

## Extension 15: The $\text{SO}_2/\text{O}_2/\text{SO}_3$ Equilibrium and the Manufacture of Sulfuric Acid

### 1. Introduction

One of the most important ideas that emerged from Unit 15 in the book was that different equilibrium concentrations of reactants and products can exist, depending on the starting concentrations of both, even though the equilibrium constant does not change at that temperature. We illustrated this with both the hydrogen and iodine reaction and the reaction of ethanoic acid and ethanol.

In this extension, we examine the way that sulfuric acid,  $\text{H}_2\text{SO}_4$ , was prepared in the past. We then look at the way it is manufactured now. **As with the reaction of hydrogen and nitrogen in the Haber process, the contact process involves compromise conditions so that yield and reaction rate are both commercially feasible.**

During this extension, we refer to equilibrium constant,  $K_p$ , in terms of equilibrium pressures of reactants and products and to the equilibrium constant,  $K_c$ , in terms of equilibrium molar concentrations of reactants and products. The Appendix discusses the conversion of  $K_p$  to  $K_c$ .

### 2. The importance of sulfuric acid

Sulfuric acid (also written as sulphuric acid, old name 'oil of vitriol') is one of the most important chemical feedstocks and is produced worldwide on a massive scale. It used to be stated that the wealth of a country is indicated by the volume of sulfuric acid produced by its industry. Since some countries now import chemicals made using sulfuric acid, rather than making those products themselves, the relationship between a country's gross national product and the amount of sulfuric acid it produced is more complicated than it was. Today, China, the USA, India, Russia and Morocco collectively produce more acid than all other countries put together. Annual world production of sulfuric acid is about 270 million tonnes ( $2.7 \times 10^{11}$  kg) and the world market for sulfuric acid is worth about \$80 billion. In the USA, manufacturers and users of sulfuric acid have even created a magazine solely about sulfuric acid, entitled (rather unimaginatively!) *Sulfuric Acid Today*. The **European Sulphuric Acid Association** (ESA, <https://www.sulphuric-acid.eu/>) brings together producers of the acid in Europe.

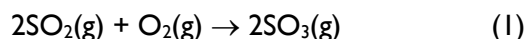
**Table 1** Uses of sulfuric acid

Use in manufacture	Percentage of sulfuric acid used for that purpose
Phosphate fertilizers	50
Metal processing and cleaning	10
Non-fertilizer phosphates	6
Fibres	5
Hydrofluoric acid	2
Paints and pigments	2
Pulp and Paper	1
Others	24

(data from <http://www.essentialchemicalindustry.org/chemicals/sulfuric-acid.html>)

### 3. Making H<sub>2</sub>SO<sub>4</sub> in the lab

The first stage in making sulfuric acid in the lab is to make sulfur trioxide:



The oxidation number of sulfur increases in this reaction, from +4 (in SO<sub>2</sub>) to +6 (in SO<sub>3</sub>). Therefore reaction (1) is an example of an oxidation reaction.

Fig 15.1 shows the traditional laboratory method. SO<sub>2</sub> and O<sub>2</sub> are dried by bubbling the gases through bottles of concentrated sulfuric acid. Sulfuric acid is very greedy for water (it is said to be hygroscopic) and is an excellent drying agent for gases with which it does not react. For this reason, we shouldn't read anything special into the use of the acid to dry gases in the preparation of SO<sub>3</sub>. The use of concentrated sulfuric acid to dry the sulfur dioxide and oxygen gases is simply a matter of convenience and the bubbles of sulfur dioxide through the acid serve as a useful indicator of gas flow rate, which should be slow. To achieve a high enough temperature, four Bunsen flames are used to heat the platinised asbestos. To resist the high temperatures, the platinised asbestos is held in a silica tube.

Platinum chloride is used to catalyse the conversion of SO<sub>2</sub> into SO<sub>3</sub>. In the lab, platinum is often used in the form of platinised asbestos, made by impregnating asbestos fibres with chloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>) and roasting the fibres in a hot flame, producing platinum chloride, PtCl<sub>2</sub>.

The preparation of SO<sub>3</sub> is carried out in a fume cupboard. The melting point of SO<sub>2</sub> and O<sub>2</sub> are well below that of the temperature of salt/ice and unused reactants are pumped away. The sulfur trioxide collects as colourless frozen crystals. The melting point of SO<sub>3</sub> is only 17 °C, so that it is easily crystallized.

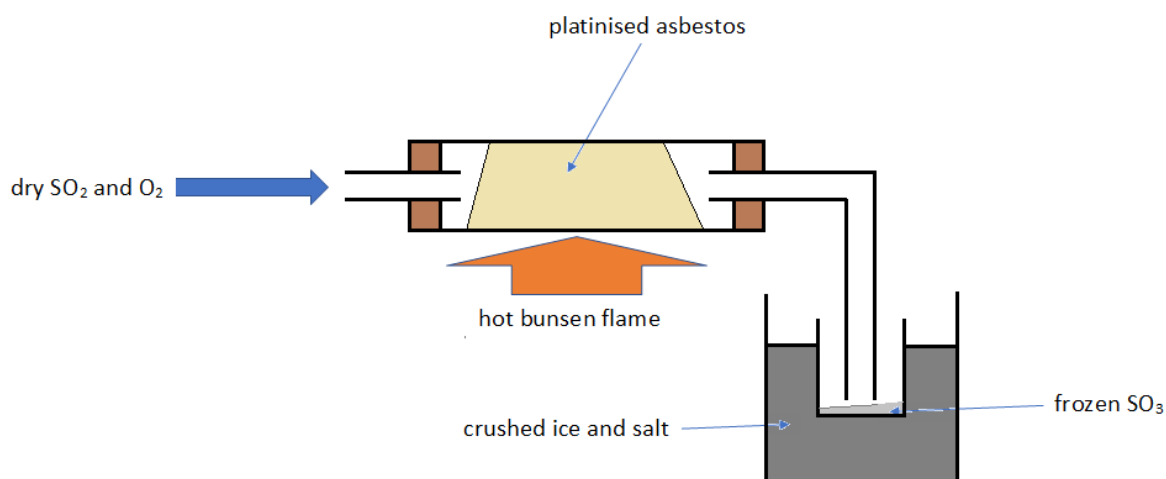


Fig. 15.1 Laboratory preparation of sulfur trioxide (sulphur trioxide).

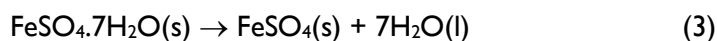
Crystalline sulfur trioxide reacts violently with water. If we use excess water, the product is dilute sulfuric acid.



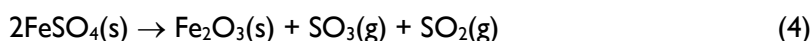
The oxidation number of sulfur remains at +6 during this reaction.

## 4. Historical interlude: older methods for manufacturing sulfuric acid

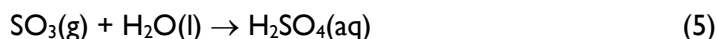
Sulfuric acid has been known for over 700 years. Early preparation depended upon distilling green crystals of iron(II) sulfate (also known as *green vitriol* or ferrous sulfate) and so the acid was known as *oil of vitriol*. Sulfuric acid produced by this method was also referred to as Nordhausen Oil of Vitriol, after the German city of the same name. The reaction may be thought of as occurring in two stages. First, the loss of water of crystallisation on heating:



When the anhydrous iron(II) sulfate is more strongly heated, sulfur dioxide and sulfur trioxide gases are produced:

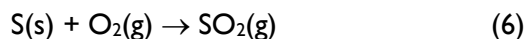


The sulfur trioxide then reacts with the water of the first stage, producing sulfuric acid:



Distillation of the solution produced more concentrated sulfuric acid.

As sulfuric acid became more important, larger quantities were needed. This led to the **Lead Chamber Process**, so-called because the reactions were carried out in large acid-resistant lead-lined containers. Sulfur was first burned in air to produce sulfur dioxide gas:



The conversion of  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$  was achieved by reacting  $\text{SO}_2$  with steam in the presence of nitric oxide gas ( $\text{NO}(\text{g})$ ) which acts as a catalyst: the overall reaction for this stage is reaction equation (5) above. The acid produced by this process was known as **chamber acid**, and it was about 70% pure.

The modern method for the manufacture of sulfuric acid is known as the **Contact Process**. It is described below. The acid produced is pure and highly concentrated. The Contact Process was first patented by Peregrine Phillips in 1831. The Contact Process has taken over from the Lead Chamber process as the process of choice to manufacture sulfuric acid on a massive international scale.

## 5. The $\text{SO}_2/\text{SO}_3$ equilibrium

As with the lab method of preparing sulfuric acid, the first stage of the Contact Process involves the conversion of  $\text{SO}_2$  to  $\text{SO}_3$  and before proceeding further we will examine this equilibrium in greater detail. We represent the reaction as:



where, as is customary, the two arrows emphasise that this reaction will achieve an equilibrium concentration of sulfur dioxide and sulfur trioxide<sup>1</sup>.

<sup>1</sup> Strictly speaking, we should use the single arrow in equation (7) as we are displaying the reaction enthalpy change,  $\Delta H$ , and  $\Delta H$  only applies to the theoretical case of complete conversion.

Since reaction (7) is exothermic, the equilibrium constant falls with increasing temperature. Since there is a change in the number of molecules of gaseous species during the reaction (three molecules forming two), the values of the equilibrium constant in terms of equilibrium partial pressure ( $K_p$ ) and equilibrium molar concentrations ( $K_c$ ) are different (Table 1). These quantities are defined as follows:

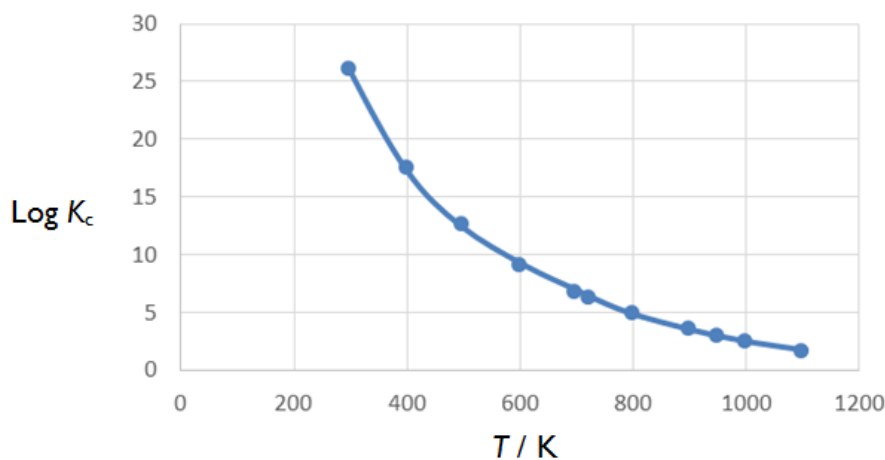
$$K_p = \frac{(p_{\text{SO}_3})^2}{p_{\text{O}_2} \times (p_{\text{SO}_2})^2} \quad \text{bar}^{-1} \qquad K_c = \frac{(c_{\text{SO}_3})^2}{c_{\text{O}_2} \times (c_{\text{SO}_2})^2} \quad \text{mol}^{-1} \text{ dm}^3$$

(Values of Standard Gibbs Energy changes  $\Delta G^\ominus$  for reaction (7) are also included in Table 1. The importance of this quantity, and its relation to  $K_p$ , will become clear after reading Unit 16 and the calculation of  $\Delta G^\ominus$  from  $\Delta S^\ominus$  and  $\Delta H^\ominus$  is discussed in Appendix 1).

**Table 2** Thermodynamic data for  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$

$T / \text{K}$	$\Delta G^\ominus / \text{kJ mol}^{-1}$	$K_p \text{ bar}^{-1}$	$K_c \text{ mol}^{-1} \text{ dm}^3$
300	-141.5	$4.36 \times 10^{24}$	$1.09 \times 10^{26}$
723	-62.0	$3.00 \times 10^4$	$1.81 \times 10^6$

Fig. 15.2 shows the variation of  $\log K_c$ , between 300 and 1100 K. ( $\log K_c$  compresses the values of  $K_c$  so trends are easier to see).



**Fig. 15.2**  $\log K_c$  for  $\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$  against reaction temperature

As with the Haber-Bosch process, there are two factors to be taken into account in order to maximise yield of sulfur trioxide.

The first is the yield of  $\text{SO}_3(\text{g})$ . At 298 K,  $K_c$  is very large indeed, but it falls very rapidly with increasing temperature. Low concentrations of sulfur dioxide in dry air ( $\approx 10\%$  by volume) at about 1.5 bar pressure are used in the Contact process and although it does not affect the equilibrium constant this low concentration of  $\text{SO}_2$  reduces the number of moles (i.e. yield) of  $\text{SO}_3$  product at equilibrium in accordance with Le Chatelier's Principle<sup>2</sup>. Calculations show that at the 'compromise'

<sup>2</sup> The independence of  $K_c$  upon concentration is discussed on pages 270-271 of the book.

temperature of 723 K (450 °C), there is still 99.5% conversion of SO<sub>2</sub> to SO<sub>3</sub>. Above this temperature, the yield of SO<sub>3</sub> falls off rapidly. This is discussed further in s6 below.

The second factor is the rate at which equilibrium is attained. Reaction (7) is extremely slow at room temperature even in the presence of a catalyst. The higher the temperature, the faster the rate. The 'compromise' temperature of 723 K (450 °C) is used to satisfy both the kinetic and yield requirements. Operating at high pressures would increase the yield of SO<sub>3</sub> and the rate of reaction, but the improvements are not justified by the costs of the high pressure pumps that would be needed and so the reaction (unlike the Haber-Bosch process) is carried out at just above atmospheric pressure, about 1.5 bar (≈ 1.5 atm). Such a pressure is enough to force the reactants and products through the pipes and converters.

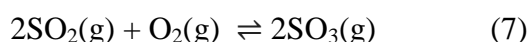
The catalyst used in the Contact Process is not platinum (which is expensive and easily deactivated by impurities) but vanadium (V) Oxide, (vanadium pentoxide, V<sub>2</sub>O<sub>5</sub>).

## 6. Yield of SO<sub>2</sub>

Manufacturers are most interested in the yield of a product – here the yield of SO<sub>3</sub>(g). There are several definitions of the word 'yield' used. One definition of yield is that it is the percentage by mass of product obtained experimentally compared to the theoretical yield of product if the reaction went to completion. This is the usual way that yields are calculated in organic synthesis in the laboratory (see p132 in the book).

$$\text{percentage yield} = \frac{\text{experimental yield}}{\text{theoretical yield}} \times 100\%$$

Another definition of yield is that it is the percentage of the number of moles of a reactant converted to a product. For example in the reaction:



2 mol of SO<sub>2</sub> react with 1 mol of O<sub>2</sub>, producing 2 mol of SO<sub>3</sub>. Suppose we start with *a* moles of SO<sub>2</sub> and that *x* moles of O<sub>2</sub> are used up at equilibrium. Equation (7) shows that there will be 2*x* moles of SO<sub>2</sub> used up and 2*x* moles of SO<sub>3</sub> present at equilibrium.

The maximum number of moles of SO<sub>3</sub> that can be produced is equal to the initial amount of SO<sub>2</sub>, *a* moles. The % molar conversion of SO<sub>2</sub> to SO<sub>3</sub> is:

$$\frac{100 \times \text{number of moles of SO}_3 \text{ at equilibrium}}{\text{maximum number of moles of SO}_3 \text{ possible at equilibrium}} = 100 \times \frac{2x}{a}$$

If virtually all of the SO<sub>2</sub> is converted at that temperature, then 2*x* = *a* and the conversion is 100%.

Appendix 3 shows in detail how the percentage conversion may be calculated from a knowledge of *K<sub>c</sub>* at that temperature, the total pressure and the starting amounts of SO<sub>2</sub> and O<sub>2</sub>. The calculations confirm that the yield of SO<sub>3</sub> does not improve appreciably with higher pressure and that above 723 K, the yield falls off significantly.

## 7. The Contact Process

### Stage 1: conversion of S to SO<sub>2</sub>

The reactants in stage 1 are pure sulfur and oxygen (in air). Most of the sulfur used in the Contact Process is obtained as a waste product from the purification of crude oil.

The solid sulfur is sprayed into a furnace and burned in a blast of dry air (excess oxygen) at about 1000 °C. The reaction is strongly exothermic and the sulfur burns with a blue flame:



The emerging gases are very hot and contain about 10% SO<sub>2</sub> and oxygen-depleted air (with [O<sub>2</sub>] ≈ 10%). The hot gases are passed through heat exchangers to extract heat which is then re-used elsewhere. This cools the gas mixture to about 450 °C as it enters stage 2.

### Stage 2: conversion of SO<sub>2</sub> to SO<sub>3</sub>

The reaction:

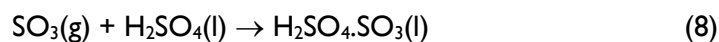


takes place at 450°C and at about 1.5 bar pressure over a bed of vanadium (V) oxide. The air/SO<sub>2</sub> mixture (plus any SO<sub>3</sub> that has already been produced) is passed through four beds of catalyst before proceeding to stage 3. The purpose of the four beds is to allow the SO<sub>2</sub> gas time to convert to SO<sub>3</sub>. The beds help the reaction to achieve equilibrium in order to maximise the yield of SO<sub>3</sub>.

Since reaction (7) is exothermic, heat exchangers take some of the heat away so that the yield of SO<sub>3</sub> is not reduced by too high a temperature.

### Stage 3: conversion of SO<sub>3</sub> to H<sub>2</sub>SO<sub>4</sub>

If SO<sub>3</sub> is passed into water, the heat generated by reaction (5) (above), causes the acid solution to form a fine mist. Instead, the sulfur trioxide is dissolved in concentrated sulfuric acid itself, making a fuming acid called oleum. Oleum has the formula H<sub>2</sub>SO<sub>4</sub>.SO<sub>3</sub>:



The oleum is a fuming liquid. It may be subsequently diluted to make 'ordinary' concentrated sulfuric acid, which contains about 98% acid.

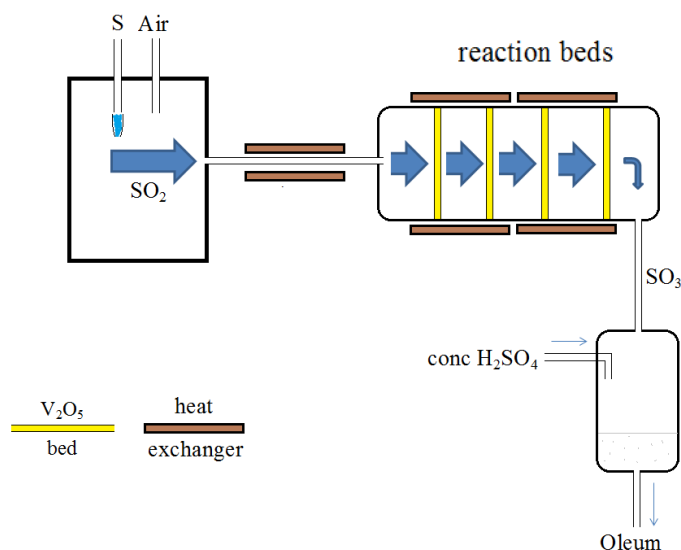


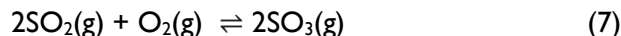
Fig. 15.3 Simplified block diagram of the Contact process

## Appendix I: calculating $\Delta G^\ominus$ from $\Delta S^\ominus$ and $\Delta H^\ominus$

Unit 16 introduced an expression for the standard Gibbs Energy change of a reaction that takes place at temperature  $T$  K:

$$\Delta G^\ominus = \Delta H^\ominus - T \cdot \Delta S^\ominus \quad (\text{A1})$$

The standard enthalpy change,  $\Delta H^\ominus$ , of the reaction:



is calculated following the pattern outlined in Unit 13 (p227) in the book:

$$\Delta H^\ominus = 2\Delta H_f^\ominus(\text{SO}_3(\text{g})) - (2\Delta H_f^\ominus(\text{SO}_2(\text{g})) + \Delta H_f^\ominus(\text{O}_2(\text{g})))$$

$\Delta H_f^\ominus(\text{O}_2(\text{g}))$  is zero and  $\Delta H_f^\ominus(\text{SO}_3(\text{g}))$  and  $\Delta H_f^\ominus(\text{SO}_2(\text{g}))$  are obtained from tables or from the NIST chemical database and

$$\Delta H^\ominus = (2 \times -395.77) - [(2 \times -296.81) + 0] = -197.9 \text{ kJ mol}^{-1}$$

The standard entropy change,  $\Delta S^\ominus$ , of reaction (7) is calculated in a similar way from standard entropy data:

$$\Delta S^\ominus = 2S^\ominus(\text{SO}_3(\text{g})) - (2S^\ominus(\text{SO}_2(\text{g})) + S^\ominus(\text{O}_2(\text{g})))$$

Although  $\text{O}_2(\text{g})$  is an element in its standard state,  $S^\ominus(\text{O}_2(\text{g}))$  is not zero. All entropies are positive and in units of  $\text{J mol}^{-1} \text{K}^{-1}$ :

$$\Delta S^\ominus = (2 \times 256.77) - [(2 \times 248.22) + 205.15] = -188.05 \text{ J mol}^{-1} \text{K}^{-1}$$

$\Delta S^\ominus$  must be in units of  $\text{kJ mol}^{-1}$  in order to produce  $\Delta G^\ominus$  in  $\text{kJ mol}^{-1}$ .

$$\Delta S^\ominus = -188.05 \text{ J mol}^{-1} \text{K}^{-1} = -0.18805 \text{ kJ mol}^{-1} \text{K}^{-1}$$



Substituting into equation (A1):

$$\Delta G^\ominus(\text{reaction (7)}) = -197.9 - [T \times (-0.18805)] \quad (\text{A2})$$

This allows us to calculate  $\Delta G^\ominus$  at temperature  $T$  K. For example, at 723 K:

$$\Delta G^\ominus(\text{reaction (7)}) = -197.9 - [723 \times (-0.18805)] = -62.0 \text{ kJ mol}^{-1}$$

In doing so, we are assuming that  $\Delta H^\ominus$  and  $\Delta S^\ominus$  are independent of temperature.  $\Delta G^\ominus$  is related to the **thermodynamic equilibrium constant**,  $K$  by the expression:

$$K = \exp\left(-\frac{\Delta G^\ominus}{RT}\right) \quad (\text{A3})$$

(see Unit 16, p. 290), where  $\Delta G^\ominus$  is now in units of  $\text{J mol}^{-1} \text{ K}^{-1}$  and  $R$ , the universal gas constant is in the units of  $\text{J mol}^{-1} \text{ K}^{-1}$ :

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

For example,

$$K(\text{reaction (7) at 723 K}) = \exp\left[-\frac{-61960}{(8.314 \times 723)}\right] = 3.00 \times 10^4$$

$K$  is unitless, but numerically equal to  $K_p$ .

The data points for Fig. 15.2 were obtained using equation (A2).

## Appendix 2: the conversion of $K_p$ to $K_c$

We have already noted that the thermodynamic equilibrium constant is unitless and that it is *numerically equal* to the equilibrium constant for the reaction in units of  $\text{bar}^3$ ,  $K_p$ :

$$K = K_p \quad (\text{A4})$$

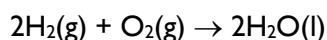
By 'numerically equal' we mean that they have the same number, although  $K$  is unitless and  $K_p$  is not. The conversion of  $K_p$  to the more familiar  $K_c$ , the equilibrium constant in terms of molar concentrations is accomplished by the equation:

$$K_c = \frac{K_p}{(RT)^{\Delta n}} \quad (\text{A5})$$

where  $R$  is the universal gas constant and  $T$  is the temperature (in kelvin).  $\Delta n$  is defined from the balanced chemical equation for the reaction, as follows:

$$\Delta n = [\text{sum of number of gas molecules produced}] - [\text{sum of number of gas molecules reacted}] \quad (\text{A6})$$

Any solid or liquid reactants or products are ignored (i.e. they are assigned zero number of molecules) in calculating  $\Delta n$ . For example, for the reaction in which liquid water is produced:

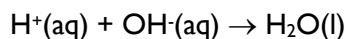
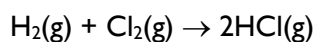


<sup>3</sup> Standard states are now defined in terms of pressure in bar, not atm. Therefore, pressure in bar is implied in assigning the standard symbol,  $\ominus$  in  $\Delta G^\ominus$ .



$$\Delta n = [0] - [2 + 1] = -3$$

If there is **no change in the number of molecules of gaseous species or if there are no gaseous species in the reaction equation** as in the two examples:



then  $\Delta n = 0$  and  $K_p$  and  $K_c$  are numerically equal – but they have different units:

$$K_p = K_c$$

(Remember that  $K$  is always numerically equal to  $K_p$ ). In Unit 16 in the book, and to make things simpler to introduce the subject, we only carried out calculations of  $K_c$  from  $\Delta G^\circ$  for reactions where  $\Delta n = 0$ .

Re-arrangement of equation (A3) permits conversion of  $K_c$  to  $K_p$ :

$$K_p = K_c \times (RT)^{\Delta n} \quad (\text{A7})$$

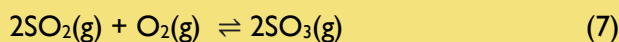
Experimental measurements of  $K_p$  are often reported in units of (standard) atmospheres as well as in units involving bar. The units of  $R$  used in equations (A6) and (A7) depend upon which unit of pressure is used: with  $R$  in units containing atm (for the case where  $K_p$  is in atm) or with  $R$  in units containing bar (where  $K_p$  is in bar) respectively:

$$R = 0.082057 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}; \quad R = 0.083145 \text{ dm}^3 \text{ bar K}^{-1} \text{ mol}^{-1}$$

In both cases  $R$  is not used in its most familiar units of ( $R = 8.3145$ ) J mol<sup>-1</sup> K<sup>-1</sup>. This is because  $K_c$  is expressed in units involving molar concentration (mol dm<sup>-3</sup>), so that the volume term in the units of  $R$  must also be in dm<sup>3</sup>.

### EXAMPLE 1

To illustrate this, we may apply equation (A7) to reaction (1), in which the reactants and products are gaseous and for which  $K_p = 4.36 \times 10^{24} \text{ bar}^{-1}$  at 300 K:



$$\Delta n = [2] - [2+1] = -1$$

$$K_c = \frac{K_p}{(RT)^{\Delta n}}$$

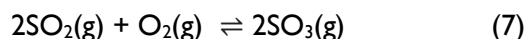
$$K_c = 7.36 \times 10^{24} / (0.083145 \times 298)^{-1} = 1.09 \times 10^{26}$$

Inspection of reaction equation (1) gives the units of  $K_c$  as:

$$(\text{mol dm}^{-3})^2 / (\text{mol dm}^{-3})^3 = \text{mol}^{-1} \text{ dm}^3$$

### Appendix 3 Calculation of yield of SO<sub>3</sub>(g)

As before, we start with the reaction:



Suppose we start with  $a$  moles of SO<sub>2</sub> and  $b$  moles of O<sub>2</sub> and no SO<sub>3</sub>. Suppose that the number of mols of O<sub>2</sub> used up is  $x$ . It then follows that there are  $2x$  moles of SO<sub>2</sub> used up and  $2x$  moles of SO<sub>3</sub> present at equilibrium. The number of moles of SO<sub>2</sub> at equilibrium is  $(a - 2x)$ . The number of mols of O<sub>2</sub> at equilibrium is  $(b - x)$  mols. The total number of mols at equilibrium,  $n_{\text{total}}$ , is:

$$n_{\text{total}} = \text{mols of unused O}_2 + \text{mols of unused SO}_2 + \text{mols of SO}_3$$

or

$$n_{\text{total}} = (b - x) + (a - 2x) + 2x = (a + b - x) \quad (\text{A8})$$

How do we find  $x$ ? The next stage is to find the relationship between these quantities and  $K_c$ . If we substitute the equilibrium concentrations in terms of  $a$ ,  $b$  and  $x$  into the expression:

$$K_c = \frac{(c_{\text{SO}_3})^2}{c_{\text{O}_2} \times (c_{\text{SO}_2})^2}$$

and remembering that molar concentration is the number of mols divided by the container volume and since  $(2x)^2 = 4x^2$ , we arrive at the expression:

$$K_c = \frac{4x^2/V}{[(b-x)/V][(a-2x)^2/V]} \quad (\text{A9})$$

where  $V$  is the volume of the container in which equilibrium has been achieved. Two of the  $V$  terms cancel, giving:

$$K_c = \frac{4x^2V}{(b-x)(a-2x)^2} \quad (\text{A10})$$

All the reactants and products are gases. Assuming that the ideal gas applies here (a reasonable assumption because the pressures used are about 1 bar), the total pressure of the gas mixture at equilibrium and at temperature  $T$ , symbolised  $P_T$ , is given by:

$$P_T V = n_{\text{total}} RT = (a + b - x) RT$$

or

$$V = n_{\text{total}} RT / P_T = (a + b - x) RT / P_T \quad (\text{A11})$$

The advantage of using equation (A11) is that the container volume is now expressed in terms of the total pressure, something that is easier to control and measure than container volume. We then substitute the right hand side of equation (A11) - the bit in bold - into the  $V$  term in equation (A10), yielding:

$$K_c = \frac{4x^2(a+b-x)RT}{(a-2x)^2(b-x)P_T} \quad (\text{A12})$$

Experiments provide  $K_c$  values at different temperatures. We know the starting number of moles  $a$  and  $b$  but we don't know  $x$ . We know  $R$ , the gas constant and the reaction temperature  $T$ . We also know the total pressure of the reacting mixture at equilibrium,  $P_T$ , in bar. By trial and error, we find the value of  $x$  that makes the RHS of equation (A12) equal the experimental value of  $K_c$ .

### Some % $\text{SO}_2$ conversions calculated using equation (A12)

#### $T = 723 \text{ K}$

Experiments show that for reaction (7) at 723 K (the 'compromise temperature'),  $K_c = 1.8 \times 10^6 \text{ mol}^{-1} \text{ dm}^3$ .  $R = 0.083145 \text{ dm}^3 \text{ bar K}^{-1} \text{ mol}^{-1}$ . Suppose that  $P_T = 1.5 \text{ bar}$ . Equation (A12) then becomes:

$$1.8 \times 10^6 = \frac{4x^2(a+b-x)(0.083145 \times 723)}{(a-2x)^2(b-x) \times 1.50} \quad (\text{A13})$$

We now have to select our amounts of reactant in the initial mixture. Suppose that  $a = 1.000 \text{ mol}$  and  $b = 10.00 \text{ mol}$  (an excess of oxygen). One way of finding out  $x$  is to incorporate the RHS of equation (A13) into an excel sheet. We know that  $x$  cannot be greater than 0.500, since (from equation (A7)) the maximum amount of  $\text{SO}_3$  that can be made is 1.000 mol  $\text{SO}_3$ .  $x$  is therefore between 0 and 0.500. After a number of attempts, it is found that the value of  $x$  that makes the RHS equal to  $1.8 \times 10^6$  is 0.4976.

The % molar conversion of  $\text{SO}_2$  to  $\text{SO}_3$  is then calculated using the formula introduced in s6 above:

$$100 \times \frac{2x}{a} = 2 \times 0.4976/1.00 = 99.5\%$$

We conclude that about 99.5% of the  $\text{SO}_2$  is converted to  $\text{SO}_3$  under these conditions.

If the total pressure (alone) is changed, to  $P_T = 5 \text{ bar}$ , then the %  $\text{SO}_2$  conversion is found to be 99.7%, not much of an increase for the considerable additional cost of installing and supplying energy to high pressure gas pumps.

#### $T = 900 \text{ K}$

Again,  $a = 1.000 \text{ mol}$  and  $b = 10.00 \text{ mol}$ ,  $P_T = 1.5 \text{ bar}$ . At 900 K,  $K_c = 3.45 \times 10^3 \text{ mol}^{-1} \text{ dm}^3$ . Trial and error gives  $x = 0.4442$  and the %  $\text{SO}_2$  conversion as 88.8%. Economically, this is a significant fall from about 99.5% at 723 K.

#### $T = 1000 \text{ K}$

Again,  $a = 1.000 \text{ mol}$  and  $b = 10.00 \text{ mol}$ ,  $P_T = 1.5 \text{ bar}$ . At 1000 K,  $K_c = 273 \text{ mol}^{-1} \text{ dm}^3$ : a marked reduction. It is not surprising then, the %  $\text{SO}_2$  conversion falls to 68.0 %.

## References

1. From the Essential Chemical Industry site of York University:

<http://www.essentialchemicalindustry.org/chemicals/sulfuric-acid.html>

2. Short article, revised by Jenny Simpson and Jonathon Petherick, on the manufacture of sulfuric acid and superphosphate fertiliser:

<https://nzic.org.nz/ChemProcesses/production/IB.pdf>

