition</td>
<td></td>
</tr>
<tr>
<td>volume% SO₃</td>
<td>0</td>
</tr>
<tr>
<td>volume% SO₂</td>
<td>10</td>
</tr>
<tr>
<td>volume% O₂</td>
<td>11</td>
</tr>
<tr>
<td>volume% N₂</td>
<td>79</td>
</tr>
<tr>
<td>volume% CO₂</td>
<td>0</td>
</tr>
<tr>
<td>feed gas temperature, K</td>
<td>690</td>
</tr>
<tr>
<td>bed pressure, bar</td>
<td>1.2</td>
</tr>
<tr>
<td>kg-mole SO₂ per kg-mole of feed gas</td>
<td>calculated</td>
</tr>
<tr>
<td>2nd catalyst bed</td>
<td></td>
</tr>
<tr>
<td>input gas temperature, K</td>
<td>700</td>
</tr>
<tr>
<td>bed pressure, bar</td>
<td>1.2</td>
</tr>
<tr>
<td>3rd catalyst bed</td>
<td></td>
</tr>
<tr>
<td>input gas temperature, K</td>
<td>710</td>
</tr>
<tr>
<td>bed pressure, bar</td>
<td>1.2</td>
</tr>
</tbody>
</table>

18.3 Calculation Results

The results of a 3 catalyst bed calculation with the above specifications are given in Table 18.2. They are plotted in Figs. 18.1 and 18.2. They show that 98% of 1st catalyst bed feed SO₂ is oxidized to SO₃ after 3 catalyst beds.

Table 18.2. Results of 3 catalyst bed calculation with Table 18.1 specifications. They are calculated in Appendix S. They are plotted in Fig. 18.1.

<table>
<thead>
<tr>
<th>Description</th>
<th>Intercept temperature, K</th>
<th>Intercept % SO₂ oxidized</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st catalyst bed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>feed</td>
<td>690</td>
<td>0</td>
</tr>
<tr>
<td>intercept</td>
<td>893.3</td>
<td>69.2</td>
</tr>
<tr>
<td>2nd catalyst bed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>input</td>
<td>700</td>
<td>69.2</td>
</tr>
<tr>
<td>intercept</td>
<td>773.1*</td>
<td>94.2</td>
</tr>
<tr>
<td>3rd catalyst bed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>input</td>
<td>710</td>
<td>94.2</td>
</tr>
<tr>
<td>intercept</td>
<td>721.0*</td>
<td>98.0</td>
</tr>
</tbody>
</table>

* These temperatures are 0.1 K lower than those calculated in Sections 15.2 and 16.3. The differences are due to different roundings.

18.4 3 Catalyst Bed Graphs

Fig. 18.1 shows Table 18.2's results as temperature % SO₂ oxidized points. Fig. 18.2 shows the results as:

(a) an equilibrium curve with 1.2 bar pressure in all beds

(b) heatup and cooldown paths.
Fig. 18.1. Plot of Table 18.2 catalyst bed input and intercept points. The intercepts are the same as those in Sections 12.2, 15.2.1 and 16.4.

Fig. 18.2. Equilibrium curve and straight lines between Fig. 18.1's calculated points. The straight line heatup paths closely approximate the 'real' heatup paths in Chapters 11 through 17.
18.4.1 Straight heatup paths

Previous chapters indicate that heatup paths are slightly curved, Fig. 11.6. This and subsequent chapters represent heatup paths as straight lines between:

input and intercept points, Figs. 18.1 and 18.2.

This:

(a) simplifies graphing
(b) closely represents the previous chapters' 'real' heatup paths
(c) has no effect on intercept calculations, Fig. 18.1.

18.4.2 SO₂ oxidation efficiency

The following sections describe the effects of six industrial variables on 3-bed SO₂ oxidation efficiency. Except where gas input temperature is variable, input gas temperature is 690 K, all beds.

18.5 Minor Effect - SO₃ in Feed Gas

Industrial sulfur burning gas contains ~0.2 volume% SO₃ when it reaches an acid plant's 1ˢᵗ catalyst bed, Chapter 3. This SO₃ slightly affects:

- equilibrium curves
- heatup paths
- equilibrium curve-heatup path intercepts,

Chapter 17 and Appendix P.

18.5.1 Effect of SO₃ on intercept % SO₂ oxidized

0.2 volume% SO₃ in acid plant feed gas has little effect on intercept % SO₂ oxidized, Table 18.3. The effect is noticeable after 1 and 2 beds – but not after 3 beds.

Nevertheless, feed SO₃ is included in our calculations, whenever specified.

18.6 Minor Effect – CO₂ in Feed Gas

Metallurgical and waste acid regeneration gases contain up to 8 volume% CO₂ – from fuels and waste acid hydrocarbons. This CO₂ has no effect on SO₂ + ½O₂ → SO₃ equilibrium curves but it does affect:

- heatup path slope
- intercept temperature and % SO₂ oxidized.

The effect is quite small, especially after 3 beds, Fig. 18.3.
Table 18.3. Comparison of intercept $\% SO_2$ oxidized values for feed gas containing 0 and 0.2 volume% SO$_3$. The difference after 3 beds is very small. The 1st catalyst bed feed gas contains 9.8 volume% SO$_2$, 11 volume% O$_2$, the specified amount of SO$_3$, remainder N$_2$. Gas pressure is 1.2 bar in all beds. Gas input temperature is 690 K, all beds.

<table>
<thead>
<tr>
<th>Feed Gas Type</th>
<th>0.0 volume% SO$_3$</th>
<th>0.2 volume% SO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metallurgical or acid-regeneration</td>
<td>69.9</td>
<td>69.7</td>
</tr>
<tr>
<td>Sulfur-burning feed gas</td>
<td>95.2</td>
<td>95.1</td>
</tr>
<tr>
<td>% SO$_2$ oxidized</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1st catalyst bed
feed
intercept

2nd catalyst bed
input
intercept

3rd catalyst bed
input
intercept

Fig. 18.3. Heatup paths and intercepts for 0 and 10 volume% CO$_2$ 1st catalyst bed feed gas. CO$_2$ heatup paths are steeper than non CO$_2$ heatup paths because CO$_2$ heat capacity > N$_2$ heat capacity, Appendix G. The steeper paths give higher intercept % SO$_2$ oxidized values in each catalyst bed.
18.7 Minor Effect – Bed Pressure

Industrial catalyst bed pressures are typically 1.1 to 1.4 bar. They are highest in 1st catalyst beds and lowest in last beds – due to dissipation of mechanical energy as gas passes through the beds.

The effect of bed pressure on intercept % $SO_2$ oxidized is shown in Fig. 18.4. It is small, especially after 3 catalyst beds.

![Graph showing effect of bed pressure on SO2 oxidation efficiency](image)

Fig. 18.4. Effect of gas pressure on intercept $SO_2$ oxidation efficiency. The lines show that % $SO_2$ oxidized increases with increasing pressure, all beds. After 3 catalyst beds the effect is small.

18.7.1 Validity of constant pressure specification

Figs. 18.1 through 18.4 specify the same pressure in all 3 catalyst beds. This specification is not necessary – the Appendix S worksheet can specify individual bed pressures. It is, however, convenient for graphing.

Fig. 18.5 compares intercept % $SO_2$ oxidized results for:

(a) 1.2 bar pressure in all beds

(b) 1.3, 1.2 and 1.1 bar pressure in beds 1, 2 and 3.

The difference between the results is tiny, especially after 3 beds.
18.8 Minor Effect – SO₂ Strength in Feed Gas

SO₂ strength in industrial catalytic oxidation feed gas varies from ~8 volume% to ~12 volume%, Table 7.2. The strength depends mainly on the preceding SO₂ production process.

Fig. 18.6 describes the effect of SO₂ concentration on intercept SO₂ oxidation efficiency. It indicates that:

(a) 1ˢᵗ and 2ⁿᵈ bed SO₂ oxidation efficiency decreases significantly with increasing volume% SO₂ in feed gas
(b) 3ʳᵈ bed SO₂ oxidation efficiency is only slightly affected by feed SO₂ concentration.

Industrial plants could send higher SO₂ strength gas to their acid plant – by enriching their combustion air with oxygen (Miller and Parekh, 2004). This strong SO₂ would:

(a) give a large production of sulfuric acid per Nm³ of gas passed through the acid plant
(b) only slightly lower SO₂ oxidation efficiency.

It would, however, tend to give catalyst overheating and degradation in the 1ˢᵗ catalyst bed, Section 12.11. For this reason, 12 volume% SO₂ is about the maximum strength used in industrial acid plants.
Fig. 18.6. Effect of 1st catalyst bed feed gas SO₂ strength on intercept SO₂ oxidation efficiency. The effect is significant after beds 1 and 2 but not after bed 3. The lower SO₂ oxidation efficiency with higher SO₂ strength is explained in Section 11.13.1 and Fig. 12.3.

18.9. Minor Effect – O₂ Strength in Feed Gas

Fig. 18.7 shows the effect of feed gas O₂ strength on intercept SO₂ oxidation efficiency.

Fig. 18.7. Effect of volume% O₂ in feed gas on intercept SO₂ oxidation efficiency. % SO₂ oxidized increases with increasing O₂ strength – but the effect is small, especially after 3 catalyst beds.
% $SO_2$ oxidized increases with increasing $O_2$ strength. However, the effect is quite small, especially after 3 catalyst beds.

8 to 16 volume% $O_2$ in Fig. 18.8 are equivalent to volume% $O_2$/volume% $SO_2$ ratios of:

0.8 and 1.6.

These are typical industrial $O_2/SO_2$ ratios, Table 7.2.

**18.10 Summary of Minor Effects**

Sections 18.5 through 18.9 indicate that:

<table>
<thead>
<tr>
<th>Volume% $SO_3$ in feed gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot; $CO_2$ &quot;</td>
</tr>
<tr>
<td>&quot; $SO_2$ &quot;</td>
</tr>
<tr>
<td>&quot; $O_2$ &quot;</td>
</tr>
</tbody>
</table>

catalyst bed pressure

have little effect on 3 bed catalytic $SO_2$ oxidation efficiency. Also, these variables are often not readily adjusted – because they are either:

(a) the result of their preceding $SO_2$ production process or:
(b) the consequence of atmospheric pressure and the pressure required to move gas through catalyst beds and other equipment.

In fact, the only truly adjustable parameters in industrial $SO_2$ oxidation are catalyst bed input gas temperatures, next section.

**18.11 Major Effect – Catalyst Bed Input Gas Temperatures**

Catalyst bed input gas temperatures are readily adjusted by heating and cooling the gas in boilers, economizers, heat exchangers etc. Industrial input temperatures vary from ~660 K to 720 K, Table 7.2.

Figs. 18.8 and 18.9 show how catalyst bed input gas temperature affects intercept $SO_2$ oxidation efficiency. Efficiency increases significantly with decreasing input gas temperature.

This is because:

(a) low gas input temperatures give low intercept temperatures, Fig. 18.8.

(b) low intercept temperatures give high $SO_2$ oxidation efficiencies.

This result suggests that industrial catalyst bed input gases should always be as cool as possible – consistent with steady, well controlled, long term catalyst bed operation.
Fig. 18.8. Three catalyst bed oxidation with 660 and 720 K input gas, all beds. 660 K input gas gives significantly more SO$_2$ oxidation. Notice that two catalyst beds with 660 K input gas give more SO$_2$ oxidation than three catalyst beds with 720 K input gas. The graph is the top portion of a graph like Fig. 18.3.

Fig. 18.9. Intercept % SO$_2$ oxidized values as a function of catalyst bed gas input temperature. SO$_2$ oxidation efficiency is seen to increase with decreasing input gas temperature.
18.12 Discussion of Book's Assumptions

This book makes three assumptions:

(a) that all processes are proceeding under steady state conditions, i.e. that temperatures and compositions are not changing with time anywhere in the system

(b) that there are no conductive, convective plus radiative heat losses from the system's catalyst beds

(c) that intercept (equilibrium) SO$_2$ oxidation is achieved in all catalyst beds.

This section discusses these three assumptions.

18.12.1 Steady state assumption

Sulfur burning acid plants operate steadily almost all the time. The main significance of this is that temperature is constant at every point in the plant's catalyst beds. It means that none of the gas's heat is being used to heat catalyst.

Metallurgical and spent acid regeneration plants are not quite so steady, but the steady state assumption is still reasonable.

18.12.2 No heat loss assumption

The assumption of no conductive, convective plus radiative heat loss from catalytic SO$_2$ oxidation converters is not perfectly correct. There is always some heat loss. Nevertheless:

(a) gas-in-catalyst bed residence times are short (~2 seconds per bed, Fig. 8.4)

(b) catalyst converters are well insulated

so that heat loss per kg-mole of gas is probably quite small.

Fig. 18.10 demonstrates the effect that heat loss would have on our SO$_2$ oxidation calculations.

18.12.3 Intercept attainment assumption

It is not easy to know how close industrial catalytic SO$_2$ oxidation comes to equilibrium. Our opinion is that it comes quite close, especially if the beds are run somewhat above their catalyst activation temperature. The effect of non-attainment is demonstrated in Fig. 18.10.
Fig. 18.10. Effect of:

- conductive, convective plus radiative heat loss
- non-attainment of equilibrium

on a 1st catalyst bed's final % SO$_2$ oxidized. The two effects are seen to offset each other. (The heat loss heatup path is steeper because less heat is available to warm the gas.)

18.13 Summary

This chapter combines Chapter 12 to 17's intercept calculations in a single worksheet. It then shows how:

- SO$_3$ concentration in feed gas
- CO$_2$
- SO$_2$
- O$_2$
- catalyst bed pressure
- catalyst bed input gas temperature

affect intercept (equilibrium) catalytic SO$_2$ oxidation efficiency.

Only input gas temperature has a significant effect. Cool input gas (but warm enough for rapid SO$_2$ oxidation) gives highly efficient SO$_2$ oxidation. Warmer input gas gives less efficient oxidation.

Reference
CHAPTER 19

After-$\text{H}_2\text{SO}_4$-Making $\text{SO}_2$ Oxidation

Many acid plants:

(a) catalytically oxidize most of their input $\text{SO}_2$ to $\text{SO}_3$ in 3 (occasionally 2 or 4) catalyst beds, Fig. 19.1

then:

(b) make $\text{H}_2\text{SO}_4(\ell)$ from the resulting $\text{SO}_3(g)$

then:

(c) catalytically oxidize the $\text{SO}_2$ remaining in step (b)'s exit gas – in 1 (occasionally 2) additional catalyst beds

then:

(d) make $\text{H}_2\text{SO}_4(\ell)$ from (c)'s new $\text{SO}_3$.

The process is called double contact acidmaking because gas and sulfuric acid are contacted twice, steps (b) and (d).

The (a) and (c) reaction is:

$$\text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) \xrightarrow{700-900 \text{ K}} \text{SO}_3(g) \quad (1.1).$$

in feed gas          catalyst

The (b) and (d) reaction is:

$$\text{SO}_3(g) + \text{H}_2\text{O}(\ell) \xrightarrow{350-380 \text{ K}} \text{H}_2\text{SO}_4(\ell) \quad (1.2).$$

in Eqn.(1.1) in strong in strengthened
product gas sulfuric acid sulfuric acid
Fig. 19.1. Schematic of 3-1 double contact sulfuric acid plant. The plant consists of:

3 catalyst beds before intermediate \( \text{H}_2\text{SO}_4 \) making
intermediate \( \text{H}_2\text{SO}_4 \) making, Eqn. (1.2)
1 catalyst bed after intermediate \( \text{H}_2\text{SO}_4 \) making
final \( \text{H}_2\text{SO}_4 \) making (not shown).

The increase in % \( \text{SO}_2 \) oxidized after each bed is notable. Other industrial versions of double contact acid plants are:

2 catalyst beds before \( \text{H}_2\text{SO}_4 \) making, 2 beds after
4 catalyst beds before \( \text{H}_2\text{SO}_4 \) making, 1 bed after, Chapter 20.

*See Table 19.3 (end of this chapter) for industrial after \( \text{H}_2\text{SO}_4 \) making catalyst bed data.
19.1 Double Contact Advantage

Double contact acidmaking always gives more efficient $\text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{SO}_3$ oxidation than single contact acidmaking. This leads to:

(a) more efficient $\text{SO}_3$ (hence $\text{H}_2\text{SO}_4$) production
(b) less $\text{SO}_2$ emission to the environment or a smaller $\text{SO}_2$-from-gas scrubbing plant.

The reason for double contact's high $\text{SO}_2$ oxidation efficiency is given in Figs. 19.6 and 19.7.

19.2 Objectives

The objectives of this chapter are to:

(a) show how after-intermediate-$\text{H}_2\text{SO}_4$-making $\text{SO}_2$ oxidation:
   equilibrium curves
   heatup paths
   heatup path-equilibrium curve intercepts
   are calculated

and to:

(b) calculate the $\text{SO}_2$ oxidation efficiency of Fig. 19.1's 3-1 double contact acid plant
(c) compare (b)'s $\text{SO}_2$ oxidation efficiency with that of a 4 catalyst bed single contact acid plant
(d) identify the extra costs of double contact acidmaking.

19.3 After-$\text{H}_2\text{SO}_4$-Making Calculations

The starting point for this chapter's calculations is the product gas from a specific:

3 catalyst bed + intermediate $\text{H}_2\text{SO}_4$ making

sequence, Fig. 19.2.

The exit gas from the 3 catalyst beds is specified to be that in Section 16.4. It contains:

- 0.098 kg-mole $\text{SO}_3$ (Fig. 19.2)
- 0.002 kg-mole $\text{SO}_2$
- 0.061 kg-mole $\text{O}_2$
- 0.790 kg-mole $\text{N}_2$

per kg-mole of 1st catalyst bed feed gas.
This gas goes to intermediate H$_2$SO$_4$ making where 100% of its SO$_3$ is specified as being removed as H$_2$SO$_4$(ℓ). The gas departing this step contains:

0.000 kg-mole SO$_3$ (Fig. 19.2)
0.002 kg-mole SO$_2$
0.061 kg-mole O$_2$
0.790 kg-mole N$_2$
0.853 total kg-mole

per kg-mole of 1$^{st}$ catalyst bed feed gas. It is sent to further catalytic SO$_2$ oxidation in Fig. 19.2's 4$^{th}$ catalyst bed.

Appendix U examines the case where less than 100% of H$_2$SO$_4$ making's input SO$_3$ is made into H$_2$SO$_4$.

### 19.4 Equilibrium Curve Calculation

This chapter treats after-H$_2$SO$_4$-making SO$_2$ oxidation as a completely new problem. This is necessary because selective SO$_3$ removal from gas during H$_2$SO$_4$(ℓ) making invalidates Appendix B's before-H$_2$SO$_4$-making equations.

The after intermediate H$_2$SO$_4$ making equilibrium curve equation is:

\[
T_E = \frac{-B}{A + R * \ln \left( \frac{\Phi^{E \text{ after}}}{100 - \Phi^{E \text{ after}}} \right) * \left( \frac{100 - \frac{1}{2}e' * \Phi^{E \text{ after}}}{100} \right) * 100^{-\frac{1}{2}} * P_t^{-\frac{1}{2}}}
\]

where $T_E$, $A$, $B$, $R$ and $P_t$ are the same as in Eqn (10.13), Section 15.1,

and where:

- $e'$ and $f'$ are volume% SO$_2$ and O$_2$ in 1$^{st}$ after-intermediate-H$_2$SO$_4$-making catalyst bed input gas
- $\Phi^{E \text{ after}}$ = equilibrium percentage of after-H$_2$SO$_4$-making input SO$_2$ that is oxidized in an after-H$_2$SO$_4$-making catalyst bed.

Eqn. (19.1) is similar to before-H$_2$SO$_4$-making equilibrium Eqn. (10.13), Section 15.1. It is derived the same way.
Fig. 19.2. Double contact acidmaking flowsheet with numerical values used in this chapter's calculations. The plant consists of 3 catalyst beds followed by intermediate H2SO4 making and a 4th catalyst bed. The gas from the last catalyst bed goes to cooling and final H2SO4 making (not shown). All kg-mole values are per kg-mole of 1st catalyst bed feed gas. Gas pressure = 1.2 bar, all beds.
19.4.1 $e'$ and $f'$

$e'$ and $f'$ are volume% SO$_2$ and O$_2$ in 1$^{\text{st}}$ after-H$_2$SO$_4$-making catalyst bed input gas. They are calculated from Fig. 19.2's intermediate H$_2$SO$_4$ making exit gas quantities, as follows:

$$
e' = \text{volume\% SO}_2 = \text{mole\% SO}_2 = \frac{\text{kg-mole SO}_2}{\text{total kg-mole}} \times 100\%$$

$$= \frac{0.002}{0.853} \times 100\% = 0.234\%$$

and:

$$
f' = \text{volume\% O}_2 = \text{mole\% O}_2 = \frac{\text{kg-mole O}_2}{\text{total kg-mole}} \times 100\%$$

$$= \frac{0.061}{0.853} \times 100\% = 7.15\%$$

19.4.2 After-H$_2$SO$_4$-making % SO$_2$ oxidized defined

After-intermediate-H$_2$SO$_4$-making % SO$_2$ oxidized is defined as:

$$\% \text{SO}_2 \text{ oxidized in after-H}_2\text{SO}_4\text{-making catalyst beds} = \psi_{\text{after}} = \frac{\text{kg-mole SO}_2 \text{ in 1$^{\text{st}}$ after-H}_2\text{SO}_4\text{-making catalyst bed input gas} - \text{kg-mole SO}_2 \text{ in any after-H}_2\text{SO}_4\text{-making catalyst bed's oxidized gas}}{\text{kg-mole SO}_2 \text{ in 1$^{\text{st}}$ after-H}_2\text{SO}_4\text{-making catalyst bed input gas}} \times 100$$

(all quantities per kg-mole of 1$^{\text{st}}$ before-H$_2$SO$_4$-making catalyst bed feed gas).

When equilibrium is attained in an after-H$_2$SO$_4$-making catalyst bed, $\psi_{\text{after}}$ becomes:

$$\text{Equilibrium } \% \text{SO}_2 \text{ oxidized in after-H}_2\text{SO}_4\text{-making catalyst beds} = \psi_{\text{E after}} = \frac{\text{kg-mole SO}_2 \text{ in 1$^{\text{st}}$ after-H}_2\text{SO}_4\text{-making catalyst bed input gas} - \text{kg-mole SO}_2 \text{ in oxidized gas in any after-H}_2\text{SO}_4\text{-making catalyst bed}}{\text{kg-mole SO}_2 \text{ in 1$^{\text{st}}$ after-H}_2\text{SO}_4\text{-making catalyst bed input gas}} \text{ where equilibrium has been attained} \times 100$$

(19.3)
19.4.3 Preparation of equilibrium curve

After-intermediate-H$_2$SO$_4$-making equilibrium curves are prepared from Eqn. (19.1) as described in Appendix D. $e'$, $f'$, and $P_t$ are specified and equilibrium temperatures are calculated for a series of $\Phi^E_{\text{after}}$ values (or vice versa). Fig. 19.3 shows the after-H$_2$SO$_4$-making equilibrium curve with this chapter's specifications.

![Equilibrium curve](image)

**Fig. 19.3.** Equilibrium curve for after-H$_2$SO$_4$-making catalyst beds. It is quite similar to Chapter 10.1's before-H$_2$SO$_4$-making curves. Input gas composition and equilibrium pressure specifications are shown. The curve is only valid for these specifications. $\Phi^E_{\text{after}}$ is defined by Eqn. (19.3).

19.5 Heatup Path Calculation

After-intermediate-H$_2$SO$_4$-making heatup paths are calculated exactly as before-H$_2$SO$_4$-making heatup paths, Chapter 11 and Appendix I. Table 19.1 shows the matrix for this chapter's after-H$_2$SO$_4$-making input gas. Fig. 19.4 shows an equivalent partial heatup path.

19.6 Heatup Path Equilibrium Curve Intercept Calculation

Maximum SO$_2$ oxidation in a catalyst bed is obtained where its:

heatup path

intercepts its:

equilibrium curve.
Table 19.1. Heatup path matrix for after-intermediate-\(\text{H}_2\text{SO}_4\)-making catalyst bed. The 1\textsuperscript{st} three rows represent the equations:

\[ n_{\text{SO}_2 \text{ in}} = 0.002 \text{ kg-mole, Fig. 19.2} \tag{19.4} \]
\[ n_{\text{O}_2 \text{ in}} = 0.061 \text{ kg-mole} \tag{19.5} \]
\[ n_{\text{N}_2 \text{ in}} = 0.790 \text{ kg-mole.} \tag{19.6} \]

All values are per kg-mole of 1\textsuperscript{st} before-\(\text{H}_2\text{SO}_4\) making catalyst bed feed gas. The matrix shows that a 695 K gas temperature is equivalent to oxidation of 69.3\% of the after-\(\text{H}_2\text{SO}_4\)-making catalyst bed's input \(\text{SO}_2\). Cells D8 to F8 contain \(\Delta H^0\) values, Eqn. (11.7). Cells G8 to J8 contain \(H^0\) values.

<table>
<thead>
<tr>
<th>A</th>
<th>Equation</th>
<th>Description</th>
<th>numerical term</th>
<th>B (\text{kg-mole SO}_2) in</th>
<th>C (\text{kg-mole O}_2) in</th>
<th>D (\text{kg-mole N}_2) in</th>
<th>E (\text{kg-mole SO}_3) out</th>
<th>F (\text{kg-mole SO}_2) out</th>
<th>G (\text{kg-mole O}_2) out</th>
<th>H (\text{kg-mole N}_2) out</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>19.4</td>
<td>input (\text{SO}_2) kg-mole</td>
<td>0.0020</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>19.5</td>
<td>input (\text{O}_2) kg-mole</td>
<td>0.0610</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>19.6</td>
<td>input (\text{N}_2) kg-mole</td>
<td>0.7900</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>11.4</td>
<td>(S) balance</td>
<td>0</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>11.5</td>
<td>(O) balance</td>
<td>0</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>11.6</td>
<td>(N) balance</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>enthalpy balance</td>
<td></td>
<td></td>
<td>0</td>
<td>278</td>
<td>10.21</td>
<td>-11.66</td>
<td>-370.9</td>
<td>-278.4</td>
<td>12.37</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Matrix results per kg-mole of 1\textsuperscript{st} before-\(\text{H}_2\text{SO}_4\)-making feed gas.

\[ \text{% SO}_2 \text{oxidized} = \frac{(\text{kg-mole SO}_2 \text{ in} - \text{kg-mole SO}_2 \text{ out})}{\text{kg-mole SO}_2 \text{ in}} \times 100 \tag{Eqn. 19.2} \]

\[ = \frac{(B13-B17)}{B13} \times 100 = 69.3 \% \]
Fig. 19.4. Equilibrium curve and partial heatup path for after-intermediate-H_2SO_4-making catalyst bed. The heatup path has been calculated with matrix Table 19.1 as in Appendix I. The steepness of the heatup path is due to the small amount of SO_2 'fuel' in the input gas. The equilibrium curve and heatup path are only valid for the specified inputs. The SO_2 and O_2 inputs are equivalent to 0.234 volume% SO_2 and 7.15 volume% O_2.

This chapter's after-H_2SO_4-making SO_2 oxidation intercept is shown in Table 19.2 and Figs. 19.5/19.6. It occurs at 697.3 K with 98.9% of the after-H_2SO_4-making catalyst bed input SO_2 oxidized to SO_3.

Table 19.2. After-intermediate-H_2SO_4-making % SO_2 oxidized-temperature points near heatup path-equilibrium curve intercept. The intercept temperature is shown to be between 697.30 and 697.31 K. The points are calculated as described in Appendices D and I. They are plotted in Fig. 19.5.

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>Heatup path % SO_2 oxidized, ( \Phi^\text{after} )</th>
<th>Equilibrium % SO_2 oxidized, ( \Phi^E_{\text{after}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>697.26</td>
<td>98.354</td>
<td>98.886</td>
</tr>
<tr>
<td>697.27</td>
<td>98.490</td>
<td>98.885</td>
</tr>
<tr>
<td>697.28</td>
<td>98.635</td>
<td>98.885</td>
</tr>
<tr>
<td>697.29</td>
<td>98.760</td>
<td>98.885</td>
</tr>
<tr>
<td>697.30</td>
<td>98.896</td>
<td>98.885</td>
</tr>
<tr>
<td>697.31</td>
<td>99.031</td>
<td>98.884</td>
</tr>
<tr>
<td>697.32</td>
<td>99.166</td>
<td>98.884</td>
</tr>
<tr>
<td>697.33</td>
<td>99.302</td>
<td>98.884</td>
</tr>
<tr>
<td>697.34</td>
<td>98.884</td>
<td></td>
</tr>
<tr>
<td>697.35</td>
<td>98.884</td>
<td></td>
</tr>
</tbody>
</table>

#Input gas: 690 K; 0.002 kg-mole SO_2, 0.061 kg-mole O_2, 0.790 kg-mole N_2 (0.234 volume% SO_2, 7.15 volume% O_2); 1.2 bar equilibrium pressure.
Fig. 19.5. Equilibrium curve, heatup path and heatup path-equilibrium curve intercept for after-intermediate-$\text{H}_2\text{SO}_4$-making catalyst bed. Attainment of equilibrium in the catalyst bed gives 98.9% oxidation of the bed's input $\text{SO}_2$. The lines apply only to the graph's specified inputs and bed pressure. This graph is a blowup of Fig. 19.6. Its intercept is confirmed by a Goal Seek calculation in Appendix T. The $\text{SO}_2$ and $\text{O}_2$ inputs are equivalent to 0.234 volume% $\text{SO}_2$ and 7.15 volume% $\text{O}_2$.

Fig. 19.6. Overall view of after-intermediate-$\text{H}_2\text{SO}_4$-making $\text{SO}_2$ oxidation. The high intercept % $\text{SO}_2$ oxidized is notable. It is due to the low intercept temperature. The $\text{SO}_2$ and $\text{O}_2$ inputs are equivalent to 0.234 volume% $\text{SO}_2$ and 7.15 volume% $\text{O}_2$. 
This 98.9% efficiency is equivalent to:

- 0.001978 kg-mole SO₃
- 0.000022 kg-mole SO₂
- 0.060011 kg-mole O₂
- 0.790000 kg-mole N₂

in after-H₂SO₄-making catalyst bed exit gas, Appendix T.

**19.7 Overall SO₂ Oxidation Efficiency**

So far, this chapter has examined after-intermediate-H₂SO₄-making SO₂ oxidation efficiency. However, Section 19.6 also provides the information needed to calculate total % SO₂ oxidized after SO₂ oxidation in all of Fig. 19.2’s catalyst beds. The values are:

from Fig. 19.2: kg-mole SO₂ in 1st catalyst bed feed gas = 0.1

from Section 19.6: kg-mole SO₂ in after-intermediate-H₂SO₄-making catalyst bed exit gas = 0.000022

(both per kg-mole of 1st catalyst bed feed gas).

Total SO₂ oxidation efficiency is calculated by the equation:

\[
\text{total } \% \text{SO₂ oxidized} = \Phi_{\text{total}} = \frac{\text{kg-mole SO₂ in 1st catalyst bed feed gas} - \text{kg-mole SO₂ in last catalyst bed exit gas}}{\text{kg-mole SO₂ in 1st catalyst bed feed gas}} \times 100
\]

(19.7)

where all quantities are per kg-mole of 1st catalyst bed feed gas.

The above numerical values give:

\[
\text{Total %SO₂ oxidized after 3 before-H₂SO₄-making beds and 1 after-H₂SO₄-making catalyst bed} = \frac{(0.1 - 0.000022)}{0.1} \times 100\% = 99.98\%
\]

This is somewhat above industrial total SO₂ oxidation (99.5-99.9%: Hansen, 2004), but it confirms the high SO₂ oxidation and H₂SO₄ making efficiencies of double contact acid plants.
19.7.1 Effect of incomplete SO\textsubscript{3}-from-gas removal during intermediate H\textsubscript{2}SO\textsubscript{4} making

Chapter 9 indicates that SO\textsubscript{3}-from-gas removal during H\textsubscript{2}SO\textsubscript{4} making may be 99.9\% rather than 100\%. This would mean that 0.1\% of Fig. 19.2's H\textsubscript{2}SO\textsubscript{4} making input SO\textsubscript{3} (0.0001 kg-mole) would get through to after-H\textsubscript{2}SO\textsubscript{4}-making SO\textsubscript{2} oxidation.

Appendix U examines this situation. It shows that this small amount of SO\textsubscript{3} has little effect on double contact's overall SO\textsubscript{2} oxidation efficiency.

19.8 Double/Single Contact Comparison

Section 19.7 shows that 3 - 1 double contact acidmaking has oxidized:

99.98\% of its feed gas SO\textsubscript{2} to SO\textsubscript{3}

after all its catalyst beds. Fig. 19.7, on the other hand, shows that 4 bed single contact acidmaking has oxidized only:

98.9\% of its feed gas SO\textsubscript{2} to SO\textsubscript{3}.

This confirms double contact's SO\textsubscript{2} oxidation advantage.

Fig. 19.7. 4 catalyst bed single contact acid plant. The 3\textsuperscript{rd} catalyst bed heatup path and intercept are the same as in Figs. 16.3 and 16.4. The 4\textsuperscript{th} bed is new, Table S.4. Note that:

(a) the 4\textsuperscript{th} bed oxidizes less than half of the 3\textsuperscript{rd} bed exit SO\textsubscript{2}, while:
(b) Fig. 19.6's after-H\textsubscript{2}SO\textsubscript{4}-making bed oxidizes 98.9\% of the 3\textsuperscript{rd} bed exit SO\textsubscript{2}, Section 19.6. This explains the greater efficiency of double contact acidmaking.
19.8.1 Double contact’s extra costs

Double contact acidmaking is more efficient than single contact acidmaking. However, this extra efficiency comes with extra costs. They are for:

(a) a second H$_2$SO$_4$ making system with its associated acid handling equipment

(b) 2 additional heat exchangers (1 for cooling before-intermediate-H$_2$SO$_4$-making gas and 1 for heating after-intermediate-H$_2$SO$_4$-making gas)

(c) additional energy for moving gas and acid through the second H$_2$SO$_4$ making system.

Widespread industrial adoption of double contact acidmaking indicates, however, that the high efficiency of the process more than offsets these extra costs.

19.9 Summary

Many sulfuric acid plants:

(a) oxidize most of their feed SO$_2$ to SO$_3$ in 3 (occasionally 2 or 4) catalyst beds

(b) make H$_2$SO$_4$(ℓ) from (a)'s product SO$_3$(g), Eqn. (1.2)

(c) oxidize the SO$_2$ remaining in (b)'s exit gas to SO$_3$ - in 1 (occasionally 2) after-H$_2$SO$_4$-making catalyst beds

(d) make H$_2$SO$_4$(ℓ) from (c)'s new SO$_3$(g).

This is called double contact acidmaking because it contacts gas and acid twice, steps (b) and (d). The advantage of double contact acidmaking is that it makes SO$_3$ and H$_2$SO$_4$(ℓ) more efficiently than single contact acidmaking.

The calculations of this chapter confirm this high efficiency.

Table 19.3 (after this chapter's problems) gives industrial after-H$_2$SO$_4$-making catalyst bed operating data.

References


Problems

19.1 Calculate Fig. 19.2's overall SO$_2$ oxidation efficiency when:
Table 19.3. Details of after-intermediate H₂SO₄-making catalytic SO₂ oxidation plants.

<table>
<thead>
<tr>
<th>Operation</th>
<th>S1</th>
<th>M2</th>
</tr>
</thead>
<tbody>
<tr>
<td>number of catalyst beds</td>
<td>3 + 1&lt;sup&gt;#&lt;/sup&gt;</td>
<td>3 + 2&lt;sup&gt;#&lt;/sup&gt;</td>
</tr>
<tr>
<td>converter height × diameter, m</td>
<td>19.23 × 16.65</td>
<td>10.4 × 9.4</td>
</tr>
<tr>
<td>construction materials</td>
<td>304 stainless steel</td>
<td>carbon steel insulation brick</td>
</tr>
<tr>
<td>heat recovery system</td>
<td></td>
<td>none</td>
</tr>
</tbody>
</table>

**Input gas data**

- flowrate, thousand Nm³/hour: 297, 102
- temperature, K: 693, 685
- composition, volume%:
  - SO₃: 0.005, 0.005
  - SO₂: 0.780, 0.42
  - O₂: 4.29, 5.34
  - CO₂: 0, 0
  - N₂: 94.9, 94.9

**Catalyst bed data**

- thickness of beds, m:
  - bed 4: 1.34, 0.64
  - bed 5: 0.78

- catalyst type(s):
  - bed 4: LP110
  - bed 5: 12 mm daisy ring, VK38
  - bed 5: 9 mm daisy ring, VK69

- catalyst bed temperatures, K:
  - bed 4:
    - in: 693, 687
    - out: 716, 704
  - bed 5:
    - in: 698
    - out: 698

**Product gas to H₂SO₄ making**

- SO₃: 0.745, 0.42
- SO₂: 0.04, 0.01
- O₂: 3.94, 5.14
- CO₂: 0
- N₂: 95.3

**Design % SO₂ oxidation after all catalyst beds**

<table>
<thead>
<tr>
<th></th>
<th>S1</th>
<th>M2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>99.7</td>
<td>99.9</td>
</tr>
</tbody>
</table>

<sup>#</sup> Catalyst beds before intermediate H₂SO₄ making + beds after intermediate H₂SO₄ making.
Their equivalent before-intermediate-\(\text{H}_2\text{SO}_4\)-making details are given in Table 7.2.

<table>
<thead>
<tr>
<th>Cumerio 1 (Bulgaria)</th>
<th>Cumerio 2 (Bulgaria)</th>
<th>M6</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 + 1$^a$</td>
<td>3 + 1$^a$</td>
<td>3 + 1$^a$</td>
</tr>
<tr>
<td>19.3 x 11.6</td>
<td>22.3 x 12</td>
<td>17.3 x 12.5</td>
</tr>
<tr>
<td>304 stainless steel, gray iron posts and grids</td>
<td>brick lined carbon steel</td>
<td>304H stainless steel</td>
</tr>
<tr>
<td></td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>160</td>
<td>150</td>
<td>191</td>
</tr>
<tr>
<td>683</td>
<td>688</td>
<td>694</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.57</td>
<td>0.45</td>
<td>0.56</td>
</tr>
<tr>
<td>8.33</td>
<td>6.31</td>
<td>13.6</td>
</tr>
<tr>
<td>0.36</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>90.74</td>
<td>92.93</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.28</td>
<td>1.00</td>
<td>0.78</td>
</tr>
</tbody>
</table>

11 x 4 mm ring       12 x 6 mm ring       12 mm daisy

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>VK48 + LP110</th>
</tr>
</thead>
<tbody>
<tr>
<td>683</td>
<td>688</td>
<td>694</td>
</tr>
<tr>
<td>701</td>
<td>693</td>
<td>714</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.56</td>
<td>0.45</td>
<td>0.51</td>
</tr>
<tr>
<td>0.01</td>
<td>0.014</td>
<td>0.05</td>
</tr>
<tr>
<td>8.06</td>
<td>6.12</td>
<td>13.4</td>
</tr>
<tr>
<td>0.36</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>91.01</td>
<td>93.11</td>
<td></td>
</tr>
<tr>
<td>99.70</td>
<td>99.80</td>
<td>99.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 19.3 (cont.) Details of after-intermediate H2SO4-making catalytic SO2 oxidation plants.

<table>
<thead>
<tr>
<th>Operation</th>
<th>M4</th>
<th>Asarco Hayden</th>
</tr>
</thead>
<tbody>
<tr>
<td>number of catalyst beds</td>
<td>3 + 1*</td>
<td>3 + 1*</td>
</tr>
<tr>
<td>converter height x diameter, m</td>
<td>22.1 x 12</td>
<td>16.9 x 7.0</td>
</tr>
<tr>
<td>construction materials</td>
<td>carbon steel, aluminum coating, brick lining</td>
<td>brick lined steel</td>
</tr>
<tr>
<td>heat recovery system</td>
<td>none</td>
<td></td>
</tr>
</tbody>
</table>

**Input gas data**

- flowrate, thousand Nm³/hour: 188, 192
- temperature, K: 663, 666
- composition, volume%:
  - SO3: 0, 0
  - SO2: 0.8-1.2, 0.69
  - O2: 8.4-9.9, 8.0
  - CO2: 3.3, 1.0
  - N2: remainder, 90.0

**Catalyst bed data**

- thickness of beds, m:
  - bed 4: 1.28
  - bed 5: 0.71
- catalyst type(s):
  - bed 4: VK69
  - bed 5: LP110/VK48
- catalyst bed temperatures, K:
  - bed 4:
    - in: 663
    - out: 683
  - bed 5:
    - in: 666
    - out: 700

**Product gas to H2SO4 making**

<table>
<thead>
<tr>
<th></th>
<th>M4</th>
<th>Asarco Hayden</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO3</td>
<td>1.1</td>
<td>0.6</td>
</tr>
<tr>
<td>SO2</td>
<td>0.025</td>
<td>0.05</td>
</tr>
<tr>
<td>O2</td>
<td>8.7</td>
<td>7.77</td>
</tr>
<tr>
<td>CO2</td>
<td>3.3</td>
<td>1.2</td>
</tr>
<tr>
<td>N2</td>
<td>remainder</td>
<td>90.9</td>
</tr>
</tbody>
</table>

**Design % SO2 oxidation**

*after all catalyst beds*

#Catalyst beds before intermediate H2SO4 making + beds after intermediate H2SO4 making.
Their equivalent before-intermediate-\(H_2\text{SO}_4\)-making details are given in Table 7.2.

<table>
<thead>
<tr>
<th>Phelps Dodge Miami</th>
<th>M1</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 + 1&quot;</td>
<td>2 + 2&quot;</td>
</tr>
<tr>
<td>23.3 x 14.76</td>
<td>9.8 x 6.9</td>
</tr>
<tr>
<td>all welded stainless steel</td>
<td>carbon steel, cast iron grids</td>
</tr>
<tr>
<td></td>
<td>mild steel division plates</td>
</tr>
<tr>
<td></td>
<td>none</td>
</tr>
<tr>
<td>199</td>
<td>50</td>
</tr>
<tr>
<td>703</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>0.21</td>
</tr>
<tr>
<td>0.6</td>
<td>12.2</td>
</tr>
<tr>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>91.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.24</td>
</tr>
<tr>
<td></td>
<td>0.33</td>
</tr>
</tbody>
</table>

0.28 m of VK69 (top) daisy ring, \(V_2\text{O}_5\)
0.96 m of VK38/48 mix daisy ring, \(V_2\text{O}_5\)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>703</td>
<td>700-727</td>
</tr>
<tr>
<td>720</td>
<td>708-736</td>
</tr>
<tr>
<td></td>
<td>700-714</td>
</tr>
<tr>
<td></td>
<td>700-716</td>
</tr>
</tbody>
</table>

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>0.008</td>
</tr>
<tr>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>6.2</td>
<td>12.2</td>
</tr>
<tr>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>91.7</td>
<td></td>
</tr>
</tbody>
</table>

99.8
(a) its 1st catalyst bed feed gas contains:

12.0 volume% SO₂  
13.2 O₂  
74.8 N₂

(b) its catalyst bed input gas temperatures are:

1st catalyst bed 675 K  
2nd 685 K  
3rd 695 K  
4th 695 K.

(c) its catalyst bed pressures are all 1.2 bar

(d) 100% of the SO₃(g) in Fig. 19.2's 3rd catalyst bed exit reacts to form H₂SO₄(ℓ) during intermediate H₂SO₄ making.

Hints:

(a) The composition of Fig. 19.2's intermediate H₂SO₄ making input gas under the above conditions is given in your answer to Prob. 16.2. It is:

0.1183 kg-mole SO₃  
0.0017 " SO₂  
0.0728 " O₂  
0.7480 " N₂.

(b) All the above SO₃ is removed from this gas during intermediate H₂SO₄ making.

19.2 Calculate the equivalent SO₂ oxidation efficiency with 4 catalyst beds but no intermediate H₂SO₄ making. Use the technique described in Appendix S with all of Prob. 19.1's temperatures and pressures.
CHAPTER 20

Optimum Double Contact Acidmaking

Chapter 19 examines after-H_2SO_4-making catalytic SO_2 oxidation. It shows how after-H_2SO_4-making catalyst bed:

- equilibrium curves
- heatup paths
- heatup path-equilibrium curve intercepts

are calculated. It also shows how:

\[
\text{total SO}_2 \text{ oxidation after SO}_2 \text{ oxidation in all before and after intermediate-H}_2\text{SO}_4\text{-making catalyst beds}
\]

is calculated.

This chapter uses the latter calculation to analyze double-contact acidmaking. Its objectives are to:

(a) compare the SO_2 oxidation efficiencies of different double-contact catalyst bed arrangements, e.g.:

- 3 beds before intermediate H_2SO_4 making, 1 bed after
- 2 " " 2 beds after

(b) show which bed arrangement gives maximum SO_2 oxidation efficiency

(c) indicate the catalyst bed where low activation temperature (Cs) catalyst will most enhance total oxidation efficiency.

The calculations are based on the following specifications and Eqn. 19.7.

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st catalyst bed feed gas</td>
<td>10 volume% SO_2 11 volume% O_2</td>
</tr>
<tr>
<td>Input gas temperature, all beds</td>
<td>690 K</td>
</tr>
<tr>
<td>Bed pressure, all beds</td>
<td>1.2 bar</td>
</tr>
<tr>
<td>Intercept specification</td>
<td>equilibrium is achieved in all beds</td>
</tr>
<tr>
<td>SO_3-from-gas removal during H_2SO_4 making</td>
<td>100%</td>
</tr>
</tbody>
</table>
20.1 **Total % \(SO_2\) Oxidized After All Catalyst Beds**

All of this chapter's efficiency comparisons are based on total % \(SO_2\) oxidized after all catalyst beds, defined as:

\[
\text{total \% \(SO_2\) oxidized} = \Phi_{\text{total}} = \left(\frac{\text{kg-mole } SO_2 \text{ in 1st catalyst bed feed gas} - \text{kg-mole } SO_2 \text{ in last catalyst bed exit gas}}{\text{kg-mole } SO_2 \text{ in 1st catalyst bed feed gas}}\right) \times 100
\]

(all quantities per kg-mole of 1\(^{st}\) catalyst bed feed gas).

20.2 **Four Catalyst Beds**

Most industrial acid plants have 4 catalyst beds. The arrangements of these beds in order of decreasing industrial use are:

- 3 catalyst beds before intermediate H\(_2\)SO\(_4\) making; 1 catalyst bed after
- 2 " " " 2 "
- 4 " " " 0 "

Fig. 20.1 compares the total \(SO_2\) oxidation efficiencies of these arrangements. The theoretical 1 - 3 arrangement is also shown.

![Graph](image)

**Fig. 20.1.** Total \(SO_2\) oxidation efficiencies of 4 four-catalyst-bed arrangements. The 3 - 1 bed arrangement is seen to be the most efficient.
The figure indicates that:

(a) double contact acidmaking is always more efficient than single contact acidmaking.

(b) the 3-1 bed arrangement gives maximum $\text{SO}_2$ oxidation.

These results explain the widespread industrial use of the 3-1 process.

20.3 Improved Efficiency with 5 Catalyst Beds

Fig. 20.2 shows the efficiencies of 5 five-catalyst-bed $\text{SO}_2$ oxidation systems. It confirms that:

(a) double contact acid plants are always more efficient than single contact plants

(b) the single after-intermediate-$\text{H}_2\text{SO}_4$-making bed arrangement is the most efficient.

![Graph showing SO$_2$ oxidation efficiency with 5 five-catalyst bed arrangements. The 4-1 arrangement is the most efficient. It is, however, only slightly more efficient than the 3-2 arrangement.]

Fig. 20.2. $\text{SO}_2$ oxidation efficiency of 5 five-catalyst bed arrangements. The 4-1 arrangement is the most efficient. It is, however, only slightly more efficient than the 3-2 arrangement.

20.3.1 Benefit from each additional bed

Figs. 20.1 and 20.2 indicate that the single after-intermediate-$\text{H}_2\text{SO}_4$-making bed arrangement gives maximum $\text{SO}_2$ oxidation efficiency. Fig 20.3 examines this further by comparing $\text{SO}_2$ oxidation efficiency with 1 to 4 beds before $\text{H}_2\text{SO}_4$ making - 1 bed after. As expected, overall efficiency with this arrangement increases with each additional before-$\text{H}_2\text{SO}_4$-making bed.
Fig. 20.3. SO₂ oxidation efficiency of acid plants with 1 catalyst bed after intermediate H₂SO₄ making. Oxidation efficiency increases with increasing number of before-intermediate-H₂SO₄-making beds. However, the difference between 3 - 1 and 4 - 1 plants is very small.

Fig. 20.4. Effect of catalyst bed gas input temperature on double contact SO₂ oxidation efficiency. Efficiency falls slightly with increasing gas input temperature.
20.4 Input Gas Temperature Effect

Fig 20.4 shows the effect of gas input temperature on:

\[ 3 - 1 \text{ acid plant } SO_2 \text{ oxidation efficiency}. \]

It indicates that total \% \( SO_2 \) oxidized:

(a) is always high
(b) increases with decreasing input gas temperature.

20.5 Best Bed for Cs Catalyst

Cs-enhanced catalyst is useful in permitting cool input gas – because it deactivates at a relatively cool temperature, Chapter 8.

However, Cs catalyst is costly, so many acid plants use it in only 1 catalyst bed. Fig. 20.5 indicates that the best location for the Cs catalyst bed is after \( H_2SO_4 \) making – where it gives maximum total \( SO_2 \) oxidation.

Prevention of catalyst overheating may, however, lead it to be used in the 1st catalyst bed (Fig. 12.7) – even though this is not the best \( SO_2 \) oxidation efficiency location.

![Graph showing SO2 oxidation efficiency](image)

**Fig. 20.5.** 3 - 1 acid plant with one Cs catalyst bed (660 K gas input) and three K, Na catalyst beds (690 and 720 K). Maximum \( SO_2 \) oxidation is obtained with the Cs catalyst in bed 4, i.e. after \( H_2SO_4 \) making. Bed 3 (just before \( H_2SO_4 \) making) is nearly as good. The calculations are all based on Table 20.1's values – except for gas input temperature.
20.6 Triple Contact Acid Plant

At the time of writing, there are no industrial triple contact acid plants. These plants would be more complex than their double contact counterparts, so they would have to give a significant SO₂ oxidation advantage.

As the following values show, 1 - 1 - 1 acid plants would be slightly less efficient than this chapter's 3 - 1 plants.

<table>
<thead>
<tr>
<th>Plant Type</th>
<th>SO₂ Oxidation Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 - 1 double contact</td>
<td>99.99 %</td>
</tr>
<tr>
<td>1 - 1 - 1 triple contact</td>
<td>99.97 %</td>
</tr>
</tbody>
</table>

(all calculations based on Table 20.1 specifications).

This and the complexity of triple contact plants explain why none has been built.

20.7 Summary

Double contact acidmaking is more efficient than single contact acidmaking. This has made it the most used industrial process. The reason for its high efficiency is its efficient oxidation of SO₂ in its after-H₂SO₄-making catalyst bed(s), Chapter 19.

The most efficient double contact plants have one catalyst bed after H₂SO₄ making, remainder before. 3 - 1 plants are more efficient than 2 - 2 plants. 4 - 1 plants are more efficient than 2 - 3 and 3 - 2 plants.

Cool catalyst bed input gas gives high SO₂ oxidation efficiency in single and double contact acid plants. Low deactivation temperature Cs catalyst is beneficial in this respect, Chapters 8 and 12.

Cs catalyst is costly so many acid plants use it in only one catalyst bed. From the SO₂ oxidation efficiency point of view, it is best used after intermediate H₂SO₄ making.

Industrial SO₂ oxidation efficiencies are slightly lower than those in this chapter — because equilibrium is not quite attained in industrial processes. However, the trends in the chapter are instructive as to best double contact practice.
CHAPTER 21

Enthalpies and Enthalpy Transfers

Chapters 10 through 20 indicate that rapid, efficient multi catalyst bed $\text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{SO}_3$ oxidation requires:

(a) warm 1\textsuperscript{st} catalyst bed feed gas (∼690 K)
(b) cooling of gas between beds and before H\textsubscript{2}SO\textsubscript{4} making.

Fig. 21.1 indicates how these requirements are achieved for a single contact sulfur-burning acid plant with 3 catalyst beds. It shows that:

(a) 690 K 1\textsuperscript{st} catalyst bed feed gas is obtained by cooling sulfur burning exit gas in a boiler and steam superheater
(b) 700 K 2\textsuperscript{nd} catalyst bed input gas is obtained by cooling ∼890 K 1\textsuperscript{st} catalyst bed exit gas in a second boiler
(c) 710 K 3\textsuperscript{rd} catalyst bed input gas is obtained by cooling ∼770 K 2\textsuperscript{nd} catalyst bed exit gas in a steam superheater
(d) 470 K H\textsubscript{2}SO\textsubscript{4} making input gas is obtained by cooling ∼720 K 3\textsuperscript{rd} catalyst bed exit gas in an economizer (boiler feed water heater).

The final products of the flowsheet are (i) cool SO\textsubscript{3} rich gas ready for H\textsubscript{2}SO\textsubscript{4} making and (ii) superheated steam.

Steps (a) to (d) all require transfer of heat to water or steam.

This chapter examines these heat transfers. Its objectives are to calculate:

(a) the enthalpies of (i) catalyst bed input and output gases and (ii) H\textsubscript{2}SO\textsubscript{4} making input gas
(b) heat transfers that will give these enthalpies.

These values pave the way for Chapter 22's examination of catalyst bed and H\textsubscript{2}SO\textsubscript{4} making temperature control.
21.1 Input and Output Gas Enthalpies

Fig. 21.1's catalyst bed input and output gas enthalpies can be calculated directly on our heatup path-equilibrium curve worksheets, Table 21.1. Table 21.1's 3rd catalyst bed input gas enthalpy is, for example:

\[
H_{\text{input gas}} = \text{kg-mole SO}_3 \text{ in } \times H_{710}^{\circ} \text{SO}_3 \\
+ \text{kg-mole SO}_2 \text{ in } \times H_{710}^{\circ} \text{SO}_2 \\
+ \text{kg-mole O}_2 \text{ in } \times H_{710}^{\circ} \text{O}_2 \\
+ \text{kg-mole N}_2 \text{ in } \times H_{710}^{\circ} \text{N}_2
\]
\[ = B34 \times \text{-D28} \\
+ B35 \times \text{-E28} \\
+ B36 \times \text{-F28} \\
+ B37 \times \text{-G28} \]  

where B34 etc. are Table 21.1 cell references.

Cells D28-G28 each contain -H°, Eqn. (11.7). This explains their negative signs in Eqn. (21.1).

Table 21.1's cell H43 contains Eqn. (21.1) exactly as shown in the cell beside it. It shows that Fig. 21.1's 3rd catalyst bed input gas enthalpy is:

-25.94 MJ

per kg-mole of 1st catalyst bed feed gas.

21.1.1 Output gas enthalpy

Table 21.1's 3rd catalyst bed output gas enthalpy is calculated the same way. It is described by the equation:

\[ H_{\text{output gas}} = \text{kg-mole SO}_3 \text{ out} \times H^o_{721.1} \text{SO}_3 \\
+ \text{kg-mole SO}_2 \text{ out} \times H^o_{721.1} \text{SO}_2 \\
+ \text{kg-mole O}_2 \text{ out} \times H^o_{721.1} \text{O}_2 \\
+ \text{kg-mole N}_2 \text{ out} \times H^o_{721.1} \text{N}_2 \\
= B38 \times H28 \\
+ B39 \times I28 \\
+ B40 \times J28 \\
+ B41 \times K28 \]  

where 721.1 K is the 3rd catalyst bed intercept temperature.

Table 21.1's cell H44 contains Eqn. (21.2) exactly as shown beside it. It shows that Fig. 21.1's 3rd catalyst bed output gas enthalpy is:

-25.94 MJ

per kg-mole of 1st catalyst bed feed gas.
Table 21.1. Bottom half of Table O.1's 3rd catalyst bed heatup path-equilibrium curve intercept worksheet. Input and output gas enthalpies are shown in rows 43 and 44. Note that they are the same. This is because our heatup path calculations assume no convective, conductive or radiative heat loss during catalytic SO_2 + \( \frac{1}{2} \)O_2 \rightarrow SO_3 oxidation, Section 11.9. 1st and 2nd catalyst bed enthalpies are calculated similarly – using Tables J.2 and M.2.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>3rd catalyst bed heatup path matrix.</td>
<td>Eqns. 14.6 to 14.8 are from Section 14.6. Eqns. 14.9* is from Appendix K. Eqns. 16.1 to 16.4 are from Section 16.3.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>Equation</td>
<td>description</td>
<td>numerical term</td>
<td>kg-mole SO_2</td>
<td>kg-mole SO_2</td>
<td>kg-mole O_2</td>
<td>kg-mole N_2</td>
<td>kg-mole SO_3</td>
<td>kg-mole SO_3</td>
<td>kg-mole O_2</td>
</tr>
<tr>
<td>21</td>
<td>16.1</td>
<td>input SO_2 kg-mole</td>
<td>0.0942</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>22</td>
<td>16.2</td>
<td>input SO_2 kg-mole</td>
<td>0.0058</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>23</td>
<td>16.3</td>
<td>input O_2 kg-mole</td>
<td>0.0629</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>24</td>
<td>16.4</td>
<td>input N_2 kg-mole</td>
<td>0.7900</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>25</td>
<td>14.6</td>
<td>S balance</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>26</td>
<td>14.7</td>
<td>O balance</td>
<td>0</td>
<td>-3</td>
<td>-2</td>
<td>-2</td>
<td>0</td>
<td>3</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>27</td>
<td>14.8</td>
<td>N balance</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>28</td>
<td>14.9*</td>
<td>enthalpy balance</td>
<td>0</td>
<td>369.9</td>
<td>277.7</td>
<td>-12.67</td>
<td>-12.28</td>
<td>-369.1</td>
<td>-277.1</td>
<td>13.24</td>
</tr>
<tr>
<td>29</td>
<td></td>
<td>3rd catalyst bed input gas temperature ( = \frac{710}{\text{intercept temperature, cell A14} = \frac{721.1}{=0.0311*F30-9.797}}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| 30| Matrix results equivalent to suggested intercept temperature in cell J30 (and A14) | \( = (0.0311*F30-9.797) \)
| 31| kg-mole SO_2, In | 0.0942 |
| 32| kg-mole SO_2, In | 0.0058 |
| 33| kg-mole O_2, In | 0.0629 |
| 34| kg-mole N_2, In | 0.7900 |
| 35| kg-mole SO_3, out | 0.0980 |
| 36| kg-mole SO_2, out | 0.0020 |
| 37| kg-mole O_2, out | 0.0610 |
| 38| kg-mole N_2, out | 0.7900 |
| 39| all per kg-mole of 1st catalyst bed feed gas | Input gas enthalpy = \( = -25.64 \) =B34*-D28+B35*-E28+B36*-F28+B37*-G28 |
| 40| | Output gas enthalpy = \( = -25.94 \) =B38*+H28+B39*+I28+B40*+J28+B41*+K28 |
| 41| | Goal Seek calculation |
| 42| | Equilibrium curve % SO_2 oxidized - heatup path % SO_2 oxidized = \( = 0.0 \) =F11-I39 |

238
21.1.2 First and second bed enthalpies

1\textsuperscript{st} and 2\textsuperscript{nd} catalyst bed input and output gas enthalpies are calculated from Tables J.2 and M.2 exactly as described above. They are summarized in Table 21.2.

21.2 H\textsubscript{2}SO\textsubscript{4} Making Input Gas Enthalpy

Fig. 21.1's H\textsubscript{2}SO\textsubscript{4}-making input SO\textsubscript{3}, SO\textsubscript{2}, O\textsubscript{2} and N\textsubscript{2} quantities are shown in Table 21.1. They are the 3\textsuperscript{rd} catalyst bed exit (intercept) quantities.

However, their 470 K enthalpies are not shown in the table. They are accounted for by the equation:

\[
\begin{align*}
H_{\text{H2SO4 making input gas}} &= \text{kg-mole SO}_3 \text{ out} \times (0.07144 \times 470 - 420.6) \\
&+ \text{kg-mole SO}_2 \text{ out} \times (0.05161 \times 470 - 314.3) \\
&+ \text{kg-mole O}_2 \text{ out} \times (0.03333 \times 470 - 10.79) \\
&+ \text{kg-mole N}_2 \text{ out} \times (0.03110 \times 470 - 9.797) \\
&= 0.098 \times -387.0 \\
&+ 0.002 \times -290.0 \\
&+ 0.061 \times 4.88 \\
&+ 0.790 \times 4.82 \\
&= -34.40 \text{ MJ per kg-mole of 1\textsuperscript{st} catalyst bed feed gas.}
\end{align*}
\]

where:

'kg-mole SO\textsubscript{3} out' is kg-mole SO\textsubscript{3} out of the 3\textsuperscript{rd} catalyst bed and into H\textsubscript{2}SO\textsubscript{4} making and:

\((0.07144 \times 470 - 420.6)\) is \(H^0_{\text{SO}_3}^{470}\)

and so on.

21.3 Heat Transfers

21.3.1 Heat transfer from 3\textsuperscript{rd} bed exit gas to economizer water

This section calculates how much heat must be removed from Fig. 21.1's:

721.1 K 3\textsuperscript{rd} catalyst bed exit gas
to cool it to the figure's specified:

\[ 470 \text{ K} \text{ H}_2\text{SO}_4 \text{ making input gas temperature.} \]

This heat removal is calculated by the equation:

\[ Q = \sum |\Delta H| = |H_{H_2SO_4 \text{ making input gas}} - H_{3rd \text{ bed exit gas}}| \quad (21.4). \]

The enthalpies in this equation are those calculated in Sections 21.1.1 and 21.2, giving:

\[ Q = \sum |\Delta H| = |-34.40 - (-25.94)| \]

\[ = 8.46 \text{ MJ per kg-mole of 1st catalyst bed feed gas.} \]

So, per kg-mole of 1st catalyst bed feed gas, 8.46 MJ must be removed from 721.1 K 3rd catalyst bed exit gas to cool it to the specified 470 K H₂SO₄ making input gas temperature. The heat is, of course, transferred to water in Fig. 21.1's economizer.

21.3.2 1–2 and 2–3 heat transfers

Heat transfers from gas between beds 1 and 2 and 2 and 3 are calculated exactly as described above. They are tabulated in Table 21.2.

Table 21.2. Summary of Fig. 21.1's temperatures, enthalpies and heat transfers. Note the continuing decrease in the gas's enthalpy as heat is transferred from gas to water and steam in Fig. 21.1's boiler, superheater and economizer. All temperatures but the last are from Tables J.2, M.2 and 21.1. Note that a catalyst bed's input enthalpy is always the same as its output enthalpy. This is due to our assumption that there is no conductive, convective or radiative heat loss from the gas.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Temp. K</th>
<th>Enthalpy $^a$</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st catalyst bed feed gas</td>
<td>690</td>
<td>-17.31</td>
<td></td>
</tr>
<tr>
<td>1st catalyst bed exit</td>
<td>893.3</td>
<td>-17.31</td>
<td></td>
</tr>
<tr>
<td>(intercept) gas</td>
<td></td>
<td></td>
<td>heat transfer to 1-2 boiler water $\rightarrow$</td>
</tr>
<tr>
<td>2nd catalyst bed input gas</td>
<td>700</td>
<td>-23.81</td>
<td></td>
</tr>
<tr>
<td>2nd catalyst bed exit</td>
<td>773.2</td>
<td>-23.81</td>
<td></td>
</tr>
<tr>
<td>(intercept) gas</td>
<td></td>
<td></td>
<td>heat transfer to superheater steam $\rightarrow$</td>
</tr>
<tr>
<td>3rd catalyst bed input gas</td>
<td>710</td>
<td>-25.94</td>
<td></td>
</tr>
<tr>
<td>3rd catalyst bed exit</td>
<td>721.1</td>
<td>-25.94</td>
<td></td>
</tr>
<tr>
<td>(intercept) gas</td>
<td></td>
<td></td>
<td>heat transfer to economizer water $\rightarrow$</td>
</tr>
<tr>
<td>$H_2SO_4$ making input gas</td>
<td>470</td>
<td>-34.40</td>
<td></td>
</tr>
</tbody>
</table>

$^a$MJ per kg-mole of 1st catalyst bed feed gas.
21.4 Heat Transfer Rate

The rate at which heat is transferred from Fig. 21.1's 3rd catalyst bed exit gas to its economizer water is calculated from:

Section 21.3.1's heat transfer amount, MJ per kg-mole of 1st catalyst bed feed gas and:

a specified 1st catalyst bed feed gas input rate, Nm³ per hour, e.g. 100 000 Nm³/hour.

Heat transfer rate is given by the equation:

\[
\text{heat transfer rate} = Q \times \frac{1\text{st catalyst bed feed gas input rate, Nm}^3/\text{hr}}{22.4 \text{ Nm}^3 \text{ of feed gas per kg-mole of feed gas}}
\]  (21.5).

With Table 21.2's 8.46 MJ economizer heat transfer (Q), it is:

\[
3\text{rd catalyst bed exit gas to economizer = heat transfer rate } \\
= 8.46 \text{ of 1st catalyst bed feed gas} \times \frac{100 000 \text{ Nm}^3 \text{ of 1st catalyst bed feed gas per hour}}{22.4 \text{ Nm}^3 \text{ of feed gas per kg-mole of feed gas}} \]  (21.6)

\[
= 38 000 \text{ MJ per hour.}
\]

21.4.1 Extension

This chapter has examined a very simple acid plant. Its techniques are, however, readily extended to complex industrial acidmaking situations.

21.5 Summary

Catalyst bed gas enthalpies are readily calculated on our heatup path-equilibrium curve intercept worksheets.

These enthalpies are conveniently used to calculate the amount of heat that must be removed to cool a catalyst bed's output gas to a specified temperature.

The enthalpies and heat removal quantities are all calculated per kg-mole of 1st catalyst bed feed gas.

The heat removal quantities (plus 1st catalyst bed feed gas input rate) are readily used to determine the cooling requirements (MJ/hour) of each of Fig. 21.1's gas cooling devices.
The next chapter builds on this information to show how catalyst bed and \( \text{H}_2\text{SO}_4 \) making input gas temperatures are controlled by bypassing gas around the cooling devices.

**Problems**

21.1 Prepare a table like Table 21.2 for:

<table>
<thead>
<tr>
<th>SO(_2)</th>
<th>O(_2)</th>
<th>N(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.0 %</td>
<td>13.2 %</td>
<td>74.8 %</td>
</tr>
</tbody>
</table>

1\(^{st}\) catalyst bed feed gas and the following catalyst bed gas input temperatures:

<table>
<thead>
<tr>
<th>Bed</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(^{st})</td>
<td>675</td>
</tr>
<tr>
<td>2(^{nd})</td>
<td>685</td>
</tr>
<tr>
<td>3(^{rd})</td>
<td>695</td>
</tr>
</tbody>
</table>

Assume that:

(a) the pressure in all catalyst beds is 1.2 bar

(b) heatup path-equilibrium curve intercepts are attained in all beds

(c) the 3\(^{rd}\) catalyst bed exit gas enters \( \text{H}_2\text{SO}_4 \) making at 470 K.

**Hints**

1. Use your Problem 12.3, 15.1 and 16.1 spreadsheets to calculate input and output gas enthalpies (as described in Section 21.1).

2. Use your Prob. 16.1 3\(^{rd}\) catalyst bed output quantities and Eqn. (21.3) to calculate \( \text{H}_2\text{SO}_4 \) making's input gas enthalpy.

21.2 Calculate the rate, MJ/hour, at which heat must be transferred from 3\(^{rd}\) catalyst bed exit gas to economizer water to obtain the above specified 470 K \( \text{H}_2\text{SO}_4 \) making gas. 100 000 \( \text{Nm}^3 \) per hour of 1\(^{st}\) catalyst bed feed gas is entering the 1\(^{st}\) catalyst bed.
CHAPTER 22

Control of Gas Temperature by Bypassing

This chapter describes how:

catalyst bed and H₂SO₄ making input gas temperatures

are controlled by bypassing gas around Fig. 21.1's heat transfer equipment.

22.1 Bypassing Principle

The principle of bypassing is that when a portion of a hot gas stream is bypassed around a gas cooling device (e.g. Fig. 21.1's economizer):

the bypassed portion is not cooled.

Then, when the bypassed portion and the cooled portion are recombined (Fig. 22.1), the product gas stream is:

warmer

than when all the gas is being passed through the cooling device.

Most acid plant heat transfer devices are provided with bypass capability, Fig. 22.2.

22.2 Objective

The objective of this chapter is to show how bypassing can be used to adjust the temperatures of acid plant gases. It examines:

(a) how bypassing gas around Fig. 21.1's economizer can be used to adjust the temperature of the economizer's output gas

(b) how bypassing can be used to maintain a constant economizer output gas temperature while the economizer's input gas temperature is varying.

Both calculations also estimate the fraction of economizer input gas that must be bypassed around the economizer to achieve a specified output gas temperature.
SO\textsubscript{3} rich output gas to H\textsubscript{2}SO\textsubscript{4} making 470 K design temperature

Fig. 22.1. Blowup of Chapter 21's economizer. Bypassing of input gas around the economizer (dotted line) is shown. Bypassing results in a warmer recombined output gas stream.

Fig. 22.2. Photograph of gas bypass flue around cross flow gas-to-gas heat exchanger. In this case, the amount of bypass is controlled by manually adjusting a butterfly valve in the bypass flue (note chain below the valve). In most cases, the valve is controlled automatically by a thermocouple placed just beyond the heat exchanger exit gas/bypass gas re-combination point.
22.3 Gas to Economizer Heat Transfer

Fig. 21.1's economizer cools Table 21.1's 3rd catalyst bed exit (intercept) gas from:

\[ 721.1 \text{ K} \]

to:

\[ 470 \text{ K} \] (its design output gas temperature).

The gas's enthalpies at 721.1 and 470 K are, Sections 21.1.1 and 21.2:

\[ -25.94 \text{ MJ} \]

and

\[ -34.40 \text{ MJ} \]

which means that:

\[ 8.46 \text{ MJ} \]

of heat must be transferred from the 721.1 K economizer input gas to give 470 K output gas, Section 21.3.1.

All enthalpies and heats are per kg-mole of 1st catalyst bed feed gas.

22.3.1 Design heat transfer rate

The Fig. 22.1 economizer's design heat transfer rate with:

(a) the above 8.46 MJ heat transfer per kg-mole of 1st catalyst bed feed gas

and:

(b) 100 000 Nm\(^3\) per hour of 1st catalyst bed feed gas (the flowrate used throughout this chapter)

is:

\[
\text{3rd catalyst bed economizer heat} = 8.46 \text{ MJ per kg-mole} \times \frac{100 000 \text{ Nm}^3}{22.4 \text{ Nm}^3} \times \frac{1\text{st catalyst bed feed gas/hour}}{} = 38 000 \text{ MJ per hour (21.6).}
\]

This value is referred to later in the chapter.
22.4 Heat Transfer Requirement for 480 K Economizer Output Gas

The temperature of Fig. 22.1's economizer output gas can be changed by:

bypassing a portion of the economizer input gas around the economizer.

This section shows how 480 K output gas is obtained. It calculates:

(a) the enthalpy of 480 K economizer output gas, per kg-mole of 1st catalyst bed feed gas
(b) the amount of heat that must be transferred from 721.1 K 3rd catalyst bed exit gas to give (a)'s enthalpy
(c) the percentage of 3rd catalyst bed exit gas that must be bypassed around the economizer to give (b)'s heat transfer.

22.4.1 Enthalpies and heat transfer

The enthalpy of 721.1 K 3rd catalyst bed exit (intercept) gas is:

\[-25.94 \text{ MJ (Section 21.1.1)}.\]

The enthalpy of this gas at 480 K is:

\[-34.07 \text{ MJ (calculated by Eqn. (21.3) with 480 K in place of 470 K)}.\]

This means that:

\[8.13 \text{ MJ}\]

must be transferred from 721.1 K economizer input gas to give 480 K output gas, Fig. 22.1.

22.5 Changing Heat Transfer by Bypassing

Section 22.3.1 indicates that the Fig. 22.1 economizer has been designed to transfer:

\[38000 \text{ MJ/hour}\]

which is equivalent to:

\[8.46 \text{ MJ per kg-mole of 1st catalyst bed feed gas}.\]
However, achievement of Section 22.4's specified 480 K economizer output gas requires a transfer of only:

8.13 MJ per kg-mole of 1st catalyst bed feed gas.

22.5.1 Percent bypass

The 8.13 MJ heat transfer required for 480 K output gas is:

\[
\frac{8.13}{8.46} \times 100\% = 96\%
\]

of the economizer's 8.46 MJ design heat transfer.

Production of 480 K economizer output gas requires, therefore, that:

96% of the 3rd catalyst bed exit gas must be cooled in the economizer

and:

4% must be bypassed around it.

22.6 460 K Economizer Output Gas

This section:

(a) calculates how much heat must be transferred from Fig. 22.1's 721.1 K economizer input gas to give 460 K economizer output gas

(b) indicates how this heat transfer may be obtained.

22.6.1 Enthalpies and heat transfer

The enthalpy of 721.1 K 3rd catalyst bed exit gas is:

-25.94 MJ.

The enthalpy of this gas at 460 K is:

-34.74 MJ (from Eqn. (21.3) with 460 K in place of 470 K).

This means that:

8.80 MJ

of heat must be transferred from 721.1 K gas to cool it to 460 K.
This requirement is greater than the cooling capacity (8.46 MJ) of the Section 22.3.1 economizer. Bypassing of gas around the economizer won't help because bypassing only decreases heat transfer.

This shows that if the temperature of the economizer output gas must be 460 K, the Section 22.3.1 economizer must be enlarged to transfer:

\[ 8.80 \text{ MJ per kg-mole of 1st catalyst bed feed gas} \]

or more. This 8.80 MJ and 100 000 Nm\(^3\) per hour of 1st catalyst bed feed gas is equivalent to 39 000 MJ/hour, Eqn. (21.6).

### 22.7 Bypassing for 460, 470 and 480 Economizer Output Gas

Production of 460 K, 470 K and 480 K economizer gas from 721.1 K 3rd catalyst bed exit gas requires transfer of:

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Cooling Requirement (MJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>460</td>
<td>8.80</td>
</tr>
<tr>
<td>470</td>
<td>8.46</td>
</tr>
<tr>
<td>480</td>
<td>8.13</td>
</tr>
</tbody>
</table>

all per kg-mole of 1st catalyst bed feed gas. These are equivalent to:

<table>
<thead>
<tr>
<th>Percentage</th>
<th>100.0%</th>
<th>95.6%</th>
<th>91.3%</th>
</tr>
</thead>
</table>

of Section 22.6.1's 39 000 MJ per hour economizer capacity and to bypassing:

<table>
<thead>
<tr>
<th>Percentage</th>
<th>0%</th>
<th>4.4%</th>
<th>8.7%</th>
</tr>
</thead>
</table>

of the gas stream around the economizer.

### 22.8 Bypassing for 470 K Economizer Output Gas

While Input Gas Temperature is Varying

This section shows how Section 22.6.1's 39 000 MJ/hour economizer is used to obtain:

470 K economizer output gas

while its input gas is varying from:
The enthalpies of Table 21.2's 3\textsuperscript{rd} catalyst bed exit gas at 725, 715 and 470 K are:

\begin{align*}
725 \text{ K} & : -25.81 \text{ MJ} \\
715 \text{ K} & : -26.15 \text{ MJ} \\
470 \text{ K} & : -34.40 \text{ MJ}
\end{align*}

per kg-mole of Fig 21.1 1\textsuperscript{st} catalyst bed feed gas (calculated with Eqn. (21.3) and the appropriate temperatures).

They indicate that:

(a) cooling 725 K economizer input gas to 470 K requires transfer of:

8.59 MJ

from the gas.

(b) cooling 715 K economizer input gas to 470 K requires transfer of:

8.25 MJ

from the gas.

These are equivalent to 97.6 and 93.8 % of Section 22.6.1's:

8.80 MJ (39 000 MJ/hour)

economizer.

So, operating the economizer to cool its input gas from 725 K to 470 K requires bypassing 2.4% of the gas. Cooling it from 715 K to 470 K requires opening the bypass valve to 6.2%.

Notably, gas is being passed through the bypass flue in both cases. This allows up and down temperature control.

\textbf{22.9 Industrial Bypassing}

This chapter's calculations assume that bypassing is:

100% effective

i.e. that bypassing 10% of a gas stream around a cooling device decreases heat transfer by 10%.
Acid plant designers suggest, however, that industrial bypass efficiency is more closely represented by an equation like:

\[
\text{industrial bypass} = (\text{theoretical bypass})^n
\]  
(22.1)

where \( n = \sim 1.1 \).

This means that the industrial bypass required to give Section 22.8's 6.2% theoretical bypass is:

\[
\text{industrial bypass} = (6.2\%)^{1.1}
\]  
(22.2)

\[
= 7.4\%
\]

22.9.1 Inefficiency explained

Bypassing gas around a cooling device inadvertently:

(a) increases the residence time of the remaining gas in the cooling device which in turn:

(b) increases heat transfer from this gas to economizer water.

This partially offsets bypassing's heat transfer decrease -- lowering its effectiveness.

22.10 Summary

Bypassing various fractions of a gas stream around a cooling device provides control over the device's output gas (Fig. 22.1) temperature.

Operating with gas always flowing in the bypass flue allows the cooling device's exit gas temperature to be adjusted upwards and downwards -- by increasing or decreasing the amount the bypass valve is open.

A cooling device should be designed for its maximum anticipated cooling duty, i.e. for:

- maximum expected gas flow

and:

- maximum expected gas temperature drop.

This permits all lesser cooling duties to be obtained by bypassing.

Also, the bypass flue and control valve should be large enough to give sufficient bypassing for the smallest anticipated cooling duty.
Problems
All heat transfer rates in these problems are based on 100 000 Nm$^3$ of 1st catalyst bed feed gas per hour.

22.1 Problem 21.2 shows that cooling Prob. 21.1's 710.4 K 3rd catalyst bed exit gas to 470 K requires transfer of:

8.23 MJ per kg of 1st catalyst bed feed gas.

It also shows that with 100 000 Nm$^3$ per hour of 1st catalyst bed feed gas, this is equivalent to a:

36 740 MJ per hour

economizer.

Determine:

(a) the percentage of economizer input gas that will have to be bypassed around the economizer to give 480 K H$_2$SO$_4$ making input gas

(b) the size (MJ per hour) of economizer that will be required to give 460 K H$_2$SO$_4$ making input gas (with 100 000 Nm$^3$ per hour 1st catalyst bed feed gas).

22.2 Industrial practice indicates that Prob. 22.1's 3rd catalyst bed exit gas varies between 705 K to 715 K.

What fraction of Prob. 22.1's 3rd catalyst bed exit gas will have to be bypassed around Prob. 22.1 (b)'s economizer to give 470 K H$_2$SO$_4$ making input gas when the economizer input gas is:

(a) 715 K

(b) 710.5 K

(c) 705 K?

Is gas always flowing through the bypass flue?

22.3 What would the industrial (a), (b) and (c) bypasses be if Eqn. (22.2) is obeyed with $n = 1.1$?
CHAPTER 23

H₂SO₄ Making

Sulfuric acid is made by:

(a) catalytically oxidizing an acid plant's feed SO₂(g) to SO₃(g)

(b) making H₂SO₄(ℓ) from the resulting SO₃(g).

The reactions are:

\[
\begin{align*}
SO_2(g) + \frac{3}{2}O_2(g) & \rightarrow SO_3(g) \quad \text{in dry feed gas catalyst} & \text{700-900 K} (1.1) \\
SO_3(g) + H_2O(\ell) & \rightarrow H_2SO_4(\ell) \quad \text{in strong sulfuric acid} & \text{350-380 K} (1.2)
\end{align*}
\]

Reaction (1.2) produces strengthened sulfuric acid because it consumes H₂O(ℓ) and makes H₂SO₄(ℓ).

Chapters 10 to 22 examine SO₂ oxidation. This chapter and Chapter 24 examine H₂SO₄ making. They do so from the points of view of:

(a) mass flows, this chapter

and:

(b) acid temperature control, next chapter.

Industrial final-H₂SO₄-making ('absorption') data are also provided, Table 23.2.
Fig. 23.1 is a simplified sulfuric acidmaking flowsheet. Its inputs are:

(a) moist 5 volume% H₂O(g), SO₂, O₂, N₂ gas from gas cleaning and cooling
(b) water.

Its outputs are:

(a) 98 mass% H₂SO₄, 2 mass% H₂O sulfuric acid
(b) dilute SO₂, O₂, N₂ gas.

All other flows are internal.

**Fig. 23.1.** Simplified single contact sulfuric acid production flowsheet. Its inputs are moist feed gas and water. Its outputs are 98 mass% H₂SO₄, 2 mass% H₂O sulfuric acid and dilute SO₂, O₂, N₂ gas. The acid output combines gas dehydration tower acid, H₂SO₄ making tower acid and liquid water. The equivalent sulfur burning acid plant sends moist air (rather than moist feed gas) to dehydration. Appendix V gives an example sulfur burning calculation.

### 23.1 Objectives

The objectives of this chapter are to calculate:

(a) the mass of 98 mass% H₂SO₄, 2 mass% H₂O sulfuric acid that is produced from Fig. 23.1’s inputs

(b) the mass of water needed to make this acid

both per kg-mole of dry 10 volume% SO₂, 11 volume% O₂, 79 volume% N₂ 1ˢᵗ catalyst bed feed gas.

Molar and mass balances are used.
23.2 Mass Balances

Acid compositions are given in mass%. It is easier, therefore, to base acid flow calculations on kg rather than kg-mole. This requires, however, that connections be made between the:

- molar (gas) calculations of Chapters 10 to 22
- and the:
- mass (liquid) calculations of this chapter.

The connective calculations are:

- conversion of kg-mole \( SO_3 \) in \( H_2SO_4 \) making tower input gas to kg \( SO_3 \).
- conversion of kg-mole \( H_2O(g) \) in moist acid plant input gas to kg \( H_2O(g) \).

Once these conversions are made, the remainder of the calculations can be based on mass.

23.3 \( SO_3 \) Input Mass

The gas entering Fig. 23.1’s \( H_2SO_4 \) making (‘absorption’) tower is specified to be Section 16.3’s 3rd catalyst bed exit gas. It contains:

\[
\begin{align*}
0.098 & \text{ kg-mole } SO_3 \\
0.002 & \text{ " } SO_2 \\
0.061 & \text{ " } O_2 \\
0.790 & \text{ " } N_2
\end{align*}
\]

per kg-mole of dry 10 volume% \( SO_2 \), 11 volume% \( O_2 \), 79 volume% \( N_2 \) 1st catalyst bed feed gas.

Only the \( SO_3 \) participates in \( H_2SO_4 \) making. It is specified that it all ends up as \( H_2SO_4(l) \), Reaction (1.2).

The mass of \( SO_3 \) equivalent to 0.098 kg-mole is given by the equation:

\[
\text{mass } SO_3 = \text{ kg-mole } SO_3 \times 80 \text{ kg } SO_3 \text{ per kg-mole } SO_3
\]

\[
= 0.098 \times 80
\]

\[
= 7.84 \text{ kg per kg-mole of dry 1st catalyst bed feed gas} \quad (23.1).
\]

(80 is the molecular weight of \( SO_3 \).)

23.4 $\text{H}_2\text{O}(g)$ Input from Moist Acid Plant Input Gas

Fig. 23.1 shows that its moist acid plant input gas contains 5 volume% $\text{H}_2\text{O}(g)$. The remaining 95 volume% is dry 1st catalyst bed feed gas. These are equivalent to 5 and 95 mole% respectively.

This gas is dehydrated in Fig. 23.1's dehydration tower. Its $\text{H}_2\text{O}(g)$ reacts with strong sulfuric acid in the tower to form:

slightly weakened sulfuric acid.

The reaction is:

$$\text{H}_2\text{O}(g) + \text{H}_2\text{SO}_4(\ell) \rightarrow \text{H}_2\text{SO}_4(\ell) + \text{H}_2\text{O}(\ell)$$

(6.2).

This section calculates the mass of $\text{H}_2\text{O}(g)$ in 5 mole% $\text{H}_2\text{O}(g)$ input gas. It is specified that all of this $\text{H}_2\text{O}(g)$ ends up in Reaction (6.2)'s slightly weakened acid.

23.4.1 $\text{H}_2\text{O}(g)$ in moist input gas

The amount of $\text{H}_2\text{O}(g)$ in Fig. 23.1's moist input gas is given by the equation:

$$\text{kg-mole } \text{H}_2\text{O}(g) \text{ in moist input gas} = \frac{5 \text{ mole% } \text{H}_2\text{O}(g) \text{ in moist input gas}}{100\%} \times \text{kg-mole moist input gas}$$

(23.2).

Similarly, the quantity of dry 1st catalyst bed feed gas in the moist acid plant input gas is:

$$\text{kg-mole of dry 1st catalyst bed feed gas in moist input gas} = \frac{95 \text{ mole% dry 1st catalyst bed feed gas in moist input gas}}{100\%} \times \text{kg-mole moist input gas}$$

(23.3).

The amount of input $\text{H}_2\text{O}(g)$ per kg-mole of dry 1st catalyst bed feed gas is obtained by dividing Eqn. (23.2) by Eqn. (23.3), i.e.:

$$\frac{\text{kg-mole } \text{H}_2\text{O}(g) \text{ in moist input gas}}{\text{kg-mole of dry 1st catalyst bed feed gas in moist input gas}} = \frac{5}{95} = 0.0526 \text{ kg-mole } \text{H}_2\text{O}(g) \text{ per kg-mole of dry 1st catalyst bed feed gas}$$

(23.4).
23.4.2 Mass $H_2O(g)$ in moist input gas

Mass $H_2O(g)$ in the above moist gas is given by the equation:

$$\text{mass } H_2O(g) \text{ in moist acid} = 0.0526 \text{ kg-mole of } H_2O(g) \text{ per kg-mole of dry 1st catalyst bed feed gas} \times 18 \text{ kg } H_2O(g) \text{ per kg-mole of } H_2O(g)$$

$$= 0.947 \text{ kg } H_2O(g) \text{ per kg-mole of dry 1st catalyst bed feed gas}$$

(18 is the molecular weight of $H_2O$.)

The above sections determine:

(a) mass $SO_3(g)$ entering Fig. 23.1's $H_2SO_4$ making tower acid

(b) mass $H_2O(g)$ entering Fig. 23.1's dehydration tower acid.

These masses plus mass input liquid water form Fig. 23.1's acid product.

The next sections calculate:

(a) the mass of output 98 mass% $H_2SO_4$, 2 mass% $H_2O$ sulfuric acid produced by these inputs

(b) the mass of liquid water needed to make this acid product.

23.5 Water for Product Acid

The water entering the Fig. 23.1 acid plant is adjusted to give the plant's specified product, in this case:

$$98 \text{ mass}\% \ H_2SO_4$$
$$2 \text{ mass}\% \ H_2O$$

sulfuric acid.

This water and the $H_2O(g)$ in moist input gas provide all the $H_2O$ for this acid. The $H_2O$ is used for:

(a) the reaction:

$$SO_3(g) + H_2O \rightarrow H_2SO_4(\ell)$$

and:

(b) the 2 mass% $H_2O$ in the product acid.
23.6 Calculation of Mass Water In and Mass Acid Out

This section calculates:

(a) the mass of H$_2$SO$_4$ produced from Section 23.3's SO$_3$(g)

(b) the mass of liquid water required to make this H$_2$SO$_4$ plus the specified 2 mass% H$_2$O in the plant's product acid

(c) the total mass of product acid

all per kg-mole of dry 1st catalyst bed feed gas.

The calculations use:

(a) SO$_3$(g) and H$_2$O(g) input Eqns. (23.1) and (23.5)

(b) sulfur and total mass balances

(c) a 98 mass% H$_2$SO$_4$, 2 mass% H$_2$O acid composition specification.

The H$_2$SO$_4$ making tower's input SO$_2$, O$_2$ and N$_2$ are ignored—because they pass unreacted through the acid plant and into the environment.

23.6.1 S balance

The S mass balance for Fig. 23.1's H$_2$SO$_4$ making tower (excluding SO$_2$) is:

\[
\text{mass S in SO}_3 \text{ into H}_2\text{SO}_4 \text{ making tower} = \text{mass S in product H}_2\text{SO}_4
\]

Since SO$_3$ and H$_2$SO$_4$ contain 40 mass% and 32.7 mass% S respectively, this equation becomes:

\[
\frac{40\%/100\%}{\text{mass SO}_3 \text{ into H}_2\text{SO}_4 \text{ making tower}} = 32.7\%/100\% \times \text{mass output H}_2\text{SO}_4
\]

or:

\[
\frac{0}{\text{mass SO}_3 \text{ into H}_2\text{SO}_4 \text{ making tower}} = -0.4 \times 32.7\% \times \text{mass output H}_2\text{SO}_4
\]  

(23.6).

23.6.2 Total mass balance

The total mass balance for Fig. 23.1 (excluding SO$_2$, O$_2$ and N$_2$ in H$_2$SO$_4$ making tower input and output gas) is:
mass SO₃ into H₂SO₄ making tower + mass H₂O(g) in + mass water in
   = mass H₂SO₄ out + mass H₂O out

or:
0 = -mass SO₃ into H₂SO₄ making tower - mass H₂O(g) in - mass water in
   + mass H₂SO₄ out + mass H₂O out

(23.7).

23.6.3 Output acid composition specification

The output acid composition is put into equation form by combining the equations:

mass H₂SO₄ in output acid = \( \frac{98 \text{ mass} \% \text{ H}_2\text{SO}_4 \text{ in output acid}}{100\%} \) * mass output acid

mass H₂O in output acid = \( \frac{2 \text{ mass} \% \text{ H}_2\text{O in output acid}}{100\%} \) * mass output acid

to give:

\[
\frac{\text{mass H}_2\text{SO}_4 \text{ in output acid}}{\text{mass H}_2\text{O in output acid}} = \frac{98}{2}
\]
or:

2 * mass H₂SO₄ in output acid = 98 * mass H₂O in output acid

or:

0 = -2 * mass H₂SO₄ in output acid + 98 * mass H₂O in output acid

(23.8).

23.6.4 Solving for mass H₂SO₄ out and mass water in

The above four sections contain 5 variables:

mass SO₃ into H₂SO₄ making tower
mass H₂O(g) in
mass water in
mass H₂SO₄ out
mass H₂O out.

They also contain 5 equations, (23.1) and (23.5-23.8). The solutions to all these equations are obtained by solving matrix Table 23.1, as described in Appendix H.
Table 23.1. Matrix for determining the mass of $H_2SO_4$ produced by the Fig. 23.1 acid plant. The water requirement is also determined. All numerical values are per kg-mole of dry 1st catalyst bed feed gas. The solution to the matrix is given below it.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Description</td>
<td>equation</td>
<td>numerical term</td>
<td>mass $SO_3$ into $H_2SO_4$ making tower</td>
<td>mass $H_2O$ in moist Input gas</td>
<td>mass $H_2O$ in output gas</td>
<td>mass $H_2SO_4$ in output acid</td>
<td>mass $H_2O$ in output acid</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mass $SO_3$ into $H_2SO_4$ making tower</td>
<td>23.1</td>
<td>7.840</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>mass $H_2O$ in moist feed gas</td>
<td>23.5</td>
<td>0.947</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>S balance*</td>
<td>23.6</td>
<td>0</td>
<td>-0.4</td>
<td>0</td>
<td>0</td>
<td>0.327</td>
<td>0</td>
</tr>
<tr>
<td>total mass balance#</td>
<td>23.7</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>output acid composition specification</td>
<td>23.8</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-2</td>
<td>98</td>
</tr>
</tbody>
</table>

* Excluding $SO_2$, $O_2$ and $N_2$ entering and leaving Fig. 23.1’s $H_2SO_4$ making tower.

The solution to the matrix, with all values kg per kg-mole of dry 1st catalyst bed feed gas, is:

- mass $SO_3$ in $H_2SO_4$ making tower input gas = 7.840
- mass $H_2O(g)$ in moist input gas = 0.947
- mass input water = 0.999
- mass $H_2SO_4$ in output acid = 9.590
- mass $H_2O$ in output acid = 0.196

These are the only values that satisfy all the equations in the matrix.

23.6.5 Mass output sulfuric acid

Total output acid mass is given by the equation:

$$mass \text{ output acid} = mass \text{ $H_2SO_4$ in output acid} + mass \text{ $H_2O$ in output acid}$$

(23.9).

With the above values, it is:

mass output acid = 9.590 + 0.196 = 9.8 kg per kg-mole of dry 1st catalyst bed feed gas.

23.6.6 Flows with 100 000 Nm$^3$ per hour dry 1st catalyst bed feed gas

The above masses are all per kg-mole of dry 1st catalyst bed feed gas. With 100 000 Nm$^3$ per hour (4464 kg-mole per hour) of dry 1st catalyst bed feed gas, these masses are equivalent to:
<table>
<thead>
<tr>
<th>Flow</th>
<th>kg/hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₃ in H₂SO₄ making tower input gas</td>
<td>35 000</td>
</tr>
<tr>
<td>H₂O in moist input gas</td>
<td>4 200</td>
</tr>
<tr>
<td>water in</td>
<td>4 500</td>
</tr>
<tr>
<td>H₂SO₄ in output acid</td>
<td>42 800</td>
</tr>
<tr>
<td>H₂O in output acid</td>
<td>900</td>
</tr>
<tr>
<td>output acid</td>
<td>43 700</td>
</tr>
</tbody>
</table>

Of course, these flows will double if the 1st catalyst bed feed gas input rate is doubled, etc.

23.7 Interpretations

23.7.1 H₂SO₄ production vs. SO₃ in H₂SO₄ making tower input gas

Fig. 23.2 shows mass H₂SO₄ out of Fig. 23.1’s H₂SO₄ making tower as a function of the tower’s input SO₃ quantity. H₂SO₄ production (kg) increases linearly with increasing SO₃ input mass (kg).

This is because each kg-mole of SO₃ into the H₂SO₄ making tower produces a kg-mole of H₂SO₄, i.e.:

\[
\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4
\]  

(23.10).

In terms of mass, each 80 kg of input SO₃ gives 98 kg of output H₂SO₄. This is equivalent to:

\[
\frac{98}{80} = 1.225
\]

kg H₂SO₄ out per kg of input SO₃. This is confirmed by the slope of Fig. 23.2’s H₂SO₄ making line.

\[\text{slope} = 1.225\]

Fig. 23.2. Mass H₂SO₄ out of H₂SO₄ making tower as a function of mass SO₃ into H₂SO₄ making tower. The line is straight with a slope of 1.225 (Section 23.7.1).
23.7.2 Water requirement vs. \( \text{H}_2\text{O(g)} \) in moist input gas

Fig. 23.3 shows Fig. 23.1’s acid plant water requirement as a function of volume\% \( \text{H}_2\text{O(g)} \) in its moist input gas. As expected, water requirement falls with increasing \( \text{H}_2\text{O(g)} \) in moist feed gas.

Fig. 23.3 also shows that no liquid water is required when the moist input gas contains 9.8 volume\% \( \text{H}_2\text{O(g)} \) (under the specific conditions of the Table 23.1 matrix). At this point, all the output acid's \( \text{H}_2\text{O} \) requirement is provided by \( \text{H}_2\text{O(g)} \) in Fig. 23.1's feed gas.

Finally, the figure indicates that moist input gas containing more than 9.8 volume\% \( \text{H}_2\text{O(g)} \) cannot produce the specified 98 mass\% \( \text{H}_2\text{SO}_4 \) acid – because it brings too much \( \text{H}_2\text{O} \) into the system. 10 volume\% \( \text{H}_2\text{O(g)} \) moist input gas would produce, for example, \( \sim 97\frac{1}{2} \) mass\% \( \text{H}_2\text{SO}_4 \) acid.

23.7.3 Water requirement vs. acid strength

Fig. 23.4 shows the Fig. 21.1 acid plant's water requirement as a function of specified mass\% \( \text{H}_2\text{SO}_4 \) in product acid (constant volume\% \( \text{H}_2\text{O(g)} \) in moist acid plant input gas).
Water requirement increases with decreasing mass\% \( \text{H}_2\text{SO}_4 \) in acid (i.e. with increasing specified mass\% \( \text{H}_2\text{O} \) in acid).

Note that liquid water is needed even when the acid plant's product is 100\% \( \text{H}_2\text{SO}_4 \). It is needed for the:

\[
\text{H}_2\text{O} + \text{SO}_3 \rightarrow \text{H}_2\text{SO}_4
\]

\( \text{H}_2\text{SO}_4 \) making reaction.

![Graph showing liquid water requirement vs. mass \( \text{H}_2\text{SO}_4 \) in product acid](image)

**Fig. 23.4.** Fig. 23.1 acid plant water requirement as a function of mass\% \( \text{H}_2\text{SO}_4 \) in acid plant product acid. Water requirement increases with decreasing specified mass\% \( \text{H}_2\text{SO}_4 \) (i.e. with increasing specified mass\% \( \text{H}_2\text{O} \)) in acid.

### 23.7.4 Water requirement vs. mass \( \text{SO}_3 \) into \( \text{H}_2\text{SO}_4 \) making tower

Fig. 23.5 shows the effect of:

- mass \( \text{SO}_3 \) into \( \text{H}_2\text{SO}_4 \) making tower
- acid plant liquid water requirement.

both per kg-mole of dry 1\text{st} catalyst bed feed gas. Water requirement increases with increasing mass \( \text{SO}_3 \).
The increased requirement is made up of:

(a) water needed for Fig. 23.2's increasing H\textsubscript{2}SO\textsubscript{4} production, Reaction (23.10)

(b) water for the 2 mass\% H\textsubscript{2}O in product acid that goes with this increased H\textsubscript{2}SO\textsubscript{4} production.

![Graph showing water requirement vs. mass SO\textsubscript{3} into H\textsubscript{2}SO\textsubscript{4} making tower.](image)

**Fig. 23.5.** Acid plant water requirement as a function of mass SO\textsubscript{3} into H\textsubscript{2}SO\textsubscript{4} making tower. The water requirement increases with increasing SO\textsubscript{3} input mass, Section 23.7.4. With a 100\% H\textsubscript{2}SO\textsubscript{4} product, the slope is 0.225 (Fig. 23.2). With 2 mass\% H\textsubscript{2}O, 98 mass\% H\textsubscript{2}SO\textsubscript{4} product acid, it is 0.25 (as shown). It varies, therefore, with product acid composition.

23.8 Summary

Sulfuric acid compositions are expressed in mass\%. For this reason, acidmaking calculations are more easily done with mass (rather than molar) balances. This chapter uses mass balances to calculate an acid plant's:

(a) H\textsubscript{2}SO\textsubscript{4} production

(b) water requirement

(kg per kg-mole of dry 1\textsuperscript{st} catalyst bed feed gas and kg per hour).

H\textsubscript{2}SO\textsubscript{4} production increases with increasing SO\textsubscript{3} mass in H\textsubscript{2}SO\textsubscript{4} making tower input gas, both per kg-mole of dry 1st catalyst bed feed gas. Acid plant water requirement increases commensurately.
Water requirement also increases with:

(a) decreasing H₂O(g) concentration in moist acid plant feed gas
and

(b) increasing specified mass% H₂O in product acid.

Problem

23.1 The moist gas entering a Fig. 23.1 acid plant contains 6 volume% H₂O(g) and 94 volume% dry 1\textsuperscript{st} catalyst bed feed gas.

The dry portion of input gas contains 12 volume% SO₂, 13.2 volume% O₂ and 74.8 volume% N₂.

This gas is:

(a) dehydrated with strong sulfuric acid
(b) oxidized in 3 catalyst beds
(c) sent to H₂SO₄ making.

The H₂SO₄ making tower input gas (i.e. cooled 3\textsuperscript{rd} catalyst bed exit gas) contains:

- 0.1183 kg-mole SO₃
- 0.0017 " " SO₂
- 0.0728 " " O₂
- 0.7480 " " N₂

per kg-mole of dry 1\textsuperscript{st} catalyst bed feed gas (Problem 16.1).

The plant is producing 98.5 mass% H₂SO₄, 1.5 mass% H₂O sulfuric acid.

All the input H₂O(g) and all the SO₃ entering the H₂SO₄ making tower end up in the plant's acid product.

Calculate:

(a) the mass of H₂SO₄ produced
(b) the mass of sulfuric acid produced
(c) the mass of input water needed to make this sulfuric acid

all per kg-mole of dry 1\textsuperscript{st} catalyst bed feed gas.

Calculate also the flows of these materials, kg per hour, when 100 000 Nm³ per hour of dry 1\textsuperscript{st} catalyst bed feed gas are entering the acid plant.


## Table 23.2. Details of packed bed H₂SO₄-from-SO₃ plants.

<table>
<thead>
<tr>
<th>Plant</th>
<th>S1</th>
<th>M2</th>
</tr>
</thead>
<tbody>
<tr>
<td>input gas flowrate, thousand Nm³/hour</td>
<td>296</td>
<td>110</td>
</tr>
<tr>
<td>estimated SO₃ utilization efficiency</td>
<td></td>
<td>99.9</td>
</tr>
</tbody>
</table>

### Packed bed details

<table>
<thead>
<tr>
<th></th>
<th>S1</th>
<th>M2</th>
</tr>
</thead>
<tbody>
<tr>
<td>number of packed beds</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>height × diameter, m</td>
<td>9.85 × 8.3</td>
<td>18.5 × 6.5</td>
</tr>
<tr>
<td>construction material</td>
<td>310/304 stainless steel</td>
<td>brick lined carbon steel</td>
</tr>
<tr>
<td>ceramic packing</td>
<td>7.5 cm saddles</td>
<td>5.1 &amp; 7.6 cm saddles</td>
</tr>
<tr>
<td>packing height, m</td>
<td>2.44</td>
<td>4</td>
</tr>
<tr>
<td>acid distributor type</td>
<td>trough and downcomer</td>
<td>buried pipe distributor</td>
</tr>
<tr>
<td>mist eliminator type</td>
<td>candles</td>
<td>hanging fiber bed</td>
</tr>
<tr>
<td>exit gas mist concentration, g/Nm³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>acid flowrate, m³/hour</td>
<td>1060</td>
<td>762</td>
</tr>
</tbody>
</table>

### Temperature data, K

<table>
<thead>
<tr>
<th></th>
<th>S1</th>
<th>M2</th>
</tr>
</thead>
<tbody>
<tr>
<td>inlet gas</td>
<td>408</td>
<td>463</td>
</tr>
<tr>
<td>outlet gas</td>
<td>355</td>
<td>345</td>
</tr>
<tr>
<td>inlet acid</td>
<td>355</td>
<td>345</td>
</tr>
<tr>
<td>outlet acid</td>
<td>365</td>
<td>356</td>
</tr>
<tr>
<td>acid cooling method</td>
<td></td>
<td>plate heat exchanger</td>
</tr>
</tbody>
</table>

### Gas composition in, vol.%

<table>
<thead>
<tr>
<th></th>
<th>SO₃</th>
<th>SO₂</th>
<th>O₂</th>
<th>CO₂</th>
<th>N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.745</td>
<td>0.04</td>
<td>3.9</td>
<td>0</td>
<td>95.3</td>
</tr>
<tr>
<td>M2</td>
<td>0.42</td>
<td>0.01</td>
<td>5.14</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Gas composition out, vol.%

<table>
<thead>
<tr>
<th></th>
<th>SO₃</th>
<th>SO₂</th>
<th>O₂</th>
<th>CO₂</th>
<th>N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td></td>
<td>0.04</td>
<td>3.97</td>
<td>0</td>
<td>96.0</td>
</tr>
<tr>
<td>M2</td>
<td></td>
<td>0.01</td>
<td>5.16</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- no tail gas scrubbing
- NaOH scrubbing

### Acid comp., mass% H₂SO₄

<table>
<thead>
<tr>
<th></th>
<th>into tower</th>
<th>out of tower</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>98.4</td>
<td>98.5</td>
</tr>
<tr>
<td>M2</td>
<td>98.5</td>
<td>98.5</td>
</tr>
</tbody>
</table>

### Acid plant products, mass% H₂SO₄

<table>
<thead>
<tr>
<th></th>
<th>S1</th>
<th>M2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>98.5</td>
<td>98.5</td>
</tr>
</tbody>
</table>
The data are for FINAL H$_2$SO$_4$ making in double contact plants.

<table>
<thead>
<tr>
<th></th>
<th>Cumerio 1 (Bulgaria)</th>
<th>Cumerio 2 (Bulgaria)</th>
<th>M6</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>19.2 x 7</td>
<td>21.02 x 7</td>
<td>20.5 x 7.1</td>
</tr>
<tr>
<td></td>
<td>brick lined carbon steel</td>
<td>brick lined carbon steel</td>
<td>brick lined carbon steel</td>
</tr>
<tr>
<td>7.6 &amp; 5.1 cm saddles</td>
<td>3.5</td>
<td>5.1 cm saddles</td>
<td>7.6 cm saddles</td>
</tr>
<tr>
<td>Lurgi pipes and tubes</td>
<td>distribution plates</td>
<td>high efficiency candles</td>
<td>troughs and downcomers</td>
</tr>
<tr>
<td>1</td>
<td>19.2 x 7</td>
<td>21.02 x 7</td>
<td>20.5 x 7.1</td>
</tr>
<tr>
<td>brick lined carbon steel</td>
<td>3.5</td>
<td>5.1 cm saddles</td>
<td>7.6 cm saddles</td>
</tr>
<tr>
<td>Lurgi pipes and tubes</td>
<td>distribution plates</td>
<td>high efficiency candles</td>
<td>troughs and downcomers</td>
</tr>
<tr>
<td>1</td>
<td>19.2 x 7</td>
<td>21.02 x 7</td>
<td>20.5 x 7.1</td>
</tr>
<tr>
<td>brick lined carbon steel</td>
<td>3.5</td>
<td>5.1 cm saddles</td>
<td>7.6 cm saddles</td>
</tr>
<tr>
<td>Lurgi pipes and tubes</td>
<td>distribution plates</td>
<td>high efficiency candles</td>
<td>troughs and downcomers</td>
</tr>
<tr>
<td>1</td>
<td>19.2 x 7</td>
<td>21.02 x 7</td>
<td>20.5 x 7.1</td>
</tr>
<tr>
<td>brick lined carbon steel</td>
<td>3.5</td>
<td>5.1 cm saddles</td>
<td>7.6 cm saddles</td>
</tr>
<tr>
<td>Lurgi pipes and tubes</td>
<td>distribution plates</td>
<td>high efficiency candles</td>
<td>troughs and downcomers</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>750</th>
<th>700</th>
<th>707</th>
</tr>
</thead>
<tbody>
<tr>
<td>453</td>
<td>355</td>
<td>355</td>
<td></td>
</tr>
<tr>
<td>355</td>
<td>333</td>
<td>350</td>
<td></td>
</tr>
<tr>
<td>384</td>
<td>353</td>
<td>372</td>
<td></td>
</tr>
<tr>
<td>shell and tube</td>
<td>shell and tube</td>
<td>shell and tube</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>0.56</th>
<th>0.45</th>
<th>0.51</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.014</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>8.06</td>
<td>6.12</td>
<td>13.40</td>
<td></td>
</tr>
<tr>
<td>0.36</td>
<td>0.31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>91.01</td>
<td>93.11</td>
<td>remainder (inerts)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>0.0022</th>
<th>0.0018</th>
<th>0.027</th>
<th>0.017</th>
<th>0.05</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0022</td>
<td>0.0018</td>
<td>0.027</td>
<td>0.017</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>8.1</td>
<td>6.12</td>
<td>13.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.36</td>
<td>0.31</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>91.51</td>
<td>93.55</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

no scrubbing      no scrubbing      no scrubbing

<table>
<thead>
<tr>
<th></th>
<th>98.5</th>
<th>98.3</th>
<th>98.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>98.55</td>
<td>98.31</td>
<td></td>
<td>98.6</td>
</tr>
<tr>
<td>94-98.5</td>
<td>94-98.5</td>
<td></td>
<td>93, 99 oleum (20%)</td>
</tr>
</tbody>
</table>
Table 23.2 (cont.). Details of packed bed H₂SO₄-from-SO₃ plants.

<table>
<thead>
<tr>
<th>Plant</th>
<th>M4</th>
<th>Asarco Hayden</th>
</tr>
</thead>
<tbody>
<tr>
<td>input gas flowrate, thousand Nm³/hour</td>
<td>158</td>
<td>170</td>
</tr>
<tr>
<td>estimated SO₃ utilization efficiency</td>
<td>99.9</td>
<td>99.9</td>
</tr>
</tbody>
</table>

**Packed bed details**
- number of packed beds: 1
- height × diameter, m: 20.4 × 7.5 (OD) 17.8 × 6.7
- construction material: brick lined carbon steel
- ceramic packing: 5.1 & 7.6 cm saddles 7.6 cm saddles
- packing height, m: 5.9 3.66
- acid distributor type: submerged distributor pipe SX troughs
- mist eliminator type: Brink mist eliminator (C fiber) candles
- exit gas mist concentration, g/Nm³: <0.05
- acid flowrate, m³/hour: 940 450

**Temperature data, K**
- inlet gas: 453 455
- outlet gas: 350 355
- inlet acid: 350 355
- outlet acid: 360 377
- acid cooling method

**Gas composition in, vol.%**
- SO₂: 1.1 0.6
- SO₃: 0.025 0.05
- O₂: 8.7 7.77
- CO₂: 3.3 1.2
- N₂: remainder remainder

**Gas composition out, vol.%**
- SO₂: 0.026 0.05
- O₂: 8.8 7.77
- CO₂: 3.3 1.2
- N₂: remainder remainder

**Acid comp., mass% H₂SO₄**
- into tower: 98.5 98.0
- out of tower: 98.5

**Acid plant products, mass% H₂SO₄**
- 98.5 93/98
The data are for FINAL H$_2$SO$_4$ making in double contact plants.

<table>
<thead>
<tr>
<th>Phelps Dodge Miami</th>
<th>M1</th>
</tr>
</thead>
<tbody>
<tr>
<td>204</td>
<td>50</td>
</tr>
<tr>
<td>99.9</td>
<td>99.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.5 × 8.5</td>
<td>8.5 × 4</td>
<td></td>
</tr>
<tr>
<td>carbon steel shell</td>
<td>brick lined carbon steel</td>
<td></td>
</tr>
<tr>
<td>5.1 cm saddles and intalox saddles</td>
<td>7.6 cm saddles</td>
<td></td>
</tr>
<tr>
<td>5.3</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>pipe and perforated arms</td>
<td>pipe</td>
<td></td>
</tr>
<tr>
<td>high efficiency candles</td>
<td>mesh pads (tent and flat)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>950</td>
<td>227</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>516</th>
<th>472-494</th>
</tr>
</thead>
<tbody>
<tr>
<td>348</td>
<td>339-366</td>
<td></td>
</tr>
<tr>
<td>348</td>
<td>347-358</td>
<td></td>
</tr>
<tr>
<td>375</td>
<td>358-375</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>0.008-0.012</td>
</tr>
<tr>
<td>7.25</td>
<td>10.2-12.2</td>
</tr>
<tr>
<td>1.1</td>
<td>1.0</td>
</tr>
<tr>
<td>88.5</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.155</td>
<td>0.008-0.012</td>
</tr>
<tr>
<td>7.475</td>
<td>10.2-12.2</td>
</tr>
<tr>
<td>1.134</td>
<td>1.0</td>
</tr>
<tr>
<td>91.236</td>
<td></td>
</tr>
</tbody>
</table>

scrubbing available, if needed  no scrubbing

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>98.5</td>
<td>98.5</td>
</tr>
<tr>
<td>98.8</td>
<td>98.8</td>
</tr>
<tr>
<td>94.5</td>
<td>93.5</td>
</tr>
</tbody>
</table>
Chapter 24

Acid Temperature Control and Heat Recovery

H$_2$SO$_4$ is made by the reaction of SO$_3$(g) with H$_2$O(ℓ) in strong sulfuric acid, i.e.:

\[
SO_3(g) + H_2O(\ell) \rightarrow H_2SO_4(\ell)
\]

The reaction is exothermic. It releases about 130 MJ of heat per kg-mole of SO$_3$(g).

A result of this is that H$_2$SO$_4$ making's output acid is ~25 K warmer than its inlet acid. Fig. 24.1 describes the process.

24.1 Objectives

The objectives of this chapter are to:

(a) show how Fig. 24.1's output acid temperature is calculated
(b) describe the factors which affect this temperature
(c) indicate how output acid is cooled for recycling and shipping
(d) describe how heat-in-acid is recovered as steam.

24.2 Calculation of Output Acid Temperature

This section shows how Fig. 24.1's output acid temperature is calculated. It uses:

(a) Fig. 24.1's temperatures and acid compositions
Fig. 24.1. Fig. 23.1's single contact H₂SO₄ making tower. Its temperatures and gas compositions are used in Section 24.1 and 24.2's calculations. The calculations assume that all input SO₃(g) reacts to form H₂SO₄(ℓ). Note that output gas temperature = input acid temperature. (Hay et al., 2003).

(b) Fig. 24.1's input and output gas quantities
(c) mass and enthalpy balances
(d) Appendix G's enthalpy vs. temperature equations
(e) H₂SO₄(ℓ)-H₂O(ℓ) enthalpy of mixing Eqn. (24.2).

Appendix W calculates Fig. 24.1's input and output H₂SO₄ and H₂O masses. They are listed in Table 24.1.

24.2.1 H₂SO₄(ℓ)-H₂O(ℓ) enthalpy-of-mixing

Mixing of H₂SO₄(ℓ) and H₂O(ℓ) releases heat. This means that the enthalpy of sulfuric acid is lower than the combined enthalpies of its components.

Calorimetric measurements indicate that the enthalpy of mixing H₂SO₄(ℓ) and H₂O(ℓ) is given by the equation:

\[
\Delta H_{\text{mix}}^{\text{H}_2\text{SO}_4} = -1.82 \cdot \text{mass\% H}_2\text{O in sulfuric acid}
\]

MJ per kg-mole of H₂SO₄

(for acid containing up to ~10 mass% H₂O [Duecker and West, 1966]).
Table 24.1. Fig. 24.1’s inputs and outputs. Input and output kg-mole of SO₃, SO₂, O₂, and N₂ are from Fig. 24.1. Input and output H₂SO₄ and H₂O masses are calculated in Appendix W. They are all used to calculate Fig. 24.1’s output acid temperature. The H⁺ values have been calculated by the equations in Appendix G. (kg-mole H₂SO₄ = kg H₂SO₄/98, kg-mole H₂O = kg H₂O/18)

<table>
<thead>
<tr>
<th>Substance</th>
<th>mass, kg</th>
<th>kg-mole</th>
<th>specified temperature, K</th>
<th>H⁺, MJ per kg-mole of substance</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₃(g) in</td>
<td>0.098</td>
<td>480</td>
<td>-386.31</td>
<td></td>
</tr>
<tr>
<td>SO₂(g) in</td>
<td>0.002</td>
<td>480</td>
<td>-289.53</td>
<td></td>
</tr>
<tr>
<td>O₂(g) in</td>
<td>0.061</td>
<td>480</td>
<td>5.208</td>
<td></td>
</tr>
<tr>
<td>N₂(g) in</td>
<td>0.790</td>
<td>480</td>
<td>5.131</td>
<td></td>
</tr>
<tr>
<td>H₂SO₄(ℓ) in</td>
<td>360.237</td>
<td>3.676</td>
<td>-806.06**</td>
<td></td>
</tr>
<tr>
<td>H₂O(ℓ) in</td>
<td>5.486</td>
<td>0.305</td>
<td>-281.91</td>
<td></td>
</tr>
<tr>
<td>SO₃(g) out</td>
<td>0.002</td>
<td>350</td>
<td>-296.24</td>
<td></td>
</tr>
<tr>
<td>O₂(g) out</td>
<td>0.061</td>
<td>350</td>
<td>0.876</td>
<td></td>
</tr>
<tr>
<td>N₂(g) out</td>
<td>0.790</td>
<td>350</td>
<td>1.088</td>
<td></td>
</tr>
<tr>
<td>H₂SO₄(ℓ) out</td>
<td>369.827</td>
<td>3.774</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>H₂O(ℓ) out</td>
<td>3.736</td>
<td>0.208</td>
<td>?</td>
<td></td>
</tr>
</tbody>
</table>

*per kg-mole of 1st catalyst bed feed gas. **H⁺, as described by Eqn. (24.2) with 1.5 mass% H₂O in input acid. ***H⁺, as described by Eqn. (24.2) with 1.0 mass% H₂O in output acid.

The enthalpy of H₂SO₄-in-acid may, therefore, be represented by:

\[
H_{T}^{\circ} = H_{T}^{\circ} + \text{mass\% H}_2\text{O in sulfuric acid} - 1.82 \times \text{mass\% H}_2\text{O in sulfuric acid} \tag{24.2}
\]

(MJ per kg-mole of H₂SO₄).

This equation gives all the heat of mixing to H₂SO₄ rather than to (H₂SO₄ + H₂O). It allows \(H_{T}^{\circ}\) to be used without change in our acid temperature calculations.

### 24.2.2 H₂SO₄ making enthalpy balance

The H₂SO₄ making tower enthalpy balance may be written:

\[
\text{input gas enthalpy} + \text{input acid enthalpy} = \text{output gas enthalpy} + \text{output acid enthalpy} + \text{conductive, convective, plus radiative heat loss} \tag{24.3}
\]

It is simplified by assuming that:

\[
\text{conductive, convective and radiative heat loss} = 0
\]
This gives the final enthalpy equation:

\[
\text{output acid enthalpy} = \{ \text{input gas enthalpy} + \text{input acid enthalpy} \} - \text{output gas enthalpy} \tag{24.4}
\]

24.2.3 Output acid enthalpy

Eqn (24.4) may be expanded to:

\[
\text{output acid enthalpy} = \begin{align*}
\text{kg-mole } \text{SO}_3(g) \text{ in } & \times \ H_{480 \text{ K}}^\circ \text{SO}_3(g) \\
+ \text{kg-mole } \text{SO}_2(g) \text{ in } & \times \ H_{480 \text{ K}}^\circ \text{SO}_2(g) \\
+ \text{kg-mole } \text{O}_2(g) \text{ in } & \times \ H_{480 \text{ K}}^\circ \text{O}_2(g) \\
+ \text{kg-mole } \text{N}_2(g) \text{ in } & \times \ H_{480 \text{ K}}^\circ \text{N}_2(g) \\
+ \text{kg-mole } \text{H}_2\text{SO}_4(\ell) \text{ in } & \times \ H_{350 \text{ K}}^\circ \text{H}_2\text{SO}_4(\ell) \\
+ \text{kg-mole } \text{H}_2\text{O}(\ell) \text{ in } & \times \ H_{350 \text{ K}}^\circ \text{H}_2\text{O}(\ell) \\
- \text{kg-mole } \text{SO}_2(g) \text{ out } & \times \ H_{310 \text{ K}}^\circ \text{SO}_2(g) \\
- \text{kg-mole } \text{O}_2(g) \text{ out } & \times \ H_{310 \text{ K}}^\circ \text{O}_2(g) \\
- \text{kg-mole } \text{N}_2(g) \text{ out } & \times \ H_{310 \text{ K}}^\circ \text{N}_2(g)
\end{align*}
\]

where the quantities and enthalpies are those listed in Table 24.1.

With Table 24.1's numerical values:

\[
\text{output acid enthalpy} = -3094.5 \text{ MJ per kg-mole of } 1^{\text{st}} \text{ catalyst bed feed gas} \tag{24.6}
\]
24.2.4 Output acid temperature

Output acid enthalpy is related to the output quantities and enthalpies of \( \text{H}_2\text{SO}_4(\ell) \) and \( \text{H}_2\text{O}(\ell) \) by the equation:

\[
\text{Output acid enthalpy} = \text{kg-mole output } \text{H}_2\text{SO}_4 \times H_{\text{H}_2\text{SO}_4}^{\text{out}}(\ell) + \text{kg-mole output } \text{H}_2\text{O} \times H_{\text{H}_2\text{O}}^{\text{out}}(\ell)
\]

(24.7).

This equation is combined with Table G.1 and Eqn. (24.2) to give:

\[
\text{Output acid enthalpy} = \frac{\text{kg-mole output } \text{H}_2\text{SO}_4}{\text{H}_2\text{SO}_4} \times \left( 0.1485 \times T_{\text{out}} - 858.3 - 1.82 \times \frac{\text{mass}\% \text{H}_2\text{O}}{\text{in output acid}} \right) + \frac{\text{kg-mole output } \text{H}_2\text{O}}{\text{H}_2\text{O}} \times (0.07568 \times T_{\text{out}} - 308.4)
\]

(24.8)

where:

\[ (0.1485 \times T_{\text{out}} - 858.3 - 1.82 \times \text{mass}\% \text{H}_2\text{O} \text{ in output acid}) \]

is the enthalpy (\( H \)) of \( \text{H}_2\text{SO}_4(\ell) \) in acid at temperature \( T_{\text{out}} \), Appendix G and Eqn. (24.2) and where:

\[ 0.07568 \times T_{\text{out}} - 308.4 \]

is the enthalpy (\( H^\circ \)) of \( \text{H}_2\text{O}(\ell) \) at temperature \( T_{\text{out}} \), Appendix G (both MJ/kg-mole).

24.2.5 Final enthalpy equation

Substitution of Table 24.1's values of:

\[
\begin{align*}
\text{kg-mole output } \text{H}_2\text{SO}_4 &= 3.774 \\
\text{kg-mole output } \text{H}_2\text{O} &= 0.208
\end{align*}
\]

(per kg-mole of 1\text{st} catalyst bed feed gas)
and:

\[
\text{mass\% H}_2\text{O in output acid} = 1.0
\]

gives:

\[
-3094.5 = 3.774 \frac{\text{kg-mole}}{\text{H}_2\text{SO}_4(\ell)} \times \left( 0.1485 \times T_{\text{out}} - 858.3 - 1.82 \times 1.0 \right) \text{mass\% H}_2\text{O in output acid} \\
+ 0.208 \frac{\text{kg-mole}}{\text{H}_2\text{O}(\ell)} \times (0.07568 \times T_{\text{out}} - 308.4)
\]

(24.9)

from which:

\[
T_{\text{out}} = T_{\text{outlet acid}} = 374 \text{ K}
\]

(as is readily confirmed by inserting 374 K in the right side of Eqn. (24.9).

Perhaps the simplest way to solve Eqn. (24.9) is by the following small Excel Goal Seek calculation.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>kg-mole H\text{2SO}_4(\ell) out =</td>
<td>3.774</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>kg-mole H\text{2O}(\ell) out =</td>
<td>0.208</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>(T_{\text{out}}) =</td>
<td>374</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Output acid enthalpy =</td>
<td>-3094.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>(=B1*(0.1485<em>B4 - 858.3 - 1.82</em>1) + B2*(0.07568*B4 - 308.4))</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Tools
Goal Seek
Set cell: \(B5\)
To value: -3094.5
By changing cell: \(B4\)
OK, OK.

24.2.6 Result

The resulting 374 K output acid temperature is 24 K higher than Table 24.1's 350 K input acid temperature. The next few sections examine the factors that affect this output acid temperature.

24.3 Effect of Input Acid Temperature

Fig. 24.2 shows the effect of H\text{2SO}_4 making's input acid temperature on its output acid
temperature.

Output acid temperature increases with increasing input acid temperature, but the increase is less than 1:1. This is because:

(a) output acid mass > input acid mass, Table 24.1

(b) output gas temperature (hence output gas enthalpy) increases with increasing input acid temperature (Fig. 24.1) leaving less enthalpy for the output acid.

\[
\begin{array}{c}
\text{480 K input gas} \\
\text{output gas temperature = input acid temperature} \\
\text{98.5 mass\% H}_2\text{SO}_4, \ 1.5 \text{ mass\% H}_2\text{O input acid} \\
\text{99.0 mass\% H}_2\text{SO}_4, \ 1.0 \text{ mass\% H}_2\text{O output acid} \\
slope = 0.94
\end{array}
\]

**Fig. 24.2.** Effect of Fig. 24.1's input acid temperature on its output acid temperature (with Table 24.1's input and output masses). A straight line relationship is shown. Note that the slope is less than 1, as explained in Section 24.3.

### 24.4. Effect of Input Gas Temperature

Fig. 24.3 shows the effect of H\textsubscript{2}SO\textsubscript{4} making's input gas temperature on its output acid temperature. Output acid temperature increases slightly with increasing input gas temperature.

This is because hotter input gas brings slightly more enthalpy to H\textsubscript{2}SO\textsubscript{4} making, giving slightly more enthalpy and a slightly higher temperature to the output acid.
Fig. 24.3. Effect of input gas temperature on Fig. 24.1's output acid temperature (with Table 24.1's input and output masses). Output acid temperature increases slightly with increasing input gas temperature. Output gas temperature remains unaltered at the 350 K input acid temperature.

24.5 Effect of Output Acid Composition on Output Acid Temperature

Fig. 24.4 shows the effect of output acid composition on output acid temperature. Output acid temperature increases with increased mass% H₂SO₄ in output acid. This is because:

(a) the amount of circulating acid decreases with increasing mass% H₂SO₄ in output acid, Fig. W.1 while:

(b) heat release by Reaction (1.2) remains constant

(both per kg-mole of 1st catalyst bed feed gas).

24.6 Effect of Input Gas SO₃ Concentration on Output Acid Temperature

Fig. 24.5 shows the effect of Fig. 24.1's input gas SO₃ concentration on its output acid temperature. Output acid temperature decreases slightly with increasing SO₃-in-input-gas concentration. The smallness of the decrease shows why H₂SO₄ making can accept varying input SO₃ concentrations with an almost constant output acid temperature.

Of course, output acid temperature will increase if mass% H₂SO₄ in output acid is allowed to increase with increasing volume% SO₃ in H₂SO₄ making tower input gas, Fig. 24.4. This is the case when input acid flowrate and mass% H₂SO₄ are kept constant while volume% SO₃ in input gas increases. This is usual industrial practice.
98.5 mass% H₂SO₄, 1.5 mass% H₂O input acid
350 K input acid and output gas
480 K input gas
Table 24.1's input and output gas quantities

Fig. 24.4. Effect of specified output acid mass% H₂SO₄ on Fig. 24.1's output acid temperature. Output acid temperature increases with increasing output acid % H₂SO₄ as explained in Section 24.6. % H₂SO₄ in output acid is increased by slowing the rate at which acid is cycling through the H₂SO₄ making tower (and vice versa).

98.5 mass% H₂SO₄, 1.5 mass% H₂O input acid
99.0 mass% H₂SO₄, 1.0 mass% H₂O output acid
350 K input acid and output gas
480 K input gas

Fig. 24.5. Effect of SO₃(g)-in-input-gas concentration on H₂SO₄ making output acid temperature. Output acid temperature decreases slightly with increasing SO₃(g) concentration. The volume% SO₃ values have been calculated as described in Chapter 16 starting with 8, 9, 10, 11 and 12 volume% SO₂ in 1st catalyst bed feed gas.
24.7 Acid Cooling

The above discussion indicates that acid is heated by Reaction (1.2) as it cycles through the H₂SO₄ making tower. It is evident from this that the recycling acid must be cooled to prevent the system from overheating.

This is done by passing the acid through water cooled:

(a) shell and tube (Figs. 9.5 and 24.6) (Chemetics, 2004)
and

(b) plate and frame (Haslego, 2005)

heat exchangers. Both involve counter current, indirect heat exchange between:

- cool water

and:

- warm acid.

![Fig. 24.6. Inside an acid cooler. Fig. 9.5 gives an external view. Tubes start through the tube 'sheet', shown here. They extend almost to the far end of the cooler where there is another tube 'sheet'. Cool water enters at this end and flows through the tubes to the far end. Between the tube 'sheets', the tubes are surrounded by warm acid moving turbulently around them. Heat transfers from the warm acid to the cool water (through the tube walls). The tube entering from the right contains a thermocouple. The polymer tubes in the foreground surround metal rods. The rods are bare between the tube 'sheets'. An electrical potential applied between them and the water tubes anodically protects the tubes against acid side corrosion.](image-url)
The cooled acid is recycled to the H$_2$SO$_4$ making tower or sent to product storage. The warmed water is cooled with atmospheric air and recycled to the acid coolers.

Dehydration tower acid is cooled the same way.

**24.8 Target Acid Temperatures**

Sulfuric acid:

(a) corrosivity

(b) H$_2$SO$_4$, SO$_3$ and H$_2$O vapor pressures

increase with increasing acid temperature. It is important, therefore, that acid temperature be kept relatively cool.

Conversely, the rate of H$_2$SO$_4$ making Reaction (1.2) decreases with decreasing acid temperature – which means that input acid temperature must not be too cool. 380 K is a typical output acid temperature (~100 K warmer in acid heat to steam recovery plants, next section).

**24.9 Recovery of Acid Heat as Steam**

The acid cooling described in Section 24.7 is straightforward and efficient but it doesn't make use of hot acid's energy.

Recent acid plants rectify this by recovering much of the acid's heat as steam (for electricity production etc.). All major acid plant designers are working on this technology (Friedman and Friedman, 2004).

Fig. 24.7 describes one version of the process. It is for double contact (Fig. 9.6) acidmaking.

Its core feature is passage of:

hot (~485 K) intermediate H$_2$SO$_4$ making tower exit acid

through the tubes of a:

shell and tube water to steam boiler.

The products of the process are:

(a) cool new acid
Fig. 24.7. Schematic of acid heat to steam energy recovery system, after Puricelli et al., 1998. It is for intermediate H$_2$SO$_4$ making, Fig. 9.6. Note (i) the double packed bed H$_2$SO$_4$ making tower and (ii) boiler. Industrial acid heat recovery H$_2$SO$_4$ making towers are ~25 m high and 10 m diameter. They produce 2000 to 4000 tonnes of H$_2$SO$_4$ per day. For photographs see Sulfur, 2004.
(b) 10 bar (gage) steam.

24.9.1 Double packed bed \( H_2SO_4 \) making tower

A second key feature of Fig. 24.7's version of the process is its double packed bed \( H_2SO_4 \) making tower – through which:

- strong \( SO_3 \) gas ascends
- strong sulfuric acid descends

around ceramic packing.

**Bottom packed bed**

The bottom packed bed is fed with slightly diluted return acid from the heat-from-acid boiler. \( H_2O \) in the acid reacts with ascending \( SO_3 \) gas to form \( H_2SO_4 \) by Reaction (1.2). Input acid composition and flowrate are controlled to give hot (~485 K) acid boiler feed, Fig. 24.7.

**Top packed bed**

The top packed bed is fed with cool acid from the final \( H_2SO_4 \) making tower. Its principal purpose is to absorb \( H_2SO_4(g) \), \( H_2O(g) \) and \( SO_3(g) \) rising from the bottom bed's hot acid.

24.9.2 Materials of construction

Passage of hot, strong sulfuric acid though tubes surrounded by hot water and steam requires strongly corrosion resistant materials. Accidental mixing of water and strong acid causes rapid corrosion throughout the \( H_2SO_4 \) making system.

Acid flowrates also have to be kept at carefully prescribed velocities.

Alloys currently used in heat-from-acid energy recovery systems are:

- anodically protected Saramet® (Aker Kvaerner, www.chemetics.ca)

(Friedman and Friedman, 2004).

Outokumpu builds a similar heat-from-acid recovery system. It uses a Venturi absorber in place of Fig. 24.7's bottom packed bed (Outokumpu, 2005).
24.10 Summary

H$_2$SO$_4(\ell)$ is made by the reaction of SO$_3(g)$ with the H$_2$O(\ell) in strong sulfuric acid.

Heat is released by the reaction, so that H$_2$SO$_4$ making's output sulfuric acid is ~25 K warmer than its input acid.

Output acid temperature increases markedly with increasing input acid temperature and decreasing acid circulation rate. Corrosion rates increase with increasing temperature so that excessive temperatures must be avoided.

They are avoided by cooling the recycle acid in water cooled 'shell and tube' or 'plate and frame' heat exchangers.

Acid plants (especially sulfur burning plants) are now often built with 'acid heat to steam' energy recovery systems. These significantly increase acidmaking energy efficiency.

References


Problems

24.1 The inputs to an H₂SO₄ making tower are:

(a) last catalyst bed exit gas (480 K) containing:

- 0.1183 kg-mole SO₃
- 0.0017 " SO₂
- 0.0728 " O₂
- 0.7480 " N₂

per kg-mole of 1st catalyst bed feed gas

(b) 98.6 mass% H₂SO₄, 1.4 mass% H₂O sulfuric acid, 350 K.

The outputs are:

(c) exit gas (350 K) containing:

- 0.0000 kg-mole SO₃
- 0.0017 " SO₂
- 0.0728 " O₂
- 0.7480 " N₂

per kg-mole of 1st catalyst bed feed gas.

(d) 99.2 mass% H₂SO₄, 0.8 mass% H₂O sulfuric acid.

Calculate the tower's:

1. H₂SO₄ and H₂O input masses, kg
2. H₂SO₄ and H₂O output masses, kg
3. total enthalpy of the inputs, MJ
4. enthalpy of the output gas

(all per kg-mole of 1st catalyst bed feed gas).

Calculate also:

5. the temperature of the tower's output acid (assume that there are no convective, conductive plus radiative heat losses from the tower).
Hints:

Use:

(a) matrix Table W.1 (with appropriate changes) to calculate the H₂SO₄ and H₂O masses

(b) Table 24.1 (with appropriate changes) to calculate the total input enthalpy and gas output enthalpy

(c) Section 24.2 to calculate the output acid temperature.
Appendix A

Sulfuric Acid Properties

A.1 Sulfuric Acid Specific Gravity at Constant Temperature

### A.2 Specific Gravity of Sulfuric Acid at Elevated Temperatures


<table>
<thead>
<tr>
<th>Mass %H₂SO₄</th>
<th>303 K</th>
<th>313 K</th>
<th>323 K</th>
<th>333 K</th>
<th>353 K</th>
<th>373 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1.8205</td>
<td>1.8107</td>
<td>1.8013</td>
<td>1.7922</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>99</td>
<td>1.8242</td>
<td>1.8145</td>
<td>1.8050</td>
<td>1.7958</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>98</td>
<td>1.8261</td>
<td>1.8163</td>
<td>1.8068</td>
<td>1.7976</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>97</td>
<td>1.8264</td>
<td>1.8166</td>
<td>1.8071</td>
<td>1.7977</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>96</td>
<td>1.8255</td>
<td>1.8157</td>
<td>1.8060</td>
<td>1.7965</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>95</td>
<td>1.8236</td>
<td>1.8137</td>
<td>1.8040</td>
<td>1.7944</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>94</td>
<td>1.8210</td>
<td>1.8109</td>
<td>1.8011</td>
<td>1.7914</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>93</td>
<td>1.8176</td>
<td>1.8074</td>
<td>1.7974</td>
<td>1.7876</td>
<td>1.7681</td>
<td>1.7485</td>
</tr>
<tr>
<td>92</td>
<td>1.8136</td>
<td>1.8033</td>
<td>1.7932</td>
<td>1.7832</td>
<td>1.7633</td>
<td>1.7439</td>
</tr>
<tr>
<td>91</td>
<td>1.8090</td>
<td>1.7986</td>
<td>1.7883</td>
<td>1.7783</td>
<td>1.7581</td>
<td>1.7388</td>
</tr>
<tr>
<td>90</td>
<td>1.8038</td>
<td>1.7933</td>
<td>1.7829</td>
<td>1.7729</td>
<td>1.7525</td>
<td>1.7331</td>
</tr>
<tr>
<td>89</td>
<td>1.7979</td>
<td>1.7874</td>
<td>1.7770</td>
<td>1.7669</td>
<td>1.7464</td>
<td>1.7269</td>
</tr>
<tr>
<td>88</td>
<td>1.7914</td>
<td>1.7809</td>
<td>1.7705</td>
<td>1.7602</td>
<td>1.7397</td>
<td>1.7202</td>
</tr>
<tr>
<td>87</td>
<td>1.7842</td>
<td>1.7736</td>
<td>1.7632</td>
<td>1.7529</td>
<td>1.7324</td>
<td>1.7129</td>
</tr>
<tr>
<td>86</td>
<td>1.7763</td>
<td>1.7657</td>
<td>1.7552</td>
<td>1.7449</td>
<td>1.7245</td>
<td>1.7050</td>
</tr>
<tr>
<td>85</td>
<td>1.7678</td>
<td>1.7571</td>
<td>1.7466</td>
<td>1.7364</td>
<td>1.7161</td>
<td>1.6966</td>
</tr>
<tr>
<td>84</td>
<td>1.7585</td>
<td>1.7479</td>
<td>1.7375</td>
<td>1.7274</td>
<td>1.7072</td>
<td>1.6878</td>
</tr>
<tr>
<td>83</td>
<td>1.7487</td>
<td>1.7382</td>
<td>1.7279</td>
<td>1.7179</td>
<td>1.6979</td>
<td>1.6787</td>
</tr>
</tbody>
</table>
A.3 Sulfuric Acid Freezing Points

Fig. A.2. Sulfuric acid freezing point temperature versus mass % H₂SO₄ in acid. The dashed lines show metastable phases. Source: Gable, C.M., Betz, H.F. and Maron, S.H. (1950) Phase equilibria of the system sulfur trioxide-water, *Journal of the American Chemical Society*, Vol. 72, 1445-1448. www.chemistry.org

Fig. A.3. Sulfuric acid freezing point temperature versus mass % H₂SO₄ in acid (90-100%). Source: Gable, C.M., Betz, H.F. and Maron, S.H. (1950) Phase equilibria of the system sulfur trioxide-water, *Journal of the American Chemical Society*, Vol. 72, 1445-1448. www.chemistry.org

<table>
<thead>
<tr>
<th>H$_2$SO$_4$ (mass%)</th>
<th>Temperature (K)</th>
<th>H$_2$SO$_4$ (mass%)</th>
<th>Temperature (K)</th>
<th>H$_2$SO$_4$ (mass%)</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.81</td>
<td>272.41</td>
<td>54.16</td>
<td>243.11</td>
<td>84.27</td>
<td>281.16</td>
</tr>
<tr>
<td>2.41</td>
<td>271.94</td>
<td>55.37</td>
<td>243.90</td>
<td>84.32</td>
<td>281.57</td>
</tr>
<tr>
<td>5.37</td>
<td>270.73</td>
<td>56.36</td>
<td>244.38</td>
<td>84.37</td>
<td>281.38</td>
</tr>
<tr>
<td>8.42</td>
<td>269.16</td>
<td>57.64</td>
<td>244.64</td>
<td>84.90</td>
<td>281.28</td>
</tr>
<tr>
<td>10.71</td>
<td>267.86</td>
<td>58.09</td>
<td>244.59</td>
<td>85.32</td>
<td>281.10</td>
</tr>
<tr>
<td>13.30</td>
<td>265.99</td>
<td>60.04</td>
<td>243.63</td>
<td>86.69</td>
<td>278.24</td>
</tr>
<tr>
<td>16.95</td>
<td>262.71</td>
<td>60.76</td>
<td>243.14</td>
<td>86.85</td>
<td>278.27</td>
</tr>
<tr>
<td>20.48</td>
<td>258.52</td>
<td>62.78</td>
<td>240.34</td>
<td>87.94</td>
<td>275.40</td>
</tr>
<tr>
<td>23.91</td>
<td>253.05</td>
<td>64.46</td>
<td>236.40</td>
<td>88.63</td>
<td>273.00</td>
</tr>
<tr>
<td>26.23</td>
<td>248.34</td>
<td>64.69</td>
<td>236.44</td>
<td>89.00</td>
<td>271.64</td>
</tr>
<tr>
<td>27.89</td>
<td>244.19</td>
<td>65.68</td>
<td>236.02</td>
<td>89.83</td>
<td>268.36</td>
</tr>
<tr>
<td>29.79</td>
<td>238.66</td>
<td>67.47</td>
<td>234.62</td>
<td>90.63</td>
<td>263.82</td>
</tr>
<tr>
<td>31.83</td>
<td>231.82</td>
<td>68.98</td>
<td>231.78</td>
<td>91.64</td>
<td>257.68</td>
</tr>
<tr>
<td>32.62</td>
<td>228.02</td>
<td>69.70</td>
<td>230.30</td>
<td>92.38</td>
<td>252.28</td>
</tr>
<tr>
<td>33.53</td>
<td>223.56</td>
<td>69.74</td>
<td>230.24</td>
<td>92.57</td>
<td>249.83</td>
</tr>
<tr>
<td>34.46</td>
<td>218.38</td>
<td>71.18</td>
<td>232.55</td>
<td>93.12</td>
<td>244.76</td>
</tr>
<tr>
<td>35.28</td>
<td>213.77</td>
<td>72.32</td>
<td>233.28</td>
<td>93.63</td>
<td>239.16</td>
</tr>
<tr>
<td>35.70</td>
<td>211.09</td>
<td>73.13</td>
<td>233.49</td>
<td>93.77</td>
<td>238.14</td>
</tr>
<tr>
<td>35.77</td>
<td>211.02</td>
<td>73.68</td>
<td>233.13</td>
<td>93.81</td>
<td>238.39</td>
</tr>
<tr>
<td>36.20</td>
<td>211.67</td>
<td>74.33</td>
<td>238.43</td>
<td>94.21</td>
<td>244.06</td>
</tr>
<tr>
<td>37.79</td>
<td>214.33</td>
<td>75.08</td>
<td>244.11</td>
<td>94.77</td>
<td>248.54</td>
</tr>
<tr>
<td>38.73</td>
<td>215.88</td>
<td>75.91</td>
<td>250.19</td>
<td>95.24</td>
<td>253.37</td>
</tr>
<tr>
<td>40.50</td>
<td>217.26</td>
<td>76.59</td>
<td>254.79</td>
<td>96.03</td>
<td>258.09</td>
</tr>
<tr>
<td>42.41</td>
<td>219.27</td>
<td>77.04</td>
<td>257.88</td>
<td>96.46</td>
<td>263.05</td>
</tr>
<tr>
<td>42.64</td>
<td>219.52</td>
<td>77.95</td>
<td>263.18</td>
<td>97.23</td>
<td>267.57</td>
</tr>
<tr>
<td>43.49</td>
<td>222.05</td>
<td>79.33</td>
<td>269.79</td>
<td>97.79</td>
<td>271.02</td>
</tr>
<tr>
<td>44.41</td>
<td>224.53</td>
<td>79.71</td>
<td>271.60</td>
<td>98.40</td>
<td>273.46</td>
</tr>
<tr>
<td>46.19</td>
<td>229.35</td>
<td>80.34</td>
<td>274.24</td>
<td>98.69</td>
<td>275.80</td>
</tr>
<tr>
<td>47.21</td>
<td>231.51</td>
<td>81.40</td>
<td>277.41</td>
<td>99.07</td>
<td>277.97</td>
</tr>
<tr>
<td>47.75</td>
<td>233.14</td>
<td>81.69</td>
<td>277.44</td>
<td>99.85</td>
<td>282.17</td>
</tr>
<tr>
<td>49.47</td>
<td>236.37</td>
<td>82.72</td>
<td>280.13</td>
<td>99.98</td>
<td>283.37</td>
</tr>
<tr>
<td>50.81</td>
<td>238.80</td>
<td>83.61</td>
<td>281.21</td>
<td>100.00</td>
<td>283.35</td>
</tr>
<tr>
<td>53.08</td>
<td>242.03</td>
<td>83.90</td>
<td>281.40</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( \text{H}_2\text{SO}_4 ) (mass%)</th>
<th>Temperature (K)</th>
<th>( \text{H}_2\text{SO}_4 ) (mass%)</th>
<th>Temperature (K)</th>
<th>( \text{H}_2\text{SO}_4 ) (mass%)</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35.77</td>
<td>211.02</td>
<td>64.46</td>
<td>236.40</td>
<td>69.74</td>
<td>230.24</td>
</tr>
<tr>
<td>36.31</td>
<td>207.69</td>
<td>66.27</td>
<td>231.34</td>
<td>70.01</td>
<td>229.50</td>
</tr>
<tr>
<td>36.86</td>
<td>203.78</td>
<td>67.45</td>
<td>226.86</td>
<td>70.89</td>
<td>226.71</td>
</tr>
<tr>
<td>37.12</td>
<td>201.79</td>
<td>67.80</td>
<td>225.54</td>
<td>71.70</td>
<td>223.65</td>
</tr>
<tr>
<td>37.55</td>
<td>199.90</td>
<td>67.91</td>
<td>225.99</td>
<td>72.40</td>
<td>220.15</td>
</tr>
<tr>
<td>38.31</td>
<td>201.61</td>
<td>68.56</td>
<td>221.20</td>
<td>72.42</td>
<td>220.85</td>
</tr>
<tr>
<td>38.58</td>
<td>203.09</td>
<td>68.71</td>
<td>228.82</td>
<td>72.78</td>
<td>223.92</td>
</tr>
<tr>
<td>38.88</td>
<td>204.59</td>
<td>69.74</td>
<td>230.24</td>
<td>73.36</td>
<td>228.85</td>
</tr>
<tr>
<td>40.08</td>
<td>209.73</td>
<td></td>
<td></td>
<td>73.68</td>
<td>233.13</td>
</tr>
<tr>
<td>39.56</td>
<td>207.71</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>41.18</td>
<td>214.41</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>41.69</td>
<td>216.28</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>42.64</td>
<td>219.52</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A.4. Oleum Specific Gravity

![Specific Gravity of oleum versus mass% equivalent H\(_2\)SO\(_4\).](image)

**Fig. A.4.** Specific Gravity of oleum versus mass% equivalent \( \text{H}_2\text{SO}_4 \). Source: *Chemical Plant Control Data, 8th Ed.* 1963, Chemical Construction Corporation, New York, 43-44.
A.5 Electrical Conductivity of Sulfuric Acid

Fig. A.5. Electrical conductivity versus mass% \( \text{H}_2\text{SO}_4 \) in sulfuric acid. Source: Roughton, J.E. (1951) The electrical conductivity of aqueous solutions of sulphuric acid from 25°C to 155°C, *J. Appl. Chem.*, I, Supplementary Issue, No. 2., 141 144.

A.6 Absolute Viscosity of Sulfuric Acid

Fig. A.6. Absolute viscosity of sulfuric acid versus mass% \( \text{H}_2\text{SO}_4 \) in sulfuric acid. For viscosity in kg m\(^{-1}\) s\(^{-1}\), multiply cP by 0.001. Source: Bright, N.F., Hutchinson, H. and Smith, D., (1946) The viscosity and density of sulfuric acid and oleum, *J. Soc. Chem. Ind.* 65, 385 388.
Appendix B

Derivation of Equilibrium Equation (10.12)

This appendix examines catalytic oxidation of SO$_2$ in SO$_2$, O$_2$, N$_2$ feed gas by the reaction:

$$\text{SO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{SO}_3(\text{g}) \quad (1.1).$$

It derives equilibrium Eqn. (10.12):

$$K_E = \left( \frac{\Phi^E}{100 - \Phi^E} \right) \cdot \left( \frac{100 - \frac{1}{2}e \cdot \Phi^E}{100 - f \cdot \frac{1}{2}e \cdot \Phi^E} \right)^{\frac{1}{2}} \cdot P_t^{-\frac{1}{2}} \quad (10.12)$$

from Reaction (1.1)'s equilibrium equation:

$$K_E = \frac{p_{SO_3}^E}{p_{SO_2}^E \cdot (p_{O_2}^E)^{\frac{1}{2}}} \quad (10.3)$$

where:

$K_E = \text{equilibrium constant, dependent only on temperature, bar}^{-\frac{1}{2}}$

$p_{SO_2}^E$, $p_{O_2}^E$, $p_{SO_3}^E = \text{equilibrium partial pressures of SO}_2$, O$_2$ and SO$_3$, bar

$\Phi^E = \text{equilibrium \% SO}_2 \text{ oxidized, Section 10.1.1}$

$e = \text{volume\% SO}_2 \text{ in Fig. 10.1 feed gas}$

$f = \text{volume\% O}_2 \text{ in Fig. 10.1 feed gas}$

$\{ \text{remainder N}_2 \}$

$P_t = \text{total equilibrium gas pressure, bar.}$

*CO$_2$ and Ar behave like N$_2$, Appendix F. The effects of SO$_3$-in-feed-gas are examined in Appendix P.
B.1 Modified Equilibrium Equation

\( P_{SO_2}^E, P_{O_2}^E \) and \( P_{SO_3}^E \) in Eqn. (10.3) are related to gas composition by the equations:

\[
\begin{align*}
    P_{SO_2}^E &= X_{SO_2}^E \cdot P_t \\ 
    P_{O_2}^E &= X_{O_2}^E \cdot P_t \\ 
    P_{SO_3}^E &= X_{SO_3}^E \cdot P_t
\end{align*}
\]

(B.1)

(B.2)

(B.3)

where \( X^E \) is equilibrium mole fraction of each gas and \( P_t \) is total equilibrium gas pressure. These three equations assume ideal gas behavior (based on the low pressure, ~1 bar, of industrial SO\(_2\) oxidation).

Eqns. (10.3) and (B.1) to (B.3) combine to give:

\[
K_E = \frac{X_{SO_3}^E}{X_{SO_2}^E \cdot \left( X_{O_2}^E \right)^{\frac{1}{2}}} \cdot P_t^{-\frac{1}{2}}
\]

(B.4)

B.2 Mole Fractions Defined

Mole fraction of SO\(_3\) in SO\(_3\), SO\(_2\), O\(_2\), N\(_2\) gas is defined as:

\[
X_{SO_3} = \frac{n_{SO_3}}{n_t} = \frac{n_{SO_3}}{n_{SO_3} + n_{SO_2} + n_{O_2} + n_{N_2}}
\]

(B.5)

where \( n_t \) is total kg-mole of gas and \( n_{SO_3}, n_{SO_2}, n_{O_2} \) and \( n_{N_2} \) are kg-mole of SO\(_3\), SO\(_2\), O\(_2\) and N\(_2\) in the gas.

Likewise:

\[
\begin{align*}
    X_{SO_2} &= \frac{n_{SO_2}}{n_t} = \frac{n_{SO_2}}{n_{SO_3} + n_{SO_2} + n_{O_2} + n_{N_2}} \\ 
    X_{O_2} &= \frac{n_{O_2}}{n_t} = \frac{n_{O_2}}{n_{SO_3} + n_{SO_2} + n_{O_2} + n_{N_2}}
\end{align*}
\]

(B.6)

(B.7)

The next six sub-sections use these equations to derive Eqn. (10.12) from Eqn. (B.4). Sulfur, oxygen and nitrogen balances are used.
B.3 Feed and Oxidized Gas Molar Quantities

The derivation is begun by:

(a) specifying that the Fig. 10.1 feed gas contains:
    \[ e \text{ volume}\% \text{ SO}_2 \]
    \[ f \text{ volume}\% \text{ O}_2 \]
    \[ 100 - e - f \text{ volume}\% \text{ N}_2 \]

(b) assuming 1 kg-mole of Fig. 10.1 feed gas.

B.3.1 Feed gas molar quantities

The molar quantity of SO\(_2\) in 1 kg-mole of Fig. 10.1 feed gas is given by the equation:

\[
\text{kg-mole of SO}_2 \text{ in 1 kg-mole of Fig. 10.1 feed gas} = \frac{\text{mole}\% \text{ SO}_2 \text{ in feed gas}}{100\%} \times 1 \text{ kg-mole of feed gas}.
\]

Also, because mole\% = volume\% (Appendix E):

\[
\text{kg-mole of SO}_2 \text{ in 1 kg-mole of Fig. 10.1 feed gas} = \frac{\text{volume}\% \text{ SO}_2 \text{ in feed gas}}{100\%} \times 1 \text{ kg-mole of feed gas} = \frac{e}{100} \times 1 = \frac{e}{100} = \frac{e}{100} \quad (\text{B.8}).
\]

Likewise:

\[
\text{kg-mole of O}_2 \text{ in 1 kg-mole of Fig. 10.1 feed gas} = \frac{f}{100} \quad (\text{B.9})
\]

\[
\text{kg-mole of N}_2 \text{ in 1 kg-mole of Fig. 10.1 feed gas} = \frac{100 - e - f}{100} = 1 - \frac{e}{100} - \frac{f}{100} \quad (\text{B.10}).
\]

B.3.2 Oxidized gas molar quantities

Oxidized gas in the Fig. 10.1 catalyst bed contains:
\[ n_{SO_3} \quad \text{kg-mole SO}_3 \]
\[ n_{SO_2} \quad \text{kg-mole SO}_2 \]
\[ n_{O_2} \quad \text{kg-mole O}_2 \]
\[ n_{N_2} \quad \text{kg-mole N}_2 \]

per kg-mole of Fig. 10.1 feed gas. \( n_{SO_3}, n_{SO_2} \) and \( n_{O_2} \) vary down the catalyst bed as
\[ SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_3(g) \] oxidation proceeds.

**B.3.3 Molar balances**

S, O and N molar balances are now used to relate Fig. 10.1's feed gas composition to oxidized gas molar quantities. The balances are all based on 1 kg-mole of feed gas.

**S balance**

The sulfur balance is:

\[ \text{kg-mole } S \text{ in feed gas} = \text{kg-mole } S \text{ in oxidized gas} \]  
(B.11).

1 mole of \( SO_3 \) and \( SO_2 \) each contain 1 mole of S, so Eqns. (B.11) and (B.8) may be combined to give:

\[ 1 \times \frac{e}{100} = 1 \times n_{SO_3} + 1 \times n_{SO_2} \]  
(B.12)

or:

\[ \frac{e}{100} = n_{SO_3} + n_{SO_2} \]  
(B.13)

or:

\[ n_{SO_2} = \frac{e}{100} - n_{SO_3} \]  
(B.14)

where:

\[ \frac{e}{100} = \text{kg-mole of feed SO}_2 \text{ in Fig. 10.1 feed gas} \]

\( n_{SO_3} \) and \( n_{SO_2} \) = kg-mole of \( SO_3 \) and \( SO_2 \) in oxidized gas

(all per kg-mole of Fig. 10.1 feed gas).
\textit{O balance}

The oxygen balance is:

\[
\frac{\text{kg-mole O in feed gas}}{\text{kg-mole O in oxidized gas}} = \frac{\text{kg-mole O in feed gas}}{\text{kg-mole O in oxidized gas}} \quad (\text{B.15}).
\]

1 mole of \( \text{SO}_3 \) contains 3 moles of O while 1 mole of \( \text{SO}_2 \) and \( \text{O}_2 \) each contain 2 moles of O - so Eqns. (B.15), (B.8) and (B.9) become:

\[
2 \frac{e}{100} + 2 \frac{f}{100} = 3n_{\text{SO}_3} + 2n_{\text{SO}_2} + 2n_{\text{O}_2} \quad (\text{B.16})
\]

where \( \frac{f}{100} = \text{kg-mole of feed O}_2 \text{ per kg-mole of Fig. 10.1 feed gas.} \)

Dividing both sides of Eqn. (B.16) by 2 gives:

\[
\frac{e}{100} + \frac{f}{100} = \frac{3}{2}n_{\text{SO}_3} + n_{\text{SO}_2} + n_{\text{O}_2} \quad (\text{B.17})
\]

or:

\[
n_{\text{O}_2} = \frac{e}{100} + \frac{f}{100} - \frac{3}{2}n_{\text{SO}_3} - n_{\text{SO}_2} \quad (\text{B.18}).
\]

Further, because \( n_{\text{SO}_2} = \frac{e}{100} - n_{\text{SO}_3} \) \quad (Eqn. B.14)

\[
n_{\text{O}_2} = \frac{e}{100} + \frac{f}{100} - \frac{3}{2}n_{\text{SO}_3} - \left( \frac{e}{100} - n_{\text{SO}_3} \right) \quad (\text{B.19})
\]

\[
= \frac{f}{100} - \frac{1}{2}n_{\text{SO}_3} \quad (\text{B.20})
\]

where \( n_{\text{SO}_3} = \text{kg-mole SO}_3 \text{ in oxidized catalyst bed gas.} \)
**N balance**

The nitrogen balance is:

\[
\frac{\text{kg-mole N in feed gas}}{\text{kg-mole N in oxidized gas}} = \text{N balance} \tag{B.21}.
\]

Of course, nitrogen doesn’t react during SO₂ oxidation so that it enters and leaves the catalyst as N₂ (only). Each mole of N₂ contains 2 moles of N so that Eqns. (B.21) and (B.10) become:

\[
2 \left(1 - \frac{e}{100} - \frac{f}{100}\right) = 2n_{N₂} \tag{B.22}
\]

or:

\[
n_{N₂} = 1 - \frac{e}{100} - \frac{f}{100} \tag{B.23}
\]

where: \(1 - \frac{e}{100} - \frac{f}{100}\) = kg-mole of feed N₂ per kg-mole of Fig. 10.1 feed gas.

**Total kg-moles of oxidized gas**

Total kg-mole of Fig. 10.1 oxidized gas (per kg-mole of Fig. 10.1 feed gas) is:

\[
n_T = n_{SO₃} + n_{SO₂} + n_{O₂} + n_{N₂} \tag{B.24}.
\]

Combining this with Eqns. (B.14), (B.20) and (B.23) gives:

\[
n_T = n_{SO₃} + \left(\frac{e}{100} - n_{SO₃}\right) + \left(\frac{f}{100} - \frac{1}{2} n_{SO₃}\right) + \left(1 - \frac{e}{100} - \frac{f}{100}\right)
\]

\[
= 1 - \frac{1}{2} n_{SO₃} \tag{B.26}.
\]

Note that the \(\frac{1}{2} n_{SO₃}\) term represents kg-mole of O₂ consumed in oxidizing \(n_{SO₃}\) kg-mole of SO₂ to SO₃.

**B.4 Mole fractions in oxidized gas**

The mole fractions of SO₃, SO₂ and O₂ in Fig. 10.1’s oxidized gas are:
\[ X_{SO_3} = \frac{n_{SO_3}}{n_t} = \frac{n_{SO_3}}{1 - \frac{1}{2} \cdot n_{SO_3}} \quad \text{from Eqn. (B.26)} \tag{B.27} \]

\[ X_{SO_2} = \frac{n_{SO_2}}{n_t} = \frac{\frac{e}{100} - n_{SO_3}}{1 - \frac{1}{2} \cdot n_{SO_3}} \quad \text{from Eqn. (B.14) and (B.26)} \tag{B.28} \]

\[ X_{O_2} = \frac{n_{O_2}}{n_t} = \frac{f - \frac{1}{2} \cdot n_{SO_3}}{1 - \frac{1}{2} \cdot n_{SO_3}} \quad \text{from Eqn. (B.20) and (B.26)} \tag{B.29}. \]

**B.5 Equation Applicability**

Eqns. (B.5) to (B.29) apply everywhere in the Fig. 10.1 catalyst bed. Of course:

(a) \( n_{SO_3} \) increases as feed gas descends the catalyst bed and oxidation proceeds

(b) \( n_{SO_2} \) and \( n_{O_2} \) decrease as feed gas descends the catalyst bed and oxidation proceeds

(c) \( n_{N_2} \) doesn't change in the catalyst bed because \( N_2 \) doesn't take part in \( SO_2 \) oxidation.

**B.6 Equilibrium Equation**

Fig. 10.1 describes a catalyst bed in which \( SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_3(g) \) oxidation comes to equilibrium near the bottom of the bed. Eqn. (B.4) describes this equilibrium in terms of \( SO_3, SO_2 \) and \( O_2 \) mole fractions, \( X_{SO_3}^E, X_{SO_2}^E \) and \( X_{O_2}^E \).

This section shows how the equilibrium values of \( n_{SO_1}, n_{SO_2} \) and \( n_{O_2} \), i.e.:

\[
\begin{align*}
    n_{SO_3}^E \\
    n_{SO_2}^E \\
    n_{O_2}^E
\end{align*}
\]

are represented in equilibrium Eqn. (B.4) (where \( E = \text{equilibrium} \)).
B.6.1 Equilibrium mole fractions

At equilibrium, oxidized gas $\text{SO}_3$, $\text{SO}_2$ and $\text{O}_2$ mole fractions are:

(from Eqn. B.27)

$$X_{\text{SO}_3} = \frac{n_{\text{SO}_3}^E}{n_t^E} = \frac{n_{\text{SO}_3}^E}{\left(1 - \frac{1}{2}n_{\text{SO}_3}^E\right)} \quad \text{(B.30)}$$

(from Eqn. B.28)

$$X_{\text{SO}_2} = \frac{n_{\text{SO}_2}^E}{n_t^E} = \frac{\left(\frac{e}{100} - n_{\text{SO}_3}^E\right)}{\left(1 - \frac{1}{2}n_{\text{SO}_3}^E\right)} \quad \text{(B.31)}$$

(from Eqn. B.29)

$$X_{\text{O}_2} = \frac{n_{\text{O}_2}^E}{n_t^E} = \frac{\left(\frac{f}{100} - \frac{1}{2}n_{\text{SO}_3}^E\right)}{\left(1 - \frac{1}{2}n_{\text{SO}_3}^E\right)} \quad \text{(B.32)}.$$

These equilibrium equations are now combined with Eqn. (B.4) to relate $n_{\text{SO}_3}^E$ to equilibrium constant $K_E$.

B.7 Equilibrium Constant and Molar Quantities

With the Eqn. (B.30)-(B.32) expressions for mole fractions, equilibrium Eqn. (B.4):

$$K_E = \frac{X_{\text{SO}_3}^E \cdot \left[p_{\text{O}_2}^E\right]^{\frac{1}{2}}}{X_{\text{SO}_2}^E} \cdot \left(X_{\text{O}_2}^E\right)^{\frac{1}{2}}$$

becomes:

$$K_E = \frac{\frac{n_{\text{SO}_3}^E}{\left(1 - \frac{1}{2}n_{\text{SO}_3}^E\right)} \cdot \left(\frac{\frac{e}{100} - n_{\text{SO}_3}^E}{\left(1 - \frac{1}{2}n_{\text{SO}_3}^E\right)}\right)^{\frac{1}{2}} \cdot \left(\frac{\frac{f}{100} - \frac{1}{2}n_{\text{SO}_3}^E}{\left(1 - \frac{1}{2}n_{\text{SO}_3}^E\right)}\right)^{\frac{1}{2}}}{\left[p_{\text{O}_2}^E\right]^{\frac{1}{2}} \cdot \left[p_{\text{SO}_3}^E\right]^{\frac{1}{2}}} \quad \text{(B.33)}$$
or, multiplying top and bottom by \(1 - \frac{1}{2} n^e_{SO_3}\)

\[
K_E = \frac{n^E_{SO_3}}{\left(1 - \frac{1}{2} n^e_{SO_3}\right)^{\frac{1}{2}}} \cdot p_t^{\frac{1}{2}}
\]  
(B.34)

\[
K_E = \frac{n^E_{SO_3}}{\left(1 - \frac{1}{2} n^e_{SO_3}\right)^{\frac{1}{2}}} \cdot \left(\frac{e}{100} - n^E_{SO_3}\right) \cdot \left(\frac{f}{100} - \frac{1}{2} n^e_{SO_3}\right)^{\frac{1}{2}}
\]

or:

\[
K_E = \frac{n^E_{SO_3}}{\left(1 - \frac{1}{2} n^e_{SO_3}\right)^{\frac{1}{2}}} \cdot \left(\frac{e}{100} - n^E_{SO_3}\right) \cdot \left(\frac{f}{100} - \frac{1}{2} n^e_{SO_3}\right)^{\frac{1}{2}}
\]

(B.35)

where \(n^E_{SO_3}\) is kg-moles of \(SO_3\) in the Fig. 10.1 equilibrium gas, per kg-mole of feed gas.

This equation is used to calculate \(n^E_{SO_3}\) for any given equilibrium constant. \(n^E_{SO_2}\) and \(n^E_{O_2}\) are then calculated with Eqns. (B.14) and (B.20).

Eqn. (B.35) is written in terms of \(n^E_{SO_3}\) (kg-moles \(SO_3\) in equilibrium gas) rather than equilibrium \(\% SO_2\) oxidized (\(\Phi^+\)) in Eqn. (10.12). The next section shows how Eqn. (10.12) is derived from Eqn. (B.35).
B.8 Equilibrium $n_{SO_2}^E$ and $\Phi^E$

Eqn. (10.2) defines equilibrium \% $SO_2$ oxidized ($\Phi^E$) as:

\[
\text{Equilibrium } \% \text{ $SO_2$ oxidized} = \Phi^E = \frac{\text{kg-mole } SO_2 \text{ in oxidized gas}}{\text{kg-mole } SO_2 \text{ in feed gas}} \times 100
\]

or:

\[
\Phi^E = \frac{\left( \frac{e}{100} - n_{SO_2}^E \right)}{\frac{e}{100}} \times 100
\]  \hspace{1cm} (B.36)

where:

\[ e = \text{volume\% } SO_2 \text{ in Fig. 10.1 feed gas} \]

\[ n_{SO_2}^E = \text{kg-mole } SO_2 \text{ in equilibrium gas per kg-mole of feed gas.} \]

Eqn. (B.36) is expressed in terms of $n_{SO_3}^E$ by combining it with the equilibrium form of Eqn. (B.14), i.e.:

\[
\frac{n_{SO_2}^E}{n_{SO_3}^E} = \frac{e}{100} - n_{SO_3}^E
\]  \hspace{1cm} (B.14')

to give:

\[
\Phi^E = \frac{\left( \frac{e}{100} - \left( \frac{e}{100} - n_{SO_3}^E \right) \right)}{\frac{e}{100}} \times 100
\]

or:

\[
\Phi^E = \frac{n_{SO_3}^E}{\left( \frac{e}{100} \right)} \times 100
\]  \hspace{1cm} (B.37)

or:

\[
\frac{n_{SO_3}^E}{\Phi^E} = \left( \frac{e}{100} \right)
\]

where:

\[ n_{SO_3}^E = \text{kg-mole } SO_3 \text{ in equilibrium gas per kg-mole of Fig. 10.1 feed gas} \]

\[ \Phi^E = \text{equilibrium } \% \text{ $SO_2$ oxidized, Section 10.1.1} \]

\[ e = \text{volume\% } SO_2 \text{ in Fig. 10.1 feed gas.} \]
B.8.1 Substituting $\Phi^E$ for $n_{SO_3}^E$

Substituting $\left(\frac{e}{100}\right) \cdot \frac{\Phi^E}{100}$ for $n_{SO_3}^E$ in Eqn. (B.35) gives:

$$K_E = \left(\frac{e}{100} \cdot \frac{\Phi^E}{100}\right) \cdot \left(1 - \frac{1}{2} \cdot \frac{e}{100} \cdot \frac{\Phi^E}{100}\right)^{\frac{1}{2}} \cdot \frac{1}{p_t^{\frac{1}{2}}}$$

(B.39)

or:

$$K_E = \left(\frac{e}{100} \cdot \frac{\Phi^E}{100}\right) \cdot \left(1 - \frac{1}{2} \cdot \frac{e}{100} \cdot \frac{\Phi^E}{100}\right)^{\frac{1}{2}} \cdot \frac{1}{p_t^{\frac{1}{2}}}$$

(B.40)

or, dividing top and bottom by $\frac{e}{100}$:

$$K_E = \left(\frac{\Phi^E}{100} \cdot \frac{1}{1 - \frac{\Phi^E}{100}}\right) \cdot \left(1 - \frac{1}{2} \cdot \frac{e}{100} \cdot \frac{\Phi^E}{100}\right)^{\frac{1}{2}} \cdot \frac{1}{p_t^{\frac{1}{2}}}$$

(B.41)

or, multiplying top and bottom by 100:

$$K_E = \left(\frac{\Phi^E}{100 - \Phi^E}\right) \cdot \left(1 - \frac{1}{2} \cdot \frac{e}{100} \cdot \frac{\Phi^E}{100}\right)^{\frac{1}{2}} \cdot \frac{1}{p_t^{\frac{1}{2}}}$$

(B.42)

or, multiplying top and bottom by $100^\frac{1}{2}$

$$K_E = \left(\frac{\Phi^E}{100 - \Phi^E}\right) \cdot \left(100 - \frac{1}{2} \cdot \frac{e}{100} \cdot \frac{\Phi^E}{100}\right)^{\frac{1}{2}} \cdot \frac{1}{p_t^{\frac{1}{2}}}$$

(10.12).

Applications of this equation are described in Sections 10.4 and 10.5.
Appendix C

Free Energy Equations for Equilibrium Curve Calculations

Industrial catalytic \( \text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{SO}_3(g) \) oxidation approaches equilibrium at 700 to 900 K. This book's equilibrium calculations require standard free energies over this temperature range. This appendix:

(a) provides the required standard free energies from published data

(b) develops a linear equation which represents standard free energy of reaction as a function of temperature.

The free energy data are from:


Chase provides standard free energies of formation for the reactions:

\[
S + \frac{3}{2} \text{O}_2(g) \rightarrow \text{SO}_3(g) \quad \Delta_r G_{\text{SO}_3}^o \quad (C.1)
\]

\[
S + \text{O}_2(g) \rightarrow \text{SO}_2(g) \quad \Delta_r G_{\text{SO}_2}^o \quad (C.2).
\]

\[
\Delta G_{\text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{SO}_3(g)}^o
\]

is determined by subtracting Eqn. (C.2) from Eqn. (C.1), which gives:

\[
\frac{1}{2} \text{O}_2(g) \rightarrow \text{SO}_3(g) - \text{SO}_2(g)
\]

or:

\[
\text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{SO}_3(g)
\]

for which:

\[
\Delta G_{\text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{SO}_3(g)}^o = \Delta_r G_{\text{SO}_3}^o - \Delta_r G_{\text{SO}_2}^o \quad (C.3).
\]
Chase's 700 to 900 K $\Delta_r G^\circ$ values (MJ per kg-mole) for Eqns. (C.1) to (C.3) are:

<table>
<thead>
<tr>
<th>Temperature T, K</th>
<th>$\Delta_r G^\circ_{SO_3}$</th>
<th>$\Delta_r G^\circ_{SO_2}$</th>
<th>$\Delta G^\circ_{SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_3(g)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>-332.365</td>
<td>-299.444</td>
<td>-32.921</td>
</tr>
<tr>
<td>800</td>
<td>-321.912</td>
<td>-298.370</td>
<td>-23.542</td>
</tr>
<tr>
<td>900</td>
<td>-310.258</td>
<td>-296.051</td>
<td>-14.207</td>
</tr>
</tbody>
</table>

Application of Excel's 'Slope' and 'Intercept' functions to the left and right columns gives the linear equation:

$$
\Delta G^\circ_{SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_3(g)} = 0.09357^\circ T - 98.41 \text{ MJ per kg-mole of SO}_3 \quad (C.4).
$$

This equation is used for all of this book's equilibrium calculations.
Appendix D

Preparation of Fig. 10.2 Equilibrium Curve

This appendix uses Eqn. (10.13) to calculate points on the Fig. 10.2 equilibrium curve. The equation is:

\[
T_E = \frac{A + R \ln \left( \frac{\Phi^E}{100 - \Phi^E} \right) - B}{\frac{100 - \frac{1}{2} e \cdot \Phi^E}{100 - \frac{1}{2} e \cdot \Phi^E}} \left( \frac{100 - \frac{1}{2} e \cdot \Phi^E}{100 - \frac{1}{2} e \cdot \Phi^E} \right)^{\frac{1}{2}} P_t\]

(10.13)

where:

- \(T_E\) = equilibrium temperature, K
- \(A\) and \(B\) = empirical constants relating \(\Delta G^o_T\) for the reaction \(\text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{SO}_3(g)\) to temperature, i.e.: \(\Delta G^o_T = A \cdot T + B\)
- \(A = 0.09357\) MJ kg-mole SO\(_2\)\(^{-1}\) K\(^{-1}\) (Appendix C)
- \(B = -98.41\) MJ/kg-mole SO\(_2\)
- \(R\) = gas constant = 0.008314 MJ kg-mole SO\(_2\)\(^{-1}\) K\(^{-1}\)
- \(\Phi^E\) = equilibrium % \(\text{SO}_2\) oxidized
- \(e = \text{volume}\%\ \text{SO}_2\) in Fig. 10.1 feed gas \(\text{remainder inert}\)
- \(f = \text{volume}\%\ \text{O}_2\) in Fig. 10.1 feed gas
- \(P_t\) = equilibrium total pressure, bar.

The calculations are done in Excel worksheet Table D.1. The calculation sequence is:

(a) \(e, f\) and \(P_t\) are entered into cells B2, D2 and D4
(b) a value of \(\Phi^E\) is entered into cell D6, say 60\% \(\text{SO}_2\) oxidized
(c) Equation (10.13) is placed in cell A9, exactly as shown beside it
(d) the equivalent value of \(T_E\) is automatically calculated in cell A9.

(b) and (d) are repeated as desired. Cells A14 to B26 show example results.
Table D.1. Excel spreadsheet for calculating Fig. 10.2 equilibrium points from Eqn. (10.13). The calculation method is described on the previous page. Equilibrium % $SO_2$ oxidized is seen to increase with decreasing equilibrium temperature.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Specified feed gas composition</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>e, volume% $SO_2$ =</td>
<td>10</td>
<td>f, volume% $O_2$ =</td>
<td>11</td>
<td>remainder = inert</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>P, specified equilibrium pressure, bar =</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>$\phi^e$, equilibrium % $SO_2$ oxidized =</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>$T_E$, equilibrium temperature (K) equivalent to Cell D6's equilibrium % $SO_2$ oxidized =</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>923.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Example results for Fig. 10.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Equilibrium % $SO_2$ oxidized</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>30</td>
<td>1030.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>40</td>
<td>990.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>50</td>
<td>955.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>60</td>
<td>923.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>70</td>
<td>890.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>80</td>
<td>854.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>90</td>
<td>805.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>95</td>
<td>765.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>97.5</td>
<td>730.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>99</td>
<td>690.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>99.5</td>
<td>663.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>99.9</td>
<td>608.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>99.95</td>
<td>587.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

D.1 Integer Temperature Calculations

Table 12.1 is most easily interpolated when the equilibrium curve points have integer temperature values. These points are determined with Table D.1 by means of Excel's Goal Seek tool, next page.
Equilibrium % $SO_2$ oxidized at 895 K is determined, for example, by the sequence:

**Tools**  
**Goal Seek**  
Set cell: A9  
To value: 895  
Changing cell: D6  
OK  
OK.

The result is equilibrium % $SO_2$ oxidized = 68.75 % (cell D6) at 895 K (cell A9).

A table of equilibrium points may be prepared by repeating these steps at different temperatures, i.e.:

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>Results for Table 12.1 and Fig. 12.1</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Equilibrium</td>
<td>Equilibrium</td>
</tr>
<tr>
<td></td>
<td>temperature, K</td>
<td>% $SO_2$ oxidized</td>
</tr>
<tr>
<td>14</td>
<td>890</td>
<td>70.23</td>
</tr>
<tr>
<td>15</td>
<td>891</td>
<td>69.94</td>
</tr>
<tr>
<td>16</td>
<td>892</td>
<td>69.64</td>
</tr>
<tr>
<td>17</td>
<td>893</td>
<td>69.34</td>
</tr>
</tbody>
</table>

**D.2 2nd and 3rd Catalyst Bed Equilibrium Curves**

This appendix's techniques are also used to calculate 2nd and 3rd catalyst bed equilibrium curves, Table 15.1. The calculations require specification of:

   (a) the equivalent 1st catalyst feed gas composition, e and f in Eqn. (10.13)

and:

   (b) the 2nd or 3rd catalyst bed gas pressure, P, in Eqn. (10.13).

The applicability of Eqn. (10.13) to 2nd and 3rd catalyst beds is discussed in Section 15.1.
Appendix E

Proof that Volume% = Mole% (for Ideal Gases)

E.1 Definitions

Consider a gas which contains ideal gas A and ideal gas B. Volume% A and volume% B in the gas are defined as:

\[
\text{volume}\% \ A = \left( \frac{V_A}{V_A + V_B} \right) \times 100\% \quad (E.1)
\]

\[
\text{volume}\% \ B = \left( \frac{V_B}{V_A + V_B} \right) \times 100\% \quad (E.2)
\]

where \(V_A\) and \(V_B\) are the partial volumes of A and B in the gas, Section E.2. Likewise, mole% A and mole% B are defined for all gases as:

\[
\text{mole}\% \ A = \left( \frac{n_A}{n_A + n_B} \right) \times 100\% \quad (E.3)
\]

\[
\text{mole}\% \ B = \left( \frac{n_B}{n_A + n_B} \right) \times 100\% \quad (E.4)
\]

where \(n_A\) and \(n_B\) are moles of A and B in the gas.

E.2 Characterization of Partial Volumes

Consider \(n_A\) moles of ideal gas A in a freely expanding/contracting box at constant temperature \(T^\circ\) and constant pressure \(P^\circ\). The volume occupied by A is described by the ideal gas law:

\[
V_A = \frac{n_A \cdot R \cdot T^\circ}{P^\circ} \quad (E.5).
\]

Consider also \(n_B\) moles of ideal gas B in a freely expanding/contracting box at constant temperature \(T^\circ\) and constant pressure \(P^\circ\). The volume occupied by B is:

\[
V_B = \frac{n_B \cdot R \cdot T^\circ}{P^\circ} \quad (E.6).
\]
Remove a wall between the two boxes and join them. Allow the gases to mix. For ideal gases, there is no change in gas volume when the gases mix so that:

\[ V_t = V_A + V_B \]  \hspace{1cm} (E.7).

where:
- \( V_t \) = total volume of gas
- \( V_A \) = partial volume of ideal gas A
- \( V_B \) = partial volume of ideal gas B.

Eqns. (E.5) - (E.7) combine to give:

\[ V_t = V_A + V_B = \frac{(n_A + n_B)\cdot R \cdot T^o}{P} \]  \hspace{1cm} (E.8).

**E.3 Equality of Volume% and Mole%**

Volume% A and mole% A are obtained by dividing Eqn. (E.5) by Eqn. (E.8):

to give:

\[ \frac{V_A}{V_A + V_B} = \frac{n_A}{n_A + n_B} \]  \hspace{1cm} (E.9).

Both sides of Eqn. (E.9) are then multiplied by 100 to give:

\[ \left( \frac{V_A}{V_A + V_B} \right) \cdot 100 = \left( \frac{n_A}{n_A + n_B} \right) \cdot 100 \]  \hspace{1cm} (E.10).

The left side of Eqn. (E.10) is volume% A (Eqn. (E.1)) while the right side is mole% A (Eqn. (E.3)) so that the equation becomes:

\[ \text{volume}\% \text{ A} = \text{mole}\% \text{ A} \]  \hspace{1cm} (E.11)

proving that, for ideal gases, volume% = mole%.

Proof that:

\[ \text{volume}\% \text{ B} = \text{mole}\% \text{ B} \]  \hspace{1cm} (E.12)

is obtained by dividing Eqn. (E.6) by Eqn. (E.8) and so on.
Appendix F

Effect of CO₂ and Ar on Equilibrium Equations (None)

CO₂ is usually present in spent acid decomposition and metallurgical furnace offgases. Most of it passes through gas cooling/cleaning/dehydration and into the Fig. 10.1 catalyst bed. It doesn't take part in catalyst bed oxidation.

This appendix shows that CO₂ has no affect on equilibrium % $SO₂$ oxidized equations, e.g. Eqn. (10.12).

A small amount of Ar is also present in catalytic SO₂ oxidation feed gases. Like CO₂, it has no effect on equilibrium % $SO₂$ oxidized equations.

F.1 CO₂

Proof that CO₂ has no effect on Eqn. (10.12) begins by specifying that Fig. 10.1's feed gas contains:

\[
e \text{ volume\% SO}_2
\]
\[
f \text{ " " O}_2
\]
\[
c \text{ " " CO}_2
\]
\[
1 - e - f - c \text{ " " N}_2
\]

Per kg-mole of Fig. 10.1 feed gas, the molar quantities entering the Fig. 10.1 catalyst bed are:

\[
\frac{e}{100} \quad \text{kg-mole SO}_2 \text{ (Section B.3.1)}
\]
\[
\frac{f}{100} \text{ " " O}_2
\]
\[
\frac{c}{100} \text{ " " CO}_2
\]
\[
\frac{1 - e - f - c}{100} \text{ " " N}_2
\]

Molar balances

Feed gas CO₂ doesn't change the Appendix B's sulfur molar balance. It remains as:

\[
n_{SO_2} = \frac{e}{100} - n_{SO_3} \quad \text{(B.14) unchanged.}
\]
CO₂ does, however, introduce a carbon molar balance into Appendix B’s derivation. It is:

\[
\frac{\text{kg-mole C in feed gas}}{\text{kg-mole C in exit gas}} = 1 \quad \text{(F.1)}.
\]

Each mole of CO₂ contains 1 mole of C so Eqn. (F.1) becomes:

\[
1 \times \frac{c}{100} = 1 \times n_{\text{CO}_2}
\]

or:

\[
n_{\text{CO}_2} = \frac{c}{100} \quad \text{(F.2)}
\]

where \( n_{\text{CO}_2} \) is kg-mole CO₂ in Fig. 10.1 exit gas.

CO₂ changes oxygen molar balance Eqn. (B.16). It becomes:

\[
2 \times \frac{e}{100} + 2 \times \frac{f}{100} + 2 \times \frac{c}{100} = 3 \times n_{\text{SO}_3} + 2 \times n_{\text{SO}_2} + 2 \times n_{\text{O}_2} + 2 \times n_{\text{CO}_2}
\]

or:

\[
n_{\text{O}_2} = \frac{e}{100} + \frac{f}{100} + \frac{c}{100} - \frac{3}{2} n_{\text{SO}_3} - n_{\text{SO}_2} - n_{\text{CO}_2}
\]

Combining this equation with Eqns. (B14) and (F2), i.e. with:

\[
n_{\text{SO}_2} = \frac{e}{100} - n_{\text{SO}_3} \quad \text{(B.14)}
\]

and:

\[
n_{\text{CO}_2} = \frac{c}{100} \quad \text{(F.2)}
\]

gives:

\[
n_{\text{O}_2} = \frac{e}{100} + \frac{f}{100} + \frac{c}{100} - \frac{3}{2} n_{\text{SO}_3} - \left( \frac{e}{100} - n_{\text{SO}_3} \right) - \frac{c}{100}
\]

or:

\[
= \frac{f}{100} - \frac{1}{2} n_{\text{SO}_3} \quad \text{(B.20) unchanged.}
\]

N balance Eqn. (B.22) is slightly changed by CO₂ to:
\[2 \cdot \left(1 - \frac{c}{100} - \frac{f}{100} - \frac{c}{100}\right) = 2 \cdot n_{N_2}\]

or:

\[n_{N_2} = 1 - \frac{e}{100} - \frac{f}{100} - \frac{c}{100}\]  \hspace{1cm} (F.3)

**Total kg-mole of exit gas**

Including CO\(_2\), the total kg-mole of Fig. 10.1 exit gas is given by:

\[n_1 = n_{SO_3} + n_{SO_2} + n_{O_2} + n_{N_2} + n_{CO_2}\]  \hspace{1cm} (F.4)

Combining this equation with Eqns. (B.14), (B.20), (F.2) and (F.3) gives:

\[n_1 = n_{SO_3} + \left(\frac{e}{100} - n_{SO_3}\right) + \left(\frac{f}{100} - \frac{1}{2} \cdot n_{SO_3}\right) + \left(1 - \frac{e}{100} - \frac{f}{100} - \frac{c}{100}\right) + \frac{c}{100}\]

\[= 1 - \frac{1}{2} \cdot n_{SO_3}\]  \hspace{1cm} (B.26) unchanged.

**Discussion**

Eqns. (B.14), (B.20) and (B.26) are unchanged by CO\(_2\) in Fig. 10.1 feed gas. Consequently, Eqns. (B.27), (B.28), (B.29) and all further developments in Appendix B are also unchanged. So:

Eqn. (10.12) is unaffected by the presence of CO\(_2\) in feed gas.

**F.2 Ar**

All Fig. 10.1 feed gases contain a small amount of argon. With this Ar, the Section F.1 feed gas may be specified as containing:

<table>
<thead>
<tr>
<th>e</th>
<th>volume% SO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>f</td>
<td>&quot; &quot; O(_2)</td>
</tr>
<tr>
<td>c</td>
<td>&quot; &quot; CO(_2)</td>
</tr>
<tr>
<td>a</td>
<td>&quot; &quot; Ar</td>
</tr>
<tr>
<td>1 - e - f - c - a</td>
<td>&quot; &quot; N(_2)</td>
</tr>
</tbody>
</table>
Per kg-mole of Fig. 10.1 feed gas, the input molar quantities are:

\[
\begin{align*}
& \frac{e}{100} \quad \text{kg-mole SO}_2 \text{ (Section B.3.1)} \\
& \frac{f}{100} \quad \text{" " O}_2 \\
& \frac{c}{100} \quad \text{" " CO}_2 \\
& \frac{a}{100} \quad \text{" " Ar} \\

1 - \frac{e}{100} - \frac{f}{100} - \frac{c}{100} - \frac{a}{100} \quad \text{" " N}_2.
\end{align*}
\]

**Molar balances**

Section F.1’s sulfur and oxygen balances (i.e. Eqns. (B14) and (B20)) are not affected by the presence of Ar in Fig. 10.1’s feed gas. Ar does, however, introduce a new molar balance, i.e.:

\[
\text{kg-mole Ar} = \text{kg-mole Ar (F.5)}
\]

in feed gas in exit gas

or:

\[
\frac{a}{100} = n_{Ar} \quad \text{(F.6)}
\]

where \( n_{Ar} = \text{kg-mole Ar in Fig. 10.1 exit gas} \).

It also changes N balance Eqn. (B.19) to:

\[
2 \times \left( 1 - \frac{e}{100} - \frac{f}{100} - \frac{c}{100} - \frac{a}{100} \right) = 2 \times n_{N_2}
\]

or:

\[
n_{N_2} = 1 - \frac{e}{100} - \frac{f}{100} - \frac{c}{100} - \frac{a}{100} \quad \text{(F.7)}.
\]

**Total kg-mole of exit gas**

Including CO\(_2\) and Ar, total kg-mole of Fig. 10.1 exit gas is given by:

\[
n_t = n_{SO_3} + n_{SO_2} + n_{O_2} + n_{N_2} + n_{CO_2} + n_{Ar} \quad \text{(F.8)}.
\]
Combining this with Eqns. (B.14), (B.20), (F.2), (F.6) and (F.7) gives:

\[ n_t = n_{SO_3} + \left( \frac{e}{100} - n_{SO_3} \right) + \left( \frac{f}{100} - \frac{1}{2} n_{SO_3} \right) + \left( 1 - \frac{e}{100} - \frac{f}{100} - \frac{c}{100} - \frac{a}{100} \right) + \frac{c}{100} + \frac{a}{100} \]

\[ = 1 - \frac{1}{2} n_{SO_3} \quad \text{(B.26) unchanged.} \]

As with CO₂, Eqns. (B.14), (B.20) and B.26) are unchanged by Ar. Consequently, Eqns. (B.27), (B.28), B29) and all further developments in Appendix B are also unchanged. So Eqn. (10.12) is unaffected by the presence of Ar in Fig. 10.1 feed gas.

**F.3 Conclusions**

Eqn. (10.12) is unaffected by the presence of N₂, CO₂ and Ar in catalyst bed feed gas. By extension, it is unaffected by all non-reactive gases ('inerts').
Appendix G

Enthalpy Equations for Heatup Path Calculations

Catalytic $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$ heatup paths range between about 660 K and 900 K. Preparation of these heatup paths requires $SO_3$, $SO_2$, $O_2$, $N_2$, and $CO_2$ enthalpy values and equations over this temperature range. This appendix:

(a) calculates the enthalpies of $SO_3$, $SO_2$, $O_2$, $N_2$ and $CO_2$ over this range from the data in Chase, 1998#

(b) relates these enthalpies to temperature with equations of the form

$$H_T^\circ = AT + B.$$

Chase, 1998:

(a) specifies that the enthalpies of elements in their most common state (e.g. $S_{\text{rhombic}}$, $O_2(g)$) are zero at 298.15 (the conventional reference temperature, $T_r$) and:

(b) gives values for:

$$\Delta_T H_{298.15}^\circ$$, the standard enthalpy of compound formation at 298.15 K

$$\left( H_T^\circ - H_{298.15}^\circ \right)$$ for elements and compounds, listed as $H^\circ - H^\circ(T_r)$.

The enthalpies of elements and compounds at temperature $T$ are calculated by the equation:

$$H_T^\circ = H_{298.15}^\circ + \left( H_T^\circ - H_{298.15}^\circ \right)$$

Element enthalpies

$H_{298.15}^\circ$ for elements is zero (see above) so that their enthalpies at temperature $T$ are simply:

$$H_T^\circ_{\text{element}} = \left( H_T^\circ - H_{298.15}^\circ \right)_{\text{element}}$$

where Chase, 1998 provides the right hand side values, listed as $H^\circ - H^\circ(T_r)$.

Compound enthalpies (using $SO_3$ as an example)

$H_{298.15}^0$ for compounds is not zero. For $SO_3$ it is calculated by the equation:

\[
H_{298.15}^0 \text{SO}_3(g) = \Delta_f H_{298.15}^0 \text{SO}_3(g) + H_{298.15}^0 \text{S(rhomnic)} + \frac{3}{2} * H_{298.15}^0 \text{O}_2(g)
\]

(G.3).

where $\Delta_f H_{298.15}^0 \text{SO}_3(g)$ is the enthalpy of formation (298.15 K) of $SO_3$ from its elements at 298.15 K, i.e.:

\[
\text{S(rhomnic)}_{298.15} + \frac{3}{2} * \text{O}_2(g)_{298.15} \rightarrow \text{SO}_3(g)_{298.15}
\]

Chase, 1998 provides $\Delta_f H_{298.15}^0$ values for each compound to which we add the compound designation, e.g. $\Delta_f H_{298.15}^0 \text{SO}_3(g)$.

Further:

\[
H_{298.15}^0 \text{S(rhomnic)} \text{SO}_3(g) \text{ and } H_{298.15}^0 \text{O}_2(g)
\]

are both zero (because they are elements), so that Eqn. (G.3) reduces to:

\[
H_{298.15}^0 \text{SO}_3(g) = \Delta_f H_{298.15}^0 \text{SO}_3(g)
\]

(G.4).

Lastly,

\[
H_T^0 \text{SO}_3(g) = H_{298.15}^0 \text{SO}_3(g) + \left( H_T^0 - H_{298.15}^0 \right) \text{SO}_3(g)
\]

from (G.1)

which combined with Eqn. (G.4) becomes:

\[
H_T^0 \text{SO}_3(g) = \Delta_f H_{298.15}^0 \text{SO}_3(g) + \left( H_T^0 - H_{298.15}^0 \right) \text{SO}_3(g)
\]

(G.5).

where both of the right hand terms are provided by Chase (the latter as $H^0 - H^0(T_c)$).

The enthalpy units in Chase, 1998 are kJ per g-mole. This unit converts one-to-one to MJ per kg-mole, the unit used in this book.

Interestingly, Barin, 1995## provides $H_T^0$ values directly. None of the above calculations is necessary when his data are used.

G.2 An Example – Enthalpy of SO₃(g) at 600 K

Chase, 1998 lists:

\[ \Delta_f H^{\circ}_{298.15, SO_3(g)} = -395.765 \text{ MJ/kg-mole SO}_3 \]

\[ \left( H^{\circ}_{600} - H^{\circ}_{298.15} \right)_{SO_3(g)} = 18.107 \text{ MJ/kg-mole SO}_3. \]

The enthalpy of SO₃(g) at 600 K is, therefore:

\[ H^{\circ}_{600, SO_3(g)} = \Delta_f H^{\circ}_{298.15, SO_3(g)} + \left( H^{\circ}_{600} - H^{\circ}_{298.15} \right)_{SO_3(g)} \]

\[ = -395.765 + 18.107 \]

\[ = -377.658 \text{ MJ/kg-mole SO}_3 \]

as shown in Cell D5 of Table G.1.

G.2 Preparation of Equations

Table G.1 uses Eqn. (G.2), Eqn. (G.5) and Chase, 1998 data to calculate the enthalpies of SO₃, SO₂, O₂, N₂ and CO₂ at 600, 700, 800 and 900 K (and H₂SO₄(ℓ) and H₂O(ℓ) at 300 to 400 K). It then prepares linear equations (in cells A9, A18, A27, A36, A45, A52 and A63) which relate these enthalpies to temperature over these ranges. Excel’s ‘Slope’ and ‘Intercept’ functions are used.

Table G.1. Enthalpy data from Chase, 1998 and H_T vs temperature equations developed from them. H_T is the enthalpy of a pure substance at temperature T.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Units in all enthalpy columns: MJ per kg-mole</td>
<td>Eqn. (G.5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>SO₃(g)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Temperature, K</td>
<td>(\Delta H^{\circ}_{298.15})</td>
<td>(H^{\circ}<em>T - H^{\circ}</em>{298.15})</td>
<td>(H^{\circ}<em>T = \Delta H^{\circ}</em>{298.15} + (H^{\circ}<em>T - H^{\circ}</em>{298.15}))</td>
</tr>
<tr>
<td>4</td>
<td>298.15</td>
<td>-395.765</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>600</td>
<td>18.107</td>
<td>-377.658</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>700</td>
<td>24.997</td>
<td>-370.768</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>800</td>
<td>32.160</td>
<td>-363.605</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>900</td>
<td>39.531</td>
<td>-356.234</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>(H^{\circ}_{SO_3T} = 0.07144^*T - 420.6)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>SO₂(g)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Temperature, K</td>
<td>(\Delta H^{\circ}_{298.15})</td>
<td>(H^{\circ}<em>T - H^{\circ}</em>{298.15})</td>
<td>(H^{\circ}<em>T = \Delta H^{\circ}</em>{298.15} + (H^{\circ}<em>T - H^{\circ}</em>{298.15}))</td>
</tr>
<tr>
<td>13</td>
<td>298.15</td>
<td>-296.842</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>600</td>
<td>13.544</td>
<td>-283.298</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>700</td>
<td>18.548</td>
<td>-278.294</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>800</td>
<td>23.721</td>
<td>-273.121</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>900</td>
<td>29.023</td>
<td>-267.819</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>(H^{\circ}_{SO_2T} = 0.05161^*T - 314.3)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table G.1 continued.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>Units in all enthalpy columns: MJ per kg-mole</td>
<td>Eqn. (G.5)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td><strong>O₂(g)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>Temperature, K</td>
<td>ΔH₉₀₂₉₈.₁₅</td>
<td>H₀ₜ - H₀₂₉₈.₁₅</td>
<td>H₀ₜ = ΔH₀₂₉₈.₁₅ + (H₀ₜ - H₀₂₉₈.₁₅)</td>
</tr>
<tr>
<td>22</td>
<td>298.15</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>600</td>
<td>9.244</td>
<td>9.244</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>700</td>
<td>12.499</td>
<td>12.499</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>800</td>
<td>15.835</td>
<td>15.835</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>900</td>
<td>19.241</td>
<td>19.241</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>H₀₂₉₈.₁₅ = 0.03333*T - 10.79</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td><strong>N₂(g)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>Temperature, K</td>
<td>ΔH₀₂₉₈.₁₅</td>
<td>H₀ₜ - H₀₂₉₈.₁₅</td>
<td>H₀ₜ = ΔH₀₂₉₈.₁₅ + (H₀ₜ - H₀₂₉₈.₁₅)</td>
</tr>
<tr>
<td>30</td>
<td>298.15</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>600</td>
<td>8.894</td>
<td>8.894</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>700</td>
<td>11.937</td>
<td>11.937</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>800</td>
<td>15.046</td>
<td>15.046</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>900</td>
<td>18.223</td>
<td>18.223</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>H₀ₙ₉₈.₁₅ = 0.03110*T - 9.797</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36</td>
<td><strong>CO₂(g)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>Temperature, K</td>
<td>ΔH₀₂₉₈.₁₅</td>
<td>H₀ₜ - H₀₂₉₈.₁₅</td>
<td>H₀ₜ = ΔH₀₂₉₈.₁₅ + (H₀ₜ - H₀₂₉₈.₁₅)</td>
</tr>
<tr>
<td>38</td>
<td>298.15</td>
<td>-393.522</td>
<td></td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>600</td>
<td>12.907</td>
<td>-380.615</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>700</td>
<td>17.754</td>
<td>-375.768</td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>800</td>
<td>22.806</td>
<td>-370.716</td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>900</td>
<td>28.030</td>
<td>-365.492</td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>H₀₇₉₈.₁₅ = 0.05042*T - 411.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>44</td>
<td><strong>H₂SO₄(l)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>Temperature, K</td>
<td>ΔH₀₂₉₈.₁₅</td>
<td>H₀ₜ - H₀₂₉₈.₁₅</td>
<td>H₀ₜ = ΔH₀₂₉₈.₁₅ + (H₀ₜ - H₀₂₉₈.₁₅)</td>
</tr>
<tr>
<td>46</td>
<td>298.15</td>
<td>-813.989</td>
<td></td>
<td></td>
</tr>
<tr>
<td>47</td>
<td>300</td>
<td>0.257</td>
<td>-813.732</td>
<td></td>
</tr>
<tr>
<td>48</td>
<td>400</td>
<td>15.112</td>
<td>-798.877</td>
<td></td>
</tr>
<tr>
<td>49</td>
<td>H₀₇₉₈.₁₅ = 0.1485*T - 858.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td><strong>H₂O(l)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>51</td>
<td>Temperature, K</td>
<td>ΔH₀₂₉₈.₁₅</td>
<td>H₀ₜ - H₀₂₉₈.₁₅</td>
<td>H₀ₜ = ΔH₀₂₉₈.₁₅ + (H₀ₜ - H₀₂₉₈.₁₅)</td>
</tr>
<tr>
<td>52</td>
<td>298.15</td>
<td>-285.830</td>
<td></td>
<td></td>
</tr>
<tr>
<td>53</td>
<td>300</td>
<td>0.139</td>
<td>-285.691</td>
<td></td>
</tr>
<tr>
<td>54</td>
<td>320</td>
<td>1.646</td>
<td>-284.184</td>
<td></td>
</tr>
<tr>
<td>55</td>
<td>340</td>
<td>3.153</td>
<td>-282.677</td>
<td></td>
</tr>
<tr>
<td>56</td>
<td>360</td>
<td>4.664</td>
<td>-281.166</td>
<td></td>
</tr>
<tr>
<td>57</td>
<td>380</td>
<td>6.182</td>
<td>-279.648</td>
<td></td>
</tr>
<tr>
<td>58</td>
<td>400</td>
<td>7.711</td>
<td>-278.119</td>
<td></td>
</tr>
<tr>
<td>59</td>
<td>H₀₇₉₈.₁₅ = 0.07568*T - 308.4</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Appendix H

Matrix Solving
Using Tables 11.2 and 14.2 as Examples

1. Put Table 11.2 into an Excel spreadsheet with the top of the numerical term column (0.10) in cell C2. The matrix covers cells C2 to J8. Label as shown in Table 11.2.

2. Select cells B13 to B19 (by, for example, selecting cell B13, holding down the Shift key and arrowing down to cell B19).

3. Leave these cells selected then type \(=\text{mmult(minverse(D2:J8),C2:C8)}\) then simultaneously press Ctrl Shift Enter.

4. Cells B13-B19 contain the solution to the matrix. Label as shown in Table 11.2.

Subsequent problems can be solved without repeating the above steps. The Section 11.13 example problem is solved, for example, by putting 0.130, 0.143 and 0.727 into cells C2, C3 and C4 respectively. The solution appears automatically in cells B13-B19.

Table 14.2's matrix has 1 more column than Table 11.2 – and 1 more row. This means that instruction 2 (above) must select 8 cells instead of 7, say B20 to B27 in Table 14.2.

Table 14.2's solving instruction is:
Leave cells B20 through B27 selected then type \(=\text{mmult(minverse(D8:K15),C8:C15)}\) then simultaneously press Ctrl Shift Enter.
Appendix I

Enthalpy Equations in Heatup Path Matrix Cells

Heatup path calculations are simplified by putting enthalpy-as-a-function-of-temperature equations in cells D8-J8 of matrix Table 11.2. The equations are listed in Appendix G. They change Eqn. (11.7) to:

\[
0 = -\text{kg-mole SO}_2 \text{ in} \times (0.05161 \times T_{\text{feed}} - 314.3) \\
-\text{kg-mole O}_2 \text{ in} \times (0.03333 \times T_{\text{feed}} - 10.79) \\
-\text{kg-mole N}_2 \text{ in} \times (0.03110 \times T_{\text{feed}} - 9.797) \\
+\text{kg-mole SO}_3 \text{ out} \times (0.07144 \times T_L - 420.6) \\
+\text{kg-mole SO}_2 \text{ out} \times (0.05161 \times T_L - 314.3) \\
+\text{kg-mole O}_2 \text{ out} \times (0.03333 \times T_L - 10.79) \\
+\text{kg-mole N}_2 \text{ out} \times (0.03110 \times T_L - 9.797) \quad (11.7'')
\]

where:

\(0.05161 \times T - 314.3 = H^o_{T,SO_2}\) etc.

\(T_{\text{feed}} = \text{Fig. 11.3 feed gas temperature, K}\)

\(T_L = \text{Fig. 11.3 level L gas temperature, K}\).

As shown in Table I.1, Eqn. (11.7'') is put into matrix Table 11.2 by:

(a) inserting numerical values of \(T_{\text{feed}}\) and \(T_L\) into cells F10 and J10
(b) putting the Eqn (11.7'') enthalpy terms into cells D8-J8 so that:
Cell D8 contains \[-(0.05161 \cdot F10 - 314.3)\]
" E8 " " = \[-(0.03333 \cdot F10 - 10.79)\]
" F8 " " = \[-(0.03110 \cdot F10 - 9.797)\]
" G8 " " = \[(0.07144 \cdot J10 - 420.6)\]
" H8 " " = \[(0.05161 \cdot J10 - 314.3)\]
" I8 " " = \[(0.03333 \cdot J10 - 10.79)\]
" J8 " " = \[(0.03110 \cdot J10 - 9.797)\].

Note the signs.

Insertion of these equations into Table 11.2 (with 690 K and 820 K in cells F10 and J10) automatically gives the Table 11.2 result, as shown below. The temperatures in cells F10 and J10 can then be changed at will – and new heatup path points automatically calculated. Example results are shown after Table I.1. Matrix solving is described in Appendix H.

**Table I.1.** Matrix Table 11.2 with Eqn. (11.7") enthalpy equations in cells D8-J8, see above. The in-cell equations refer to \(T_{\text{feed}}\) in cell F10 and \(T_{L}\) in cell J10. Feed gas quantities in cells C2-C4 can also be changed at will as described in Section 11.13. Refer to Table 11.2 for other details.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Equation</td>
<td>description</td>
<td>numerical term</td>
<td>kg-mole SO(_2) in</td>
<td>kg-mole O(_2) in</td>
<td>kg-mole N(_2) in</td>
<td>kg-mole SO(_3) out</td>
<td>kg-mole SO(_2) out</td>
<td>kg-mole O(_2) out</td>
<td>kg-mole N(_2) out</td>
</tr>
<tr>
<td>2</td>
<td>11.1</td>
<td>feed SO(_2) kg-mole</td>
<td>0.10</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>11.2</td>
<td>feed O(_2) kg-mole</td>
<td>0.11</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>11.3</td>
<td>feed N(_2) kg-mole</td>
<td>0.79</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>11.4</td>
<td>S balance</td>
<td>0</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>11.5</td>
<td>O balance</td>
<td>0</td>
<td>-2</td>
<td>-2</td>
<td>0</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>11.6</td>
<td>N balance</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>11.7*</td>
<td>enthalpy balance</td>
<td>0</td>
<td>278.7</td>
<td>-12.21</td>
<td>-11.66</td>
<td>-362.0</td>
<td>-272.0</td>
<td>16.54</td>
<td>15.71</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>Fig. 11.3 feed gas temperature, K = 690</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>Fig. 11.3 level L gas temp, K = 820</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>Matrix results per kg-mole of feed gas contains (0.07144 \cdot J10 - 420.6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td></td>
<td>kg-mole SO(_2) in</td>
<td>0.1000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td></td>
<td>kg-mole O(_2) in</td>
<td>0.1100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td></td>
<td>kg-mole N(_2) in</td>
<td>0.7900</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>kg-mole SO(_2) out</td>
<td>0.0442</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td></td>
<td>% SO(_2) oxidized at level L = ((\text{kg-mole SO}(_2) in - kg-mole SO(_2) out) / \text{kg-mole SO}(_2) in))*100 (\text{Eqn. 10.1)}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td></td>
<td>kg-mole SO(_2) out</td>
<td>0.0558</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td></td>
<td>kg-mole O(_2) out</td>
<td>0.0879</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td></td>
<td>kg-mole N(_2) out</td>
<td>0.7900</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
I.1 Example Results

Table I.1 automatically shows that: an 820 K heatup path temperature with: 10 volume% SO₂, 11 volume% O₂, 79 volume% N₂, 690 K feed gas is equivalent to: 44.2 % oxidation of the feed gas's SO₂ in the Fig. 11.3 catalyst bed. This is one point on the feed gas's heatup path.

Other points may be calculated by:

(a) incrementally changing the cell J10 temperature

(b) tabulating these temperatures and their equivalent cell H17 % SO₂ oxidized values.

Table 11.3/Fig. 11.1 points have been calculated this way. A few of them are:

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td></td>
<td>Fig. 11.3 level L temperature, K</td>
<td>% SO₂ oxidized at level L</td>
</tr>
<tr>
<td></td>
<td></td>
<td>690</td>
<td>0.0</td>
</tr>
<tr>
<td>22</td>
<td></td>
<td>710</td>
<td>6.8</td>
</tr>
<tr>
<td>23</td>
<td></td>
<td>730</td>
<td>13.5</td>
</tr>
</tbody>
</table>

Table 12.1/Fig. 12.1 heatup path points have also been calculated this way. A few are:

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td></td>
<td>Fig. 11.3 level L temperature, K</td>
<td>% SO₂ oxidized at level L</td>
</tr>
<tr>
<td></td>
<td></td>
<td>890</td>
<td>68.09</td>
</tr>
<tr>
<td>22</td>
<td></td>
<td>891</td>
<td>68.44</td>
</tr>
<tr>
<td>23</td>
<td></td>
<td>892</td>
<td>68.76</td>
</tr>
</tbody>
</table>
Appendix J

Heatup Path-Equilibrium Curve Intercept Calculations

Figs. 11.7 and 12.1 indicate that maximum SO$_2$ oxidation in a catalyst bed occurs where a feed gas's:

heatup path

intercepts its:

equilibrium curve.

The point of interception may be determined:

(a) by re-doing Table 12.1's calculations every 0.1 K

(b) iteratively, using Excel's Goal Seek tool.

This appendix describes (b).

J.1 Calculation Strategy

Our iterative intercept strategy is to find the temperature at which a feed gas's:

heatup path $\% \text{SO}_2$ oxidized, $\Phi$.

equals its:

equilibrium curve $\% \text{SO}_2$ oxidized, $\Phi^E$.

This temperature and its equivalent $\% \text{SO}_2$ oxidized define the intercept point. The next several pages provide an intercept calculation worksheet and instructions. The worksheet is for the specific case of:

10 volume$\%$ SO$_2$

11 volume$\%$ O$_2$

79 volume$\%$ N$_2$

690 K

feed gas and 1.2 bar gas pressure. It is easily altered for different pressures and gas compositions and temperatures. All calculations are based on 1 kg-mole of 1$^{st}$ catalyst bed feed gas.
J.2 Worksheet

The top of worksheet Table J.1 is similar to equilibrium curve worksheet Table D.1. Its main components are:

(a) an equilibrium curve % $SO_2$ oxidized value in cell F11
(b) Eqn. (10.13) in cell A14 (as shown to the right of that cell)
(c) equilibrium pressure $P_t$ specified in cell K6.

The middle of the worksheet is similar to heatup path Table I.1. Its main components are:

(a) a matrix which contains Eqns. (11.1) to (11.6) – and Eqn. (11.7") with enthalpy equations in cells D28-J28
(b) feed gas temperature in cell F30 (copied from cell K5)
(c) intercept gas temperature in cell J30 (copied from cell A14)
(d) a matrix results column like that in Table I.1
(e) a heatup path % $SO_2$ oxidized value calculated in cell I39 from the matrix results.

The bottom of Table J.1 is the iterative part of the worksheet. It:

(a) subtracts:

\[ \text{heatup path } %SO_2 \text{ oxidized (cell I39)} \]

from

\[ \text{equilibrium curve } %SO_2 \text{ oxidized (cell F11)} \]

in cell G47

then:

(b) uses Excel's Goal Seek tool to determine the value of:

\[ \text{equilibrium curve } %SO_2 \text{ oxidized in cell F11} \]

which gives a zero value to cell G47.

The Goal Seek procedure is described in Section J.4.
J.3 Intercept Worksheet Preparation Instructions

1. Feed gas volume% \( \text{SO}_2 \), \( \text{O}_2 \) and \( \text{N}_2 \) are entered into cells G3, I3 and K3. Feed gas temperature is entered into cell K5. Total gas pressure is entered into cell K6.

2. Feed kg-mole \( \text{SO}_2 \), \( \text{O}_2 \) and \( \text{N}_2 \) are calculated in cells G8, I8 and K8 as shown. They are all per kg-mole of feed gas. Feed kg-mole \( \text{SO}_2 \) is repeated in cell G5 (for later 2\textsuperscript{nd} catalyst bed calculations).

3. A suggested equilibrium curve intercept \( \% \text{SO}_2 \text{ oxidized} \) value is entered in cell F11 (perhaps 69% from Table 12.1).

4. Eqn. (10.13) is entered in Cell A14 as shown.

5. Steps 3 and 4 automatically calculate the equilibrium curve temperature (cell A14) equivalent to the \( \% \text{SO}_2 \text{ oxidized} \) value in cell F11. The cell A14 temperature is automatically copied into cell J30. This links the equilibrium curve and heatup path calculations.

6. A heatup path matrix is entered as described in Tables 11.2 and I.1. Cells D28 to J28 contain enthalpy-as-a-function-of-temperature equations, Table I.1. Cells C22 to C24 contain input kg-mole \( \text{SO}_2 \), \( \text{O}_2 \) and \( \text{N}_2 \), Section 11.13.

7. The matrix is solved as described in Appendix H. The procedure is: select cell B35, shift-arrow down to cell B41, type \texttt{mmult(minverse(D22:J28),C22:C28)} then simultaneously press Ctrl Shift Enter. This is the only time the matrix must be solved.

8. Eqn. (10.1) is entered in cell I39. This automatically uses the step 7 results to calculate the heatup path \( \% \text{SO}_2 \text{ oxidized} \) value equivalent to:

   cell J30's (hence cell A14's) intercept temperature.

9. At this point, equilibrium curve temperature = heatup path temperature. But equilibrium curve \( \% \text{SO}_2 \text{ oxidized} \) (cell F11) ≠ heatup path \% \( \text{SO}_2 \text{ oxidized} \) (cell I39). So this is not the intercept.

The 'actual' intercept value is determined by the Goal Seek calculation in Section J.4.
Table J.1. Worksheet for calculating 1st catalyst bed heatup path-equilibrium curve intercept. Preparation instructions are given in Section J.3. Operating instructions are given in Section J.4. Notice that equilibrium curve % SO₂ oxidized (cell F11) ≠ heatup path % SO₂ oxidized (cell I39). So 894.2 K in cells A14 and J30 is not the intercept temperature. The intercept value is calculated in Table J.2.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1ST CATALYST BED</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1st catalyst bed feed gas composition from Fig. 11.2</td>
<td></td>
<td></td>
<td></td>
<td>e. volume % SO₂ =</td>
<td>10</td>
<td>f. volume % O₂ =</td>
<td>11</td>
<td>volume % N₂ =</td>
<td>79</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1st catalyst bed feed kg-mole SO₂ (for Eqs. (10.10) = e/100 = G/3100 (Eqs. 11.1)</td>
<td></td>
<td></td>
<td></td>
<td>SO₂ =</td>
<td>0.1</td>
<td>feed gas temperature, K =</td>
<td>690</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1st catalyst bed feed kg-mole from above feed gas composition, Eqs. (11.1) etc.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Suggested equilibrium curve intercept % SO₂ oxidized, φ₂’ =</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>69.0</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Equilibrium curve temperature equivalent to cell F11's suggested % SO₂ oxidized, Eqs. (10.13)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>894.2 = (-0.41)×0.9357×0.09314+(N[0]×100+11) ×(100-0.5×G/3100×100)/(3.5×G/3100×100+0.5×φ₂’×0.5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(10.13)</td>
</tr>
<tr>
<td>13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Heatup path matrix (kg means in feed gas; out means in intercept gas)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Equation description</td>
<td>numerical term</td>
<td>kg-mole SO₂</td>
<td>kg-mole O₂</td>
<td>kg-mole N₂</td>
<td>kg-mole SO₂</td>
<td>kg-mole O₂</td>
<td>kg-mole N₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>11.1 feed SO₂ kg-mole</td>
<td>0.10</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>11.2 feed O₂ kg-mole</td>
<td>0.11</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>11.3 feed N₂ kg-mole</td>
<td>0.79</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>11.4 S balance</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>11.5 Q balance</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>11.6 N balance</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>11.7* enthalpy balance</td>
<td>0</td>
<td>278.7</td>
<td>-123</td>
<td>-116</td>
<td>-256.7</td>
<td>-282</td>
<td>16.01</td>
<td>18.01</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>feed gas temperature =</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>690</td>
</tr>
<tr>
<td>25</td>
<td>intercept temperature from cell A14 =</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>894.2</td>
</tr>
<tr>
<td>26</td>
<td>=A14</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>=A14</td>
</tr>
<tr>
<td>27</td>
<td>Matrix results equivalent to suggested intercept temperature in cell J30 (and A14)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>kg-mole SO₂ in</td>
<td>0.1000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>kg-mole O₂ in</td>
<td>0.1100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>kg-mole N₂ in</td>
<td>0.7900</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>kg-mole SO₂ out</td>
<td>0.0955</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>kg-mole SO₂ out</td>
<td>0.0305</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>kg-mole O₂ out</td>
<td>0.0752</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>kg-mole N₂ out</td>
<td>0.7900</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>per kg-mole of feed gas</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>Goal Seek calculation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>Equilibrium curve % SO₂ oxidized - heatup path % SO₂ oxidized =</td>
<td>-0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>=F11-J39</td>
</tr>
</tbody>
</table>

329
J.4 Goal Seek Instructions

Table J.1 is set up so that equilibrium curve temperature always = heatup path temperature. The only remaining question is at what temperature does:

\[
\text{heatup path } \% \text{SO}_2 \text{ oxidized} = \text{equilibrium curve } \% \text{SO}_2 \text{ oxidized}?
\]

This is determined by:

1. Putting 'equilibrium curve 'SO\(_2\) oxidized' - heatup path 'SO\(_2\) oxidized' in cell G47, as shown.
2. Using Goal Seek to adjust:

   \[
   \text{equilibrium curve } \% \text{SO}_2 \text{ oxidized} \text{ (cell F11)}
   \]

   until cell G47 = zero, i.e. until:

   \[
   \text{heatup path } \% \text{SO}_2 \text{ oxidized} = \text{equilibrium curve } \% \text{SO}_2 \text{ oxidized}.
   \]

The Goal Seek procedure is:

**Tools**

**Goal Seek**

**Set cell:** G47

**To value:** 0

**Changing cell:** F11

**OK**

**OK.**

The results are shown in worksheet Table J.2. The intercept point is 69.2 % SO\(_2\) oxidized (in cells F11 and I39), 893.3 K (in cells A14 and J30) -- as is readily checked by comparison with Table 12.1.

Intercept kg-mole SO\(_2\), SO\(_2\), O\(_2\) and N\(_2\) (per kg-mole of feed gas) are also provided in cells B38 to B41. They are used in Chapter 14 and 15's multi-catalyst bed calculations.

J.5 Another Example

Table J.3 is a worksheet for 13 volume% SO\(_2\), 14.3 volume% O\(_2\) and 72.7 volume% N\(_2\), 690 K feed gas and a 1.2 bar equilibrium pressure. The heatup path-equilibrium curve intercept for this new gas is determined by:

(a) entering these new specifications in cells G3, I3, K3, K5 and K6

(b) repeating Section J.4's Goal Seek instructions.
Table J.2. Table J.1 worksheet after Goal Seek has found the heatup path-equilibrium curve intercept: 893.3 K, 69.2% SO₂ oxidized.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1ST CATALYST BED</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1st catalyst bed feed gas composition from Fig. 11.2</td>
<td>e, volume% SO₂ =</td>
<td>10</td>
<td>f, volume% O₂ =</td>
<td>11</td>
<td>volume% N₂ =</td>
<td>79</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1st catalyst bed feed kg-mole SO₂ (for Eqn. (10.1) = e/100 = G3/100 (Eqn. 11.1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>catalyst bed pressure P₁, bar =</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1st catalyst bed feed kg-mole from above feed gas composition, Eqn. (11.1) etc.</td>
<td>%SO₂ =</td>
<td>0.1</td>
<td>%O₂ =</td>
<td>0.11</td>
<td>%N₂ =</td>
<td>0.79</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>= e/100 = G3/100 = f/100 = l/3/100 = k/3/100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Suggested equilibrium curve intercept % SO₂ oxidized, Φ° =</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Equilibrium curve temperature equivalent to cell F11's suggested % SO₂ oxidized, Eqn. (10.13)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>893.3 = (0.98411/0.09257+0.008314<em>LN(10)/(1))((1/10)/(0.5</em>G3/F11)2)/(1-0.5<em>G3/F11/100)2/(0.5</em>G3/F11/100)2/(0.5<em>G3/F11/100)2/(0.5</em>G3/F11/100)2/(0.5*G3/F11/100)2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>(10.13)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>Heatup path matrix (in means 'in feed gas', out means 'in intercept gas')</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>Equation</td>
<td>numerical term</td>
<td>kg-mole SO₂ in</td>
<td>kg-mole O₂ out</td>
<td>kg-mole N₂ out</td>
<td>kg-mole SO₂ out</td>
<td>kg-mole SO₂ out</td>
<td>kg-mole O₂ out</td>
<td>kg-mole N₂ out</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>11.1 feed SO₂ kg-mole</td>
<td>0.10</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>11.2 feed O₂ kg-mole</td>
<td>0.11</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>11.3 feed N₂ kg-mole</td>
<td>0.79</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>11.4 S-balance</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>11.5 O-balance</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>11.6 N-balance</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>11.7 * enthalpy balance</td>
<td>0</td>
<td>278.7</td>
<td>-12.21</td>
<td>-11.66</td>
<td>-356.8</td>
<td>-268.2</td>
<td>18.99</td>
<td>17.99</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>feed gas temperature =</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>intercept temperature from cell A14 =</td>
<td>690</td>
<td>893.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>=K5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>33</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>Matrix results equivalent to suggested intercept temperature in cell J30 (and A14)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>kg-mole SO₂ in</td>
<td>0.1000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>kg-mole O₂ in</td>
<td>0.1100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>kg-mole N₂ in</td>
<td>0.7900</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>kg-mole SO₂ out</td>
<td>0.0692</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>kg-mole O₂ out</td>
<td>0.0308</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>kg-mole N₂ out</td>
<td>0.0754</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>Equilibrium curve % SO₂ oxidized - heatup path % SO₂ oxidized =</td>
<td>0.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: Φ° is the suggested equilibrium curve intercept % SO₂ oxidized, and the heatup path % SO₂ oxidized is calculated based on the equilibrium curve temperature. The matrix results are equivalent to the suggested intercept temperature in cell J30 (and A14).
Table J.3. Worksheet for 13 volume% $SO_2$, 14.3 volume% $O_2$, 72.7 volume% $N_2$, 690 K feed gas (1.2 bar) after Goal Seek has found the intercept.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1ST CATALYST BED</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1st catalyst bed feed gas specification</td>
<td>$e$, volume% $SO_2 = 13.0$</td>
<td>$f$, volume% $O_2 = 14.3$</td>
<td>volume% $N_2 = 72.7$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1st catalyst bed feed kg-mole $SO_2 = e/100 = G3/100 = $</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Eqn. (11.1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Feed gas temperature, $K = 690$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Gas pressure in feed gas, bar = 1.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1st catalyst bed feed kg-mole from feed gas composition</td>
<td>kg-mole $SO_2 = 0.13$</td>
<td>kg-mole $O_2 = 0.143$</td>
<td>kg-mole $N_2 = 0.727$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>$= e/100 = G3/100 = f/100 = s/100 = k3/100$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Equilibrium curve intercept % $SO_2$ oxidized = 62.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Equilibrium curve temperature equivalent to cell F11's suggested % $SO_2$ oxidized, from Eqn. (10.13)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>$924.5 = (-38.41)(0.00357+0.00314<em>LN(F11/100-F11)'(/100-0.5</em>G3<em>F11/100))/(0.5</em>G3*F11/100)<em>0.5</em>K^0.5)$ (10.13)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Heatup path metric</td>
<td>(in means in feed gas, out means in intercept gas)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Equation description</td>
<td></td>
<td>numerical term $=G8$ etc.</td>
<td>kg-mole $SO_2$ in</td>
<td>kg-mole $O_2$ in</td>
<td>kg-mole $N_2$ in</td>
<td>kg-mole $SO_2$ out</td>
<td>kg-mole $SO_2$ out</td>
<td>kg-mole $O_2$ out</td>
<td>kg-mole $N_2$ out</td>
</tr>
<tr>
<td>16</td>
<td>Feed $SO_2$, kg-mole</td>
<td>0.130</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>17</td>
<td>Feed $O_2$, kg-mole</td>
<td>0.143</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>18</td>
<td>Feed $N_2$, kg-mole</td>
<td>0.727</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>19</td>
<td>S balance</td>
<td>11.4</td>
<td>0</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>O balance</td>
<td>11.5</td>
<td>0</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>21</td>
<td>N balance</td>
<td>11.6</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>22</td>
<td>Enthalpy balance</td>
<td>11.7</td>
<td>0</td>
<td>278.7</td>
<td>-12.21</td>
<td>-11.66</td>
<td>-354.6</td>
<td>-295.6</td>
<td>20.02</td>
<td>18.95</td>
</tr>
<tr>
<td>23</td>
<td>Feed gas temperature = 690</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>Equilibrium temperature from cell A10 = 924.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>Matrix results equivalent to suggested intercept temperature in cell J30 (and A14)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>$= 0.07144*J30 - 420.6$ from Appendix AHUP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>$= 0.07144*J30 - 420.6$ from Appendix AHUP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>$= 0.07144*J30 - 420.6$ from Appendix AHUP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>$= 0.07144*J30 - 420.6$ from Appendix AHUP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>$= 0.07144*J30 - 420.6$ from Appendix AHUP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>$= 0.07144*J30 - 420.6$ from Appendix AHUP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>$= 0.07144*J30 - 420.6$ from Appendix AHUP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>$= 0.07144*J30 - 420.6$ from Appendix AHUP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>$= 0.07144*J30 - 420.6$ from Appendix AHUP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>$= 0.07144*J30 - 420.6$ from Appendix AHUP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>$= 0.07144*J30 - 420.6$ from Appendix AHUP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>$= 0.07144*J30 - 420.6$ from Appendix AHUP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>$= 0.07144*J30 - 420.6$ from Appendix AHUP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>$= 0.07144*J30 - 420.6$ from Appendix AHUP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>$= 0.07144*J30 - 420.6$ from Appendix AHUP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>$= 0.07144*J30 - 420.6$ from Appendix AHUP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>$= 0.07144*J30 - 420.6$ from Appendix AHUP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>$= 0.07144*J30 - 420.6$ from Appendix AHUP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>$= 0.07144*J30 - 420.6$ from Appendix AHUP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>46</td>
<td>$= 0.07144*J30 - 420.6$ from Appendix AHUP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>47</td>
<td>$= 0.07144*J30 - 420.6$ from Appendix AHUP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Appendix K

2nd Catalyst Bed Heatup Path Calculations

Table K.1 shows a 2nd catalyst bed heatup path matrix with enthalpy-as-a-function-of-temperature equations in cells D15 to K15. The only difference between this matrix and the Table 14.2 matrix is that Eqn. 14.9 in row 15 has been changed to:

\[
0 = -\text{kg-mole SO}_3 \text{ in} \times (0.07144 \times T_{\text{input}} - 420.6) \\
- \text{kg-mole SO}_2 \text{ in} \times (0.05161 \times T_{\text{input}} - 314.3) \\
- \text{kg-mole O}_2 \text{ in} \times (0.03333 \times T_{\text{input}} - 10.79) \\
- \text{kg-mole N}_2 \text{ in} \times (0.03110 \times T_{\text{input}} - 9.797) \\
+ \text{kg-mole SO}_3 \text{ out} \times (0.07144 \times T_L - 420.6) \\
+ \text{kg-mole SO}_2 \text{ out} \times (0.05161 \times T_L - 314.3) \\
+ \text{kg-mole O}_2 \text{ out} \times (0.03333 \times T_L - 10.79) \\
+ \text{kg-mole N}_2 \text{ out} \times (0.03110 \times T_L - 9.797)
\]  \hspace{1cm} (14.9")

where:

\[ (0.07144 \times T - 420.6) = H^t_{\text{SO}_3} \text{ etc.} \]

\[ T_{\text{input}} = \text{Fig. 14.2's 2nd catalyst bed input gas temperature, K} \]

\[ T_L = \text{Fig. 14.2's 2nd catalyst bed level L gas temperature, K} \]

Eqn. (14.9") is put into Table 14.2's solved matrix by:

(a) inserting numerical values of \(T_{\text{input}}\) and \(T_L\) into cells F17 and J17

(b) putting the Eqn (14.9") enthalpy terms into cells D15 to K15 so that:
cell D15 contains = -(0.07144 * F17 - 420.6)
" E15 " " = -(0.05161 * F17 - 314.3)
" F15 " " = -(0.03333 * F17 - 10.79)
" G15 " " = -(0.03110 * F17 - 9.797)
" H15 " " = (0.07144 * J17 - 420.6)
" I15 " " = (0.05161 * J17 - 314.3)
" J15 " " = (0.03333 * J17 - 10.79)
" K15 " " = (0.03110 * J17 - 9.797).

Note the (-) signs

Insertion of these terms (with 700 K and 760 K in cells F17 and J17) automatically gives the same result as in Table 14.2. The temperatures in cells F17 and J17 can now be changed at will – and heatup path points automatically calculated. Example results are shown below the worksheet.
Table K.1 Table 14.2 with (i) input and level L temperatures in cells F17 and J17 and (ii) enthalpy equations in cells D15 to K15. A change in either temperature automatically gives a new % SO₂ oxidized result.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>All calculations are based on 1 kg-mole of 1st catalyst bed feed gas.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>kg-mole SO₂ in 1 kg-mole of 1st catalyst bed feed gas</td>
<td>0.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2nd catalyst bed matrix

<table>
<thead>
<tr>
<th>Equation</th>
<th>Description</th>
<th>Numerical Term</th>
<th>kg-mole SO₂ in</th>
<th>kg-mole SO₂ in</th>
<th>kg-mole O₂ in</th>
<th>kg-mole N₂ in</th>
<th>kg-mole SO₂ out</th>
<th>kg-mole SO₂ out</th>
<th>kg-mole O₂ out</th>
<th>kg-mole N₂ out</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>14.2</td>
<td>input SO₂ kg-mole</td>
<td>0.0692</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>14.3</td>
<td>input SO₂ kg-mole</td>
<td>0.0308</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>14.4</td>
<td>input O₂ kg-mole</td>
<td>0.0754</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>14.5</td>
<td>input N₂ kg-mole</td>
<td>0.7900</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>14.6</td>
<td>S balance</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>13</td>
<td>14.7</td>
<td>O balance</td>
<td>0</td>
<td>-3</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>14</td>
<td>14.8</td>
<td>N balance</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>14.9*</td>
<td>enthalpy balance</td>
<td>0</td>
<td>370.6</td>
<td>278.2</td>
<td>-12.54</td>
<td>-11.97</td>
<td>-366.3</td>
<td>-275.1</td>
<td>14.54</td>
</tr>
<tr>
<td>16</td>
<td></td>
<td>Fig. 14.2 input gas temperature = 700</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td></td>
<td>heating path temperature = 760</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Heat up path result per kg-mole of 1st catalyst bed feed gas contains = (0.0311 * F17 - 9.797)

<table>
<thead>
<tr>
<th>kg-mole SO₂ in</th>
<th>0.0692</th>
<th>0.0308</th>
<th>0.0754</th>
<th>0.7900</th>
<th>0.0897</th>
<th>0.0103</th>
<th>0.0652</th>
<th>0.7900</th>
</tr>
</thead>
</table>

Several Table 14.3/ Fig. 14.3 heating path points calculated with the above worksheet are:

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>Fig. 14.2 level L temperature, K</td>
<td>% SO₂ oxidized at level L</td>
</tr>
<tr>
<td>31</td>
<td>700</td>
<td>69.2</td>
</tr>
<tr>
<td>32</td>
<td>705</td>
<td>70.9</td>
</tr>
<tr>
<td>33</td>
<td>710</td>
<td>72.8</td>
</tr>
</tbody>
</table>
Appendix L

Equilibrium Equation for Multi-Catalyst Bed SO₂ Oxidation

This appendix shows that the equilibrium equation developed for the 1ˢᵗ catalyst bed of a multi-catalyst bed 'converter' (Eqn. 10.13) also applies to the converter's:

2ⁿᵈ, 3ʳᵈ (and 4ᵗʰ) pre-H₂SO₄-making catalyst beds.

It also indicates that the 1ˢᵗ catalyst bed equation does not apply to beds which follow:

(a) selective removal of SO₃(g) during H₂SO₄ making, Reaction (1.2)
or:

(b) addition of air between beds (as is occasionally done industrially).

L.1 Proof

Examination of Appendix B and Chapter 10 shows that if the:

\[ \begin{align*}
    & \text{kg-mole S} \\
    & \text{kg-mole O} \\
    & \text{kg-mole N}
\end{align*} \]

inputs to a 2ⁿᵈ catalyst bed are the same as those entering the preceding 1ˢᵗ catalyst bed (per kg-mole of 1ˢᵗ catalyst bed feed gas), then:

equilibrium Eqn. (10.13) applies to both beds.

These 1ˢᵗ and 2ⁿᵈ bed inputs are, of course, the same if nothing is added to or removed from the gas as it passes between the beds. Industrially this is almost always the case so that Eqn. (10.13) almost always applies to both beds.

The following empirical calculation serves to emphasize this point.

Table J.2 shows that 1 kg-mole of its 1ˢᵗ catalyst bed feed gas contains:

\[ \begin{align*}
    0.10 \text{ kg-mole SO}_2 &= \frac{e}{100} \\
    0.11 \text{ kg-mole O}_2 &= \frac{f}{100} \\
    0.79 \text{ kg-mole N}_2 &= 1 - \frac{e}{100} - \frac{f}{100}
\end{align*} \]

where e and f are volume% SO₂ and O₂ in the 1ˢᵗ catalyst bed feed gas.
kg-mole S, O and N equivalent to the above quantities are (Section B.3.1):

\[
\text{kg-mole S} = 1 \times \frac{e}{100} = 0.10
\]

\[
\text{kg-mole O} = 2 \times \frac{e}{100} + 2 \times \frac{f}{100} = 0.42
\]

\[
\text{kg-mole N} = 2 \times \left(1 - \frac{e}{100} - \frac{f}{100}\right) = 1.58
\]

Table J.2 also shows that the 1\textsuperscript{st} catalyst bed exit (intercept) gas contains:

- 0.0692 kg-mole \( \text{SO}_3 \)
- 0.0308 kg-mole \( \text{SO}_2 \)
- 0.0754 kg-mole \( \text{O}_2 \)
- 0.7900 kg-mole \( \text{N}_2 \)

which are equivalent to:

\[
\text{kg-mole S} = 1 \times 0.0692 \text{ kg-mole } \text{SO}_3 + 1 \times 0.0308 \text{ kg-mole } \text{SO}_2 = 0.10
\]

\[
\text{kg-mole O} = 3 \times 0.0692 \text{ kg-mole } \text{SO}_3 + 2 \times 0.0308 \text{ kg-mole } \text{SO}_2 + 2 \times 0.0754 \text{ kg-mole } \text{O}_2 = 0.42
\]

\[
\text{kg-mole N} = 2 \times 0.79 \text{ kg-mole } \text{N}_2 = 1.58
\]

(all per kg-mole of 1\textsuperscript{st} catalyst bed feed gas).

This exit gas flows without addition or removal through its gas cooler and into the 2\textsuperscript{nd} catalyst bed – which leads to the conclusions that:

(a) \( \text{kg-mole S into } 1\textsuperscript{st} \text{ catalyst bed} = \text{kg-mole S into } 2\textsuperscript{nd} \text{ catalyst bed} = 0.10 = 1 \times \frac{e}{100} \) \hspace{1cm} (L.1)

(b) \( \text{kg-mole O into } 1\textsuperscript{st} \text{ catalyst bed} = \text{kg-mole O into } 2\textsuperscript{nd} \text{ catalyst bed} = 0.42 = 2 \times \frac{e}{100} + 2 \times \frac{f}{100} \) \hspace{1cm} (L.2)

(c) \( \text{kg-mole N into } 1\textsuperscript{st} \text{ catalyst bed} = \text{kg-mole N into } 2\textsuperscript{nd} \text{ catalyst bed} = 1.58 = 2 \left(1 - \frac{e}{100} - \frac{f}{100}\right) \) \hspace{1cm} (L.3)

(b) Eqn. (10.13) therefore applies to both catalyst beds.
Item (b) arises because Eqns. (B14), (B20), (B23) (B26) (and all subsequent Appendix B equations) are the same for both catalyst beds.

The above calculation can be generalized to a series of catalyst beds as long as nothing is added to or removed from the gas stream between beds.

L.2 Inapplicability

1st catalyst bed equilibrium Eqn. (10.13) does not, however, apply to beds which follow:

(a) selective removal of SO₃ during H₂SO₄-making

(b) addition of air between beds.

This is because Eqns. (L.1), (L.2) and (L.3), hence Eqns. (B.14), (B.20), (B23) and (B.26) would not apply to bed 2 (and subsequent beds) if SO₃ were removed or air were added between beds 1 and 2.
Appendix M

2\textsuperscript{nd} Catalyst Bed Intercept Calculations

Chapter 15 indicates that maximum SO$_2$ oxidation in a 2\textsuperscript{nd} catalyst bed occurs where the bed's:

\begin{equation*}
\text{heatup path} \quad \text{equilibrium curve}.
\end{equation*}

The point of interception may be determined:

(a) by interpolation, Table 15.1
(b) iteratively with Excel's Goal Seek tool, described here.

M.1 Calculation Strategy

Our iteration strategy here is much like that in Appendix J. It consists of finding the temperature at which a 2\textsuperscript{nd} catalyst bed's:

\begin{equation*}
\text{equilibrium curve } \% \text{SO}_2\text{ oxidized, } \Phi^E \quad \text{is the same as its}
\end{equation*}
\begin{equation*}
\text{heatup path } \% \text{SO}_2\text{ oxidized, } \Phi.
\end{equation*}

This temperature and its equivalent \% SO$_2$ oxidized define the 2\textsuperscript{nd} catalyst bed intercept point.

All calculations in this appendix are based on the gas composition, temperature and pressure specifications in Fig. 14.2. The calculations are all per kg-mole of 1\textsuperscript{st} catalyst bed feed gas.

M.2 Specifications (Fig. 14.2)

This appendix's specifications are:

1\textsuperscript{st} catalyst bed feed gas composition:

- 10 volume\% SO$_2$
- 11 volume\% O$_2$
- 79 volume\% N$_2$

2\textsuperscript{nd} catalyst bed input gas quantities:

- 0.0692 kg-mole SO$_3$
- 0.0308 kg-mole SO$_2$
- 0.0754 kg-mole O$_2$
- 0.7900 kg-mole N$_2$

per kg-mole of 1\textsuperscript{st} catalyst bed feed gas.

2\textsuperscript{nd} catalyst bed gas input temperature and bed pressure:

700 K \quad 1.2 \text{ bar}
M.3 Worksheet

All quantities are per kg-mole of 1st catalyst bed feed gas.
The 2nd catalyst bed intercept worksheet (below) is prepared as follows:
1. 1st catalyst bed feed gas volume % SO\textsubscript{2} and volume% O\textsubscript{2} are entered in cells G3 and I3. 1st catalyst bed input kg-mole SO\textsubscript{2} is calculated in cell G5.
2. 2nd catalyst bed input gas quantities are entered in cells E8, G8, I8 and K8. They are Fig. 14.2's 1st catalyst bed intercept quantities. They are automatically copied into cells C21-C24.
3. 2nd catalyst bed gas input temperature and catalyst bed pressure are entered in cells K5 and K6.
4. An equilibrium curve intercept % SO\textsubscript{2} oxidized is suggested in cell F11 (perhaps 94% from Table 15.1).
5. Eqn. (10.13) is entered in cell A14 as shown beside the cell.
6. Steps 4 and 5 automatically calculate the cell A14 equilibrium curve temperature that is equivalent to cell F11's % SO\textsubscript{2} oxidized. The cell A14 temperature is then automatically copied into cell J30, as shown. This links the 2nd bed equilibrium curve and heatup path calculations.
7. The Appendix K heatup path matrix is entered into cells C21 to K28. Cells D28 to K28 contain enthalpy-as-a-function-of-temperature equations, Appendix K (-H\textsubscript{T} in cells D28 to G28). Cells C21 to C24 contain Fig. 14.2's 2nd catalyst bed input kg-mole SO\textsubscript{3}, SO\textsubscript{2}, O\textsubscript{2} and N\textsubscript{2}.
8. The matrix is solved as described in Appendix H. The procedure is: select cell B34, shift-arrow down to cell B41. With these cells still selected, type mmult(minverse(D21:K28),C21:C28) then simultaneously press Ctrl Shift Enter
9. Eqn. (14.1) is entered in cell I39 as shown beside it. This automatically uses step 8's results to calculate the heatup path % SO\textsubscript{2} oxidized equivalent to cell J30's (hence cell A14's) intercept temperature.
10. At this point, equilibrium curve temperature = heatup path temperature. But equilibrium curve % SO\textsubscript{2} oxidized (cell F11) ≠ heatup path % SO\textsubscript{2} oxidized (cell I39). So this is not the intercept.
The actual 2nd catalyst bed intercept value is determined by the Goal Seek calculation in Section M.4.
Table M.1. Worksheet for determining 2nd catalyst bed heatup path-equilibrium curve intercept. The non-zero 'equilibrium curve % \( \text{SO}_2 \text{ oxidized} \) - heatup path % \( \text{SO}_2 \text{ oxidized} \) value in cell G47 indicates that cell F11's suggested 94% \( \text{SO}_2 \text{ oxidized} \) is not the intercept value. The actual intercept value is calculated in Table M.2.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>2</strong>&lt;sup&gt;nd&lt;/sup&gt; CATALYST BED</td>
<td>All quantities are per kg-mole of 1&lt;sup&gt;st&lt;/sup&gt; catalyst bed feed gas</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2&lt;sup&gt;nd&lt;/sup&gt; catalyst bed feed gas specifications from Fig. 14.2</td>
<td>e. volume % ( \text{SO}_2 ) =</td>
<td>10</td>
<td>f. volume % ( \text{O}_2 ) =</td>
<td>11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1&lt;sup&gt;st&lt;/sup&gt; catalyst bed feed kg-mole ( \text{SO}_2 ) for Eqn. (14.1) = ( 0.1 \times 100 = 0.3/100 )</td>
<td>Eqn. (11.1) =</td>
<td>0.1</td>
<td>2&lt;sup&gt;nd&lt;/sup&gt; catalyst bed input gas temperature, ( \text{K} ) =</td>
<td>700</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>( \text{SO}_2 )</td>
<td>0.0692</td>
<td>( \text{SO}_2 )</td>
<td>0.0308</td>
<td>( \text{O}_2 )</td>
<td>0.0754</td>
<td>( \text{N}_2 )</td>
<td>0.79</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Suggested 2&lt;sup&gt;nd&lt;/sup&gt; catalyst bed equilibrium curve intercept % ( \text{SO}_2 ) oxidized, ( \alpha^2 ) =</td>
<td>94.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>2&lt;sup&gt;nd&lt;/sup&gt; catalyst bed equilibrium curve temperature equivalent to cell F11's % ( \text{SO}_2 ) oxidized, from Eqn. (10.13)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>( T_{750} \text{K} = (68.41 \times 0.09355 \times 0.008314 \times (\text{F11}/100) \times (100-0.5^2 \times (\text{F11}/100)) (0.5^2 \times (0.6^2) \times (0.5^2 \times (0.5^2) \times (0.5^2))) )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>(10.13)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>( T_{750} \text{K} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>2&lt;sup&gt;nd&lt;/sup&gt; catalyst bed heatup path matrix. Eqns. 14.12 to 14.18 are from Sections 14.5 and 14.6. Eqn. 14.9&lt;sup&gt;th&lt;/sup&gt; from Appendix K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Equation</td>
<td>description</td>
<td>numerical term ( \times 10^6 )</td>
<td>kg-mole ( \text{SO}_2 )</td>
<td>kg-mole ( \text{SO}_2 )</td>
<td>kg-mole ( \text{O}_2 )</td>
<td>kg-mole ( \text{N}_2 )</td>
<td>kg-mole ( \text{SO}_2 )</td>
<td>kg-mole ( \text{SO}_2 )</td>
<td>kg-mole ( \text{O}_2 )</td>
</tr>
<tr>
<td>15</td>
<td>14.2</td>
<td>input ( \text{SO}_2 ) kg-mole</td>
<td>0.0692</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>16</td>
<td>14.3</td>
<td>input ( \text{SO}_2 ) kg-mole</td>
<td>0.0308</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>17</td>
<td>14.4</td>
<td>input ( \text{O}_2 ) kg-mole</td>
<td>0.0754</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>18</td>
<td>14.5</td>
<td>input ( \text{N}_2 ) kg-mole</td>
<td>0.7900</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>19</td>
<td>14.6</td>
<td>( \text{O} ) balance</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>14.7</td>
<td>( \text{D} ) balance</td>
<td>0</td>
<td>-3</td>
<td>-2</td>
<td>-2</td>
<td>0</td>
<td>3</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>21</td>
<td>14.8</td>
<td>( \text{N} ) balance</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>22</td>
<td>14.9&lt;sup&gt;th&lt;/sup&gt;</td>
<td>enthalpy balance</td>
<td>0</td>
<td>307.6</td>
<td>273.2</td>
<td>-0.76</td>
<td>-1.97</td>
<td>-365.2</td>
<td>-274.3</td>
<td>15.04</td>
</tr>
<tr>
<td>23</td>
<td>2&lt;sup&gt;nd&lt;/sup&gt; catalyst bed input gas temperature =</td>
<td>700</td>
<td>Intercept temperature, cell A14 =</td>
<td>775.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>2&lt;sup&gt;nd&lt;/sup&gt; catalyst bed input gas temperature =</td>
<td>700</td>
<td>Intercept temperature, cell A14 =</td>
<td>775.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>31</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>Matrix results equivalent to suggested intercept temperature in cell J30 and A14 = ( (0.0311 \times 50.8787) ) (Appendix AHJJP)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>kg-mole ( \text{SO}_2 ) in</td>
<td>0.0692</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>kg-mole ( \text{SO}_2 ) in</td>
<td>0.0308</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>kg-mole ( \text{O}_2 ) in</td>
<td>0.0754</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>kg-mole ( \text{N}_2 ) in</td>
<td>0.7900</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>kg-mole ( \text{SO}_2 ) out</td>
<td>0.0948</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>kg-mole ( \text{SO}_2 ) out</td>
<td>0.0052</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>kg-mole ( \text{O}_2 ) out</td>
<td>0.0265</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>kg-mole ( \text{N}_2 ) out</td>
<td>0.7900</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>all per kg-mole of 1&lt;sup&gt;st&lt;/sup&gt; catalyst bed feed gas</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>43</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>44</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>46</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>47</td>
<td>Equilibrium curve % ( \text{SO}_2 ) oxidized - heatup path % ( \text{SO}_2 ) oxidized =</td>
<td>-0.8</td>
<td>( = \text{F11}=39 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
M.4 Goal Seek Instructions

Table M.1 is set up so that equilibrium curve temperature always = heatup path temperature. The only remaining question is at what temperature does:

\[ \text{heatup path } % \text{SO}_2 \text{ oxidized} = \text{equilibrium curve } % \text{SO}_2 \text{ oxidized?} \]

This is determined by:

1. Putting 'equilibrium curve % SO\textsubscript{2} oxidized - heatup path % SO\textsubscript{2} oxidized' in cell G47, as shown in Table M.1.

2. Using Goal Seek to adjust:

\[ \text{equilibrium curve } % \text{SO}_2 \text{ oxidized} \text{ (cell F11)} \]

until cell G47 = zero, i.e. until:

\[ \text{heatup path } % \text{SO}_2 \text{ oxidized} = \text{equilibrium curve } % \text{SO}_2 \text{ oxidized}. \]

The Goal Seek procedure is:

Tools
Goal Seek
Set Cell G47
To Value 0
Changing Cell F11
OK
OK.

The results are shown in Table M.2. The intercept point is 94.2% SO\textsubscript{2} oxidized (in cells F11 and J39), 773.2 K (in cells A14 and J30) – as is readily checked with Table 15.1.
Table M.2. Table M.1 after Goal Seek has found the intercept. It is 773.2 K (cells A14 and J30), 94.2% SO₂ oxidized (cells F11 and I39). This result is the same as that obtained by interpolating Table 15.1's temperature-% SO₂ oxidized values.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2nd CATALYST BED</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>All quantities are per kg-mole of 1st catalyst bed feed gas</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1st catalyst bed feed gas specifications from Fig. 14.2</td>
<td>e, volume% SO₂ = 10</td>
<td>l, volume% O₂ = 11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1st catalyst bed feed kg-mole SO₂ for Eqn. (14.1) = e/100 = G3/100</td>
<td>Eqn. (11.1)</td>
<td>0.1</td>
<td>2nd catalyst bed input gas temperature, K = 770</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2nd catalyst bed input kg-mole from Fig. 14.2</td>
<td>SO₂ = 0.0692</td>
<td>SO₂ = 0.0308</td>
<td>O₂ = 0.0754</td>
<td>N₂ = 0.79</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Suggested 2nd catalyst bed equilibrium curve intercept % SO₂ oxidized, θ* = 94.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>2nd catalyst bed equilibrium curve temperature equivalent to cell F11's % SO₂ oxidized, from Eqn. (10.13)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>773.2 = -498.411 + 0.0083141*[NIF11(100-F11)<em>[0.5</em>(0.93F11/100)(0.5-0.5G3/F11)(0.5K0.9) - 0.5)]</td>
<td>(10.13)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>2nd catalyst bed heatup path matrix, Eqs. 14.2 to 14.8 are from Sections 14.5 and 14.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Eqn. 14.9 is from Appendix K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>2nd catalyst bed heatup path matrix, Eqs. 14.2 to 14.8 are from Sections 14.5 and 14.6.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Eqn. 14.9 is from Appendix K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>29</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>31</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>33</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>34</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>38</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>39</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>41</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>42</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>43</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>44</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>46</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>47</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Appendix N

3rd Catalyst Bed Heatup Path Worksheet

Table N.1 is a 3rd catalyst bed heatup path worksheet. It is a copy of worksheet Table K.1* with:

(a) Eqns. (16.1) to (16.4) in place of Eqns. (14.2) to (14.5), rows 8 to 11
(b) Chapter 16's 710 K 3rd catalyst bed input gas temperature in cell F17
(c) a 715 K 3rd bed heatup path temperature in cell J17
(d) 3rd instead of 2nd in all captions.

With these changes, the worksheet automatically gives the result that 715 K in the 3rd catalyst bed is generated by a total of 95.9% SO₂ oxidation (including oxidation in the preceding 1st and 2nd beds), cell H25.

The table's matrix doesn't have to be re-solved for this or any other calculation. A few other heatup path points are:

<table>
<thead>
<tr>
<th>M</th>
<th>Fig. 16.2 level L temperature, K</th>
<th>% SO₂ oxidized at level L</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>710</td>
<td>94.20</td>
</tr>
<tr>
<td>32</td>
<td>712</td>
<td>94.89</td>
</tr>
<tr>
<td>33</td>
<td>714</td>
<td>95.57</td>
</tr>
<tr>
<td>34</td>
<td>716</td>
<td>96.25</td>
</tr>
</tbody>
</table>

*Steps for copying the worksheet are:
Edit
Move or Copy Sheet
To book: (new book)
Create a copy ✓
OK.

Changes (a) – (d) are then made. Finally, the worksheet is saved in the Chapter 16 file with an appropriate name, e.g. Table N.1.
Table N.1. 3rd catalyst bed heatup path matrix with enthalpy equations in cells D15-K15. The numerical quantities in cells C8-C11 are Table M.2's 2nd catalyst bed intercept quantities.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>All calculations are based on 1 kg-mole of 1st catalyst bed feed gas.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>kg-mole SO(_2) in 1 kg-mole of 1st catalyst bed feed gas</td>
<td>0.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>3rd catalyst bed matrix</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Equation</td>
<td>description</td>
<td>numerical term</td>
<td>kg-mole SO(_3)</td>
<td>kg-mole SO(_2)</td>
<td>kg-mole O(_2)</td>
<td>kg-mole N(_2)</td>
<td>kg-mole SO(_3)</td>
<td>kg-mole SO(_2)</td>
<td>kg-mole O(_2)</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>8</td>
<td>16.1</td>
<td>input SO(_2) kg-mole</td>
<td>0.0942</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>16.2</td>
<td>input SO(_2) kg-mole</td>
<td>0.0058</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>16.3</td>
<td>input O(_2) kg-mole</td>
<td>0.0629</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>16.4</td>
<td>input N(_2) kg-mole</td>
<td>0.7900</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>14.6</td>
<td>S balance</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>13</td>
<td>14.7</td>
<td>O balance</td>
<td>0</td>
<td>-3</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>14</td>
<td>14.8</td>
<td>N balance</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>15</td>
<td>14.9</td>
<td>enthalpy balance</td>
<td>0</td>
<td>369.9</td>
<td>277.7</td>
<td>-12.87</td>
<td>-12.28</td>
<td>-369.5</td>
<td>-277.4</td>
<td>13.04</td>
</tr>
<tr>
<td>16</td>
<td></td>
<td>Fig. 16.2 input gas temperature = 710</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td></td>
<td>heatup path temperature = 715</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td></td>
<td>Heatup path result per kg-mole of 1st catalyst bed feed gas</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>kg-mole SO(_3) in</td>
<td>0.0942</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>kg-mole SO(_2) in</td>
<td>0.0058</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>kg-mole O(_2) in</td>
<td>0.0629</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>kg-mole N(_2) in</td>
<td>0.7900</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td></td>
<td>heatup path temper-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td></td>
<td>ature in 3rd catalyst bed</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>kg-mole SO(_3) out</td>
<td>0.0959</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>kg-mole N(_2) out</td>
<td>0.7900</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Heating path result per kg-mole of 1st catalyst bed feed gas:

\[-(0.0311 * F17 - 9.797)\]
Appendix O

3rd Catalyst Bed Intercept Worksheet

Table O.1 is a 3rd catalyst bed heatup path-equilibrium curve intercept worksheet. It is a copy of Table M.2 with:

(a) Fig. 16.2's 3rd catalyst bed input gas quantities in cells E8, G8, I8 and K8

(b) Eqns. (16.1) to (16.4) in place of Eqns. (14.2) to (14.5), rows 21 to 24

(c) Fig. 16.2's specified 710 K 3rd catalyst bed input gas temperature in cell K5 and its specified 1.2 bar 3rd bed pressure in cell K6

(d) 3rd instead of 2nd in all captions.

The worksheet is operated exactly like worksheet Table M.2. The result is shown in Table O.1. It indicates that the 3rd catalyst bed intercept point under Fig. 16.2's specified conditions is:

\[ 721.1 \text{ K, } 98.0\% \text{ } SO_2 \text{ oxidized (after 3 beds).} \]

*Copied as described in Appendix N.*
Table O.1. 3rd catalyst bed intercept worksheet after Appendix M's Goal Seek instructions have been carried out. The intercept is shown to be 721.1 K, 98.0% SO₂ oxidized – which gives a zero value in cell G47.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3rd CATALYST BED</td>
<td>All quantities are per kg-mole of 1st catalyst bed feed gas.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1st catalyst bed feed gas composition from Fig. 11.2</td>
<td>e, volume% SO₂ = 10 f, volume% O₂ = 11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1st catalyst bed kg-mole SO₂ (for Eqn. (14.1)) = e/100 = 0.0942 (Eqn. (11.1))</td>
<td>0.1 3rd catalyst bed input gas temperature, K = 710</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3rd catalyst bed pressure P₁ bar = 1.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>3rd catalyst bed input kg-mole from Section 15.2.4 SO₂ = 0.0942 SO₂ = 0.0058 O₂ = 0.0629 N₂ = 0.79</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Suggested 3rd catalyst bed equilibrium curve intercept % SO₂ oxidized, δ₈ = 98.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>3rd catalyst bed equilibrium curve temperature equivalent to cell F11% % SO₂ oxidized, Eqn. (10.13)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>721.1 = 0.0942x(0.0058+0.00343x10^5x0^2) = 721.1 (110-0.5x3) = 721.1 (110-0.5x3) = 721.1 (110-0.5x3) = 721.1 (110-0.5x3) = 721.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>3rd catalyst bed heatup path matrix. Eqns. 14.8 to 14.8 are from Section 14.6. Eqns. 14.9 is from Appendix K. Eqns. 16.1 to 16.4 are from Section 16.2.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Equation</td>
<td>description</td>
<td>numerical term</td>
<td>kg-mole SO₂</td>
<td>kg-mole SO₂</td>
<td>kg-mole O₂</td>
<td>kg-mole N₂</td>
<td>kg-mole SO₂</td>
<td>kg-mole SO₂</td>
<td>kg-mole O₂</td>
</tr>
<tr>
<td>11</td>
<td>16.1</td>
<td>input SO₂ kg-mole</td>
<td>0.0942</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>16.2</td>
<td>input SO₂ kg-mole</td>
<td>0.0058</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>13</td>
<td>16.3</td>
<td>input O₂ kg-mole</td>
<td>0.0029</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>14</td>
<td>16.4</td>
<td>input N₂ kg-mole</td>
<td>0.7900</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>14.6</td>
<td>S balance</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>16</td>
<td>14.7</td>
<td>O balance</td>
<td>0</td>
<td>-3</td>
<td>-2</td>
<td>-2</td>
<td>0</td>
<td>3</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>17</td>
<td>14.8</td>
<td>N balance</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>18</td>
<td>14.9</td>
<td>enthalpy balance</td>
<td>0</td>
<td>369.9</td>
<td>277.7</td>
<td>12.87</td>
<td>12.28</td>
<td>369.1</td>
<td>277.1</td>
<td>13.24</td>
</tr>
<tr>
<td>19</td>
<td>3rd catalyst bed input gas temperature = 710</td>
<td>intercept temperature, cell A14 = 721.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>=K5</td>
<td>=A14</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>Matrix results equivalent to suggested intercept temperature in cell J20 (and A14) = (0.2311x10^-9x797) (Appendix G)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>kg-mole SO₂ in</td>
<td>0.0942</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>kg-mole SO₂ in</td>
<td>0.0058</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>kg-mole O₂ in</td>
<td>0.0029</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>kg-mole N₂ in</td>
<td>0.7900</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>kg-mole SO₂ out</td>
<td>0.0980</td>
<td>heatup path % SO₂ oxidized (δ) equivalent to 3rd catalyst bed intercept temperature in cell J20 = 98.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>kg-mole SO₂ out</td>
<td>0.0020</td>
<td>1st catalyst bed feed gas kg-mole SO₂ - 3rd catalyst bed kg-mole SO₂ out</td>
<td>1.100 = 98.0 = (G5x1.3)+(G4*100) (14.1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>kg-mole O₂ out</td>
<td>0.0610</td>
<td>1st catalyst bed feed gas kg-mole SO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>kg-mole N₂ out</td>
<td>0.7900</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>all per kg-mole of 1st catalyst bed feed gas</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>Goal Seek calculation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>Equilibrium curve % SO₂ oxidized - heatup path % SO₂ oxidized = 0.0 = F11-139</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

347
Appendix P

Effect of SO₃ in Fig. 10.1 Feed Gas on Equilibrium Equations

About 2% of (SO₂ + SO₃) in sulfur-burning furnace/waste heat boiler offgas is SO₃. Sulfur burning offgas isn't water quenched/cleaned so its SO₃ isn't absorbed. It enters the Fig. 10.1 catalyst bed.

This appendix describes how SO₃-in-feed-gas affects equilibrium Equations (10.12) and (10.13).

Including SO₃, Fig. 10.1’s feed gas contains:

\[
\begin{align*}
&d \quad \text{volume\% SO₃} \\
e \quad \text{" " SO₂} \\
f \quad \text{" " O₂} \\
100 - d - e - f \quad \text{" " N₂.}
\end{align*}
\]

Per kg-mole of Fig. 10.1 feed gas, the input molar quantities are:

\[
\begin{align*}
\frac{d}{100} & \quad \text{kg-mole SO₃ (Section B.3.1)} \\
\frac{e}{100} & \quad \text{" " SO₂} \\
\frac{f}{100} & \quad \text{" " O₂} \\
1 - \frac{d}{100} - \frac{e}{100} - \frac{f}{100} & \quad \text{" " N₂.}
\end{align*}
\]

P.1 Molar balances

Sulfur

SO₃ in Fig. 10.1 feed gas changes Appendix B’s sulfur balance:

\[
\text{kg-mole S in feed gas} = \text{kg-mole S in oxidized gas} \quad (B.11)
\]

to:

\[
1 \times \frac{d}{100} + 1 \times \frac{e}{100} = 1 \times n_{SO₃} + 1 \times n_{SO₂}
\]

or:
\[ \frac{d}{100} + \frac{e}{100} = n_{SO_3} + n_{SO_2} \]

or:

\[ n_{SO_2} = \frac{d}{100} + \frac{e}{100} - n_{SO_3} \]  \hspace{1cm} (P.1)

**Oxygen**

SO$_3$ in Fig. 10.1 feed gas changes its oxygen balance:

\[ \text{kg-mole O in feed gas} = \text{kg-mole O in oxidized gas} \]  \hspace{1cm} (B.15).

to:

\[ 3 \frac{d}{100} + 2 \frac{e}{100} + 2 \frac{f}{100} = 3n_{SO_3} + 2n_{SO_2} + 2n_{O_2} \]

or:

\[ \frac{3}{2} \left( \frac{d}{100} \right) + \frac{e}{100} + \frac{f}{100} = \frac{3}{2}n_{SO_3} + n_{SO_2} + n_{O_2} \]

or:

\[ n_{O_2} = \frac{3}{2} \left( \frac{d}{100} \right) + \frac{e}{100} + \frac{f}{100} - \frac{3}{2}n_{SO_3} - n_{SO_2} \]

Further, because

\[ n_{SO_2} = \frac{d}{100} + \frac{e}{100} - n_{SO_3} \]  \hspace{1cm} (Eqn. [P.1])

\[ n_{O_2} = \frac{3}{2} \left( \frac{d}{100} \right) + \frac{e}{100} + \frac{f}{100} - \frac{3}{2}n_{SO_3} - \left( \frac{d}{100} + \frac{e}{100} - n_{SO_3} \right) \]

or:

\[ = \frac{f}{100} + \frac{1}{2} \frac{d}{100} - \frac{1}{2}n_{SO_3} \]  \hspace{1cm} (P.2)

**Nitrogen**

SO$_3$ in feed gas changes N balance Eqn.(B.22) slightly to:

\[ 2 \left( 1 - \frac{d}{100} - \frac{e}{100} - \frac{f}{100} \right) = 2n_{N_2} \]

or:

\[ n_{N_2} = 1 - \frac{d}{100} - \frac{e}{100} - \frac{f}{100} \]  \hspace{1cm} (P.3).
P.2 Total kg-mole of oxidized gas

Total kg-mole of oxidized gas is still given by Eqn. (B.24), i.e.:

\[ n_t = n_{SO_3} + n_{SO_2} + n_{O_2} + n_{N_2} \]

Combining this with Eqns. (P.1), (P.2) and (P.3) gives:

\[
\frac{d}{100} + \frac{e}{100} - n_{SO_3} + \left( \frac{1}{2} \frac{d}{100} - \frac{1}{2} n_{SO_3} \right) + \left( \frac{1}{2} \frac{e}{100} - \frac{f}{100} \right) = 1 + \frac{1}{2} \frac{d}{100} - \frac{1}{2} n_{SO_3}
\]

(P.4).

P.3 Mole fractions in oxidized gas

With SO₃-in-feed gas, the mole fractions of SO₃, SO₂ and O₂ in Fig. 10.1 oxidized gas are:

\[
X_{SO_3} = \frac{n_{SO_3}}{n_t} = \frac{n_{SO_3}}{1 + \frac{1}{2} \frac{d}{100} - \frac{1}{2} n_{SO_3}}
\]

from Eqn. (P.4) (P.5)

\[
X_{SO_2} = \frac{n_{SO_2}}{n_t} = \frac{d}{100} + \frac{e}{100} - n_{SO_3} \left( 1 + \frac{1}{2} \frac{d}{100} - \frac{1}{2} n_{SO_3} \right)
\]

from Eqns. (P.1) and (P.4) (P.6)

\[
X_{O_2} = \frac{n_{O_2}}{n_t} = \frac{f}{100} + \frac{1}{2} \frac{d}{100} - \frac{1}{2} n_{SO_3} \left( 1 + \frac{1}{2} \frac{d}{100} - \frac{1}{2} n_{SO_3} \right)
\]

from Eqns. (P.2) and (P.4) (P.7).

P.4 New equilibrium equation

With the Eqns. (P.5) to (P.7) expressions for mole fraction, equilibrium Eqn. (B.4)

\[
K_E = \frac{X_{SO_3}^E}{X_{SO_2}^E (X_{O_2}^E)^{1/2}}
\]

(B.4).

becomes:
\[ K_E = \left( \frac{\frac{n_{SO_3}^E}{1 + \frac{1}{2} \frac{d}{100} - \frac{1}{2} n_{SO_3}^E}}{1 + \frac{1}{2} \frac{d}{100} - \frac{1}{2} n_{SO_3}^E} \right) \cdot \left( \frac{\frac{f}{100} + \frac{1}{2} \frac{d}{100} - \frac{1}{2} n_{SO_3}^E}{1 + \frac{1}{2} \frac{d}{100} - \frac{1}{2} n_{SO_3}^E} \right) \cdot P_t^{-\frac{1}{2}} \] (P.8)

or, multiplying top and bottom by \( 1 + \frac{1}{2} \frac{d}{100} - \frac{1}{2} n_{SO_3}^E \)

\[ K_E = \left( \frac{n_{SO_3}^E}{1 + \frac{1}{2} \frac{d}{100} - \frac{1}{2} n_{SO_3}^E} \right) \cdot \left( \frac{f}{100} + \frac{1}{2} \frac{d}{100} - \frac{1}{2} n_{SO_3}^E \right) \cdot P_t^{-\frac{1}{2}} \] (P.9)

or, multiplying top and bottom by: \( 1 + \frac{1}{2} \frac{d}{100} - \frac{1}{2} n_{SO_3}^E \)

\[ K_E = \left( \frac{n_{SO_3}^E}{1 + \frac{1}{2} \frac{d}{100} - \frac{1}{2} n_{SO_3}^E} \right) \cdot \left( \frac{f}{100} + \frac{1}{2} \frac{d}{100} - \frac{1}{2} n_{SO_3}^E \right) \cdot P_t^{-\frac{1}{2}} \] (P.10)

or:

\[ K_E = \left( \frac{n_{SO_3}^E}{\frac{d}{100} + \frac{e}{100} - n_{SO_3}^E} \right) \cdot \left( \frac{\frac{f}{100} + \frac{1}{2} \frac{d}{100} - \frac{1}{2} n_{SO_3}^E}{\frac{f}{100} + \frac{1}{2} \frac{d}{100} - \frac{1}{2} n_{SO_3}^E} \right) \cdot P_t^{-\frac{1}{2}} \] (P.10)

Eqn. (P.10) is written in terms of \( n_{SO_3}^E \). The next few sections show how it is expressed in terms of % \( SO_2 \) oxidized.
P.5 \%SO\textsubscript{2} oxidized in Equilibrium Equation

Equilibrium \%SO\textsubscript{2} oxidized with SO\textsubscript{3} in feed gas is defined exactly as in Section B.8 and Chapter 10. The definition is:

\[
\text{Equilibrium } \%\text{SO}_2 \text{ oxidized} = \Phi^E = \frac{\text{kg-mole SO}_2 \text{ - kg-mole SO}_3 \text{ in oxidized gas}}{\text{kg-mole SO}_2 \text{ in feed gas}} \times 100
\]

or:

\[
\Phi^E = \left( \frac{e}{100} - \frac{n_{SO_3}^E}{100} \right) \times 100
\]

(Eq. (B.36))

Eqn. (B.36) is expressed in terms of \(n_{SO_3}^E\) by combining it with the equilibrium form of Eqn. (P.1), i.e.:

\[
n_{SO_2}^E = \frac{d}{100} + \frac{e}{100} - n_{SO_3}^E
\]

to give:

\[
\text{Equilibrium } \%\text{SO}_2 \text{ oxidized} = \Phi^E = \left( \frac{e}{100} - \frac{d}{100} + \frac{e}{100} - n_{SO_3}^E \right) \times 100
\]

(P.11)

or:

\[
\Phi^E = \left( \frac{n_{SO_3}^E - \frac{d}{100}}{e} \right) \times 100
\]

(P.12)

or:

\[
\left( \frac{e}{100} \right) \times \Phi^E = n_{SO_3}^E - \frac{d}{100}
\]

(P.13)

or:

\[
n_{SO_3}^E = \frac{d}{100} + \left( \frac{e}{100} \right) \times \Phi^E
\]

(P.14)

Substituting the right side of Eqn. (P.14) for \(n_{SO_3}^E\) in Eqn. (P.10) gives:
\[ KE = \left( \frac{d}{100} + \left( \frac{e}{100} \right) \frac{\Phi^E}{100} \right) \left( 1 + \frac{d}{2 \cdot 100} \right) \left( \frac{d}{100} + \left( \frac{e}{100} \right) \frac{\Phi^E}{100} \right) \frac{1}{2} * P_t^{1/2} \]  

(P.15)

or, rearranging the bottom left term:

\[ KE = \left( \frac{d}{100} + \left( \frac{e}{100} \right) \frac{\Phi^E}{100} \right) \left( 1 + \frac{e}{2 \cdot 100} \right) \left( \frac{f}{100} + \left( \frac{e}{100} \right) \frac{\Phi^E}{100} \right) \frac{1}{2} * P_t^{1/2} \]  

(P.16)

or:

\[ KE = \left( \frac{d}{100} + \left( \frac{e}{100} \right) \frac{\Phi^E}{100} \right) \left( 1 - \frac{1}{2} \cdot \frac{e}{100} \right) \left( \frac{f}{100} - \frac{1}{2} \cdot \frac{e}{100} \right) \frac{1}{2} * P_t^{1/2} \]  

(P.17)

and, multiplying top and bottom by 100:

\[ KE = \left( \frac{d + e*\Phi^E}{100} \right) \left( 1 - \frac{1}{2} \cdot \frac{e}{100} \right) \left( \frac{f}{100} - \frac{1}{2} \cdot \frac{e}{100} \right) \frac{1}{2} * P_t^{1/2} \]  

(P.18)

or, multiplying top and bottom by \(100^2\)

\[ KE = \left( \frac{d + e*\Phi^E}{100} \right) \left( 100 - \frac{1}{2} \cdot e*\Phi^E \right) \frac{1}{2} * P_t^{1/2} \]  

(P.19)

Comparison of Eqn. (P.19) with Eqns. (B41) and (10.12) shows that the only difference between the two is the presence of \(d\) (volume\% SO\(_3\) in feed gas) in the top left term.
The meanings of the terms are also clear:

\[ e \cdot \frac{\Phi^E}{100} \]

represents the equilibrium amount of SO\(_2\) oxidized to SO\(_3\) in the catalyst bed

upper left term represents equilibrium production of SO\(_3\) in the catalyst bed + the amount of SO\(_3\) in the original feed gas

lower left term represents amount of SO\(_2\) remaining after equilibrium oxidation of SO\(_2\) to SO\(_3\) in the catalyst bed

upper right term represents the total amount of gas remaining after equilibrium oxidation of SO\(_2\) to SO\(_3\) because each mole of SO\(_2\) oxidized consumes 0.5 mole of O\(_2\)

lower right term represents the amount of O\(_2\) remaining after equilibrium oxidation of SO\(_2\) to SO\(_3\) because each mole of SO\(_2\) oxidized consumes 0.5 mole of O\(_2\).

**P.6 Equilibrium % SO\(_2\) Oxidized as a Function of Temperature**

The effect of temperature on equilibrium % SO\(_2\) oxidized is determined by combining Eqns. (P.19) and (10.11), i.e.:

\[ T_E = \frac{-B}{A + R\ln(K_E)} \]

(as described in Section 10.3)

where:

- \( T_E \) = equilibrium temperature
- \( A \) and \( B \) = empirical constants for relating \( \Delta_r G_{SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_3(g)}^o \) to temperature,

Section 10.3 and Appendix C:

\[ A = 0.09357 \text{ MJ kg-mole SO}_2^{-1} \text{ K}^{-1} \]
\[ B = -98.41 \text{ MJ/kg-mole SO}_2 \]

The result is:

\[ T_E = \frac{-B}{A + R\ln \left( \frac{d + e \cdot \frac{\Phi^E}{100}}{e \cdot \frac{1 - \frac{\Phi^E}{100}}{100}} \right) \left( \frac{100 - \frac{1}{2} \cdot e \cdot \frac{\Phi^E}{100}}{\frac{f - \frac{1}{2} \cdot e \cdot \frac{\Phi^E}{100}}{100}} \right)^{\frac{1}{2}} \}

(17.1).
Appendix Q

**SO₃-in-Feed-Gas Intercept Worksheet**

Table Q.1 is a 1st catalyst bed worksheet for calculating heatup path-equilibrium curve intercepts with SO₃-in-feed-gas. The worksheet is similar to those in Appendices M and O.

**Preparation instructions**
1. Enter the data, equations and matrix as shown. This might be done by (i) copying Table O.1 and (ii) making appropriate changes to the copy. Copying instructions are given in Appendix N.
2. Suggest an equilibrium curve % SO₂ oxidized value in cell F11, say 65%.
3. Enter equilibrium curve Eqn. (17.1) into cell A14 as shown, not Eqn. (10.13).
4. Solve the matrix as described in Appendix M. Once solved, the matrix doesn't need re-solving.

**Operating instructions**
1. Find the intercept by means of Section M.4's Goal Seek instructions.

**Result**
The result is as shown in the worksheet – the intercept is 890.3 K, 69.7% SO₂ oxidized.

**Other calculations**
Catalyst bed pressure, feed gas composition and feed gas input temperature can now be changed at will. Only the Goal Seek procedure needs to be repeated to find the new intercept.

**Comment**
SO₃, SO₂, O₂ and N₂ input quantities are represented in Table Q.1's matrix by Eqns. (17.2), (17.3), (11.2) and (11.3). A more general representation is:

\[
\text{kg-mole SO₃ in} = E8 \quad \text{kg-mole SO₂ in} = G8 \quad \text{kg-mole O₂ in} = I8 \quad \text{kg-mole N₂ in} = K8
\]

where E8 etc. are cell designations

This causes any change in feed gas composition (Cells E2, G2, I2, K2) to be reflected in the matrix. It allows new intercepts to be calculated at will (using only Goal Seek).
Table Q.1. 1st catalyst bed intercept calculation worksheet with SO₃ in feed gas. The use of Eqn. (17.1) in cell A14 is notable. Cells D28 to G28 contain \( \frac{f}{F} \) values. Cells H28 to K28 contain \( H \) values.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><strong>1ST CATALYST BED</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>\textbf{1st bed feed gas specification, Section 17.1.2}</td>
<td>( d \text{, volume}% \text{SO}_2 = 0.2 )</td>
<td>( e \text{, volume}% \text{SO}_3 = 0.8 )</td>
<td>( f \text{, volume}% \text{O}_2 = 11 )</td>
<td>( \text{volume}% \text{N}_2 = 79 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>( 1st \text{ catalyst bed feed kg-mole} \text{SO}_2 \text{(Eqn. (14.1))} = e(100 - G3/100) \text{ (Eqn. (17.2))} )</td>
<td>0.098</td>
<td>1st catalyst bed \text{input gas temperature, K} = 890</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>( 1st \text{ catalyst bed input kg-mole from above feed gas specification, Eqn. (17.2)} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>( \text{SO}_2 = 0.002 \text{ kg-mole} )</td>
<td>( \text{SO}_3 = 0.098 \text{ kg-mole} )</td>
<td>( \text{O}_2 = 0.11 \text{ kg-mole} )</td>
<td>( \text{N}_2 = 0.79 \text{ kg-mole} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>( \text{kg-mole gas} = a(100) + G3/100 )</td>
<td>( a = 890/100 = G3/100 )</td>
<td>( &lt;6100 &gt;100 &lt;6100 &gt;100 &lt;K3/100 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>( 1st \text{ catalyst bed pressure, atm} = 1.2 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>( \text{Suggested equilibrium curve intercept } % \text{SO}_3 \text{ oxidized, } a^* = 65.7 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>( \text{Equilibrium curve temperature equivalent to cell F11's } % \text{SO}_3 \text{ oxidized, from Eqn. (17.1)} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>( 890.3 )</td>
<td>( = (994.1)(0.0935+0.083141/(E3+G3/F11/100)(G3/(1.1F11/100))(G100-0.2(73/F11/100)(3.52(32/F11/100)<em>(0.5</em>H)*0.5))) )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>( \text{feed gas temperature } = 690 \text{ K} )</td>
<td>( \text{intercept temperature, cell A14 } = 890.3 \text{ K} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>( \text{Matrix results equivalent to suggested intercept temperature in cell J32 (and A14)} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>( \text{kg-mole SO}_2 \text{ ln} = 0.0020 )</td>
<td>( \text{kg-mole SO}_3 \text{ ln} = 0.0880 )</td>
<td>( \text{kg-mole O}_2 \text{ ln} = 0.1100 )</td>
<td>( \text{kg-mole N}_2 \text{ ln} = 0.7900 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>( \text{kg-mole SO}_2 \text{ out} = 0.0270 )</td>
<td>( \text{kg-mole SO}_3 \text{ out} = 0.0297 \text{ kg-mole SO}_2 \text{ ln} \times \text{kg-mole SO}_3 \text{ ln} \times 100 = 69.7 )</td>
<td>( = (G5-B39)/(G5*100) )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>( \text{kg-mole O}_2 \text{ out} = 0.0759 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>( \text{kg-mole N}_2 \text{ out} = 0.7900 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>( \text{all per kg-mole of 1st catalyst bed feed gas} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>( \text{Goal: Seek calculation} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>( \text{Equilibrium curve } % \text{SO}_3 \text{ oxidized - heatup path } % \text{SO}_3 \text{ oxidized = 0.0 } )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

357
Appendix R

CO$_2$- and SO$_3$-in-Feed-Gas Intercept Worksheet

Table R.1 is a worksheet for calculating 1$^\text{st}$ catalyst bed heatup path-equilibrium curve intercepts with CO$_2$ and SO$_2$ in feed gas. It is similar to that in Appendix Q.

This is the final form of our 1$^\text{st}$ catalyst bed worksheets. It can be used for all of the book's 1$^\text{st}$ catalyst bed calculations.

**Preparation instructions**

1. Enter the data, equations and matrix as shown. This might be done by (i) copying Table Q.1 and by (ii) making appropriate changes to the copy. CO$_2$ enlarges the matrix so that it has to be re-solved (once) as described in Appendix H.
2. Suggest an equilibrium curve % SO$_2$ oxidized value in cell F11, say 65%.
3. Enter Eqn. (17.1) into cell A14, as shown.
4. Solve the matrix as described in Appendix H.

The worksheet is now ready to operate.

**Operating instructions**

1. Find the intercept using Section M.4's Goal Seek instructions.

**Result**

As shown, the intercept with 10% CO$_2$ in feed gas is:

\[ 887.2 \text{ K}, \ 71.0\% \text{ SO}_2 \text{ oxidized}. \]

**Other Calculations**

The worksheet is readily used for other specified bed pressures and input gas compositions and temperatures. Once the new data are entered, only Goal Seek is required.
Table R.1. 1st catalyst bed intercept calculations with SO₃ and CO₂ in feed gas. Note the 2 new CO₂ columns, new input CO₂ and C balance rows and 2 new CO₂ result rows. The use of Eqn (17.1) in cell A14 is notable. Cells D28-H28 contain -H⁺ values. Cells I28-M28 contain H⁺ values.

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
<th>K</th>
<th>L</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H⁺ Catalyst Bed</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>All quantities are per kg-mole of 1st catalyst bed feed gas</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1st bed feed gas specification, Section 17.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1st catalyst bed feed kg-mole SO₂ (f Eqn. (14.1)) = 0.0100 x G3/100 (E 11.1) 0.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>feed gas temperature, K = 880</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>bed gas pressure, bar = 1.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1st catalyst bed feed kg-mole from feed gas specification, Eqn. (11.1) etc.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Suggested equilibrium curve intercept % SO₂ oxidized, D⁰⁺ = 71.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Equilibrium temperature equivalent to cell F11% % SO₂ oxidized, from Eqn. (17.1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>887.2 = (68.41)0.09357 + 0.005341 H2(1.03+G3/F11/100) [(1.0-F11/100) x (3.5+0.5G3/F11/100)] x (0.5)x 0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>(17.1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>1st Catalyst Bed heatup path matrix (in means 'in input gas', out means 'in intercept gas')</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>18</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Equation</td>
<td>Description</td>
<td>numerical term</td>
<td>kg-mole SO₂ in</td>
<td>kg-mole SO₂ in</td>
<td>kg-mole SO₂ out</td>
<td>kg-mole O₂ in</td>
<td>kg-mole CO₂ out</td>
<td>kg-mole SO₂ out</td>
<td>kg-mole CO₂ out</td>
<td>kg-mole N₂ out</td>
<td>kg-mole CO₂ out</td>
</tr>
<tr>
<td>17</td>
<td>11.1</td>
<td>input SO₂ kg-mole</td>
<td>0.1000</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>18</td>
<td>11.2</td>
<td>input O₂ kg-mole</td>
<td>0.1100</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>19</td>
<td>17.8</td>
<td>input N₂ kg-mole</td>
<td>0.8000</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>17.4</td>
<td>input CO₂ kg-mole</td>
<td>0.1000</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>21</td>
<td>14.6</td>
<td>S balance</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>22</td>
<td>17.6</td>
<td>O balance</td>
<td>0</td>
<td>-3</td>
<td>-2</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>23</td>
<td>11.6</td>
<td>N balance</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>24</td>
<td>17.5</td>
<td>C balance</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>25</td>
<td>17.7</td>
<td>enthalpy balance</td>
<td>0</td>
<td>371.3</td>
<td>279.7</td>
<td>-1.22</td>
<td>-1.66</td>
<td>376.2</td>
<td>357.2</td>
<td>266.5</td>
<td>16.78</td>
<td>17.80</td>
</tr>
<tr>
<td>26</td>
<td>28</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>Matrix results equivalent to intercept temperature in cell J30 (and A14)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>29</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>feed gas temperature = 880</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>31</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>heatup path % SO₂ oxidized (b) equivalent to intercept temperature in cell J30 and A14 =</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>kg-mole SO₂ in</td>
<td>0.0000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>kg-mole SO₂ out</td>
<td>0.0710</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>kg-mole O₂ in</td>
<td>0.1100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>kg-mole O₂ out</td>
<td>0.0745</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>kg-mole N₂ in</td>
<td>0.6900</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>kg-mole N₂ out</td>
<td>0.8900</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>kg-mole CO₂ in</td>
<td>0.1000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>kg-mole CO₂ out</td>
<td>0.1000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>all per kg-mole of 1st catalyst bed feed gas</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>Goal Seek calculation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>Equilibrium curve % SO₂ oxidized - heatup path % SO₂ oxidized =</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>44</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>46</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>47</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

359
Appendix S

3-Catalyst-Bed 'Converter' Calculations#

All calculations in this appendix are per kg-mole of 1st catalyst bed feed gas. They are based on the specifications in Table 18.1. This appendix shows how 3-catalyst-bed 'converter' calculations are done. Three areas in the same Excel worksheet are used, Tables S.1, S.2 and S.3. The 3 beds are linked by kg-mole SO₃, SO₂, O₂, N₂ and CO₂ passing between beds 1 and 2 and beds 2 and 3.

Each area is arranged so that the same cells in all three areas have the same meaning. For example, cells K6, AK6 and BK6 all contain catalyst bed pressure.

The objectives of the 3-bed calculations are to determine, for any set of Table 18.1 specifications:

(a) the percentage of feed SO₂ that is oxidized to SO₃ after the feed gas has passed through 3 catalyst beds

(b) kg-mole of SO₃, SO₂, O₂, N₂ and CO₂ departing the 3rd catalyst bed. These kg-mole values are used for Chapter 19's double contact acid plant calculations.

S.1 1st Catalyst Bed Calculations (Cells A1 through M47)

The objectives of the 1st catalyst bed worksheet area are to calculate:

(a) 1st bed heatup path-equilibrium curve intercept temperature and % SO₂ oxidized

(b) kg-mole of SO₃, SO₂, O₂, N₂ and CO₂ in the 1st bed intercept gas, per kg-mole of feed gas. These kg-mole pass between the 1st and 2nd catalyst beds.

Setup and Operation

The 1st catalyst bed worksheet area is set up exactly like Table R.1. It may be copied from that table as described in Appendix N. Only the feed gas composition specification is different, Table 18.1. The intercept is found by Section M.4's Goal Seek procedure (Appendix M). The results are 893.3 K, 69.2 % SO₂ oxidized and:

0.0692 kg-mole SO₃  0.0308 kg-mole SO₂  0.0754 kg-mole O₂  0.79 kg-mole N₂  0 kg-mole CO₂

in the intercept gas (as confirmed by Section 12.2).

These intercept quantities are automatically copied into the 2nd catalyst bed worksheet area as described in the next section.

# A 4th catalyst bed worksheet is added at the end of this appendix. It is used to prepare Fig. 19.7.
<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
<th>K</th>
<th>L</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TABLE 5.1, 1st CATALYST BED</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>All quantities are per kg-mole of 1st catalyst bed feed gas</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3. bed feed gas specification, Table 18.1</td>
<td>d,vol% SO₂ = 0</td>
<td>e,vol% SO₂ = 10</td>
<td>f,vol% O₂ = 11</td>
<td>vol% N₂ = 79</td>
<td>vol% CO₂ = 0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1st catalyst bed feed kg-mole SO₂ (for Eqn. (14.1)) = a/100 = G3/100 (Eqn. 11.1)</td>
<td>0.1</td>
<td>feed gas temperature, K = 690</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>catalyst bed gas pressure, bar = 1.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1st catalyst bed feed gas kg-mole from feed gas specification, Eqn. (11.1) etc.</td>
<td>SO₂ = 0</td>
<td>SO₂ = 0.1</td>
<td>O₂ = 0.11</td>
<td>N₂ = 0.79</td>
<td>CO₂ = 0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Suggested equilibrium curve intercept % SO₂ oxidized, 0θ = 69.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Equilibrium curve temperature equivalent to cell F11’s % SO₂ oxidized, Eqn. (17.1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>893.3 = [-(0.41)×(0.9)^357+0.008314×LN((E3+G3+F11/100)/G3)] ×((100-0.5×G3+F11/100)/(0.5×G3+F11/100)) = (17.1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>17.1 catalyst bed heattup path matrix (θ means ‘in input gas’, out means ‘in intercept gas’):</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Equation</td>
<td>description</td>
<td>number</td>
<td>kg-mole SO₂ in</td>
<td>kg-mole SO₂ out</td>
<td>kg-mole O₂ in</td>
<td>kg-mole O₂ out</td>
<td>kg-mole N₂ in</td>
<td>kg-mole N₂ out</td>
<td>kg-mole CO₂ in</td>
<td>kg-mole CO₂ out</td>
<td>kg-mole CO₂ out</td>
</tr>
<tr>
<td>17</td>
<td></td>
<td>input SO₂ kg-mole</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>18</td>
<td></td>
<td>input SO₂ kg-mole</td>
<td>0.1000</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>19</td>
<td></td>
<td>input O₂ kg-mole</td>
<td>0.1100</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td>input N₂ kg-mole</td>
<td>0.7900</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>21</td>
<td></td>
<td>input CO₂ kg-mole</td>
<td>0.0000</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>22</td>
<td></td>
<td>balance</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>23</td>
<td></td>
<td>D balance</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>24</td>
<td></td>
<td>D balance</td>
<td>0</td>
<td>2</td>
<td>2</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>25</td>
<td></td>
<td>N balance</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>26</td>
<td></td>
<td>C balance</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>27</td>
<td></td>
<td>enthalpy balance</td>
<td>371.3</td>
<td>278.7</td>
<td>12.21</td>
<td>-11.66</td>
<td>376.2</td>
<td>-356.8</td>
<td>-268.2</td>
<td>18.99</td>
<td>17.99</td>
<td>-366.0</td>
</tr>
<tr>
<td>28</td>
<td></td>
<td>feed gas temperature = 690</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>29</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>31</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>33</td>
<td></td>
<td>Matrix results equivalent to intercept temperature in cell J30 (and A14)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>34</td>
<td></td>
<td>kg-mole SO₂ in</td>
<td>0.0000</td>
<td>-(0.0311×36-9.797)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td></td>
<td>kg-mole SO₂ out</td>
<td>0.1000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36</td>
<td></td>
<td>kg-mole O₂ in</td>
<td>0.1100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td></td>
<td>kg-mole N₂ in</td>
<td>0.7900</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>38</td>
<td></td>
<td>kg-mole CO₂ in</td>
<td>0.0000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>39</td>
<td></td>
<td>kg-mole SO₂ out</td>
<td>0.0692</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td></td>
<td>kg-mole SO₂ out</td>
<td>0.0306</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>41</td>
<td></td>
<td>kg-mole O₂ out</td>
<td>0.0754</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>42</td>
<td></td>
<td>kg-mole N₂ out</td>
<td>0.7900</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>43</td>
<td></td>
<td>kg-mole CO₂ out</td>
<td>0.0000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>44</td>
<td></td>
<td>per kg-mole of 1st catalyst bed feed gas</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td></td>
<td>per 1st catalyst bed feed gas</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>46</td>
<td></td>
<td>Goal seek calculation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>47</td>
<td></td>
<td>Equilibrium curve % SO₂ oxidized - heattup path % SO₂ oxidized = 0.0 = F11-33</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

361
S.2 2\textsuperscript{nd} Catalyst Bed Calculations (Cells AA1 through AM47)

The objectives of the 2\textsuperscript{nd} catalyst bed worksheet area are to:

(a) automatically copy 1\textsuperscript{st} catalyst bed exit (intercept) gas quantities into the 2\textsuperscript{nd} catalyst bed worksheet area and to determine 2\textsuperscript{nd} catalyst bed:

(b) heatup path-equilibrium curve intercept temperature and \% SO\textsubscript{2} oxidized

(c) kg-mole SO\textsubscript{3}, SO\textsubscript{2}, O\textsubscript{2}, N\textsubscript{2} and CO\textsubscript{2} in intercept gas with 1\textsuperscript{st} catalyst bed exit gas as 2\textsuperscript{nd} catalyst bed feed gas.

Setup and Operation

The 2\textsuperscript{nd} catalyst bed worksheet area is set up much like the 1\textsuperscript{st} (with a different input gas temperature, Table 18.1). The distinctive difference is that the input quantities in row 8 are 1\textsuperscript{st} catalyst bed exit (intercept) gas quantities from Table S.1 cells B38 through B42. The latter are automatically copied into the 2\textsuperscript{nd} catalyst bed area by the instructions:

\begin{verbatim}
=B38         in cell AE8
=B39         in cell AG8
=B40         in cell AI8
=B41         in cell AK8
=B42         in cell AM8.
\end{verbatim}

The 2\textsuperscript{nd} bed intercept is then found by Section M.4's Goal Seek procedure. The intercept results are 773.1 K, 94.2\% SO\textsubscript{2} oxidized and:

\begin{verbatim}
 0.0942 kg-mole SO\textsubscript{3}
 0.0058 kg-mole SO\textsubscript{2}
 0.0629 kg-mole O\textsubscript{2}
 0.7900 kg-mole N\textsubscript{2}
 0.0000 kg-mole CO\textsubscript{2}
\end{verbatim}

in 2\textsuperscript{nd} catalyst bed intercept gas (as confirmed by Section 15.2.2).

These gas quantities are automatically copied into the 3\textsuperscript{rd} catalyst bed area as described in the next section.
<table>
<thead>
<tr>
<th>TABLE S.2, 2nd CATALYST BED</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Column</strong></td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>d.wt% SO₂</td>
</tr>
<tr>
<td>a.wt% SO₂</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>SO₂</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>6</td>
</tr>
<tr>
<td>7</td>
</tr>
<tr>
<td>8</td>
</tr>
<tr>
<td>9</td>
</tr>
<tr>
<td>10</td>
</tr>
<tr>
<td>11</td>
</tr>
<tr>
<td>12</td>
</tr>
<tr>
<td>13</td>
</tr>
<tr>
<td>14</td>
</tr>
<tr>
<td>15</td>
</tr>
<tr>
<td>16</td>
</tr>
<tr>
<td>17</td>
</tr>
<tr>
<td>18</td>
</tr>
<tr>
<td>19</td>
</tr>
<tr>
<td>20</td>
</tr>
<tr>
<td>21</td>
</tr>
<tr>
<td>22</td>
</tr>
<tr>
<td>23</td>
</tr>
<tr>
<td>24</td>
</tr>
<tr>
<td>25</td>
</tr>
<tr>
<td>26</td>
</tr>
<tr>
<td>27</td>
</tr>
<tr>
<td>28</td>
</tr>
<tr>
<td>29</td>
</tr>
<tr>
<td>30</td>
</tr>
<tr>
<td>31</td>
</tr>
<tr>
<td>32</td>
</tr>
<tr>
<td>33</td>
</tr>
<tr>
<td>34</td>
</tr>
<tr>
<td>35</td>
</tr>
<tr>
<td>36</td>
</tr>
<tr>
<td>37</td>
</tr>
<tr>
<td>38</td>
</tr>
</tbody>
</table>

363
S.3 3rd Catalyst Bed Calculations (cells BA1 through BM47)

The objectives of the 3rd catalyst bed area are to:

(a) automatically copy 2nd catalyst bed exit (intercept) gas quantities into the 3rd catalyst bed worksheet area and to determine 3rd catalyst bed:

(b) heatup path-equilibrium curve intercept temperature and % SO2 oxidized

(c) kg-mole of SO3, SO2, O2, N2 and CO2 in intercept gas (for Chapter 19's calculations)

with 2nd catalyst bed exit gas as 3rd catalyst bed input gas.

Setup and Operation

The 3rd catalyst bed worksheet area is set up like the 2nd (with a different input gas temperature, Table 18.1). The row 8 quantities are automatically copied from the 2nd bed area by the instructions:

=AB38 in cell BE8  
=AB39 in cell BG8  
=AB40 in cell BI8  
=AB41 in cell BK8  
=AB42 in cell BM8.

The 3rd catalyst bed intercept is found by means of Section M.4’s Goal Seek procedure. The results are 721.0 K, 98.0% SO2 oxidized and:

0.098 kg-mole SO3  
0.002 kg-mole SO2  
0.061 kg-mole O2  
0.79 kg-mole N2  
0 kg-mole CO2

in 3rd catalyst bed intercept gas (as confirmed by Section 16.3). This gas now goes to cooling and H2SO4-making, Chapter 19.
<table>
<thead>
<tr>
<th>BA</th>
<th>BB</th>
<th>BC</th>
<th>BD</th>
<th>BE</th>
<th>BF</th>
<th>BG</th>
<th>BH</th>
<th>BI</th>
<th>BJ</th>
<th>BK</th>
<th>BL</th>
<th>BM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TABLE 9.3, 3rd CATALYST BED</td>
<td>All quantities are per kg-mole of 1st catalyst bed feed gas</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1st bed feed gas specification. Table 9.1</td>
<td>d,vol% SO₂ = 0 e,vol% SO₂ = 10 f,vol% O₂ = 11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1st catalyst bed feed kg-mole SO₂ (for Eqn. (14.1)) = e/100 = BG3/100 (Eqn. 11.1)</td>
<td>0.1 input gas temperature, K = 710</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>catalyst bed gas pressure, bar = 1.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2nd catalyst bed feed gas kg-mole from cell AB38-AB42 2nd catalyst bed intercept data</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>SO₂ = 0.0942 SO₂ = 0.0058 O₂ = 0.0629 N₂ = 0.7900 CO₂ = 0.0000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Suggested equilibrium curve intercept % SO₂ oxidized, δ₀ = 98.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>3rd catalyst bed equilibrium curve temperature equivalent to cell BF11's % SO₂ oxidized, Eqn. (17.1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>721.0 = -(68.4190.09355+0.006314<em>LN[(BE3+BG3)<em>BF11/100]/BG3</em>(1+BF11/100)</em>((100-0.5BG3)<em>BF11/100)/(B3-0.5BG2</em>BF11/100)<em>0.5</em>BF10*0.5)] (17.1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Equation matrix input data</td>
<td>in means 'in input gas', out means 'in intercept gas'</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>16.1 input SO₂ kg-mole</td>
<td>0.0942 0 0 0 0 0 0 0 0 0 0 0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>16.2 input SO₂ kg-mole</td>
<td>0.0058 0 1 0 0 0 0 0 0 0 0 0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>16.3 input O₂ kg-mole</td>
<td>0.0629 0 0 1 0 0 0 0 0 0 0 0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>16.4 input N₂ kg-mole</td>
<td>0.7900 0 0 0 1 0 0 0 0 0 0 0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>16.5 input CO₂ kg-mole</td>
<td>0.0000 0 0 0 0 1 1 0 0 0 0 0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>16.6 SO balance</td>
<td>0 -1 -1 0 0 0 1 1 0 0 0 0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>16.7 O balance</td>
<td>0 -3 -2 -2 0 -2 3 2 2 0 2 0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>16.8 N balance</td>
<td>0 0 0 2 0 0 0 2 0 2 0 0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>16.9 CO balance</td>
<td>0 0 0 0 -1 -1 0 0 0 0 0 0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>16.10 enthalpy balance</td>
<td>0 369.9 277.7 -12.87 -12.28 375.2 -369.1 -277.1 13.24 12.63 -374.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>input gas temperature = 710 intercept temperature, cell BA14 = 721.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>Matrix results equivalent to intercept temperature in cell BJ30 (and BA14)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>kg-mole SO₂ In</td>
<td>0.0942</td>
<td>-(0.0311*BF30-0.797)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>kg-mole SO₂ In</td>
<td>0.0058</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>kg-mole O₂ In</td>
<td>0.0629</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>kg-mole N₂ In</td>
<td>0.7900</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>kg-mole CO₂ In</td>
<td>0.0000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>kg-mole SO₂ out</td>
<td>0.0980</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>kg-mole SO₂ out</td>
<td>0.0020</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>kg-mole O₂ out</td>
<td>0.0610</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>kg-mole N₂ out</td>
<td>0.7900</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>kg-mole CO₂ out</td>
<td>0.0000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>all per kg-mole of 1st catalyst bed feed gas</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>Goal Seek calculation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>Equilibrium curve % SO₂ oxidized = heatup path % SO₂ oxidized = 0.0 = BF11-BF39</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

365
<table>
<thead>
<tr>
<th>CA</th>
<th>CB</th>
<th>CG</th>
<th>CD</th>
<th>CE</th>
<th>CF</th>
<th>CG</th>
<th>CH</th>
<th>CI</th>
<th>CJ</th>
<th>CK</th>
<th>CL</th>
<th>CM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TABLE S.4, 4th CATALYST BED</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>All quantities are per kg-mole of 5th catalyst bed feed gas</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1st bed feed gas specification, Table 18.1</td>
<td>d, vol% SO₂ = 0.060, vol% O₂ = 11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3rd catalyst bed feed gas kg-mole SO₂ = 0.010 = CG3/100 (Eqn. 11.1)</td>
<td>0.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>input gas temperature, K = 890</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>catalyst bed feed gas pressure, bar = 1.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>2nd catalyst bed feed gas kg-mole from cell BB38-BB42 2nd catalyst bed feed gas</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>SO₂ = 0.0020</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>O₂ = 0.0810</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>N₂ = 0.7900</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>CO₂ = 0.0000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>=BB38</td>
<td>=BB39</td>
<td>=BB40</td>
<td>=BB41</td>
<td>=BB42</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Suggested equilibrium curve intercept % SO₂ oxidized, θ =</td>
<td>98.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>4th catalyst bed equilibrium curve temperature equivalent to cell CF11’s % SO₂ oxidized, Eqn. (17.1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>692.6 = -(0.41)ln(0.0957+0.0973*(ln(CE3+CG3<em>CF11/100)+(CG3</em>11<em>CF11/100)+(1500-0.5</em>(CG3<em>CF11/100)+CG3</em>0.5<em>CG3</em>CF11/100)<em>0.5</em>CE6*0.5))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>Equation description</td>
<td>number</td>
<td>kg-mole SO₂</td>
<td>kg-mole SO₂</td>
<td>kg-mole SO₂</td>
<td>kg-mole O₂</td>
<td>kg-mole O₂</td>
<td>kg-mole SO₂</td>
<td>kg-mole SO₂</td>
<td>kg-mole O₂</td>
<td>kg-mole O₂</td>
<td>kg-mole SO₂</td>
</tr>
<tr>
<td>18</td>
<td>input SO₂ kg-mole</td>
<td>0.0080</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>19</td>
<td>input SO₂ kg-mole</td>
<td>0.0020</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>input O₂ kg-mole</td>
<td>0.0010</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>21</td>
<td>input N₂ kg-mole</td>
<td>0.7900</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>22</td>
<td>input CO₂ kg-mole</td>
<td>0.0000</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>23</td>
<td>14.6 S balance</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>24</td>
<td>17.6 O balance</td>
<td>0</td>
<td>-2</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>25</td>
<td>17.5 C balance</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>26</td>
<td>17.7 enthalpy balance</td>
<td>0</td>
<td>371.3</td>
<td>278.7</td>
<td>-12.21</td>
<td>-11.66</td>
<td>376.2</td>
<td>-371.1</td>
<td>-278.5</td>
<td>12.30</td>
<td>11.75</td>
<td>-376.1</td>
</tr>
<tr>
<td>27</td>
<td>input gas temperature = 690</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>Interception temperature, cell CA14 = 692.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>=CF5 =CA14</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>Matrix results equivalent to intercept temperature in cell CA14 (and CA14)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>kg-mole SO₂</td>
<td>0.0000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>kg-mole SO₂</td>
<td>0.0060</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>kg-mole SO₂</td>
<td>0.0020</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>kg-mole SO₂</td>
<td>0.0010</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>kg-mole SO₂</td>
<td>0.7900</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>kg-mole SO₂</td>
<td>0.0000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>kg-mole SO₂</td>
<td>0.0090</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>kg-mole SO₂</td>
<td>0.0000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>kg-mole SO₂</td>
<td>0.0011</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>kg-mole SO₂</td>
<td>0.0000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>kg-mole SO₂</td>
<td>0.7900</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>kg-mole SO₂</td>
<td>0.0000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>kg-mole SO₂</td>
<td>0.0030</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>All per kg-mole of 1st catalyst bed feed gas</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>Goal Seek calculation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>46</td>
<td>Equilibrium curve % SO₂ oxidized - heatup path % SO₂ oxidized =</td>
<td>0.0 =CF11-C139</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Appendix T

Worksheet for Calculating After-Intermediate-H₂SO₄-Making Heatup Path Equilibrium Curve Intercepts

A worksheet for calculating after-intermediate-H₂SO₄-making heatup path-equilibrium curve intercepts is shown on the following page. It uses Fig. 19.2’s after-intermediate-H₂SO₄-making catalyst bed input gas composition, quantities and temperature (P₁ = 1.2 bar). It calculates the percentage of after H₂SO₄ making catalyst bed input SO₂ that is oxidized to SO₃ when the intercept is attained, Eqn. 19.3. Operating instructions are given in Appendix J.
<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1&lt;sup&gt;st&lt;/sup&gt; AFTER H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt; MAKING CATALYST BED</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1&lt;sup&gt;st&lt;/sup&gt; after H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt; making catalyst bed input gas composition, Section 19.4.1</td>
<td>( x' ), volume% SO&lt;sub&gt;2&lt;/sub&gt; = 0.234</td>
<td>( f' ), volume% O&lt;sub&gt;2&lt;/sub&gt; = 7.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1&lt;sup&gt;st&lt;/sup&gt; after H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt; making catalyst bed input kg-mole SO&lt;sub&gt;2&lt;/sub&gt;, Section 19.3</td>
<td>0.002</td>
<td>feed gas temperature, ( K = 690 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>gas pressure in bed ( P_B ), bar = 12</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1&lt;sup&gt;st&lt;/sup&gt; after H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt; making catalyst bed input kg-mole, Section 19.3</td>
<td>SO&lt;sub&gt;2&lt;/sub&gt; = 0.002</td>
<td>O&lt;sub&gt;2&lt;/sub&gt; = 0.061</td>
<td>N&lt;sub&gt;2&lt;/sub&gt; = 0.79</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Suggested after H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt; making equilibrium curve. intercept % SO&lt;sub&gt;2&lt;/sub&gt; oxidized, ( q_{\text{SO2}} = 96.9 )</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Equilibrium curve temperature equivalent to cell 117's suggested % SO&lt;sub&gt;2&lt;/sub&gt; oxidized, Eqn. (19.1)</td>
</tr>
<tr>
<td>13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>697.3 = ((98.4%)/(0.09357+0.003414\times\text{cell117F11100-F11)}\times\text{[(100-0.5%G3+F11100)/(100-0.5%G3+F11100)}\times\text{0.5%K6}+0.5]) ( (19.1) )</td>
</tr>
<tr>
<td>14</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Heatup path matrix (In means in feed gas, out means in intercept gas):</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Equation</td>
</tr>
<tr>
<td>22</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>19.4 feed SO&lt;sub&gt;2&lt;/sub&gt; kg-mole</td>
</tr>
<tr>
<td>23</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>19.5 feed O&lt;sub&gt;2&lt;/sub&gt; kg-mole</td>
</tr>
<tr>
<td>24</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>19.6 feed N&lt;sub&gt;2&lt;/sub&gt; kg-mole</td>
</tr>
<tr>
<td>25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>11.4 ( \text{S balance} )</td>
</tr>
<tr>
<td>26</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>11.5 ( \text{O balance} )</td>
</tr>
<tr>
<td>27</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>11.6 ( \text{N balance} )</td>
</tr>
<tr>
<td>28</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Enthalpy balance</td>
</tr>
<tr>
<td>29</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>input gas temperature = 690</td>
</tr>
<tr>
<td>31</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>intercept temperature from cell A14 = 697.3</td>
</tr>
<tr>
<td>32</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( k_5 )</td>
</tr>
<tr>
<td>33</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( =0.07144\times30+420.6 )</td>
</tr>
<tr>
<td>34</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Matrix results equivalent to suggested intercept temperature in cell J30 (and A14)</td>
</tr>
<tr>
<td>35</td>
<td>1&lt;sup&gt;st&lt;/sup&gt; SO&lt;sub&gt;2&lt;/sub&gt; in kg-mole</td>
<td>0.0020</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>1&lt;sup&gt;st&lt;/sup&gt; O&lt;sub&gt;2&lt;/sub&gt; in kg-mole</td>
<td>0.0610</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>1&lt;sup&gt;st&lt;/sup&gt; N&lt;sub&gt;2&lt;/sub&gt; in kg-mole</td>
<td>0.7900</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>SO&lt;sub&gt;2&lt;/sub&gt; out kg-mole</td>
<td>0.001978</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>SO&lt;sub&gt;2&lt;/sub&gt; out kg-mole</td>
<td>0.00022</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>O&lt;sub&gt;2&lt;/sub&gt; out kg-mole</td>
<td>0.06011</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>N&lt;sub&gt;2&lt;/sub&gt; out kg-mole</td>
<td>0.790000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>per kg-mole of 1&lt;sup&gt;st&lt;/sup&gt; before H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt; making feed gas</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>43</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Catalytic input SO&lt;sub&gt;2&lt;/sub&gt; that is oxidized in this catalyst bed</td>
</tr>
<tr>
<td>44</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>46</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Goal Seek calculation</td>
</tr>
<tr>
<td>47</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Equilibrium curve % SO&lt;sub&gt;2&lt;/sub&gt; oxidized - heatup path % SO&lt;sub&gt;2&lt;/sub&gt; oxidized = 0.0 ( =F11-139 )</td>
</tr>
</tbody>
</table>
Appendix U

After-H₂SO₄-Making SO₂ Oxidation with SO₃ and CO₂ in Input Gas

All quantities in this appendix are per kg-mole of 1st before-H₂SO₄-making catalyst bed feed gas.

Chapter 19's SO₂ oxidation calculations assume that 100% of the SO₃ entering H₂SO₄ making reacts to form H₂SO₄(ℓ). This appendix's calculations remove that restriction. They also consider CO₂ in feed gas.

The objectives of the calculations are to determine a 1st after-H₂SO₄-making catalyst bed's:
(a) intercept temperature and % SO₂ oxidized, Φₑₐₐᵢₜₜₑᵦ
(b) intercept SO₃, SO₂, O₂, N₂ and CO₂ quantities with SO₃ and CO₂ in after-H₂SO₄-making input gas.

Total % SO₂ oxidized after:

3 before-H₂SO₄-making catalyst beds
1 after-H₂SO₄-making catalyst bed

is also calculated, Section U.6.

U.1 Equilibrium equation with SO₃ in after-H₂SO₄-making input gas

The after-H₂SO₄-making SO₂(g) + \( \frac{1}{2} \)O₂(g) → SO₃(g) equilibrium equation is:

\[
T_E = \frac{-B}{A + R \ln \left( \frac{d' + e' \Phi_{ₑₐₐᵢₜₜₑᵦ}}{100} \right) \left( \frac{100 - \frac{1}{2} e' \Phi_{ₑₐₐᵢₜₜₑᵦ}}{100} \right) \left( \frac{f' - \frac{1}{2} e' \Phi_{ₑₐₐᵢₜₜₑᵦ}}{100} \right)^{-
\frac{1}{2}}} \]

where:

\( T_E \) = equilibrium temperature, K

A and B = empirical constants for calculating \( \Delta G^\circ \) from temperature,

Eqn. (10.9) and Appendix C

\( A = 0.09357 \text{ MJ kg-mole SO}_2^{-1} \text{K}^{-1} \)
\( B = -98.41 \text{ MJ/kg-mole SO}_2 \)

R = gas constant, 0.008314 MJ/kg-mole SO₂.

\( d' \) = volume% SO₃ in 1st after H₂SO₄-making catalyst bed feed gas
\( e' \) = volume% SO₂
\( f' \) = volume% O₂

\( \{ \text{remainder} \} \) CO₂ and N₂
\( \Phi_{\text{after}} \) = equilibrium \% \( \text{SO}_2 \) oxidized, Section 19.4.2
\( P_t \) = total gas pressure, bar

It is exactly analogous to Eqn. (17.1) and is derived the same way.

**U.2 H\textsubscript{2}SO\textsubscript{4}-Making Input Gas Quantity Specification**

H\textsubscript{2}SO\textsubscript{4}-making input gas is specified to be the same as in Fig. 19.2, i.e.:

- 0.098 kg-mole SO\textsubscript{3}
- 0.002 kg-mole SO\textsubscript{2}
- 0.061 kg-mole O\textsubscript{2}
- 0.790 kg-mole N\textsubscript{2}
- 0.000 kg-mole CO\textsubscript{2}

**U.3 H\textsubscript{2}SO\textsubscript{4}-Making Exit Gas Quantity Calculation**

Chapter 19 assumes that 100\% of H\textsubscript{2}SO\textsubscript{4}-making input SO\textsubscript{3} is made into H\textsubscript{2}SO\textsubscript{4}(\ell). This appendix assumes that 99.9\% of the SO\textsubscript{3} is made into H\textsubscript{2}SO\textsubscript{4}(\ell), i.e. that 0.1\% remains in H\textsubscript{2}SO\textsubscript{4}-making exit gas. The exit gas contains, therefore:

\[
\frac{0.1\%}{100\%} \times 0.098 \text{ kg-mole SO}_3 \text{ into H}_2\text{SO}_4 \text{ making} = 0.0001 \text{ kg-mole SO}_3
\]

plus:

- 0.002 " SO\textsubscript{2}
- 0.061 " O\textsubscript{2}
- 0.790 " N\textsubscript{2}
- 0.000 " CO\textsubscript{2}

0.8531 total kg-mole.

This gas is goes forward to further SO\textsubscript{2} oxidation in a 1\textsuperscript{st} after-H\textsubscript{2}SO\textsubscript{4}-making catalyst bed.

**U.4 Calculation of H\textsubscript{2}SO\textsubscript{4}-Making Exit Gas Volume Percents**

The composition of the H\textsubscript{2}SO\textsubscript{4}-making exit gas is calculated as described in Section 19.4.1, e.g.:

\[
\text{volume}\% \text{ SO}_3 = \frac{\text{mole}\% \text{ SO}_3 \times \text{kg-mole SO}_3}{\text{total kg-mole gas}} \times 100\%
\]

\[
= \frac{0.0001 \times 100}{0.8531} = 0.012 \text{ volume}\% \text{ SO}_3 = d'
\]

Volume\% SO\textsubscript{2} and O\textsubscript{2} are calculated similarly to be:

\[
0.234 " \text{SO}_2 = e'
\]

\[
7.15 " \text{O}_2 = f'.
\]

The above after-H\textsubscript{2}SO\textsubscript{4}-making kg-mole and volume \% values are the starting points for this appendix's after-H\textsubscript{2}SO\textsubscript{4}-making intercept calculations. The calculations are described in the next two sections.
U.5 Worksheet Construction and Operation

Table U.1 shows an after-H_2SO_4-making intercept calculation worksheet. It is much like Table R.1. It includes SO_3 and CO_2 in catalyst bed input gas. Preparation and use instructions are:

1. In Excel, make a copy of Table R.1 by:
   - Edit
     - Move or Copy Sheet
     - Create a copy
   - To book: (new book)
   - OK.

2. Enter Section U.4's 1st after-H_2SO_4-making catalyst bed input volume% SO_2, SO_2 and O_2 into cells E3, G3 and I3 (empty cells J3 through M3).

3. Enter Section U.3's 1st after-H_2SO_4-making catalyst bed input kg-mole SO_3, SO_2, O_2, N_2 and CO_2 into cells E8, G8, I8, K8 & M8.

4. Re-enter Section U.3's 1st after-H_2SO_4-making catalyst bed input kg-mole SO_2 into cell G5 (for possible 2nd after-H_2SO_4-making catalyst bed calculations).

5. Enter gas input temperature and bed pressure in cells K5 and K6. Label all cells as shown.

6. Estimate an intercept % SO_2 oxidized (Φ^{after}) value in cell F11 (perhaps 99% from Table 19.2).

7. Enter Eqn. U.1 into cell A14, exactly as shown in cell B14.

8. Use Goal Seek to find the actual intercept % SO_2 oxidized (Φ^{after}) – by the instructions:

   **Tools**
   - Goal Seek
   - Set cell: G47
   - To value: 0
   - Changing cell: F11
   - OK
   - OK.

The results are shown in worksheet Table U.1. The intercept point is 98.8 % SO_2 oxidized (Φ^{after} in cells F11 and I39), 697.3 K (in cells A14 and J30).
Table 4.1: Percent sulfur dioxide and carbon monoxide in stack gases.

<table>
<thead>
<tr>
<th>Sulfur Dioxide (%)</th>
<th>Carbon Monoxide (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>0.02</td>
</tr>
<tr>
<td>0.06</td>
<td>0.03</td>
</tr>
<tr>
<td>0.07</td>
<td>0.04</td>
</tr>
<tr>
<td>0.08</td>
<td>0.05</td>
</tr>
<tr>
<td>0.09</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Note: The values above are for illustration purposes only and may not reflect real-world data.
U.6 Calculation of \% SO\textsubscript{2} Oxidized After All Catalyst Beds

Section 19.7 describes calculation of after-all-catalyst-bed SO\textsubscript{2} oxidation efficiency. The equation is:

\[
\% SO_2 \text{oxidized} = \Phi_{\text{total}} = \frac{\text{kg-mole SO}_2 \text{ in 1}\text{st catalyst bed feed gas}}{\text{kg-mole SO}_2 \text{ in 1}\text{st catalyst bed feed gas}} - \frac{\text{kg-mole SO}_2 \text{ in last catalyst bed exit gas}}{\text{kg-mole SO}_2 \text{ in 1}\text{st catalyst bed feed gas}} \times 100
\] (19.7).

This appendix repeats this calculation. Its data are:

from Fig. 19.2: \( \text{kg-mole SO}_2 \text{ in 1}\text{st catalyst bed feed gas} = 0.1 \)

from Table U.1: \( \text{kg-mole SO}_2 \text{ in after-H}_2\text{SO}_4\text{-making catalyst bed exit gas} = 0.000023 \)

so that:

\[
\text{total \% SO}_2 \text{ oxidized after 3 before-H}_2\text{SO}_4\text{-making and 1 after-H}_2\text{SO}_4\text{-making catalyst bed} = (0.1 - 0.000023) \times 100\% = 99.98\%.
\]

This result is virtually the same as with no SO\textsubscript{3} in 1\text{st after-H}_2\text{SO}_4\text{-making input gas, Section 19.7.}
Appendix V

Moist Air in H₂SO₄ Making Calculations

Chapter 23 examines the input of moist metallurgical and spent acid regeneration gases into Fig. 23.1's dehydration tower. It quantifies the amount of H₂O(g) that enters dehydration tower acid:

\[
\text{per kg-mole of dry 1st catalyst bed feed gas.}
\]

This appendix examines H₂O(g) in sulfur burning acid plants. It:

(a) shows that sulfur burning plants dehydrate sulfur burning air rather than cleaned furnace offgas
(b) quantifies the amount of H₂O(g) that enters dehydration tower acid

\[
\text{per kg-mole of dry air}
\]

and:

\[
\text{per kg-mole of dry 1st catalyst bed feed gas.}
\]

Fig. V.1 depicts the feed end of a sulfur burning sulfuric acid plant.

---

Fig. V.1. Front end of sulfur burning acid plant showing that \( \text{kg-mole dry 1st catalyst bed feed gas} = \text{kg-mole dry sulfur combustion air} \).
It shows that:

(a) kg-mole sulfur burning exit gas (i.e. kg-mole dry 1st catalyst bed feed gas) = kg-mole dry input sulfur combustion air

and therefore that:

(b) kg-mole H₂O(g) entering dehydration tower acid

\[ \text{per kg-mole of dry 1st catalyst bed feed gas} \]

has the same numerical value as kg-mole H₂O(g) entering dehydration tower acid

\[ \text{per kg-mole of dry sulfur combustion air.} \]

This greatly simplifies our sulfur burning H₂O(g) calculations, next section.

V.1 Calculation

This section duplicates Section 23.4.1's calculation of kg-mole H₂O(g) into dehydration tower acid per kg-mole of dry 1st catalyst bed feed gas.

The moist air being fed to the Fig. V.1 sulfur burning dehydration tower is specified to contain:

\[ 3 \text{ volume}\% \text{ H}_2\text{O(g)} \text{ and } 97 \text{ volume}\% \text{ dry air.} \]

These are equivalent to 3 and 97 mole\% H₂O(g) and dry air respectively.

From Eqns. (23.2) to (23.4):
\[
\begin{align*}
\text{kg-mole H}_2\text{O (g)} \text{ in moist input air} &= \frac{3 \text{ mole\% H}_2\text{O (g) in moist input air}}{100\%} \times \text{kg-mole moist input air} \quad \text{(V.1)} \\
\text{kg-mole dry air in moist input air} &= \frac{97 \text{ mole\% dry air in moist input air}}{100\%} \times \text{kg-mole moist input air} \quad \text{(V.2)}.
\end{align*}
\]

Dividing Eqn. (V.1) by Eqn. (V.2):

\[
\frac{\text{kg-mole H}_2\text{O(g) in moist input air}}{\text{kg-mole dry air in moist input air}} = \frac{3}{97}
\]

\[
= 0.031 \text{ kg-mole H}_2\text{O(g) per kg-mole of dry air.}
\]

Further, because:

\[
\text{kg-mole dry 1}\text{st catalyst bed feed gas} = \text{kg-mole dry air}
\]

\[
\text{kg-mole H}_2\text{O (g) per kg-mole of dry 1}\text{st catalyst bed feed gas} = \frac{\text{kg-mole H}_2\text{O (g) per kg-mole of dry air}}{\text{kg-mole of dry air}} = 0.031
\]

This value can be used in the remainder of Chapter 23's calculations, starting with Section 23.4.2.

It will be slightly wrong if the sulfur burning exit gas contains a small amount of SO\textsubscript{3}. 

377
Appendix W

Calculation of $\text{H}_2\text{SO}_4$ Making Tower Mass Flows

The Fig. 24.1 $\text{H}_2\text{SO}_4$ making tower’s mass flows are calculated by specifying:

- input mass $\text{SO}_3(\text{g})$ per kg-mole of 1$^{st}$ catalyst bed feed gas
- input acid composition, mass% $\text{H}_2\text{SO}_4$ and mass% $\text{H}_2\text{O}$
- output acid composition, mass% $\text{H}_2\text{SO}_4$ and mass% $\text{H}_2\text{O}$.

These specification plus total and sulfur mass balances permit calculation of the tower’s

(a) input $\text{SO}_3$, $\text{H}_2\text{SO}_4$ and $\text{H}_2\text{O}$ flows

(b) $\text{H}_2\text{SO}_4$ and $\text{H}_2\text{O}$ output flows.

W.1 Input and Output Gas Specifications

Fig. 24.1’s $\text{H}_2\text{SO}_4$ making tower input gas is specified to be Section 16.4’s 3$^{rd}$ catalyst bed exit gas. It contains:

- 0.098 kg-mole $\text{SO}_3$
- 0.002 " $\text{SO}_2$
- 0.061 " $\text{O}_2$
- 0.790 " $\text{N}_2$

per kg-mole of 10 volume% $\text{SO}_2$, 11 volume% $\text{O}_2$, 79 volume% $\text{N}_2$ 1$^{st}$ catalyst bed feed gas.

It is specified that all of the $\text{SO}_3$ in this gas reacts with $\text{H}_2\text{O}$ ($\ell$) in the tower’s input acid to form $\text{H}_2\text{SO}_4$ ($\ell$). The other gases pass unreacted out of the tower.

With this specification, the tower’s output gas contains:

- 0.000 kg-mole $\text{SO}_3$
- 0.002 " $\text{SO}_2$
- 0.061 " $\text{O}_2$
- 0.790 " $\text{N}_2$

per kg-mole of 1$^{st}$ catalyst bed feed gas, Table 24.1.

W.2 Input $\text{SO}_3(\text{g})$ Equation

The mass of input $\text{SO}_3(\text{g})$ equivalent to the above 0.098 kg-mole is given by the equation:

$$\text{mass } \text{SO}_3 = \text{kg-mole } \text{SO}_3 \times 80 \text{ kg } \text{SO}_3 \text{ per kg-mole } \text{SO}_3$$
= 0.098 * 80
= 7.84 kg per kg-mole of 1st catalyst bed feed gas. \hspace{1cm} (W.1).

(80 is the molecular weight of SO₃.)

**W.3 Input and Output Acid Composition Equations**

Fig. 24.1’s input acid is specified to contain 98.5 mass% H₂SO₄, 1.5 mass% H₂O. As Section 23.6.3 shows, this composition is described by the equation:

\[ 0 = -1.5 \times \text{mass H}_2\text{SO}_4 \text{ in input acid} + 98.5 \times \text{mass H}_2\text{O} \text{ in input acid} \] \hspace{1cm} (W.2).

The output acid is specified to contain 99.0 mass% H₂SO₄ and 1.0 mass% H₂O. It is described by:

\[ 0 = -1.0 \times \text{mass H}_2\text{SO}_4 \text{ in input acid} + 99.0 \times \text{mass H}_2\text{O} \text{ in input acid} \] \hspace{1cm} (W.3).

**W.4 Total Mass Balance Equation**

Excluding SO₂, O₂ and N₂ (which pass unreacted through the tower), Fig. 24.1’s total mass balance is:

\[ \text{mass SO}_3 \text{ in} + \text{mass H}_2\text{SO}_4 \text{ in input acid} + \text{mass H}_2\text{O} \text{ in input acid} = \text{mass H}_2\text{SO}_4 \text{ in output acid} + \text{mass H}_2\text{O} \text{ in output acid} \]

or:

\[ 0 = -\text{mass SO}_3 \text{ in} - \text{mass H}_2\text{SO}_4 \text{ in input acid} - \text{mass H}_2\text{O} \text{ in input acid} + \text{mass H}_2\text{SO}_4 \text{ in output acid} + \text{mass H}_2\text{O} \text{ in output acid} \] \hspace{1cm} (W.4).

**W.5 Sulfur Balance Equation**

Excluding SO₂ (which passes unreacted through the H₂SO₄ making tower), Fig. 24.1’s S mass balance is:

\[ \text{mass S in input SO}_3 + \text{mass S in input H}_2\text{SO}_4 = \text{mass S in output H}_2\text{SO}_4 \]

or, because SO₃ and H₂SO₄ contain 40 and 32.7 mass% S respectively:
\[
\frac{40}{100} \text{mass input } \text{SO}_3 + \frac{32.7}{100} \text{mass input } \text{H}_2\text{SO}_4 = \frac{32.7}{100} \text{mass output } \text{H}_2\text{SO}_4
\]

or

\[
0 = -0.4 \times \text{mass input } \text{SO}_3 - 0.327 \times \text{mass input } \text{H}_2\text{SO}_4 + 0.327 \times \text{mass output } \text{H}_2\text{SO}_4
\]

(W.5).

W.6 Solving for Flows

The Fig. 24.1 \text{H}_2\text{SO}_4 \text{ making tower has five flows:}

- mass \text{SO}_3 (g) in
- mass \text{H}_2\text{SO}_4 (\ell) in
- mass \text{H}_2\text{O} (\ell) in
- mass \text{H}_2\text{SO}_4 (\ell) out
- mass \text{H}_2\text{O} (\ell) out.

They are described by five equations, (W.1) to (W.5).

The numerical values of the above five flows are obtained by solving matrix Table W.1, as described in Appendix H.

The results are listed in Tables W.1 and 24.1.

| Table W.1. Matrix for determining Fig. 24.1 mass flows using Eqns. (W.1) to (W.5). |
|-----------------------------------|-------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                                  | A                | B                | C                | D                | E                | F                | G                | H                |
| Description of Mass Balance      | equation         | numerical         | mass SO3 in      | mass H2SO4 in    | mass H2O in      | mass H2SO4 in    | mass H2O in      | mass H2SO4 out   | mass H2O out     |
| total mass balance               | W4               | 0                | -1               | -1               | -1               | 1               | 1               | 1                | 1                |
| input acid composition          | W5               | 0                | -0.4             | -0.327           | 0                | 0.327           | 0               | 0                | 0                |
| output acid composition         | W3               | 0                | 0                | -1.5             | 98.5             | 0               | 0               | 0                | 0                |

W.7 Effect of Output Acid Mass% \text{H}_2\text{SO}_4 on Input and Output Acid Flows

Fig. W.1 shows the effect of specified output acid composition on input and output acid masses, per kg-mole of 1\text{st} catalyst bed feed gas. Both decrease markedly with increasing mass\% \text{H}_2\text{SO}_4 in output acid.
This is because each kg of specified composition input acid can accept more SO$_3$ when it goes (for example) from:

98.5 mass% H$_2$SO$_4$ in to 99.2 mass% H$_2$SO$_4$ out

than when it goes from:

98.5 mass% H$_2$SO$_4$ in to 98.8 mass% H$_2$SO$_4$ out

so less acid has to be circulated when 99.2 mass% H$_2$SO$_4$ is being produced.

Fig. W.1. Effect of specified output acid mass% H$_2$SO$_4$ on H$_2$SO$_4$ making tower input and output acid requirements. Input acid composition is constant at 98.5 mass% H$_2$SO$_4$, 1.5 mass% H$_2$O. #per kg-mole of 1st catalyst bed feed gas.
Answers to Numerical Problems

Answers within ± 1% of those listed here indicate correct methods of calculation.

Chapter 10

10.1 854 K
10.2 854 K
10.3 83.3% $SO_2$ oxidized
10.4

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>Answer to Problem 10.4</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Equilibrium</td>
<td>Equilibrium</td>
</tr>
<tr>
<td></td>
<td>% $SO_2$ oxidized</td>
<td>temperature,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>K</td>
</tr>
<tr>
<td>14</td>
<td>40</td>
<td>998.2</td>
</tr>
<tr>
<td>15</td>
<td>50</td>
<td>963.2</td>
</tr>
<tr>
<td>16</td>
<td>60</td>
<td>930.4</td>
</tr>
<tr>
<td>17</td>
<td>70</td>
<td>897.2</td>
</tr>
<tr>
<td>18</td>
<td>80</td>
<td>860.0</td>
</tr>
<tr>
<td>19</td>
<td>90</td>
<td>810.3</td>
</tr>
<tr>
<td>20</td>
<td>95</td>
<td>769.9</td>
</tr>
<tr>
<td>21</td>
<td>97.5</td>
<td>735.1</td>
</tr>
<tr>
<td>22</td>
<td>99</td>
<td>694.7</td>
</tr>
<tr>
<td>23</td>
<td>99.5</td>
<td>667.3</td>
</tr>
<tr>
<td>24</td>
<td>99.9</td>
<td>611.6</td>
</tr>
<tr>
<td>25</td>
<td>99.95</td>
<td>590.4</td>
</tr>
</tbody>
</table>

Problem 10.4

Feed gas
- 12.0 volume% $SO_2$
- 13.2 volume% $O_2$
- 74.8 volume% $N_2$
- 1.2 bar equilibrium pressure

$\phi^E$, equilibrium % $SO_2$ oxidized versus Equilibrium temperature, K

equilibrium curve
Chapter 11

11.1 37.4% SO₂ oxidized

11.2 46.0% SO₂ oxidized

11.3 50.3% SO₂ oxidized

11.4

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>Answer to Problem 11.4</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>Measured</td>
<td>Equivalent</td>
</tr>
<tr>
<td></td>
<td>temperature, K</td>
<td>% SO₂ oxidized</td>
</tr>
<tr>
<td>23</td>
<td>675</td>
<td>0</td>
</tr>
<tr>
<td>24</td>
<td>700</td>
<td>7.2</td>
</tr>
<tr>
<td>25</td>
<td>750</td>
<td>21.5</td>
</tr>
<tr>
<td>26</td>
<td>800</td>
<td>35.9</td>
</tr>
<tr>
<td>27</td>
<td>850</td>
<td>50.3</td>
</tr>
</tbody>
</table>

Feed gas
12.0 volume% SO₂
13.2 volume% O₂
74.8 volume% N₂
Chapter 12

12.1 and 12.2

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Equilibrium</td>
<td>Heatup path</td>
<td>Equilibrium</td>
</tr>
<tr>
<td></td>
<td>temperature</td>
<td>% SO₂ oxidized</td>
<td>% SO₂ oxidized</td>
</tr>
<tr>
<td>22</td>
<td>904</td>
<td>65.9</td>
<td>68.0</td>
</tr>
<tr>
<td>23</td>
<td>905</td>
<td>66.2</td>
<td>67.7</td>
</tr>
<tr>
<td>24</td>
<td>906</td>
<td>66.5</td>
<td>67.4</td>
</tr>
<tr>
<td>25</td>
<td>907</td>
<td>66.8</td>
<td>67.1</td>
</tr>
<tr>
<td>26</td>
<td>908</td>
<td>67.1</td>
<td>66.8</td>
</tr>
<tr>
<td>27</td>
<td>909</td>
<td>67.4</td>
<td>66.5</td>
</tr>
<tr>
<td>28</td>
<td>910</td>
<td>67.6</td>
<td>66.2</td>
</tr>
<tr>
<td>29</td>
<td>911</td>
<td>67.9</td>
<td>65.9</td>
</tr>
</tbody>
</table>

Problems 12.1 and 12.2

1.2 bar equilibrium pressure, 675 K feed gas,
12.0 volume% SO₂, 13.2 volume% O₂, 74.8 volume% N₂

12.3  (a) 1ˢᵗ catalyst bed intercept point: 907.6 K, 66.9% SO₂ oxidized

(b) intercept (exit gas) quantities (per kg-mole of 1ˢᵗ catalyst bed feed gas)

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>38</td>
<td>kg-mole SO₃ out</td>
<td>0.0803</td>
</tr>
<tr>
<td>39</td>
<td>kg-mole SO₂ out</td>
<td>0.0397</td>
</tr>
<tr>
<td>40</td>
<td>kg-mole O₂ out</td>
<td>0.0918</td>
</tr>
<tr>
<td>41</td>
<td>kg-mole N₂ out</td>
<td>0.7480</td>
</tr>
</tbody>
</table>
Chapter 13

13.1 Chapter 11 heatup path plus Chapter 12 intercept point.

Problem 13.1 heatup path with intercept point

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>Problem 13.1 heatup path with intercept point</td>
<td>Measured temperature, K</td>
<td>% SO₂ oxidized</td>
</tr>
<tr>
<td>22</td>
<td>675</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>700</td>
<td>7.2</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>750</td>
<td>21.5</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>800</td>
<td>35.9</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>850</td>
<td>50.3</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>907.6</td>
<td>66.9</td>
<td></td>
</tr>
</tbody>
</table>

Problem 13.1 graph

Chapter 14

14.1

Problem 14.1 heatup path data table

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>Problem 14.1 heatup path data table</td>
<td>2nd catalyst bed level L</td>
</tr>
<tr>
<td>31</td>
<td>685</td>
<td>66.9</td>
</tr>
<tr>
<td>32</td>
<td>710</td>
<td>74.1</td>
</tr>
<tr>
<td>33</td>
<td>730</td>
<td>79.9</td>
</tr>
<tr>
<td>34</td>
<td>750</td>
<td>85.7</td>
</tr>
<tr>
<td>35</td>
<td>770</td>
<td>91.5</td>
</tr>
</tbody>
</table>
Problem 14.1 graph

Chapter 15

15.1
15.2 2\textsuperscript{nd} catalyst bed intercept (exit gas) quantities (per kg-mole of 1\textsuperscript{st} catalyst bed feed gas)

<table>
<thead>
<tr>
<th>(B)</th>
<th>(C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>37 kg-mole SO(_3) out</td>
<td>0.1129</td>
</tr>
<tr>
<td>38 kg-mole SO(_2) out</td>
<td>0.0071</td>
</tr>
<tr>
<td>39 kg-mole O(_2) out</td>
<td>0.0755</td>
</tr>
<tr>
<td>40 kg-mole N(_2) out</td>
<td>0.7480</td>
</tr>
</tbody>
</table>

Chapter 16

16.1

![Graph showing temperature vs. SO\(_2\) oxidation percentage]

First catalyst bed feed gas
- 12 volume% SO\(_2\)
- 13.2 volume% O\(_2\)
- 74.8 volume% N\(_2\)
- 1.2 bar equilibrium pressure

Gas temperature, K

\(710.5\) K, \(98.5\%\) SO\(_2\) oxidized

\(779.1\) K, \(94.1\%\) SO\(_2\) oxidized

\(695\) K

\(685\) K

\(907.6\) K, \(86.9\%\) SO\(_2\) oxidized

\(675\) K

\(600\) to \(1000\) K

16.2 3\textsuperscript{rd} catalyst bed intercept (exit gas) quantities (per kg-mole of 1\textsuperscript{st} catalyst bed feed gas)

<table>
<thead>
<tr>
<th>(B)</th>
<th>(C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>37 kg-mole SO(_3) out</td>
<td>0.1183</td>
</tr>
<tr>
<td>38 kg-mole SO(_2) out</td>
<td>0.0017</td>
</tr>
<tr>
<td>39 kg-mole O(_2) out</td>
<td>0.0728</td>
</tr>
<tr>
<td>40 kg-mole N(_2) out</td>
<td>0.7480</td>
</tr>
</tbody>
</table>

Chapter 17

17.1 (a) 1\textsuperscript{st} catalyst bed intercept: 64.9% SO\(_2\) oxidized at 899.3 K
(b) 1st catalyst bed intercept (exit gas) quantities (per kg-mole of 1st catalyst bed feed gas. They show that the intercept (exit) gas contains a total of 0.07205 kg-mole of SO3 per kg-mole of 1st catalyst bed feed gas.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>38</td>
<td>kg-mole SO3 out</td>
<td>0.07205</td>
</tr>
<tr>
<td>39</td>
<td>kg-mole SO2 out</td>
<td>0.0379</td>
</tr>
<tr>
<td>40</td>
<td>kg-mole O2 out</td>
<td>0.0640</td>
</tr>
<tr>
<td>41</td>
<td>kg-mole N2 out</td>
<td>0.7910</td>
</tr>
</tbody>
</table>

17.2 With 10.5, 10.5, 9.0, and 70.0 volume% SO2, O2, CO2 and N2 the 1st catalyst bed intercept % SO2 oxidized is 66.5% at 899.4 K.

With 10.5, 10.5, 0, and 79.0 volume% SO2, O2, CO2, and N2 the 1st catalyst bed intercept % SO2 oxidized is 64.9% at 904.6 K.

Chapter 19

19.1 99.98% SO2 oxidized after all 4 beds (with intermediate H2SO4 making after the 3rd catalyst bed).

19.2 99.0% SO2 oxidized after all 4 beds (no intermediate H2SO4 making).

Chapter 21

21.1

<table>
<thead>
<tr>
<th>Gas</th>
<th>Temp. K</th>
<th>Enthalpy#</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st catalyst bed feed gas</td>
<td>675</td>
<td>-23.62</td>
</tr>
<tr>
<td>1st catalyst bed exit (intercept) gas</td>
<td>907.6</td>
<td>-23.62</td>
</tr>
<tr>
<td>2nd catalyst bed input gas</td>
<td>685</td>
<td>-31.21</td>
</tr>
<tr>
<td>2nd catalyst bed exit (intercept) gas</td>
<td>779.1</td>
<td>-31.21</td>
</tr>
<tr>
<td>3rd catalyst bed input gas</td>
<td>695</td>
<td>-34.08</td>
</tr>
<tr>
<td>3rd catalyst bed exit (intercept) gas</td>
<td>710.5</td>
<td>-34.08</td>
</tr>
<tr>
<td>H2SO4-making input gas</td>
<td>470</td>
<td>-42.31</td>
</tr>
</tbody>
</table>

# per kg-mole of 1st catalyst bed feed gas

21.2 36740 MJ per hour. This is the design capacity of this problem's economizer.
Chapter 22
In all Chapter 22 problems, the 1st catalyst bed feed gas flowrate is 100 000 Nm$^3$ per hour.

22.1

3rd catalyst bed exit gas enthalpies

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>Enthalpy, MJ per kg-mole of 1st catalyst bed feed gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>710.5 (Problem 21.1)</td>
<td>-34.08</td>
</tr>
<tr>
<td>480</td>
<td>-41.97</td>
</tr>
<tr>
<td>470 (Problem 21.1)</td>
<td>-42.31</td>
</tr>
<tr>
<td>460</td>
<td>-42.66</td>
</tr>
</tbody>
</table>

Economizer enthalpy transfers

<table>
<thead>
<tr>
<th>Cooling temperatures, K</th>
<th>Enthalpy transfer, MJ per kg-mole of 1st catalyst bed feed gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>710.5 to 480</td>
<td>7.89</td>
</tr>
<tr>
<td>710.5 to 470 (Problem 21.1)</td>
<td>8.23</td>
</tr>
<tr>
<td>710.5 to 460</td>
<td>8.58</td>
</tr>
</tbody>
</table>

(a) 8.23 MJ heat transfer requires 100% of Problem 21.1's economizer capacity

7.89 MJ heat transfer (cooling from 710.5 to 480 K) requires:

\[
\frac{7.89}{8.23} \times 100\% = 95.9\%
\]

of Problem 21.1's economizer capacity.

This is equivalent to a theoretical bypass of:

\[
100\% - 95.9\% = 4.1\%
\]

(b) Industrial bypass \(= (4.1\%)^{1.1} = 4.7\%\)

(c) 38 300 MJ per hour, Eqn. (21.6)
22.2

3\textsuperscript{rd} catalyst bed exit gas enthalpies

<table>
<thead>
<tr>
<th>Temperature K</th>
<th>Enthalpy, MJ per kg-mole of 1\textsuperscript{st} catalyst bed feed gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>715</td>
<td>-33.93</td>
</tr>
<tr>
<td>710.5 (Problem 21.1)</td>
<td>-34.08</td>
</tr>
<tr>
<td>705</td>
<td>-34.27</td>
</tr>
<tr>
<td>470 (Problem 21.1)</td>
<td>-42.31</td>
</tr>
</tbody>
</table>

Economizer enthalpy transfers

<table>
<thead>
<tr>
<th>Cooling temperatures, K</th>
<th>Enthalpy transfer, MJ per kg-mole of 1\textsuperscript{st} catalyst bed feed gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>715 to 470</td>
<td>8.38</td>
</tr>
<tr>
<td>710.5 to 470 (Problem 21.1)</td>
<td>8.23</td>
</tr>
<tr>
<td>705 to 470</td>
<td>8.04</td>
</tr>
</tbody>
</table>

Problem 22.1 (b)'s economizer has the heat transfer capacity of:

8.58 MJ per kg-mole of 1\textsuperscript{st} catalyst bed feed gas (@ 100 000 Nm\textsuperscript{3} of 1\textsuperscript{st} catalyst bed feed gas per hour)

(a) Cooling of 715 K 3\textsuperscript{rd} catalyst bed exit gas to 470 K requires 8.38 MJ per kg-mole of 1\textsuperscript{st} catalyst bed feed gas. This is:

\[
\frac{8.38}{8.58} \times 100\% = 97.7\% 
\]

of the Problem 22.1(b)'s economizer's capacity. It is equivalent to:

2.3% bypass

of gas around the economizer.

(b) Cooling of 710.5 K 3\textsuperscript{rd} catalyst bed exit gas to 470 K requires 8.23 MJ per kg-mole of 1\textsuperscript{st} catalyst bed feed gas. This is:

\[
\frac{8.23}{8.58} \times 100\% = 95.9\% 
\]

of the Problem 22.1(b)'s economizer's capacity. It is equivalent to:

4.1% bypass

of gas around the economizer.
(c) Cooling of 705 K 3rd catalyst bed exit gas to 470 K requires 8.04 MJ per kg-mole of 1st catalyst bed feed gas. This is:

\[
\frac{8.04}{8.58} \times 100\% = 93.7\%
\]

of the Problem 22.1(b)'s economizer's capacity. It is equivalent to:

6.3\% bypass

of gas around the economizer.

22.3

Prob. 22.2's (a), (b) and (c) bypasses are equivalent to:

<table>
<thead>
<tr>
<th>Theoretical bypass, %</th>
<th>Industrial bypass</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) 2.3</td>
<td>= 2.3/1 = 2.5%</td>
</tr>
<tr>
<td>(b) 4.1</td>
<td>= 4.1/1 = 4.7%</td>
</tr>
<tr>
<td>(c) 6.3</td>
<td>= 6.3/1 = 7.6%</td>
</tr>
</tbody>
</table>

Chapter 23

23.1 Mass SO₃ entering H₂SO₄ making tower =

\[
\text{kg-mole SO₃ per kg-mole of dry 1st catalyst bed feed gas} \times 80 \text{ kg SO₃ per kg-mole of SO₃}
\]

\[
= 0.1183 \times 80 = 9.464 \text{ kg SO₃ per kg-mole of dry 1st catalyst bed feed gas}
\]

From Eqn. (23.4):

\[
\frac{\text{kg-mole H₂O(g) in moist input gas per kg-mole of dry 1st catalyst bed feed gas in moist input gas}}{6\%} = \frac{94\%}{94\%} = 0.0638
\]

Mass input H₂O(g) = 0.638 kg-mole SO₃ per kg-mole of dry 1st catalyst bed feed gas \times 18 kg H₂O per kg-mole of H₂O

= 1.149 kg H₂O(g) per kg-mole of dry 1st catalyst bed feed gas

From Table 23.1 (for 98.5 mass% H₂SO₄, 1.5 mass% H₂O output acid):
Chapter 24

24.1 The H₂SO₄ making tower matrix with:

(a) 9.464 kg SO₃ per kg-mole of dry 1st catalyst bed feed gas (Problem 23.1)
(b) 98.6 mass% H₂SO₄, 1.4 mass% H₂O input sulfuric acid
(c) 99.2 mass% H₂SO₄, 0.8 mass% H₂O output sulfuric acid

<table>
<thead>
<tr>
<th></th>
<th><strong>A</strong></th>
<th><strong>B</strong></th>
<th><strong>C</strong></th>
<th><strong>D</strong></th>
<th><strong>E</strong></th>
<th><strong>F</strong></th>
<th><strong>G</strong></th>
<th><strong>H</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Description</td>
<td>equation</td>
<td>numerical term</td>
<td>mass SO₃ into H₂SO₄ making tower</td>
<td>mass H₂O in moist input gas</td>
<td>mass H₂O in input water</td>
<td>mass H₂SO₄ in output acid</td>
<td>mass H₂O in output acid</td>
</tr>
<tr>
<td>2</td>
<td>mass SO₃ into H₂SO₄ making tower</td>
<td>23.1</td>
<td>9.464</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>mass H₂O in moist feed gas</td>
<td>23.5</td>
<td>1.149</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>S balance</td>
<td>23.6</td>
<td>0</td>
<td>-0.4</td>
<td>0</td>
<td>0</td>
<td>0.327</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>total mass balance</td>
<td>23.7</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>output acid composition specification</td>
<td>23.8</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-1.5</td>
<td>98.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>9</strong></th>
<th><strong>Matrix solution</strong></th>
<th>mass* Kg per 100,000 Nm³ (4464 kg-mole) dry 1st catalyst bed feed gas per hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>mass SO₃ in</td>
<td>9.464</td>
</tr>
<tr>
<td>11</td>
<td>mass H₂O(g) in</td>
<td>1.149</td>
</tr>
<tr>
<td>12</td>
<td>mass water in</td>
<td>1.140</td>
</tr>
<tr>
<td>13</td>
<td>mass H₂SO₄ out</td>
<td>11.577</td>
</tr>
<tr>
<td>14</td>
<td>mass H₂O out</td>
<td>0.176</td>
</tr>
<tr>
<td>15</td>
<td>(mass acid out)</td>
<td>11.753</td>
</tr>
<tr>
<td>16</td>
<td>*kg per kg-mole of dry 1st catalyst bed feed gas</td>
<td></td>
</tr>
</tbody>
</table>

Solution (All masses are per kg-mole of dry 1st catalyst bed feed gas.)

<table>
<thead>
<tr>
<th><strong>9</strong></th>
<th><strong>Matrix solution</strong></th>
<th>mass* Kg per 100,000 Nm³ (4464 kg-mole) dry 1st catalyst bed feed gas per hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>mass SO₃ in</td>
<td>9.464</td>
</tr>
<tr>
<td>11</td>
<td>mass H₂O(g) in</td>
<td>1.149</td>
</tr>
<tr>
<td>12</td>
<td>mass water in</td>
<td>1.140</td>
</tr>
<tr>
<td>13</td>
<td>mass H₂SO₄ out</td>
<td>11.577</td>
</tr>
<tr>
<td>14</td>
<td>mass H₂O out</td>
<td>0.176</td>
</tr>
<tr>
<td>15</td>
<td>(mass acid out)</td>
<td>11.753</td>
</tr>
<tr>
<td>16</td>
<td>*kg per kg-mole of dry 1st catalyst bed feed gas</td>
<td></td>
</tr>
</tbody>
</table>
The acid temperature calculation table with:

(a) the appropriate input and output gas compositions

(b) the H$_2$SO$_4$ and H$_2$O input and output masses from the above table

(c) the mass% H$_2$SO$_4$ and H$_2$O in acid values from the above table

is:

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>The enthalpy equation for H$_2$SO$_4$ =</td>
<td>=0.1485<em>T-858.3 -1.82</em>(mass% H$_2$O in sulfuric acid)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Substance</td>
<td>kg</td>
<td>kg-mole</td>
<td>temperature, K</td>
<td>enthalpy, MJ per kg-mole</td>
</tr>
<tr>
<td>3</td>
<td>kg-mole SO$_2$(g) in</td>
<td>0.1183</td>
<td>480</td>
<td>-386.31</td>
<td>-45.700</td>
</tr>
<tr>
<td>4</td>
<td>kg-mole SO$_2$(g) in</td>
<td>0.0017</td>
<td>480</td>
<td>-289.53</td>
<td>-0.492</td>
</tr>
<tr>
<td>5</td>
<td>kg-mole O$_2$(g) in</td>
<td>0.0728</td>
<td>480</td>
<td>5.208</td>
<td>0.379</td>
</tr>
<tr>
<td>6</td>
<td>kg-mole N$_2$(g) in</td>
<td>0.7480</td>
<td>480</td>
<td>5.131</td>
<td>3.838</td>
</tr>
<tr>
<td>7</td>
<td>kg-mole H$_2$SO$_4$(l) in</td>
<td>359.639</td>
<td>3.670</td>
<td>-808.87</td>
<td>-2968.391</td>
</tr>
<tr>
<td>8</td>
<td>kg-mole H$_2$O(l) in</td>
<td>5.106</td>
<td>0.284</td>
<td>-281.91</td>
<td>-79.969</td>
</tr>
<tr>
<td>9</td>
<td>kg-mole SO$_2$(g) out</td>
<td>0.0000</td>
<td>350</td>
<td>-395.596</td>
<td>0.000</td>
</tr>
<tr>
<td>10</td>
<td>kg-mole SO$_2$(g) out</td>
<td>0.0017</td>
<td>350</td>
<td>-296.237</td>
<td>-0.504</td>
</tr>
<tr>
<td>11</td>
<td>kg-mole O$_2$(g) out</td>
<td>0.0728</td>
<td>350</td>
<td>0.876</td>
<td>0.064</td>
</tr>
<tr>
<td>12</td>
<td>kg-mole N$_2$(g) out</td>
<td>0.7480</td>
<td>350</td>
<td>1.088</td>
<td>0.814</td>
</tr>
<tr>
<td>13</td>
<td>Substance</td>
<td>kg</td>
<td>kg-mole</td>
<td>temperature, K</td>
<td>enthalpy, MJ per kg-mole</td>
</tr>
<tr>
<td>14</td>
<td>kg-mole H$_2$SO$_4$(l) out</td>
<td>371.215</td>
<td>3.788</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>kg-mole H$_2$O(l) out</td>
<td>2.994</td>
<td>0.166</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Output acid enthalpy =</td>
<td>=-3090.709 =F4+F5+F6+F7+F8+F9-F11-F12-F13-F14</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>T$_{acid}$ out</td>
<td>378</td>
<td>= output acid temperature</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>Enthalpy acid out</td>
<td>=-3090.709 =C18*(0.1485<em>B22-858.3 - 1.82</em>[0.8])+C19*(0.07568*B22-308.4)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

which shows the output acid temperature to be 378 K.
Author Index

Abeck, W. 34, 44
Al Hassen, A.Y. 11, 17
Azwell, D.E. 103, 117

Bal’zhinaeva, B.S. 98
Barin, L. 317
Bartlett, C. 30, 117
Betz, H.F. 9, 289, 290, 291
Biswa, A.K. 45
Bjerrum, N.J. 98
Boghosian, S. 98
Bright, N.F. 292
Byszewski, C. 103, 117
Buckingham, D.A. 13, 17

Chase, M.W. 304, 316
Collins, D.N. 45

Daftt, C.A. 50, 57
Davenport, 33, 45
Dunlavy, D. 20, 29
Dueker, W.W. 9, 272, 284

Eriksen, K.M. 98
Fahrer, N.S. 30
Fehrmann, R. 98
Fischer, H. 9, 16, 30, 88
Folkmann, G.E. 90, 91, 98
Friedman, L.J. 44, 69, 78, 88, 102, 103,
116, 117, 281, 283, 284
Friedman, S.J. 44, 69, 78, 88, 102, 103, 116,
117, 281, 283, 284
Fries, R.M. 9, 45, 284

Gable, C.M. 8, 9, 289, 290, 291
Gaune-Escard, M. 98
Baskell, D.R. 122, 127
Green, D.W.III 43, 45, 63, 69, 100, 104, 117
Greendel, R.W. 9, 45, 284
Guenkkel, A. 116

Hansen, L. 8, 9, 94, 98, 221, 223
Hasleogi, C. 20, 280, 284
Hatem, G. 90, 98
Hay, S. 100, 117, 272, 284
Hill, D.R. 11, 17
Holopainen, H. 45
Hopp, A. 8, 9
Hornbaker, D. 21, 30

Hultborn, K.G. 42, 45
Hutchison, H. 292

Jacob, K. 26, 30
Jondle, J. 21 30

King, M. 45
Killick, D. 11, 17
Kitto, M. 9, 12, 13, 15, 16, 17
Kola, R. 9, 16, 17, 30, 88
Lang, E. 49, 53, 57
Lapina, O.G. 90, 98
Laursen, J.K. 9, 9
Lee, M. 103, 117
Lossin, A. 42, 45
Louie, D. 9
Ludtke, P. 44

Maron, S.H. 9, 289, 290, 291
Miller, D. 27, 28, 30, 205, 210
More, A.I. 9, 16, 17, 30, 88
Muller, H. 44

Newman, C.J. 42, 45
Nichols, G.G. 35, 45
Nokelainen, J. 45

Ober, J.A. 13, 17
Oglesby, S. 35, 45
Orlando, J. 116

Parekh, U. 27, 30, 205, 210
Peippo, R. 34, 45
Perry, R. H. 43, 45, 63, 69, 100, 104, 117
Poretta, F. 117, 284
Puricelli, S.M. 8, 9, 39, 45, 54, 57, 282, 284

Rasmussen, S.G. 91, 93, 98
Rieder, J. 29, 117
Roensch, L.F. 23, 29
Rothe, U. 9, 16, 17, 30
Roughton, J.E. 292

Sander, U.H.F. 9, 12, 13, 16, 17, 21, 30, 74, 88
Salehi, M. 8, 9
Schlesinger, M. 45
Smith, D. 292

Tuller, W.N. 21, 30
Viergutz, M.D. 57
Weddick, A.J. 45
Weiss, W. 54, 57
West, J.R. 9, 272, 284
White, C.R. 50, 57
Windhager, H. 42, 45
Wiggins, B. 117, 284
Ziebold, S.A. 62, 69, 103, 116, 117
Index

Absorption, SO₃(g) 99-117, 253-269 (see also H₂SO₄ making)
Acidmaking (see H₂SO₄ making)
Acid (see Sulfuric acid)
Acid coolers
  anodic protection in 106, 280
  industrial details 106
  materials of construction 106
  photographs
    exterior 106
    interior 280
Acid (sulfuric) plant locations
  acid plant cost 15
  map 14
  reasons 15
Acid, heat recovery from 281-283
  flowsheet 282
Acid pump 101 (photo)
Acid temperature control 276-281
  input acid temperature 280
  output acid temperature
    affected by input acid temperature 277
    affected by input gas temperature 278
    affected by specified mass% H₂SO₄
      in output acid 279
    affected by volume% SO₃(g) in input
gas 279
  calculation 271-276
  Goal Seek 276
  H₂O(ℓ)-H₂SO₄(ℓ) enthalpy of
    mixing in 272
  matrix 380
  coolers for input acid temperature
  control by bypassing 107
  photographs
    exterior 106
    interior 280
  water cooling 280
  cooler bypass for input acid temperature
  control 107
  industrial acid temperatures
    final acidmaking 266-269
    intermediate acidmaking 110-115
    recovery of acid heat as steam 281-283
    target acid temperatures 281
Activation, catalyst
  melting of catalyst 90, 91
  temperature 91
  lowered by Cs in catalyst 93-94, 233

Air (sulfur burning) dehydration with strong
sulfuric acid 59
  flowsheet 60
  H₂O(g) content before 61
    " " after 63, 65
  industrial data 65
  reason for 59
  sulfuric acid composition, choice of 63
Anodic protection of acid coolers 106, 280
Argon, effect on SO₂ oxidation equilibrium
  (none) 311
Assumptions in SO₂ oxidation calculations
  attainment of equilibrium in all catalyst
  beds 209
  discussion 209
  no conductive, convective or
    radiative heat loss 131, 136, 209, 273
  steady state operation
    no heat transfer to catalyst 209
  100% SO₃ utilization during H₂SO₄
    making 214, 255, 378
    elimination of this assumption 370
Assumption in H₂SO₄ making calculations
  100% SO₃ utilization during H₂SO₄
    making 214, 255, 378
    assumption elimination 370
Blower, acid plant main 26
  location in flowsheet
    metallurgical acid plants 60
    spent sulfuric acid regeneration
      plants 60
    sulfur burning plants 26
  power, industrial 65-68
Boilers
  gas cooling device 236
  fire tube 23 (photo)
  makes steam 23
  metallurgical offgas
    waste heat boiler 34
      drawing 34
      dust removed in 34
      temperatures 33-34
    preheating boiler water in
      economizer 236
    superheating steam from 236
    sulfur burning boiler 23
Boliden Norzink mercury from gas
  removal process 42
Bypassing around heat transfer devices,
temperature controlled by
  acid 107
gas 243-251
  calculations 245-250
  flowsheet 244
  percent bypass 246-247
  industrial vs. theoretical 249-250
  inefficiency explained 250
  photograph of bypass 244
  principle 243
  up and down (continuous flow through bypass flue) 248-249

Candles, acid mist removal 102
  efficiency 102
  photograph 103
Carbon, molar balances
  in derivation of SO₂ oxidation equilibrium equation 312
  in heatup path preparation 193-197
Carbon dioxide (see CO₂)
 Catalytic SO₂(g) + \( \frac{1}{2} \)O₂(g) → SO₃(g)
 oxidation 71-98
 catalytic reaction mechanisms 90
 temperature increases rate 162
 catalyst photograph 89
 catalyst beds 3, 77-79, 94 (see also Catalyst, SO₂ oxidation, beds)
 converter for (3 to 5 catalyst beds)
 photographs
  exterior 78
  interior 3
 in double contact acid plants 229-234
 equilibrium curves for 119-128
 equilibrium equation for
  after intermediate H₂SO₄ making 214
  with SO₃ in input gas 370
 before intermediate H₂SO₄
  making 119-128, 293-303
  with SO₃ in feed gas 190
feed gas composition
 industrial
  after intermediate H₂SO₄
  making 224-227
  before intermediate H₂SO₄
  making 82-87
flowsheets
  double contact acid plant 6, 108
  single contact acid plant 100
heat release from 71
heatup paths represent 77, 129, 143-145
industrial data
  after intermediate H₂SO₄
  making 224-227
  before intermediate H₂SO₄
  making 82-87
making 82-87
industrial operation 80-81
startup 80
steady operation 80
 control 81, 243-251
 bypass 244 (photo)
 shut down 81
heatup path-equilibrium curve intercepts for 147-158
maximum SO₂ oxidation (equilibrium, intercept) 147-158
multi catalyst bed
 converter photographs 3, 78
 cooling between beds
 maximizes SO₂ oxidation 151
drawing 78
flowsheets
 double contact acidmaking 6, 108
 single contact acidmaking 100
oxygen source, feed gas
 O₂/SO₂ ratio 73
industrial
  after intermediate
  H₂SO₄ making 224-227
  before intermediate
  H₂SO₄ making 82-87
theoretical 73
purpose 119
in single contact acid plants 199-210
Catalyst, SO₂ oxidation 89-98
activation mechanism 90
activation temperature 91
 cesium affects (table) 94
temperature (table) 94
beds
 diameter 96
 industrial data
  after intermediate H₂SO₄
  making 224-227
  before intermediate H₂SO₄
  making 82-87
maintenance (screening) 97
number 229-234
photograph 3
pressures
 assumed 204-205
 industrial 26, 125
thickness
 increases with bed number 95
 explanation 95
gas residence time in
 increases with bed number 96
 explanation 97
catalytic reaction mechanism 90
cesium in catalyst
cost 233
gives low activation temperature 233
  lowers catalyst melting point 233
optimum placement of cesium
catalyst 233
phase diagram 91
composition 92
changes during use 92
choice of (table) 94
for various uses (table) 94
sulfation of 92
‘converter’, multicatalyst bed
bed thicknesses 82-87, 95, 224-227
diameter 82-87, 96, 224-227
height 82-87, 224-227
industrial data 82-87, 224-227
  after intermediate H2SO4
  making 224-227
  before intermediate H2SO4
  making 82-87
materials of construction 82-87, 224-227
  strength requirements 78
  number of beds 82-87, 224-227
photograph 78
gas residence time various beds 97
gas velocity 72
deactivation, low temperature 90
re-activation 91
solidification of catalyst layer 90
degradation, high temperature 154
affected by feed gas temperature 155
affected by SO2 concentration in feed gas 151, 155
avoidance (graph) 155
mechanism 91
temperature 91
activation
  mechanism 90
temperature 94
manufacture 91
sulfation 92
operating temperature
  industrial 82-87, 224-227
  maximum to avoid degradation 91, 94
  minimum to avoid deactivation 94
  catalyst composition affects 94
phase diagram, Cs2S2O7-V2O5 91
pieces (photograph) 89
shapes and sizes 93
quantity needed, industrial 82-87, 224-227
re-activation (catalyst layer remelting 90
  supported liquid phase 89-91
vanadium pentoxide 71-98
Catalyst beds
diameter 82-87, 95-96, 224-227
gas residence time in 96
  increases with bed number 97
  explanation 95
industrial data
  after intermediate H2SO4 making 224-227
  before intermediate H2SO4 making 82-87
maintenance (screening) 97
temperature
  increases with bed number 162
industrial data
  after intermediate H2SO4 making 224-227
  before intermediate H2SO4 making 82-87
thickness
  increases with bed number 82-87, 95
  224-227
  explanation 95
industrial data
  after intermediate H2SO4 making 224-227
  before intermediate H2SO4 making 82-87
Cesium in catalyst
congentration 92
lowers catalyst activation
temperature 233
  improves SO2 oxidation efficiency 154-155, 233
phase diagram 91
prevents 1st catalyst bed high temperature degradation 154-156
use
  avoids high temperature degradation in 1st catalyst bed 154-156
  best bed for maximum SO2 SO2 oxidation efficiency 233
Cleaning, gas
metallurgical offgas 32-44
dust concentration after cleaning 40-41
dust concentration before cleaning 40-41
settles in waste heat boiler 34
electrostatic precipitation 35-38
flowsheet 32
industrial data 36-37, 40-41
scrubbing, aqueous 39
spent sulfuric acid decomposition furnace gas 48, 54
dust
  concentration after cleaning 54
  concentration before cleaning 54
electrostatic precipitation, wet 54-55
flowsheet 48
industrial data 55
scrubbing, aqueous 54

CO₂
catalytic SO₂ oxidation efficiency
  affected by 154, 197
concentrations in:
  metallurgical offgas 36-37
  spent acid decomposition furnace offgas 51, 52
  scrubbing, not removed by 36, 40
equilibrium SO₃ oxidation equation
  (not affected by) 311
heatup paths, affected by 193-197
  calculations 193-197
  matrix 196
  graphs 197
  heat capacity effect 197
industrial CO₂ in gas concentrations 74
in catalytic SO₂ oxidation gas
  after intermediate
    H₂SO₄ making 224-227
  before intermediate
    H₂SO₄ making 82-87
intercept (equilibrium curve-heatup path)
  affected by 197, 203
  calculations 193-196
  graphs 154, 197
enthalpy 319
  vs. temperature equation 319
H₂SO₄ making, no reaction during 194
SO₂ oxidation, no reaction during 194
sulfur burning gas, none in 24-25
Condensation of H₂O(g) from gas
  direct (open or packed bed) 43
  flowsheets
    metallurgical offgas 32
    spent acid regeneration offgas 48
H₂O concentrations
  after condensation 40-41, 43
  before condensation 43
H₂O(g) equilibrium vapor pressure over water 43

indirect (heat exchanger) 43
industrial data
  metallurgical offgas 40-41
  spent acid decomposition furnace offgas 55
purpose
  decreases H₂O(g) into acidmaking 43
Consumption of sulfuric acid, worldwide
  graph, by year 13
  uses, table 15
Control
  gas dehydration, optimum sulfuric acid composition 64
H₂SO₄ making
  adjustments 107
  measurements 107
  table 107
SO₂ oxidation, catalytic
  based on temperature 81
  gas temperature controlled by bypassing gas around heat transfer devices 243-251
Cooldown paths (multicatalyst bed SO₂ oxidation) 159-164
  calculation data table 161
  flowsheet 159
  graph 162
  industrial gas cooling control of 162, 243-251
  no reaction during 161
  permits more SO₂ oxidation 163
Coolers, acid
  anodic protection from corrosion 280
  bypass temperature control 107
  industrial data 106
  materials of construction 106
  photographs
    exterior 106
    interior 280
Corrosion
  high acid velocities increase 283
  anodic protection from 280
  increases with increasing acid velocities 283
  increases with increasing acid temperature 281
  prevention of by dehydrating gas 59
  stainless steel minimizes 283
Cost, acid plant 15
Degradation (high temperature)
  of catalyst 91
  avoidance
catalyst composition choice 154
feed gas composition choice 156
feed gas temperature choice 155
indicated by pressure 97
mainly in 1st catalyst bed 155-156
mechanisms 91, 93
temperature 91
Dehydration of air and gas with strong sulfuric acid 59-69
acid compositions for 63, 65-68
acid droplet formation 62
removal from gas by mesh screen 62
drawing 62
air (sulfur burning) dehydration flowsheet 60
industrial data 65
purpose 59
cooling of dehydration acid 281
dehydration reaction 61
heat evolution 61
dehydration tower
acid residence time 64
diameter 64-67
drawing 62
gas residence time 64
height 65-67
industrial data 65-67
materials of construction 64
packed bed
bed thickness 64, 65-67
materials 62
flowsheets
air dehydration 60
gas (metallurgical and spent acid) dehydration 60
H2O(g) in gas concentrations before dehydration
air 65
gas 66-67
after dehydration
air 65
target 63
gas 66-67
target 63
equilibrium above sulfuric acid 63, 104
industrial dehydration data
air 65
gas 66-67
materials of construction, dehydration tower 64
Density oleum 291
sulfur 21
sulfuric acid 287-288
Double contact (double absorption) acid-making 229-234
advantage
efficient SO2 oxidation and H2SO4 making 109
cesium catalyst placement optimum 233
four catalyst beds 233
comparison with single contact acidmaking 109, 222, 230
costs, extra 223
flowsheets 6, 108
heat from acid recovery flowsheet 282
industrial data
catalytic SO2 oxidation after H2SO4 making 224-227
before H2SO4 making 82-87
H2SO4 making (absorption) final 266-269
intermediate 110-115
Dowa mercury from gas removal process 42
Drying of gas condensation 42, 43, 54 (see also Condensation of H2O(g) from gas)
industrial data
metallurgical gas 40-41
flowsheet 32
spent acid regeneration gas 55
flowsheet 48
dehydration 59-69 (see also Dehydration of air and gas with strong sulfuric acid)
industrial data
air 65
flowsheet 60, 62
gas 66-68
flowsheet 60, 62
Dust
adversely affects catalyst 33
in metallurgical offgas 33
concentrations before and after removal 33, 36-37, 40-41
removal
electrostatic precipitation 35-38
industrial data 36-37
mechanism of removal 35, 38
flowsheet for 32
scrubbing (aqueous) 39
industrial data 40-41
in waste heat boiler 34
in spent acid regeneration offgas 52
after removal 54
before removal 52
removal
flowsheet 48
industrial data 55
Dynawave scrubber 39

Economizer (heats boiler feed water) 236, 244, 282
bypass for gas temperature control 243-251

Electrical conductance of sulfuric acid 292

Electrostatic precipitation, dry 35-38
collection plate area 36-37, 38
corona wire, number of 36-37
current 36-37, 38
drawings 35, 38
dust removal mechanism 35, 38
dust concentration before and after 36-37
gas residence time in 38
gas velocity in 38
industrial data 36-37
mechanism of dust removal 35, 38
temperature of operation 34, 36-37
voltage 36-37, 38

Electrostatic precipitation, wet 40-41, 43

Enthalpy balance, \( H_2SO_4 \) making tower 273
calculation of product acid temperature with 271-276
no heat loss assumption 273
balances, \( SO_2 \) oxidation after intermediate \( H_2SO_4 \) making 218
before intermediate \( H_2SO_4 \) making 135, 170
no heat loss assumption 136, 209
with \( CO_2 \) in gas 195
with \( SO_3 \) in feed gas 191
data 318-319
enthalpy vs. temperature
equations 318-319
of mixing \( H_2O(\ell) \) and \( H_2SO_4(\ell) \) 272

Enthalpy (heat) transfers after catalyst beds 235-242
calculation of gas enthalpies 236
Excel worksheet 238
enthalpy drop, gas 240
enthalpy (heat) transfer devices boiler 23
industrial data 24-25
economizer 236-242
steam superheater 236
enthalpy (heat) transfers assumption of no heat loss 240
calculation 239-240
table 240
used in bypass calculations 243-251
enthalpy (heat) transfer rate calculation 241
enthalpy into catalyst bed = enthality out of catalyst bed 240
flowsheet 236

Equilibrium, \( SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_3(g) \) (see also \( SO_2 \) oxidation)
curves 119-128
effect of argon on (none) 313-315
" \( CO_2 \) on (none) 311-313
" \( O_2 \) in gas on 125
" \( SO_2 \) in gas on 126
" pressure on 125
" temperature on 121
after intermediate \( H_2SO_4 \) making 217
preparation of
after intermediate \( H_2SO_4 \) making 217
before intermediate \( H_2SO_4 \) making 306-308

equation after intermediate \( H_2SO_4 \) making 214
argon doesn’t affect 313-315
before intermediate \( H_2SO_4 \) making 124
\( CO_2 \) doesn’t affect 311-313
derivation after intermediate \( H_2SO_4 \) making 370
before intermediate \( H_2SO_4 \) making 119-128, 293-303
with \( SO_3 \) in gas 348-354
free energy data for 305
free energy vs. \( T \) equation 304-305
function of temperature 124
\( SO_3 \) in gas affects 190

Excel worksheets
equilibrium curve preparation after intermediate \( H_2SO_4 \) making 367-368
before intermediate \( H_2SO_4 \) making 306-308
gas enthalpy calculations 238
heatup path preparation
1" catalyst bed 139, 322-324
2" catalyst bed 173, 333-335
3rd catalyst bed 344-345  
with CO₂ in gas 196  
enthalpy equations in cells 322-324  
after intermediate H₂SO₄ making 218  
with SO₃ in gas 192  
intercept (heatup path-equilibrium curve preparation)  
1st catalyst bed 326-332  
2nd catalyst bed 339-343  
3rd catalyst bed 346-347  
4th catalyst bed 366  
with CO₂ in gas 358-359  
after intermediate H₂SO₄ making 367-368  
before intermediate H₂SO₄ making 360-366  
with SO₃ in feed gas 356-357

Filter, air 2, 23  
Flowsheets  
acidmaking 6  
simplified 254  
air dehydration with strong sulfuric acid 60  
bypass temperature control after 3rd catalyst bed 236-244  
catalytic SO₂ oxidation  
1 catalyst bed 120, 181  
equilibrium 157  
2 catalyst beds with gas cooling between 159, 168  
3 catalyst beds with gas cooling between 183, 185  
3-1 double contact acidmaking 212, 215  
after intermediate H₂SO₄ making 212  
double contact acid plant 6, 108  
economizer bypass 244  
photograph of bypass 244  
gas cooldown between catalyst beds 159  
gas dehydration with strong sulfuric acid 60  
H₂SO₄ making  
double contact 6, 108  
intermediate 100  
H₂SO₄ making tower 272  
heat recovery from acid (as steam) 282  
heat transfers after catalyst beds 236  
metallurgical offgas cooling, cleaning and H₂O(g) condensation 32  
multi catalyst bed SO₂ oxidation 212  
spent sulfuric acid decomposition furnace offgas cooling, cleaning and H₂O(g) condensation 48  
single contact acid plant 100  
heat transfers 236  
simplified 254  
sulfur burning 20  
Flowrates, industrial  
air dehydration 65  
catalytic SO₂ oxidation (conversion)  
after intermediate H₂SO₄ making 224-227  
before intermediate H₂SO₄ making 82-87  
gas dehydration 66-68  
H₂SO₄ making (absorption)  
final 266-269  
intermediate 110-115  
methallurgical offgas treatment  
electrostatic precipitation 36-37  
scrubbing 40-41  
waste heat boiler 36-37  
spent acid regeneration 51, 55  
sulfur burning 24-25  
Free energy (Gibbs) for SO₂(g) + ½O₂(g) → SO₃(g) reaction  
data 305  
free energy vs. temperature equation 304-305  
Freezing points, sulfuric acid 289-291  
Gas compositions, industrial SO₂ oxidation (conversion) gases  
after intermediate H₂SO₄ making 224-227  
before intermediate H₂SO₄ making 82-87  
gas dehydration gases 66-68  
final H₂SO₄ making (absorption) gas 266-269  
intermediate H₂SO₄ making (absorption) gas 110-115  
methallurgical offgas 33  
spent sulfuric acid regeneration furnace offgas 51, 52, 55  
sulfur burning offgas 24-25, 27-28  
control of 27-28  
Gas cooling  
before catalytic SO₂ oxidation 27  
between SO₂ oxidation catalyst beds  
enthalpy (heat) transfers 235-242  
graphical representation 161-162  
industrial method 162
purpose 163
for H₂O(g) condensation 42, 54
before electrostatic precipitation 34
purpose 34
before H₂SO₄ making
enthalpy transfer 239-240
purpose 105
Gas drying (H₂O(g) removal before SO₂ oxidation)
condensation by cooling
metallurgical gas 42
spent acid decomposition furnace offgas 54
derhydration with strong
sulfuric acid 59-69
air 65
flowsheets, air and gas
derhydration 60
H₂O ends up in acid plant's product
acid 254, 257, 262
metallurgical gas, industrial
data 66-68
spent acid decomposition furnace gas data 68
prevents accidental downstream
H₂SO₄(l) formation 59
sulfur burning air dehydration 60, 65
Gas temperature control 243-251 (see also
Temperature control, gas)
by bypassing gas around heat exchange
devices 243-251 (see also
Bypassing)
Goal Seek calculations
equilibrium curve 308
heattrip path-equilibrium curve
intercept 326-332
product acid temperature 276
H₂O(g) vapor pressure over water
graph 43
importance in H₂O(g) condensation 42
H₂O(g) vapor pressure over sulfuric acid
graph 104
importance in
air and gas dehydration 62-64
H₂SO₄ making (SO₂(g)+H₂O in strong sulfuric acid
→ H₂SO₄(l) in strengthened sulfuric acid
acid used rather than water 100
optimum H₂SO₄ concentrations 104
optimum acid temperatures 105
acid cooling for 105
cooler photographs 106, 280
heat from acid
recovery (as steam) 281-283
materials of construction 283
acid mist produced during 102
removal from exit gas 102-103
candles for 103 (photo)
acid pumping
photograph and data 101
acid (product) temperature
affected by input
acid temperature 277
affected by input gas temperature 278
affected by input and output acid
compositions 279
affected by SO₃ concentration
in input gas 279
calculation of 271-276
Goal Seek 276
target 281
calculation of acid production 253-261
graph 261
calculation of water requirement 253-261
graphs 262-264
candle acid mist removers
photograph 103
choice of input and output acid
compositions 104
double contact 229-234
advantage 109
extra costs 223
flowsheets 6, 108
final H₂SO₄ making vs. intermediate
H₂SO₄ making 109
flowsheets
double contact 6, 108
H₂SO₄ making tower 272
heat from acid recovery 282
single contact 100
simplified 254
heat recovery from
acid (as steam) 281-283
acid temperatures higher for 281
description 281
flowsheet 282
materials of construction 283
industrial data
final H₂SO₄ making 266-269
intermediate H₂SO₄ making 110-115
mass balances for 258
operation 105-107
control 107
adjustments 107
sensors 107
startup and shut down 105
steady operation 107
product acid temperature
calculation of 271-276
affected by input acid temperature 277
affected by input gas temperature 278
affected by mass% H2SO4 in acid 279
affected by SO3 in gas concentration 279
production distribution, intermediate vs., final 109
reaction 4
heat release 4
residence times (acid and gas) in H2SO4 making tower packing 102
single contact calculations 253-286
acid production rate
vs. input SO3(g) rate 261 (graph)
dilution water requirement
vs. H2O(g) in input gas 262
vs. %H2O in product acid 263
mass balances
for 258-260, 378-381
matrix for 260
flowsheet (simplified) 254
SO3 utilization
efficiency 110-115, 266-269
sulfuric acid reactant
industrial H2SO4 concentrations 110-115, 266-269
optimum H2SO4 concentrations 104
temperatures, acid and gas
choice of 105
industrial 110-115, 266-269
control of
input acid temperature 105
output acid temperature 105
input gas temperature 243-251
temperatures, industrial
final H2SO4 making 266-269
intermediate H2SO4 making 110-115
with heat in acid recovery
as steam 281-282
tower, packed bed, for 62
industrial data 110-115, 266-269
materials of
construction 110-115, 266-269
packed bed
materials 110-115, 266-269
photograph 4
packed bed thickness 102
residence times in
acid 102
gas 102
water not used for 100-101
water (dilution) requirement
calculation of 253-261
H2SO4 vapor pressure over sulfuric acid 104
causes downstream corrosion 105
graph 104
temperature effect 104
Heat exchange (see Heat transfer)
Heatup paths (catalytic SO2 oxidation)
1st catalyst bed 129-146
2nd catalyst bed 165-175
3rd catalyst bed 187, 344-345
after intermediate H2SO4 making 217
affected by CO2 in feed gas 154, 197
affected by SO2 in feed gas 143
affected by SO3 in feed gas 192
affected by feed gas temperature 144
balances for calculating
C 194
enthalpy 135, 170, 191, 195
no heat loss assumption 136
N 134, 169
O 134, 169
S 133, 169
not straight 144
preparation of 140-141
enthalpy equations in cells 322-324
matrices for 139, 323
straight line approximation 202
no effect on heatup path-equilibrium curve intercepts 202
Heat transfers during catalytic SO2 oxidation 235-242
cooldown path represents 159-164
gas enthalpy contents
calculation of 236
worksheet for 238
heat transfer amounts
calculation of 239-240
heat transfer rates
calculation of 241
purpose 151, 159-164
History of sulfuric acid manufacture 11-12
Industrial data
air dehydration with strong sulfuric acid 65
catalytic SO2(g) + ½O2(g) → SO3(g)
oxidation
after intermediate
H2SO4 making 224-227
before intermediate
H2SO4 making 82-87
electrostatic precipitation 36-37
gas dehydration with strong sulfuric acid 66-68
H2SO4 making, final 266-269
H2SO4 making, intermediate 110-115
metallurgical offgas treatment cooling and electrostatic precipitation 36-37
scrubbing and H2O(g) condensation 40-41
pump, acid 101
spent sulfuric acid regeneration decomposition furnace 51
gas cleaning, cooling and H2O(g) condensation 55
sulfur burning 24-25
Intercepts, heatup path-equilibrium curve, maximum SO2 oxidation efficiency predicted by 147-158
affected by CO2 in feed gas 154, 197
affected by O2 concentration in feed gas 153
affected by gas pressure 152
affected by SO2 concentration maximum industrial SO2 concentration 151
affected by SO3 in feed gas 193
affected by catalyst bed input gas temperatures 155
calculation of 147-150
assumptions 131, 150, 209
Goal Seek 326-332
graphical 148-149
initial specifications 1st catalyst bed 147-148
2nd catalyst bed 168
3rd catalyst bed 185
4th catalyst bed 366
after intermediate H2SO4 making 213-215
meaning 150
catalyst degradation predicted by 155-156

Map of sulfuric acid production worldwide 14
Mass balances sulfur 258, 379
total 258, 379
Materials of construction acid coolers 106
acid pumps 101
catalytic SO2 oxidation converters 82-87, 224-227
photograph 78
critical strengths 78
derdration towers 64-68
H2SO4 making towers 110-115, 266-269
heat from acid recovery systems 283
Matrices for SO2(g) + ½O2(g) → SO3(g) oxidation heatup paths
1st catalyst bed 139, 322-324
2nd catalyst bed 173, 333-335
after intermediate H2SO4 making catalyst bed 218
with CO2 in feed gas 196
with SO3 in feed gas 192
Matrices, H2SO4 making
H2SO4 making tower 378-381
simplified single contact acid plant 260
Mercury removal from metallurgical offgas 42
Boliden Norzink process 42
Dowa process 42
Metallurgical offgas acidmaking from 31-45
flowsheets 6, 32
condensation of H2O(g) 42
cooling 32, 34
drying
condensation 42
dehydration with strong sulfuric acid 59-69
dust contents after all gas treatment 33
after electrostatic precipitation 36-37
before electrostatic precipitation 36-37
electrostatic precipitation drawings 35, 38
precipitation mechanism 35, 38
wet 40-41
H2O(g) condensation from 42
industrial data 40-41
heat recovery from 34
in waste heat boiler 34
industrial data cooling and electrostatic precipitation 36-37
scrubbing and H2O(g) condensation 40-41
mercury removal from 42
Boliden-Norzink process 42
Dowa process 42
gas compositions 33, 74
scrubbing (aqueous) of dust from gas 39-42
waste acid product from 42
sources 33

Mixing enthalpy, \( H_2O(\ell) + H_2SO_4(\ell) \) 272

Multicatalyst bed \( SO_2 \)
- oxidation calculations 199-210, 229-234
- after intermediate \( H_2SO_4 \) making 229-234
- assumptions in calculations for 209
  - discussion 209
- cooldown paths 159-164
- heatup paths 129-146
- intercepts 199-210, 229-234
- maximizes \( SO_2 \) oxidation efficiency 159

Nitrogen
- equilibrium curve, no effect on 315
- equilibrium equation, no effect on 315
  - derivation with 293-303
- \( H_2SO_4 \) making, no reaction during 255
  - molar balance
    - equilibrium curve 298
    - heatup path 134
- \( SO_2 \) oxidation, no reaction during 298

Oleum 8
- specific gravity 291

Oxygen
- added (in air) to acid plant gas
  - before catalytic \( SO_2 \) oxidation 74
  - metallurgical offgas 32, 74
  - spent sulfuric acid regeneration gas 48, 54, 74
  - sulfur burning exit gas 28
  - before last catalyst bed 87
- concentrations in acidmaking gases
  - industrial data
    - in catalytic \( SO_2 \) oxidation gases
      - after intermediate \( H_2SO_4 \) making 274-227
      - before intermediate \( H_2SO_4 \) making 82-87
    - in gas dehydration gases 66-67
    - in \( H_2SO_4 \) making gases
      - final \( H_2SO_4 \) making 266-269
      - intermediate \( H_2SO_4 \) making 110-115
    - in metallurgical gases
      - electrostatic precipitation
        - gases 36-37
      - in scrubbing gases 40-41
      - in spent acid decomposition
        - furnace gases 55
        - control of 54
      - in sulfur burning gases 28
      - control of 27
  - industrial data 24-25
  - enrichment of combustion air
    - smelting 33
  - spent acid regeneration 50
  - sulfur burning 28
  - enthalpy 319
    - vs. temperature equation 316-319
  - in equilibrium curve equation
    - derivation 297
  - \( O_2 \) concentration effects on
    - catalytic \( SO_2 \) oxidation
      - equilibrium curves 125
      - heatup paths 153
      - intercepts 153
      - \( SO_2 \) oxidation rate 95
        - shown in reaction
          - mechanism 90
    - molar balance, catalytic
      - \( SO_2 \) oxidation equilibrium curve equation 297
        - with \( CO_2 \) in feed gas 312
        - with \( SO_3 \) in feed gas 349
      - heatup path 134
        - with \( CO_2 \) in feed gas 194
        - with \( SO_3 \) in feed gas 169
      - \( O_2/SO_2 \) ratio in catalytic \( SO_2 \)
        - oxidation feed gas 73
        - industrial 82-87
          - after intermediate \( H_2SO_4 \)
            - making 224-227
          - before intermediate \( H_2SO_4 \)
            - making 82-87
          - minimum 73
          - stoichiometric 73

Packed bed scrubber 48

Percent \( SO_2 \) oxidized (\( \Phi \)) defined 120
- equilibrium (\( \Phi^* \)) 121
- 1st catalyst bed 120, 121
- 2nd catalyst bed 166
- in after \( H_2SO_4 \) making catalyst beds 216
- total after \( SO_2 \) oxidation in all catalyst beds 221

Phase diagram \( Cs_2S_2O_7-V_2O_5 \) 91
- eutectic 91

Photographs
- acid cooler
  - exterior 280
  - interior 106
- acid mist removal 'candle' 103
- acid plant 2
- acid pump 101
- boiler, fire tube 23
bypass flue (around heat exchanger) 244

candle, acid mist remover 103
catalyst bed 3
catalyst pieces 89
fire tube boiler 23
H₂SO₄ making (absorption) tower 4
SO₂ oxidation 'converter'
  exterior 78
  interior 3
spent acid decomposition furnace 52
spinning cup sulfur burning flame 18
sulfur burning furnace
  boiler 23
  burner end 22
sulfuric acid plant 2

Precipitation, electrostatic 35-38
drawings of precipitators 35, 38
dust concentrations before & after 36-37
electrical current through 38
dry, industrial data 36-37
gas velocity through 38
gas residence time in 38
industrial data
dry electrostatic precipitators 36-37
wet electrostatic precipitators 40-41
precipitation mechanism 35, 38
principle of operation 35
potential, volts 36-37
spent acid decomposition
  furnace offgas cleaning 55
  temperature of operation
    maximum 34
    minimum 34
    explanation 34
  wet, industrial data 40-41, 55
Pressure, catalytic SO₂ oxidation beds
catalyst degradation indicated by 97
effect on equilibrium curves 125
curve equation
derivation 124, 293-303
effect on heatup paths (none) 152
effect on heatup path-equilibrium curve
  intercepts 152
  constant pressure assumption 204-205
  compared to actual pressures 205

Price, sulfuric acid 15
graph 16

Pumps
  acid, photo and details 101
  sulfur (steam heated) 21

R, gas constant 124
  in equilibrium curve equation 124

value 124
Radial flow scrubber 39
Reaction rate, catalytic SO₂ oxidation 90
  reaction mechanism 90
  slows in 2nd, 3rd and 4th catalyst beds 95
  offset by:
    increasing bed thickness 95
    increasing gas input
    temperature 162
    using higher vanadium
    catalyst 93, 94
  reasons 95
  temperature effect 90-91
Reaction rate, SO₃(g)+H₂O(l) in strong sulfuric acid
  H₂SO₄ in strengthened acid
  rapid 105
SO₃ utilization
  100% assumption 214, 255, 378
  assumption removed 370
  industrial data
    final H₂SO₄ making 266-269
    intermediate H₂SO₄
    making 110-115
  temperature effect 105
Regeneration of spent sulfuric acid 47-57
  (see also Spent sulfuric acid regeneration)
decomposition furnace
  industrial data 55
  photograph 52
  flowsheet 48
Residence times
catalyst beds 97
  increases with bed number 97
  explanation 95
dehydration packed beds
  acid 64
  gas 64
electrostatic precipitators 38
H₂SO₄ making packed beds
  final H₂SO₄ making 109
  intermediate H₂SO₄
  making 102
  gas 102

Scrubbing acid plant exit gas
  lowers SO₂(g) 100, 272
Scrubbing metallurgical gas
  dust and impurity removal 39-42
  industrial data 40, 41
Scrubbing spent acid regeneration gas
  for dust removal 54
  dust concentrations before
  and after 52, 54
Shipping and handling
product sulfuric acid 8
spent sulfuric acid 79
sulfur 20-21

Single contact acidmaking
cesium catalyst avoids catalyst degradation 155-156
comparison with double contact acidmaking 109, 222-223
less equipment and energy use 223
lower SO₂ oxidation efficiency 222
flowsheets 100
H₂SO₄ making tower 272
simplified 254
H₂SO₄ making calculations
mass flows and flowrates 253-269, 375-381
product acid temperatures 271-286
heat transfers between catalyst beds 235-242
industrial data
catalytic SO₂ oxidation (conversion) 82-87
H₂SO₄ making (absorption) 109-115
temperature control
gas (by passing) 243-251
input acid
acid coolers 280
bypass of 107
product acid 277-279

SO₂ concentrations in industrial acidmaking gases 74
in catalytic SO₂ oxidation gases after intermediate
H₂SO₄ making 224-227
before intermediate H₂SO₄ making 82-87
in gas dehydration gases 66-68
in H₂SO₄ making gases final H₂SO₄ making 266-269
intermediate H₂SO₄ making 110-115
in metallurgical gases 33
electrostatic precipitation gases 36-37
in spent acid decomposition furnace gases 54-55
control of 53
in sulfur burning gases 26-28
control of 27
produced by:
smelting and roasting of sulfide minerals 33
spent acid decomposition 47-57
sulfur burning 18-30
SO₂(g) + ½O₂(g) → SO₃(g) oxidation, catalytic 71-98 (see also SO₂ oxidation efficiency)
after intermediate H₂SO₄ making 214
catalyst for 89-98
reaction mechanism 90
double contact vs. single contact 222-223
equilibrium equation for 124
graphical representation as equilibrium curve 121, 125-126
derivation of 119-128, 293-303
with Ar in feed gas 313-315
with CO₂ in feed gas 311-313
with SO₃ in feed gas 348-354
heat release 2
heatup path representation of
SO₂ oxidation - calculations
1st catalyst bed 129-146
2nd catalyst bed 165-175
with CO₂ in feed gas 194-196
with SO₃ in feed gas 189-193
after intermediate H₂SO₄ making 217-218
matrices for
1st catalyst bed 139
2nd catalyst bed 173
3rd catalyst bed 344-345
with CO₂ in feed gas 196
with SO₃ in feed gas 192, 356-359
after intermediate H₂SO₄ making 218
intercept representation of maximum (equilibrium) SO₂ oxidation calculations
1st catalyst bed 147
Goal Seek 326
graphical 148-149
2nd catalyst bed 177
Goal Seek 339
graphical 180
3rd catalyst bed 346-347
4th catalyst bed 366
after intermediate H₂SO₄ making 217
Goal Seek 367
graphical 219-221
with CO₂ and SO₃ in feed gas 370-374
key step in sulfuric acid production 119
kinetics 89
catalyst for 71-98
faster with increasing temperature 90
industrial significance 162
slower with:
decreasing O₂ in gas 95
decreasing SO₂ in gas 95
increasing SO₃ in gas 95
offset by:
higher gas temperatures 162
thicker catalyst beds 95
maximum SO₂ oxidation
equilibrium 120
heatup path-equilibrium curve
intercept 147
SO₂ oxidation efficiency
1st catalyst bed 147-158
2nd catalyst bed 181
3rd catalyst bed 187
4th catalyst bed 366
after intermediate H₂SO₄ making
catalyst beds 219-221
cesium catalyst effect on
double contact acid plants 233
single contact acid plants 154-155
double contact-single contact
comparison 230-231
3-1 vs. 4-0 comparison 222
gas temperature effect on
double contact acid plant 233
single contact acid plant 208
O₂ in gas concentration
effect on 206
percent SO₂ oxidized defined 120
equilibrium 121
1st catalyst bed 120
2nd catalyst bed 166
after intermediate H₂SO₄ making
3rd catalyst bed 216
total 221
pressure effect on 204-205
SO₂ in gas concentration
affects 151, 154-156
SO₃ in gas concentration
affects 193
total after SO₂ oxidation in all catalyst beds including after H₂SO₄
making beds 221
1-0 acid plant 147-158
2-0 " 181
3-0 " 187
4-0 " 222, 230
5-0 " 231
1-1 " 232
2-1 " 232
3-1 " 230, 232
4-1 " 231, 232
2-2 " 230
3-2 " 231
1-3 " 230
2-3 " 231
1-4 " 231
1-1-1 " 234

SO₃ concentrations in industrial gases
1st catalyst bed feed gas 82-87
H₂SO₄ making input gases
final H₂SO₄ making 109, 224-227
intermediate H₂SO₄
making 109, 110-115
metallurgical furnace offgas 74
precipitator input and
output gas 36-37
spent sulfuric acid regeneration
furnace offgases 51-52, 74
in sulfur burning offgas 24-25
enthalpy 318
enthalpy vs.
temperature equation 316-318
produced during sulfur burning 74
enters 1st SO₂ oxidation
catalyst bed 74, 189
production from SO₂
catalytic oxidation 2
heat release 2
reacts with H₂O in sulfuric acid to make
new H₂SO₄ 4
heat release 4
removed from gas during gas cleaning
(aqueous scrubbing) 74
none in metallurgical 1st catalyst bed
feed gas 74
none in spent acid regeneration 1st
catalyst bed feed gas 74
removed from gas during subsequent
H₂SO₄ making 110-115, 224-227
in SO₂ oxidation equilibrium
equations 190, 348
in SO₂ oxidation heatup path
calculations 190-192
in SO₂ oxidation intercept
calculations 193, 356, 358
vapor pressure over sulfuric acid 104
SO₂ oxidation efficiency affected by 193
Specific gravity (see Density)
Spent sulfuric acid regeneration 47-57
acid (spent) atomization in 50
decomposition furnace 48, 52 (photo)
air (hot) for 48
lance sprayers 48
nozzles 50
spinning cup 50
acid (spent) source 49
byproduct from organic catalysis 47
compositions (table) 49
evaporation of water from 49
handling and transportation 49
acid (spent) decomposition reactions 50
decomposition gas composition 51, 52
heat requirement 50
acid (new) production 6
description of process 47
flowsheets 6, 48
percentage of world acid production 12
atomization of spent acid 50
lance sprayers 48
nozzles 50
spinning cup 50
control 53
decomposition reactions 50
flowsheets
acidmaking 6
decomposition, cooling, cleaning,
\( \text{H}_2\text{O(g)} \) condensation 48
furnace 48, 52 (photo)
acid sprayers 48, 50
composition of gas from 52
description 48
hot air for 48
photograph 52
gas composition
leaving decomposition furnace 51, 52
catalytic \( \text{SO}_2 \) oxidation feed gas 74
gas cooling, cleaning and drying 51
dust-in-gas concentration
after cleaning 54
before cleaning 52
flowsheet 48
industrial data 55
\( \text{H}_2\text{SO}_4 \) production from 6
heat recovery from furnace gases 48
hot air for spent acid decomposition 50
industrial data 55
optimum decomposition 52-54
furnace operating conditions 53
diagram 53
oxygen used for 50
\( \text{O}_2 \)-in-gas concentration affects 53
diagram 53
photograph of decomposition furnace 52
product from 52
destination 52
\( \text{SO}_3 \) formation 53
minimization 53
reason for avoiding 53
sources of spent acid
methyl methacrylate manufacture 49
petroleum refining (alkylation) 49
spent acid handling and transportation 49
sprayers, acid
lance 50
number 50
spinning cup 50
undecomposed \( \text{H}_2\text{SO}_4 \) 53
Steam superheater 20
superheats boiler steam 236
Sulfur (see also Sulfur burning)
density 20-21
filtering of 21
largest source of sulfuric acid 12
mass balances
acidmaking 258
\( \text{H}_2\text{SO}_4 \) making tower 379
melting 21
melting point 20
molar balances
catalytic \( \text{SO}_2 \) oxidation
equilibrium curve 296
with \( \text{SO}_3 \) in feed gas 348
heatup path 133
with \( \text{SO}_3 \) in feed gas 269, 191
production of 20
pumping of 20
steam heated pumps 21
solid 21
melting and filtering of 20
sources of elemental sulfur 20
sources of sulfur (all forms) 12
elemental 12, 19
smelting and roasting offgas 12, 31
spent acid regeneration 12, 47
transportation of 20
liquid 20
steam heated vehicles 21
solid 21
offloading and onloading 21
viscosity 20
vs. temperature graph 21
Sulfur burning to \( \text{SO}_2, \text{O}_2, \text{N}_2 \) gas for
sulfuric acid manufacture 19-30
flowsheets 6, 20
atomization of sulfur for 22
lance sprayers 22
photograph 22
nozzles 22, 23
spinning cup 23

70% of world’s acid produced from air dehydration
flowsheet 60
industrial data 65
boiler cools gas and recovers heat
boiler photograph 23
burners
lance sprayers
photograph 22
nozzles 22
spinning cup 23
photograph (flame) 18

control of product gas composition
target composition
control of product gas temperature
method
target temperature
dehydrated air supply
dehydrated with strong sulfuric acid
excess dry air used by
flowsheets
acidmaking
air dehydration
sulfur burning and gas cooling
furnace
photograph 22
gas composition control
target gas composition
gas temperature control
target temperature
heat release
industrial data
air dehydration
sulfur burning
process description
product gas
N₂-in-gas concentration
O₂-in-gas concentration
raising and lowering
SO₂-in-gas concentration
raising and lowering
SO₃-in-gas concentration
reaction

control
independent with oxygen
industrial data
cooling of product gas

in fire tube boiler
photograph
in steam superheater
sulfur (molten) delivery to furnace
by steam heated pump
filtering
melting
melting temperature
pumps
temperature (industrial)
through steam heated pipes
viscosity

Sulfur dioxide (see SO₂)
Sulfur trioxide (see SO₃)
Sulfuric acid (see also H₂SO₄ making)
air dehydration with
compositions for
industrial
color
compositions
measurement of
sonic
consumption, world
uses
density
electrical conductivity
freezing points
metastable
gas dehydration with
industrial data
history
manufacture flowsheet
double contact acid plant
single contact acid plant
from metallurgical offgas
from spent sulfuric acid decomposition offgas
from sulfur burning gas
oleum

specific gravity
plant (photo)
photograph
price
by year (graph)
production history
locations (map)
shipping and handling
spent sulfuric acid
sources (table)
smelting and roasting gas
spent acid regeneration gas
sulfur burning gas
spent 49 (see also Spent sulfuric acid regeneration)

reactions
- air and gas dehydration 61
- \( \text{H}_2\text{SO}_4 \) making 4
- historical processes 11-12
- phosphate fertilizer 13
- \( \text{SO}_3 \) making 2
- spent acid decomposition 50
- sulfur burning 5

transportation 8
- spent sulfuric acid 49
- sulfur 20-21

uses 15

viscosity 292

worldwide production 13

Supported liquid phase catalyst 89-91
(see also Catalyst, \( \text{SO}_2 \) oxidation)

phase diagram 91

\( \text{SO}_2 \) oxidation mechanism 90

Temperatures, industrial
- air dehydration 65
- boiler 24-25, 33-34
- catalyst bed input gas 82-87, 224-227
  - increases with bed number 162
  - explanation 162
- electrostatic precipitation 36-37
- gas dehydration 66-68
- \( \text{H}_2\text{O}(g) \) condensation
  - metallurgical gas 40-43
  - spent acid decomposition gas 55
- \( \text{H}_2\text{SO}_4 \) making (absorption)
  - final 266-269
  - heat from acid recovery
    - system 281, 282
    - intermediate 105, 110-115
  - metallurgical offgas 33
- \( \text{SO}_2 \) oxidation catalyst bed input and output gas temperatures
  - after intermediate
    - \( \text{H}_2\text{SO}_4 \) making 224-227
  - before intermediate
    - \( \text{H}_2\text{SO}_4 \) making 82-87
- spent acid decomposition furnace 51, 53
  - optimum 53
- sulfur burning furnace, 24-25

Temperature control, acid 276-281
- acid cooling 105, 280
- cooler bypass 107
- dehydration and \( \text{H}_2\text{SO}_4 \) making
  - output acid 105
  - graphs 277-279

Temperature control, gas 243-251
- by bypassing gas around heat transfer devices 243
- calculations 245-250
- flowsheet 244
- photograph 244
- principle 243
- percent bypass
  - industrial 249
  - inefficiency explained 250
  - theoretical 247
- up and down 249
  - gas always moving through bypass 249

Times, residence (see Residence times)

Triple contact acidmaking (theoretical) 234

Uses, sulfuric acid (table) 13-15

Vanadium (\( \text{V}_2\text{O}_5 \)) catalyst 89-98 (see also Catalyst, \( \text{SO}_2 \) oxidation)

Venturi scrubber 60

Viscosity
- sulfur (graph) 21
- sulfuric acid 292

Waste acid 47 (see also Spent sulfuric acid regeneration)

Waste heat boiler (drawing) 34
- dust settling in 34
- temperatures in and out 33, 34

Waste heat recovery 34

Wet sulfuric acid (WSA) process 8

World sulfuric acid production
- by year (graph) 13
- locations (map) 14