Week 4

Calculating the Equilibrium Constant

WORKBOOK

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SPECIALIST TUITION

Contents

Syllabus Content

Calculating the Equilibrium Constant (K_{eq})
- Deduce the equilibrium expression (in terms of K_{eq}) for homogeneous reactions occurring in solution
- Perform calculations to find the value of K_{eq} and concentrations of substances within an equilibrium system, and use these values to make predictions on the direction in which a reaction may proceed
- Qualitatively analyse the effect of temperature on the value of K_{eq}
- Conduct an investigation to determine K_{eq} of a chemical equilibrium system, for example:
  - K_{eq} of the iron(III) thiocyanate equilibrium

Quiz

Question 1 (10 marks)

Ammonium chloride salt dissolves in water in a reversible reaction. The heat of solution is $+15 \text{ kJ mol}^{-1}$. Ammonium is an acidic ion in solution.

(a)   Write a balanced chemical equation for this reaction, including states and enthalpy.   **1**

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(b)   If 26 g of ammonium chloride are dissolved in 250 mL of water at 25 °C, what will be the final temperature of the water? Assume that the salt dissolves completely.   **3**

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(c) With reference to Le Chatelier's principle, explain the microscopic and macroscopic effects that would result from cooling this solution. **3**

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(d) The neutral salt silver nitrate is added to the solution. Explain the expected effect on the equilibrium position, and hence explain the expected effect on the solution's pH. **3**

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1   The Equilibrium Constant

We have now spent some time examining how equilibrium systems change their position in response to disturbances. So far, however, we have only described these changes from a qualitative standpoint, using terms such as 'shifting left' and 'shifting right'. Now, we will introduce a mathematical quantity that will allow us to analyse these changes quantitatively. This is the **equilibrium constant** K_{eq}.

The Equilibrium Constant Formula

The equilibrium constant K_{eq} relates the concentrations of all species involved in a chemical system at equilibrium at a certain temperature. It is equal to the product of all concentrations on the right-hand side, over the product of all concentrations on the left-hand species:

$$K_{eq} = \frac{[\text{product 1}] \times [\text{product 2}] \times \ldots}{[\text{reactant 1}] \times [\text{reactant 2}] \times \ldots}$$

Many resources will tell you to construct the equilibrium constant by multiplying the product concentrations and reactant concentrations at equilibrium and dividing the former by the latter, whilst raising each concentration to the power of the stoichiometric coefficient in the chemical equation. Though this is a useful way of looking at it, it is important to understand why this is the case.

Let's consider the following generic equilibrium:

$$2\,A + 3\,B \rightleftharpoons 4\,C + 5\,D$$

As we have done so far, we will by convention refer to the species on the left hand side as the reactants and those on the right-hand side as the products, even though in reversible reactions all species can perform both roles. Looking at the products of the equilibrium above, it is important to note that we don't just have C and D; we have 4 moles of C and 5 moles of D. Likewise, in the reactants, we have 2 moles of A and 3 moles of B. To make things clearer, we could rewrite the chemical equation as follows:

$$A + A + B + B + B \rightleftharpoons C + C + C + C + D + D + D + D + D$$
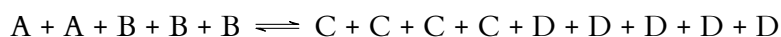
This means that when we calculate K_{eq}, we need to multiply [A] by itself twice (i.e. square it), multiply [B] by itself three times (i.e. cube it), and so on. In other words, we would calculate K_{eq} for this system as follows:

$$K_{eq} = \frac{[\text{C}]^4 [\text{D}]^5}{[\text{A}]^2 [\text{B}]^3}$$

The equilibrium constant K_{eq} is dimensionless. Although the reasons behind this are not examinable, it may interest you to know that this is because when substituted into the K_{eq} formula, all concentrations are actually representing the *reaction activity* of that species, which is equal to its concentration (in mol L^{-1}) divided by a reference concentration of $1\,\text{mol L}^{-1}$. The units cancel out, and so K_{eq} is dimensionless.

Questions

Question 1 (3 marks)

Ammonia is produced by the following equilibrium reaction:

$$N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$$
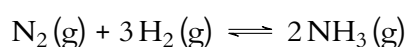
(a) Construct a formula for the equilibrium constant of this reaction. (1 mark)

(b) At equilibrium, the concentrations of ammonia, nitrogen, and hydrogen are $0.02\,\text{mol L}^{-1}$, $0.6\,\text{mol L}^{-1}$, and $0.4\,\text{mol L}^{-1}$, respectively. What is the value of the equilibrium constant? (2 marks)

Solution to Question 1

(a)
$$K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

(b)
$$K_{eq} = \frac{0.02^2}{0.6 \times 0.4^3}$$
$$= 0.01$$

Marking Criteria

(a) Provides correct expression (1 mark)

(b) Correctly substitutes values into equation (1 mark) and calculates correct value (1 mark)

Question 2 (3 marks)

Lead(II) hydroxide can exist in solution in a very one–sided equilibrium as follows:

$$Pb^{2+}(aq) + 3\,OH^-(aq) \rightleftharpoons Pb(OH)_3^-(aq)$$
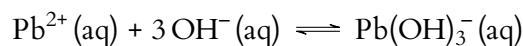
(a) Construct a formula for the equilibrium constant of this reaction. (1 mark)

(b) If this reaction has an equilibrium constant equal to 6×10^{-8} and the equilibrium concentrations of Pb^{2+} and OH^- are both 0.005 mol L^{-1}, what is the concentration of $Pb(OH)_3^-$ at equilibrium? (2 marks)

Solution to Question 2

(a)
$$K_{eq} = \frac{[Pb(OH)_3^-]}{[Pb^{2+}][OH^-]^3}$$

(b)
$$6 \times 10^{-8} = \frac{[Pb(OH)_3^-]}{0.005 \times 0.005^3}$$
$$[Pb(OH)_3^-] = 6 \times 10^{-8} \times 0.005^4$$
$$\therefore [Pb(OH)_3^-] = 3.75 \times 10^{-17}\ \text{mol L}^{-1}$$

Marking Criteria

(a) Provides correct expression (1 mark)

(b) Correctly substitutes values into equation (1 mark) and calculates correct concentration (1 mark)

Temperature Dependence

As briefly alluded to earlier, the equilibrium constant is only constant *for a given temperature*. If you change the pressure, volume or concentration of species in an equilibrium system, or if you set up the equilibrium on several different occasions under the same conditions, or if you add a catalyst, then the value of K_{eq} will always be the same. However, if you change the temperature of the system, then K_{eq} will have a different value.

The way that K_{eq} responds to temperature changes can tell us about the enthalpy change in a reaction. If the value increases when the system temperature is increased, it means that the temperature increase has favoured the species on the *numerator* of the fraction – in other words, it has caused an increase in product concentrations. This means the equation has pushed right, so the forward reaction must be endothermic.

Conversely, if the value decreases when the system temperature is increased, it implies this change has favoured the reactants, and as such the reaction has pushed left and the forward reaction must be exothermic.

State Dependence

Not all species in an equilibrium reaction actually make their way into an equilibrium constant formula. By far, the most common equilibria you will encounter for K_{eq} questions are what we call homogeneous reactions, which are where all species are in the same state, whether reactants or products. Furthermore, they are most commonly homogeneous aqueous equilibria, or homogeneous gaseous equilibria. Either way, in these cases, all species are included in the equilibrium constant formula.

However, you may encounter questions where an equilibrium includes a liquid species (rare) or a solid species (more common, especially in solubility equilibria). In these situations, the species in the liquid and solid states are **excluded** from the equilibrium constant calculation. This is because liquids and solids have fixed concentrations which do not change as an equilibrium changes position, and as such they do not affect the position of equilibrium by Le Chatelier's principle. Thus, they do not contribute to the quantitative determination of where that position is.

Gases and aqueous substances are always measured with respect to the volume of a container or a solvent. So adding or removing a gas will change the number of moles per litre of the container, and thus the concentration. Similarly with aqueous substances, changing the moles of solute doesn't affect the amount of solvent, and as such the number of moles per litre changes. However, if you remove a quantity of a liquid species from a reaction system, you are removing both moles *and* volume of the substance. Does the 'concentration' of water, in the amount of molecules of water per unit volume it occupies, change if you removed some? Not really. When you remove an amount of moles of a liquid or solid from a system, you remove an

equivalent volume of the substance with it, and the concentration remains unchanged Figure 1.
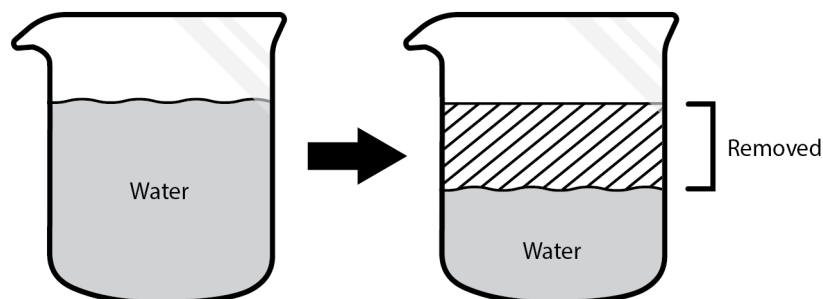

Figure 1 When we remove a certain amount of liquid (or solid) from a system, we remove moles along with volume. The amount of moles per unit volume is still exactly the same. If you have taken half the moles out, you also have half the volume left, and the concentration is unchanged.

Numerical Interpretations

Since K_{eq} is a fraction, if its value is greater than 1, it means that the concentration of products is higher overall than the concentration of reactants at equilibrium, and the reaction favours the products. If the value is lower than 1, it means that the reactants are overall favoured at equilibrium, and thus the reaction doesn't progress very far before reaching an equilibrium point. If the value is close to 1, it indicates a relative balance of species concentrations at equilibrium, i.e. a reaction that tends to sit around the middle of the position spectrum.

Numerically, this implies:

$K_{eq} \gg 1$, **products favoured**, position of equilibrium sits to the right

$K_{eq} \ll 1$, **reactants favoured**, position of equilibrium sits to the left

$K_{eq} \approx 1$, **similar concentrations**, position of equilibrium sits around midway

Remember that if a reaction doesn't progress very far before reaching equilibrium, leaving a large amount of reactants in the mixture, this actually means the *backward* reaction is quite strong and its spontaneity equals that of the forward reaction with much less concentration of reaction species. It is tempting to make the incorrect assumption that if there is a high amount of species on one side, then the reaction from that side is strong – it is in fact the reaction *towards* that side that is strong.

What if you were to write the equation for an equilibrium reaction in reverse, i.e. with the products on the reactants side and vice versa? In this case, you would still have the same chemical system, but you would have changed the definition of what is a reactant and what is a product. As such, the value of K_{eq} would be equal to the

reciprocal of its prior value. Furthermore, the temperature dependence would also go the other way, because you would have changed the sign of the enthalpy of reaction (i.e. $- \rightarrow +, + \rightarrow -$).

The Reaction Quotient

We will now introduce another quantity: the reaction quotient Q. The reaction quotient is calculated in the exact same way as the equilibrium constant, but it is defined at every point in the reaction, not just at equilibrium. As such, the reaction quotient is not a constant, but depends on the stage that the reaction is in. If the reaction quotient for a system is equal to its value of K_{eq}, then the system is at equilibrium. If the two are not equal, it means the system is approaching equilibrium. K_{eq} can be thought of as a 'special case' of Q: it is the value Q takes when the system is at equilibrium.

If $Q < K_{eq}$, then the system is approaching equilibrium from the left, i.e. shifting right. This is because there are fewer products and more reactants (lower numerator and higher denominator) at the current state of reaction than there should be at equilibrium, so it needs to move more to the right.

If $Q > K_{eq}$, then the system is approaching equilibrium from the right, i.e. shifting left. This is because there are more products and fewer reactants than there should be at equilibrium, so the system progresses towards the left.

Numerically, this implies:

$Q < K_{eq}$, **not at equilibrium**, system reacting to the right

$Q > K_{eq}$, **not at equilibrium**, system reacting to the left

$Q = K_{eq}$, system **at equilibrium**, no *net* reacting

In other words, the magnitude of Q relative to K_{eq} tells us about which way the reaction will proceed and how close it is to equilibrium. If you think there might be a mathematical relationship between Q, K_{eq}, and ΔG – which tells us the same thing – you would be entirely correct. There is an equation that links ΔG, Q and K_{eq} for any reaction, but we will not explore it in this course. However, we can qualitatively infer the values of ΔG for various values of Q:

$Q < K_{eq}$, **not at equilibrium**, $\Delta G < 0$

$Q > K_{eq}$, **not at equilibrium**, $\Delta G > 0$

$Q = K_{eq}$, system **at equilibrium**, $\Delta G = 0$

The ICE Box Method

Very commonly, you will encounter questions that tell you the initial concentrations of reactants, as well as the concentration of one species at equilibrium, and ask you to find K_{eq} and make further inferences about the system. To find K_{eq}, you need to know the concentrations of *all* species at equilibrium. This involves some delicate stoichiometric work, for which the so-called 'ICE box method' is well suited.

The acronym *ICE* stands for **I**nitial, **C**hange, **E**quilibrium. The ICE box method involves setting up a table of all the species in the reaction and writing in their initial concentrations, how they have changed, and what the final concentrations are at equilibrium. This allows you to set out your working clearly and concisely.

Let's explain the method using an example. Suppose we are answering a question that asks us to find K_{eq} for the equilibrium system $N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)$. The question tells us that, initially, 1 mol of nitrogen gas and 2 mol of hydrogen gas were placed in a 2 L chamber, while at equilibrium there were 0.12 mol of ammonia in the chamber. Your initial ICE box would look like this:

	$[N_2]$	$[H_2]$	$[NH_3]$
I	0.5	1	0
C			
E			0.06

Table 1 Starting off the ICE box with the values we know from the question.

Remember, the values we are filling in are *concentrations*, not numbers of moles. Since the chamber has a volume of 2 L, we divide all mole values in the question by 2 to arrive at concentrations.

We then focus on the initial row, where we know two of the three values, and work from here to fill in all the values of the table.

If $[NH_3]$ is initially zero, and $[NH_3]$ at equilibrium is 0.06, then the change in concentration must be $+0.06\ \text{mol L}^{-1}$. Therefore we write $+0.06$ as the change value for $[NH_3]$:

	$[N_2]$	$[H_2]$	$[NH_3]$
I	0.5	1	0
C			+0.06
E			0.06

Table 2 We need to find at least one value in the 'change' row using the data in the question, and then the rest will fall into place.

Take care to write the correct sign to indicate whether the change is an increase or decrease. This will be important in the next step. Once we know that ammonia has increased by 0.06 mol L^{-1}, we can tell by the stoichiometric ratios of the chemical equation that 0.03 mol L^{-1} of N_2 must have reacted to form this, along with 0.09 mol L^{-1} of H_2. So we can fill in the changes for these species too:

	$[N_2]$	$[H_2]$	$[NH_3]$
I	0.5	1	0
C	−0.03	−0.09	+0.06
E			0.06

Table 3 We have now used the equation to fill in the entire change row.

The final step is to use the newly discovered changes to fill in what the concentrations at equilibrium will be. If you know the initial concentration of a species, and how it changes, then you can easily work out what it is at the end:

	$[N_2]$	$[H_2]$	$[NH_3]$
I	0.5	1	0
C	−0.03	−0.09	+0.06
E	0.47	0.91	0.06

Table 4 We now have a complete ICE box.

And now we can determine the equilibrium constant:

$$\begin{aligned}
K_{eq} &= \frac{[NH_3]^2}{[N_2][H_2]^3} \\
&= \frac{0.06^2}{0.47 \times 0.91^3} \\
&= 0.01
\end{aligned}$$

A question could then ask you for a variety of things at this point. Some may require you to construct a second ICE box. For example, if the system is disturbed and re-establishes an equilibrium, you may need to do some of this *backwards*, starting at K_{eq} and then using that to fill in and complete the ICE box to find a concentration of a species.

Extreme Value Approximation

When K_{eq} is either very large or very small (in general, over 1000 or under 0.001), we can use an approximation rule to find the concentration of species at equilibrium only by knowing the initial conditions of the system. This relies on the following concepts:

- When K_{eq} is very small, the reactants don't react to any appreciable extent to make their concentrations significantly different to their starting values, so we make their initial and final concentrations equal.

- When K_{eq} is very large, the difference between the concentration of the products at equilibrium and their concentration if it were a one-way reaction is barely significant. As such, for the equilibrium concentrations of the products only, we assume that the reaction has gone the full way.

Let's consider an example of an equilibrium with a large K_{eq} to see how we can use the ICE box method to determine the concentrations at equilibrium.

Consider the equilibrium reaction $2\,NO\,(g) + O_2\,(g) \rightleftharpoons 2\,NO_2\,(g)$. At room temperature, the equilibrium constant is approximately 4×10^{13}. Let's say that 2 mol of nitrogen monoxide and 1 mol of oxygen gas are placed in a 1 L chamber to start with. How can we find their concentrations at equilibrium?

Let's start by noting that K_{eq} is so large that the equilibrium lies almost all the way to the right. Therefore, from the stoichiometric ratios in the equation, we can assume that the concentration of NO_2 at equilibrium is almost 2 M. But let's say that a small amount, say $2x$ hasn't reacted, so actually the concentration at equilibrium is $2 - 2x$ M. This means that the concentrations of O_2 and NO at equilibrium are x M and $2x$ M respectively. We can show this using an ICE box:

	[NO]	[O$_2$]	[NO$_2$]
I	2	1	0
C	$-(2-2x)$	$1-x$	$+(2-2x)$
E	$2x$	x	$2-2x$

Table 5 A tiny amount of oxygen and nitrogen have not reacted.

We can try to use the K_{eq} expression to solve for x, after which we will be able to determine all the concentrations:

$$K_{eq} = \frac{(2-2x)^2}{(2x)^2(x)}$$

$$4 \times 10^{13} = \frac{4 - 8x + 4x^2}{4x^3}$$

This is not an equation that anyone would like to solve in a Maths exam, let alone a Chemistry exam. So what are our options?

We know that x in this case is a very tiny number. So let's make the assumption that $2 - 2x \approx 2$. Then, our equation for K_{eq} looks a lot more solvable:

$$K_{eq} = \frac{2^2}{(2x)^2(x)}$$

$$4 \times 10^{13} = \frac{1}{2x^3}$$

$$x^3 = \frac{1}{8 \times 10^{13}}$$

$$x = 2.32 \times 10^{-5}$$

Therefore, the concentrations of each species at equilibrium are as follows:

$$[NO] = 2x = 4.64 \times 10^{-5} \text{ M}$$

$$[O_2] = x = 2.32 \times 10^{-5} \text{ M}$$

$$[NO_2] = 1.99995 \approx 2 \text{ M}$$

Fundamental Concepts

Equilibrium constant K_{eq} A dimensionless number for a given equilibrium reaction at a given temperature which tells us about the relative concentrations of reactants and products at equilibrium.

Equilibrium constant formula $K_{eq} = \frac{[P_1] \times [P_2] \times \dots}{[R_1] \times [R_2] \times \dots}$. Coefficients of species are converted into **powers**. Only **gaseous and aqueous** species are included as these are the only ones where concentrations change on the removal or addition of moles.

Magnitude of K_{eq} A high K_{eq} means the products are favoured at equilibrium, whereas a low value means the reactants are favoured. How K_{eq} changes in relation to changes in temperature can be predicted qualitatively if it is known whether the reaction is exothermic or endothermic.

Reaction quotient Q The reaction quotient has the same formula as K_{eq}, but is defined at all points in the reaction, so if $Q = K_{eq}$ then the system is at equilibrium. By comparing the value of Q to K_{eq}, the movement of the system, the relative reaction rates, and the sign of ΔG can all be inferred.

ICE box method **I**nitial, **C**hange, **E**quilibrium. A useful way of setting out equilibrium calculations involving K_{eq}, where a systematic series of steps allows you to find the concentration of all species at equilibrium from the data given in the question. Remember to convert to **concentrations** before entering values into the ICE box!

Approximations For **very large** or **very small** K_{eq} values, an approximation method can be used to solve for the concentration of all species at equilibrium when the starting conditions are known.

Questions

Question 3 (9 marks)

Iron(III) thiocyanate exists in an equilibrium in solution.

(a) Write a balanced chemical equilibrium for the formation of iron(III) thiocyanate in solution. (1 mark)

(b) Construct a formula for the equilibrium constant of this reaction. (1 mark)

(c) 100 mL of 0.1 M $Fe(NO_3)_3$ (aq) is mixed together with the same amount of 0.1 M KSCN. At equilibrium, the concentration of iron(III) thiocyanate is 2×10^{-2} M. What is the value of K_{eq} at this temperature? (3 marks)

(d) From your answer to part (c), predict whether this equilibrium lies further to the left or to the right at this temperature. Justify your prediction. (2 marks)

(e) If the reaction is exothermic, predict the effect on K_{eq} of decreasing the temperature of the system, and use this to explain the visible changes that would be observed. (2 marks)

Solution to Question 3

(a) Fe^{3+} (aq) + SCN^- (aq) $\rightleftharpoons$ $Fe(SCN)^{2+}$ (aq)
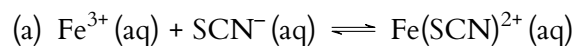
(b) $K_{eq} = \dfrac{[Fe(SCN)^{2+}]}{[Fe^{3+}][SCN^-]}$

(c) We need to find initial concentrations first. The total volume of the mixture is 200 mL. The molar amounts of both iron(III) and thiocyanate, which are in a 1:1 ratio, are calculated as follows:

$$n = cv$$
$$= 0.1 \text{ mol L}^{-1} \times 0.1 \text{ L}$$
$$= 0.01 \text{ mol}$$

Therefore $[Fe^{3+}]$ and $[SCN^-] = \frac{0.01}{0.2} = 0.05$ M. We can now set up an ICE box:

	$[Fe^{3+}]$	$[SCN^-]$	$[Fe(SCN)^{2+}]$
I	0.05	0.05	0
C			
E			0.02

By filling in the change of iron(III) thiocyanate, we can then complete the rest of the ICE box:

	$[Fe^{3+}]$	$[SCN^-]$	$[Fe(SCN)^{2+}]$
I	0.05	0.05	0
C	−0.02	−0.02	+0.02
E	0.03	0.03	0.02

Substituting the final equilibrium concentrations into K_{eq} gives us:

$$K_{eq} = \frac{0.02}{0.03 \times 0.03}$$
$$\therefore K_{eq} = 22.2$$

(d) K_{eq} is significantly larger than 1. This means the equilibrium lies further towards the right, as there are a greater proportion of products than reactants.

(e) Decreasing the temperature of an exothermic reaction favours the product side, and is therefore associated with a higher equilibrium constant. The observable effect of an increase in product concentrations would be a deeper red colour due to the increased presence of the iron(III) thiocyanate ion.

Marking Criteria

(a) Writes correct equation, with two species *combining* in the forward reaction (1 mark)

(b) Provides correct expression (1 mark)

(c) Correctly calculates initial $[Fe^{3+}]$ and $[SCN^-]$, uses ICE box method correctly to find final concentrations (1 mark), correctly solves for K_{eq} (1 mark)

(d) Identifies the equilibrium lies to the right (1 mark) and uses the value of the fraction being larger than 1 as the justification (1 mark)

(e) Recognises that K_{eq} reduces (1 mark), and links this to an increased red colour of the solution (1 mark)

Question 4 (8 marks)

Phosgene gas, $COCl_2$ (g), can reversibly decompose in an endothermic reaction to form carbon monoxide and chlorine gas.

(a) Construct a balanced chemical equation, including states and enthalpy, for this decomposition reaction. (1 mark)

(b) Construct a formula for the equilibrium constant of this reaction. (1 mark)

(c) At 300 K, the value of K_{eq} for the exothermic formation of phosgene gas from carbon monoxide and chlorine gas is 0.05. 1 mol of phosgene gas is introduced into a 4 L chamber at 300 K that contains 0.6 mol L^{-1} of carbon monoxide. Three minutes later there is 0.2 mol of phosgene gas in the chamber. Find the value of the reaction quotient at 3 minutes. Has this system reached equilibrium? (4 marks)

(d) At the 3 minute mark, after the above concentration measurements are made, the system is cooled down to 250 K. Is the system closer or further to equilibrium now? Justify your answer. (2 marks)

Solution to Question 4

(a) $COCl_2$ (g) $\rightleftharpoons$ CO (g) + Cl_2 (g) $\Delta H > 0$
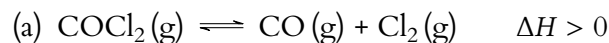
(b) $K_{eq} = \frac{[CO][Cl_2]}{[COCl_2]}$

(c) If the reaction to form phosgene gas has a K_{eq} of 0.05, then K_{eq} of the decomposition reaction at the same temperature must be the reciprocal, which is $\frac{1}{0.05} = 20$. Now we can set up an ICE box to determine the reaction quotient Q. We will then be able to work out whether or not the system is at equilibrium by comparing Q to K_{eq}.

COMMENT. *Since we do not know if the system is at equilibrium in this instance, it is good practice to write **Final** rather than **E** in the ICE box.*

	$[COCl_2]$	[CO]	$[Cl_2]$
I	0.25	0.6	0
C			
Final	0.05		

Now we know that the change in $[COCl_2]$ is –0.20. Thus, by stoichiometry, the changes for carbon monoxide and chlorine must both be +0.20. By adding these to the initial values, we can finalise the ICE box:

	$[COCl_2]$	$[CO]$	$[Cl_2]$
I	0.25	0.6	0
C	−0.20	+0.20	+0.20
Final	0.05	0.8	0.2

So $Q = \frac{0.8 \times 0.2}{0.05} = 3.2$.

Since 3.2 < 20, $Q < K_{eq}$. As such, the reaction has not yet reached equilibrium, and will keep proceeding in the forwards direction until it does.

(d) If the system is cooled down, Le Chatelier's principle predicts that the exothermic reaction will be favoured. Since the forward reaction is endothermic, this means the backward reaction will be the one favoured. This will reduce the value of K_{eq}, bringing it below 20 and moving it closer towards 3.2. As such, the system is now closer to equilibrium than it was before.

Marking Criteria

(a) Writes correct equation including enthalpy and states, and shows the phosgene decomposing rather than forming (1 mark)

(b) Provides correct expression (1 mark)

(c) Correctly sets up initial ICE box table paying close attention to which values were provided as mol and which were provided as $\mathrm{mol\,L^{-1}}$ (1 mark), correctly calculates final concentrations and reaction quotient (1 mark), recognises the equilibrium constant for the reaction as written is the reciprocal of what was provided in the question (i.e. 20) (1 mark), and reasons that because the quotient is less than the constant, the reaction is not at equilibrium (1 mark)

(d) Recognises that cooling down an endothermic reaction favours the reactants side, which lowers the value of the equilibrium constant (1 mark); states that because the quotient is now closer to the constant the system is now closer to equilibrium (1 mark)

2 Practical: Determining the Equilibrium Constant

Aim

To determine the value of the equilibrium constant for the chemical system described by $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$ at standard laboratory conditions.

Equipment

- 1 M solution of $Fe(NO_3)_3$ (aq)

- 1 M solution of KSCN (aq)

- Large test tubes

- Colorimeter or spectrophotometer

- 5 mL pipettes

- Distilled water

- 1 cm length cuvettes

Risk Assessment

This is a low risk experiment. Care must be taken using glassware, as breaks can cause cuts to skin. The spectrophotometer is a piece of electrical equipment and care should be taken handling water near electrical outlets due to the risk of electrocution.

Methods

We first need to understand the basis of the science of **colorimetry**. Colorimetry allows us to determine the concentration of a chemical species in solution by measuring the intensity of the light that passes through it. The **spectrophotometer** is an instrument used in colorimetry. It has a component called a **monochromator** which tunes the light it emits to a specific wavelength selected by the user. In this case we selected light with a wavelength of 480 nm, because this wavelength is particularly well absorbed by iron(III) thiocyanate.

We first tested four or five **reference solutions** of iron(III) thiocyanate – that is, solutions with known concentrations. We did this by first filling a small 1-cm-wide rectangular container known as a **cuvette** with a solution of iron(III) thiocyanate, and placing this into the spectrophotometer. Once switched on, the spectrophotometer shone a ray of light at 480 nm through the cuvette. The iron(III) thiocyanate absorbed some of this light, with some light unabsorbed and passing through to be detected by the photoresistor (light detector) on the other side of the cuvette.

The spectrophotometer compared the two intensities of light and determined an **absorbance** value. This was repeated for each reference solution, and their absorbance values were recorded.
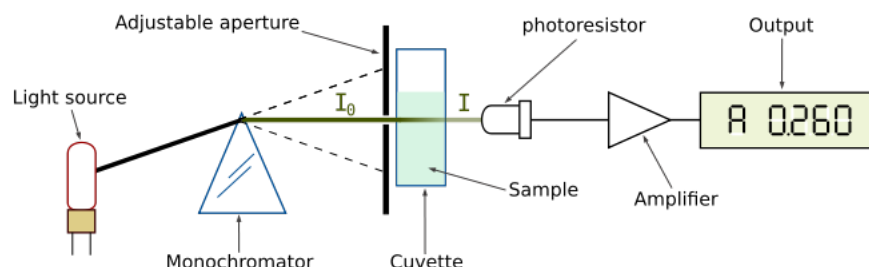

Figure 2 A schematic diagram of the components of a spectrophotometer. The wavelength is selected using a monochromator, passed through a cuvette of a known length containing the solution to be tested, and the intensity of light is detected and compared on the other side.

We observed a direct linear relationship between increasing concentration and increasing absorbance. This accords with **Beer's law**, which states that absorbance is proportional to concentration: $A \propto c$. Given this linear relationship, we were able to plot a line of best fit through the data to form a **calibration curve** (Figure 3).

Having generated this calibration curve, we then turned to determining the concentration of an unknown iron(III) thiocyanate solution. This solution was produced by mixing 100 mL each of the $Fe(NO_3)_3$ and KSCN solutions to create a 200 mL mixture containing initially 0.5 M Fe^{3+} (aq) and 0.5 M SCN^- (aq). Once this system reached an equilibrium, the concentrations of each species in the equilibrium were unknown.

Next, using a 5 mL pipette, 5 mL of the mixture was transferred into each of five clean large test tubes. Then, using a clean 5 mL pipette, a series of dilutions were performed with distilled water.

- To the first test tube, no distilled water was added.

- To the second test tube, 5 mL of distilled water was added, decreasing the concentration by a factor of 2.

- To the third test tube, 15 mL of distilled water was added, decreasing the concentration by a factor of 4.

- To the fourth test tube, 20 mL of distilled water was added, decreasing the concentration by a factor of 5.

- To the final test tube, 45 mL of distilled water was added, decreasing the concentration by a factor of 10.
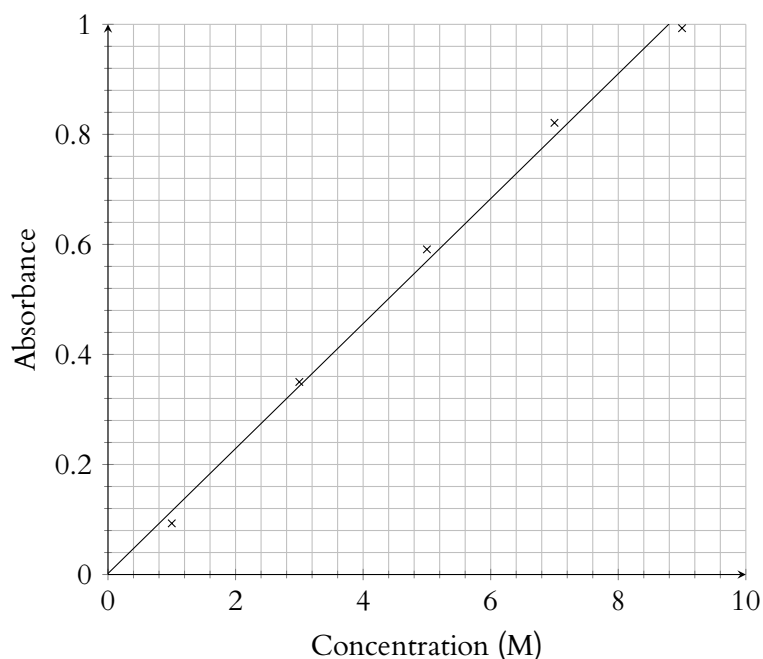
Figure 3 A calibration curve is a line of best fit drawn on a plot of absorbance against concentration when solutions of known concentrations are tested using colorimetry. The values shown here are illustrative only.

This resulted in five solutions of Fe^{3+} (aq) and SCN^- (aq), with initial concentrations of 0.5 M, 0.25 M, 0.125 M, 0.1 M and 0.05 M of each of the two species. Again, these were all initial concentrations and were not the true concentrations of the species at the time because all solutions had reacted to equilibrium.

Next, five 1 cm cuvettes were prepared by pouring a small amount of each solution to fill one cuvette. After calibrating a spectrophotometer to 480 nm and obtaining a previously determined calibration curve for the absorbance of $Fe(SCN)^{2+}$ (aq) at 480 nm, the absorbance of each cuvette was tested in the spectrophotometer. Each solution's absorbance was then matched to a concentration on the calibration curve, thus the concentration of $Fe(SCN)^{2+}$ (aq) in each solution at equilibrium was determined.

Next, for each of the five solutions, we used the ICE box method to calculate the concentration of the Fe^{3+} (aq) and SCN^- (aq) at equilibrium, as their initial concentrations were known and the final concentration of $Fe(SCN)^{2+}$ (aq) for each was now also known.

Lastly, we used this data to determine the K_{eq} for each solution.

Results and Interpretation

After testing the solution in test tubes 1 to 5, measuring their absorbances and determining the concentration of $Fe(SCN)^{2+}$ (aq) at equilibrium in each by reading off the calibration curve, we then assembled a table as follows, with K_{eq} values to be determined:

Test Tube	Absorbance	$[Fe(SCN)^{2+}]$ at Eq.	K_{eq}
1	A_1	C_1	
2	A_2	C_2	
3	A_3	C_3	
4	A_4	C_4	
5	A_5	C_5	

Then, we used the ICE box method to determine the equilibrium concentrations of Fe^{3+} (aq) and SCN^- (aq) in each solution. We were then able to find the value of K_{eq} using the following formula:

$$K_{eq} = \frac{[Fe(SCN)^{2+}]}{[Fe^{3+}][SCN^-]}$$

We can demonstrate this calculation for a test set of results. Let us assume that test tube 3, whose contents were diluted by a factor of 4 so that initial iron(III) and thiocyanate concentrations were 0.125 M, when run through the spectrophotometer, had an absorbance A_3 that when read off the calibration curve, corresponded to a iron(III) thiocyanate concentration of $C_3 = 0.094$ M. We can set up an ICE box:

	$[Fe^{3+}]$	$[SCN^-]$	$[Fe(SCN)^{2+}]$
I	0.125	0.125	0
C			
E			0.094

Recognising that the change in the concentration of iron(III) thiocyanate is +0.094, and that the stoichiometric ratio is 1:1:1, we can fill in the remainder of the ICE box:

	$[Fe^{3+}]$	$[SCN^-]$	$[Fe(SCN)^{2+}]$
I	0.125	0.125	0
C	–0.094	–0.094	+0.094
E	0.031	0.031	0.094

Now we can calculate K_{eq}:

$$K_{eq} = \frac{0.094}{0.031^2}$$
$$= 97.8$$

In this way, the K_{eq} for each original test tube was determined, and it was noted that each time the value came out very close to 97.8. This is the expected result. As long as the same equilibrium was set up at the same temperature (laboratory conditions), they have the same K_{eq} no matter what the starting concentrations were, since K_{eq} is constant for a given reaction at a given temperature.

Discussion

In this investigation, we used the technique of colorimetry to determine the equilibrium constant for a given reaction system with varying initial concentrations of reactants. The results we obtained were reliable, because after five repeats, we determined values for K_{eq} that were in agreement with each other.

Secondary sources indicate that the value of K_{eq} for this equilibrium is 98 at 25 °C[*] and 113 at 20 °C[†], which is consistent with the exothermic nature of the reaction. As our experiment was done at 25 °C, this represents an error of only 0.2%, indicating a high degree of accuracy.

Finally, the experiment had high validity because sources of error were controlled. The spectrophotometer was calibrated prior to use, and new cuvettes were used for each trial. All cuvettes used were of the same size (1 cm). Dilutions were done with clean pipettes. The other dissolved ions K^+, NO_3^-, Fe^{3+} and SCN^- do not significantly absorb at 480 nm wavelengths, and as such they do not interfere with colorimetry results.

Error may have been introduced by contaminants in the original solutions, as well as inaccuracies in the reference absorption calibration curve used for the experiment. To improve on this, the original solutions could be created as primary standards from their original solid salts, and the calibration curve could be cross referenced with other sources to check for any inaccuracies.

Conclusion

Using the technique of colorimetry, we were able to determine an average value of K_{eq} for the iron(III) thiocyanate equilibrium at 25 °C and found it to be roughly 98.

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[*] de Berg K, Maeder M, Clifford S. A new approach to the equilibrium study of iron(III) thiocyanates which accounts for the kinetic instability of the complexes particularly observable under high thiocyanate concentrations. *Inorg. Chim. Acta* 2016;445(24):155–159.   [†] Nyasulu F, Barlag R. Colorimetric determination of the iron(III)–thiocyanate reaction equilibrium constant with calibration and equilibrium solutions prepared in a cuvette by sequential additions of one reagent to the other. *J. Chem. Educ.* 2011;88(3):313–314.

Quiz Solutions

Solution to Question 5

(a) $NH_4Cl(s) \rightleftharpoons NH_4^+(aq) + Cl^-(aq)$ $\Delta H = +15 \text{ kJ mol}^{-1}$
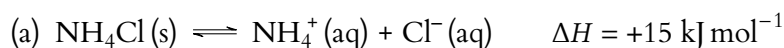
(b) For the total heat change, we need moles of ammonium chloride.

$$n = \frac{m}{M}$$
$$= \frac{26}{14.01 + 4 \times 1.008 + 35.45}$$
$$= 0.486\ldots \text{ mol}$$

Therefore, the heat change is $Q = -\Delta H = -(0.486\ldots \times 15) = -7.29\ldots$ kJ. We can then use specific heat to work out the temperature change:

$$Q = mc\Delta T$$
$$-7290.809\ldots = 250 \times 4.184 \times \Delta T$$
$$\Delta T = -6.97$$

Therefore, the final temperature of the water is $18.03\,°C$.

(c) Le Chatelier's principle states that when a system at chemical equilibrium is disturbed, the system adjusts itself so as to minimise the disturbance. When this system is cooled, the system reacts to produce more heat again, and the exothermic reaction is favoured. Thus, the system shifts to the left, and the forward rate of reaction drops whilst the backward rate of reaction increases. Macroscopically, we should notice ammonium chloride precipitating in the solution.

(d) Adding silver nitrate to the solution will result in a precipitation reaction occurring with chloride, forming insoluble silver chloride salt. The effect of this is removal of chloride ions from the equilibrium. Hence, by Le Chatelier's principle, the system shifts right to replenish these ions. As it does so, it produces more ammonium ions. Since ammonium is acidic, the pH of the solution will fall.