Unit 1 - Inorganic & Physical Chemistry

1.3.1 Chemical Equilibria

Part 1

Equilibrium Position
Equilibrium Constant
Introduction to Weak Acids & Bases
Salt Solutions

Pupil Notes
Learning Outcomes
Questions & Answers
1.3 CHEMICAL EQUILIBRIUM- part 1

Reactions at equilibrium
1. A chemical reaction is at equilibrium when the composition of the reactants and products remains constant indefinitely.

2. The equilibrium constant (K) characterises the equilibrium composition of the reaction mixture.

3. The equilibrium constant can be measured in terms of concentration or, for gases, in terms of pressure.

4. For the general reaction \( aA + bB \rightarrow cC + dD \)

\[ K = \frac{[C]^c [D]^d}{[A]^a [B]^b} \]

where \([A],[B],[C]\) and \([D]\) are the equilibrium concentrations of A, B, C and D, respectively, and \(a, b, c\) and \(d\) are the stoichiometric coefficients in a balanced reaction equation.

5. In a homogeneous equilibrium all the species are in the same phase.

6. In a heterogeneous equilibrium the species are in more than one phase.

7. The concentration of pure solids or pure liquids are constant and are given the value 1 in the equilibrium equation.

8. Equilibrium constants are independent of the particular concentrations or pressures of species in a given reaction.

9. The effects of changes in concentration or pressure on the position of equilibrium can be explained quantitatively in terms of a fixed equilibrium constant.

10. The presence of a catalyst does not affect the equilibrium constant.

11. Equilibrium constants depend on the reaction temperature.

12. For endothermic reactions a rise in temperature causes an increase in \(K\), i.e. the yield of product is increased.

13. For exothermic reactions a rise in temperature causes a decrease in \(K\), i.e. the yield of product is decreased.

Introduction to Strong and Weak

14. In aqueous solutions, strong acids are completely dissociated but weak acids are only partially dissociated.

15. Equimolar solutions of weak and strong acids differ in pH, conductivity and reaction rates but not in stoichiometry (amount) of reactions.

16. The weakly acidic nature of ethanoic acid, sulphur dioxide and carbon dioxide can be explained by reference to equations showing the equilibrium.
17 In aqueous solutions, strong bases are **completely dissociated** but weak bases are only **partially dissociated**.

18 Equimolar solutions of weak and strong bases differ in pH, conductivity but not in stoichiometry (amount) of reactions.

19 The weakly alkaline nature of ammonia, can be explained by reference to an equation showing the equilibrium.

**pH of salt solutions**

20 A soluble salt of a **strong acid** and a **strong base** dissolves in water to produce a **neutral** solution.

21 A soluble salt of a **weak acid** and a **strong base** dissolves in water to produce an **alkaline** solution.

22 A soluble salt of a **strong acid** and a **weak base** dissolves in water to produce an **acidic** solution.

23 **Soaps** are salts of weak acids and strong bases.

24 The acidity, alkalinity or neutrality of the above kinds of salt can be **explained** by reference to the appropriate **equilibria** (plural !).
1.3.1 Previous Knowledge

<table>
<thead>
<tr>
<th>Section</th>
<th>Exemplification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reversible reactions, dynamic equilibrium, altering equilibrium position.</td>
<td>This may result in costly reactants failing to be completely converted into products.</td>
</tr>
<tr>
<td>Effect of catalyst on equilibrium and the most favourable reaction conditions.</td>
<td>In a closed system, reversible reactions attain a state of dynamic equilibrium when the rates of forward and reverse reactions are equal.</td>
</tr>
<tr>
<td></td>
<td>At equilibrium, the concentrations of reactants and products remain constant, but are rarely equal.</td>
</tr>
<tr>
<td></td>
<td>To maximise profits, chemists employ strategies to move the position of equilibrium in favour of products.</td>
</tr>
<tr>
<td></td>
<td>Changes in concentration, pressure and temperature can alter the position of equilibrium.</td>
</tr>
<tr>
<td></td>
<td>A catalyst increases the rate of attainment of equilibrium but does not affect the position of equilibrium.</td>
</tr>
<tr>
<td></td>
<td>The effects of altering pressure, altering temperature, the addition or removal of reactants or products can be predicted for a given reaction.</td>
</tr>
</tbody>
</table>

This question is about the equilibrium established between hydrogen, iodine and hydrogen iodide; \( \text{H}_2 + \text{I}_2 \rightleftharpoons 2 \text{HI} \)

1.  
   a)  If the system is at equilibrium, indicate whether the statements below are True or False:

      The rate of the forward and backward reaction must be the same
      The concentration of the reactants and products is the same
      The equilibrium must have been established by reacting hydrogen with iodine
      The system must be sealed (closed)
      Iodine is purple in colour. Hydrogen and hydrogen iodide are colourless.
      Therefore as the iodine is used up, the colour of the system will gradually fade.
      The pressure of the system will remain constant

   b)  The diagram on the left below shows how the concentration of reactants and products changes when the equilibrium is established from an equimolar mixture of hydrogen and iodine.

      Draw an equivalent diagram on the axes on the right to show how the concentration of reactants and products would change if the equilibrium was established from pure hydrogen iodide under the same conditions.
2. A system at equilibrium can be disturbed - causing the equilibrium to move in a particular direction.

Le Châtelier’s principle states that if a system at equilibrium is disturbed, the equilibrium moves in the direction that tends to minimise the disturbance.

Suggest two disturbances that can be made to each of the equilibria below to bring about the desired changes;

\[ \text{a) } \text{Cl}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HClO}(\text{aq}) + \text{HCl}(\text{aq}) - \text{a decrease in the concentration of chlorine} \]

\[ \text{b) } 4 \text{HCl} + \text{O}_2 \rightleftharpoons 2 \text{Cl}_2 + 2 \text{H}_2\text{O} \ \Delta H -\text{ve} - \text{an increase in the concentration of chlorine} \]

\[ \text{c) } \text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \ \Delta H +\text{ve} - \text{shift to the right without adding or removing chemicals} \]

\[ \text{d) } \text{CH}_2=\text{CH}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CH}_3\text{CH}_2\text{OH}(\text{g}) \ \Delta H -46 \text{ kJ mol}^{-1} - \text{increase in the }\% \text{ yield ethanol} \]

\[ \text{e) } \text{HCOOH} + \text{CH}_3\text{OH} \rightleftharpoons \text{HCOOCH}_3 + \text{H}_2\text{O} \ \Delta H 0 \text{ kJ mol}^{-1} - \text{no change in equilibrium position} \]

3. A number of industrial processes involve reversible reactions. Predicting the effect of disturbing the equilibrium can be used to help find the best conditions for obtaining the maximum reaction yield.

A: low temperature B: high temperature C: high temperature

Decide which set of conditions A – C would result in the highest yield of the desired product for each of the equilibria below

\[ \text{a) Production of hydrogen iodide } \text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g}) \ \Delta H +53 \text{ kJ mol}^{-1} \]

\[ \text{b) Making hydrogen } \text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons 3 \text{H}_2(\text{g}) + \text{CO}(\text{g}) \ \Delta H +206 \text{ kJ mol}^{-1} \]

\[ \text{c) Production of methanol } \text{CO}(\text{g}) + 2 \text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g}) \ \Delta H -91 \text{ kJ mol}^{-1} \]
1.3.2 **Equilibrium Constant, K**

As you should know, an *equilibrium mixture* is rarely 50:50 - *Rates are equal* but concentrations are not.

This is due to inevitable differences in aspects such as *activation energy*, *collision geometry* etc which result in one reaction being 'favoured'.

In general, the *exothermic* reaction will have a *lower activation energy* than the *endothermic* reaction.

In general, the *exothermic* reaction will be *favoured* and the *equilibrium position* will be shifted in the direction of that reaction.

*Forward reaction favoured* ⇒ *more products* than reactants *equilibrium lies over to the right*

*Reverse reaction favoured* ⇐ *more reactants* than products *equilibrium lies over to the left*

A more mathematical approach is used to describe the equilibrium position as follows:

For the reaction: \( aA + bB + \cdots \rightleftharpoons mM + nN + \cdots \)

\[
K = \frac{[M]^m[N]^n}{[A]^a[B]^b} \cdots \]

Product concentrations raised to powers equal to coefficients

Reactant concentrations raised to powers equal to coefficients

as usual square brackets \([A]\) denote actual 'concentration of' ....

usually in mol \(l^{-1}\), but any units can be used as long as it is the same for all substances.
**Units and Deviations**

Despite the concentrations having units (which may or may not cancel out), *Equilibrium constants* (K) have no units, they are dimensionless.

In reality, *equilibrium constants* are derived using activities which can be thought of as relative or effective concentrations (a simplification). At low concentrations, in particular, the effective concentration will be the same as the actual concentration and actual concentrations can be more easily used with little risk of error. At higher concentrations, there can be significant differences. For example;

Conductivity should be directly proportional to concentration, and at low concentrations the relationship is good. The following table can illustrate this:-

<table>
<thead>
<tr>
<th>Actual Concentration (ppm mg/litre)</th>
<th>Conductivity microsiemen/centimetre at 25 °C</th>
<th>Expected Conductivity</th>
<th>Effective Concentration ('activity')</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.2</td>
<td>2.2</td>
<td>1/1 x 2.2 / 2.2 = 1</td>
</tr>
<tr>
<td>3</td>
<td>6.5</td>
<td>3 x 2.2 = 6.6</td>
<td>3/1 x 6.5 / 6.6 = 2.995</td>
</tr>
<tr>
<td>10</td>
<td>21.4</td>
<td>10 x 2.2 = 22</td>
<td>10/1 x 21.4 / 22 = 9.297</td>
</tr>
<tr>
<td>30</td>
<td>64</td>
<td>30 x 2.2 = 66</td>
<td>30/1 x 64 / 66 = 29.090</td>
</tr>
<tr>
<td>100</td>
<td>210</td>
<td>100 x 2.2 = 220</td>
<td>100/1 x 210 / 220 = 95.455</td>
</tr>
<tr>
<td>300</td>
<td>617</td>
<td>300 x 2.2 = 660</td>
<td></td>
</tr>
<tr>
<td>1 000</td>
<td>1 990</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 000</td>
<td>5 690</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 000</td>
<td>17 600</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the case of conductivity, the decrease in 'effectiveness' as the concentration increases will be due to increased interactions between ions of opposite charge which can reduce their mobility and hence their conductivity. The differences are small but become more significant at higher concentrations.

Notice that, in the calculation of effective concentration, the actual concentration is divided by a standard or reference concentration (often 1.0 mol l⁻¹) and it is this that cancels out the units.

Similarly, the relationship between absorbance and concentration of a coloured substance is linear at low concentrations but deviates at higher concentrations.

Therefore, when using colorimetry as an analytical tool, care must be taken to dilute solutions sufficiently to ensure that measurements are always within the range of concentrations where the relationship is linear.

Though beyond the scope of this course to work with activities, it will help explain why calculations involving Equilibrium Constants, such as pH calculations, may not match exactly with measured values (particularly at higher concentrations).
**Pure solids, solvents and large excess**

When a pure solid is present in an equilibrium reaction or a liquid is used as a solvent the concentration, at a given temperature, does not vary to a measurable extent and it is given the concentration value of 1 in the equilibrium equation. (This again is a result of using activity and not actual concentration).

In particular, in equilibria where water is both a solvent and a reactant, it is assumed that any decrease in water or increase in water due to the reactions will have a negligible effect on the overall concentration of water. For example, in Higher you probably examined the following equilibrium:

\[
2\text{CrO}_4^{2-} + 2\text{H}^+ (\text{aq}) \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} (l)
\]


Similarly, the dissociation of water

\[
\text{H}_2\text{O} (l) \rightleftharpoons \text{H}^+ (\text{aq}) + \text{OH}^- (\text{aq})
\]

Strictly, \( K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} \) but instead we use

\[
K_w = [\text{H}^+][\text{OH}^-] = 10^{-14} \text{ mol}^2 \text{ l}^{-2}
\]

**Equilibrium Constant & Equilibrium Position - 'same but different'**

As already mentioned, the Equilibrium Constant, \( K \) reflects which reaction is favoured and hence the position of equilibrium.

However, we sometimes use the term 'equilibrium position' loosely when describing changes in an equilibrium that would appear to contradict the idea of \( K \) being a constant. Again, in Higher you may have examined the effect of adding acid (\( \text{H}^+ \) ions) to the following equilibrium:

\[
2\text{CrO}_4^{2-} + 2\text{H}^+ (\text{aq}) \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} (l)
\]

The increase in concentration of \( \text{H}^+ \) ions increases the rate of the forward reaction so that for a while the forward reaction is faster than the reverse reaction. Visibly, the solution becomes less yellow and more orange. It is correct to say 'the equilibrium moves to the right' but strictly speaking incorrect to say 'the equilibrium position moves to the right'.

If we simply consider the two coloured ions, then \([\text{CrO}_4^{2-}] \downarrow\) (less reactant) whilst \([\text{Cr}_2\text{O}_7^{2-}] \uparrow\) (more product) and since

\[
K = \frac{[\text{Products}]}{[\text{Reactants}]}
\]

it might appear that the value of \( K \) is increasing

However, \( K = \frac{[\text{Cr}_2\text{O}_7^{2-}]}{[\text{CrO}_4^{2-}]^2 [\text{H}^+]^2} \) and \([\text{Cr}_2\text{O}_7^{2-}] \uparrow, [\text{H}^+] \uparrow\) and \([\text{CrO}_4^{2-}] \downarrow\) means that overall the value of \( K \) is unchanged - it is a constant and is unaffected by changes in concentration.
Equilibrium Constant & Temperature

Another equilibrium you probably studied at Higher was this equilibrium mixture involving two coloured gases:

\[
\text{N}_2\text{O}_4 (g) \rightleftharpoons 2 \text{ NO}_2 (g) \quad \Delta H = +\text{ve}
\]

Increasing the temperature favours the endothermic forward reaction and the equilibrium moves to the right.

\[ K = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} \]

and this time the value of K and, hence, the equilibrium position are changing.

The Equilibrium Constant is temperature dependent. In fact, equilibrium constants are always quoted at a specific temperature, quite often standard temperature which is 25 °C (298K).

As already mentioned, the dissociation of water is represented by:

\[ K_w = [\text{H}^+] [\text{OH}^-] = 10^{-14} \text{ mol}^2 \text{ l}^2 \]

This is the value at 25 °C, and since [H+] = [OH−] then both [H+] and [OH−] = 10⁻⁷ mol l⁻¹ and pH=7.

However, this constant is temperature dependent as shown in the table below.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Kw (mol² l⁻²)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.14 x 10⁻¹⁵</td>
<td>7.47</td>
</tr>
<tr>
<td>10</td>
<td>2.93 x 10⁻¹⁵</td>
<td>7.27</td>
</tr>
<tr>
<td>20</td>
<td>6.81 x 10⁻¹⁵</td>
<td>7.08</td>
</tr>
<tr>
<td>25</td>
<td>1.01 x 10⁻¹⁴</td>
<td>7.00</td>
</tr>
<tr>
<td>30</td>
<td>1.47 x 10⁻¹⁴</td>
<td>6.92</td>
</tr>
<tr>
<td>40</td>
<td>2.92 x 10⁻¹⁴</td>
<td>6.77</td>
</tr>
<tr>
<td>50</td>
<td>5.48 x 10⁻¹⁴</td>
<td>6.63</td>
</tr>
<tr>
<td>100</td>
<td>5.13 x 10⁻¹³</td>
<td>6.14</td>
</tr>
</tbody>
</table>

At all temperatures,

[H+] still = [OH−] and water is still neutral.

However, as can be seen

pH = 7 does not always mean neutral.

In reality, it is very rare that pH measurements in a school lab will be taken at 25 °C and this can be another reason why calculated pH values will not always tally with measured values.
Equilibrium Constant & Catalysts

The presence of a catalyst provides an alternative reaction pathway of lower activation energy.

However, since both reactions have their activation energies reduced by the same amount, neither reaction is favoured.

As a result, there is no change to the position of equilibrium and no change to the value of the equilibrium constant, K.

A catalyst might still be used for a reversible reaction as it will shorten the time needed to reach a stable equilibrium.

Equilibrium Constant Values

$$K = \frac{[\text{Products}]}{[\text{Reactants}]}$$

The value of K gives an indication of how far the equilibrium lies to one side of a reaction or the other.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Value of K</th>
<th>Position of equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag⁺&lt;sub&gt;(aq)&lt;/sub&gt; + 2NH₃&lt;sub&gt;(aq)&lt;/sub&gt; ⇌ [Ag(NH₃)₃]⁺&lt;sub&gt;(aq)&lt;/sub&gt;</td>
<td>$1.7 \times 10^7$ at 25°C</td>
<td>Since K &gt;&gt; 1 the equilibrium lies to the right</td>
</tr>
<tr>
<td>CH₃COOH&lt;sub&gt;(aq)&lt;/sub&gt; ⇌ CH₃COO⁻&lt;sub&gt;(aq)&lt;/sub&gt; + H⁺&lt;sub&gt;(aq)&lt;/sub&gt;</td>
<td>$1.8 \times 10^{-5}$ at 25°C</td>
<td>Since K &lt;&lt; 1 the equilibrium lies to the left</td>
</tr>
<tr>
<td>N₂O₄&lt;sub&gt;(g)&lt;/sub&gt; ⇌ 2NO₂&lt;sub&gt;(g)&lt;/sub&gt;</td>
<td>0.87 at 55°C</td>
<td>Since K ≈ 1 the equilibrium lies to neither the left nor the right</td>
</tr>
</tbody>
</table>

You will meet examples later in this Topic where K values are used in calculations - mainly pH calculations, but most of the time values of K are simply used as an indication of which reaction is favoured and as an indication of the relative position of equilibrium.
1.3.3  Using K values - Strong & Weak Acids & Bases

(Most of this section, apart from the use of K values themselves, used to be covered in the Higher course and would have been assumed knowledge by this stage. Time will show how much, and at what level, this will appear in the AdvH exam. In the meantime, Past Higher Papers may have to be used in exam preparation.)

Hydrochloric acid, along with sulphuric and nitric, have been our ‘main 3 acids’. From now on, they are our ‘main 3 strong acids’. So what does the word 'strong' tell you about an acid?

All acids start off as (polar) covalent substances.

\[ \text{HCl}(g) + \text{water} \rightarrow \text{HCl}(aq) \rightarrow \text{H}^+(aq) + \text{Cl}^-(aq) \]

When dissolved in water, the polar covalent acid molecules dissociate (split up) into ions. With strong acids this conversion is considered to be 100% and a single arrow \( \rightarrow \) is correct.

A strong acid is one that is completely dissociated into ions in solution

In reality, very few reactions are irreversible but the K values are very large showing that the equilibrium position is very far to the right.

\[ \text{HCl}(g) \rightarrow \text{H}^+(aq) + \text{Cl}^-(aq) \quad K_a = 1.3 \times 10^6 \]

Calculations of the pH of strong acids are 'easier' because we can assume 100% ionisation, but (once again) this assumption can introduce small errors into our calculations.

By contrast, organic acids such as ethanoic acid also start as polar covalent molecules but most remain as molecules when dissolved in water.

\[ \text{CH}_3\text{COOH}(l) \rightarrow \text{H}^+(aq) + \text{CH}_3\text{COO}^-(aq) \quad K_a = 1.7 \times 10^{-5} \]

A weak acid is one that is only partially dissociated into ions in solution

Equilibrium constants, known as dissociation constants \( K_a \), are available in the Data Booklet and will allow the 'strength' of weak acids to be quickly compared. For example,

<table>
<thead>
<tr>
<th>Equilibrium in aqueous solution</th>
<th>( K_a )</th>
<th>( pK_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanoic acid</td>
<td>( 1.8 \times 10^{-4} )</td>
<td>3.75</td>
</tr>
<tr>
<td>ethanoic acid</td>
<td>( 1.7 \times 10^{-5} )</td>
<td>4.76</td>
</tr>
<tr>
<td>propanoic acid</td>
<td>( 1.3 \times 10^{-5} )</td>
<td>4.87</td>
</tr>
<tr>
<td>butanoic acid</td>
<td>( 1.5 \times 10^{-5} )</td>
<td>4.83</td>
</tr>
<tr>
<td>hexanoic acid</td>
<td>( 4.3 \times 10^{-5} )</td>
<td>4.20</td>
</tr>
</tbody>
</table>

We can see that, in general, the strength of an alkanoic acid decreases as the length of the carbon chain increases. \( 10^{-4} \) is 'obviously' stronger than \( 10^{-5} \). More care is needed when comparing acids with same 'powers'.

Calculations of the pH of weak acids are 'harder' and we will have to use the dissociation constant to help calculate the concentration of \( \text{H}^+ \) ions and, hence, the pH of the solution.
**Other Weak Acids**

Other examples of weak acids are less ‘obvious’ and rely more on knowledge gained over the N5 and Higher courses. For example,

\[ \text{CO}_2 \text{ is a soluble gas that (like other non-metal oxides) will dissolve/react with water to produce an acidic solution.} \]

Solutions of \( \text{CO}_2 \) (think of fizzy drinks) lose \( \text{CO}_2 \) quickly when open to the air i.e. even the dissolving of \( \text{CO}_2 \) is a reversible reaction.

\[
\begin{align*}
\text{CO}_2 (g) & \rightleftharpoons \text{CO}_2 (aq) + \text{H}_2 \text{O} & \rightleftharpoons \text{H}_2\text{CO}_3 (aq) & \rightleftharpoons \text{H}^+(aq) + \text{HCO}_3^-(aq)
\end{align*}
\]

in air in solution carbonic acid dissociated ions

\[ K_a = 4.5 \times 10^{-7} \]

Similarly for \( \text{SO}_2 \):

\[
\begin{align*}
\text{SO}_2 (g) & \rightleftharpoons \text{SO}_2 (aq) + \text{H}_2 \text{O} & \rightleftharpoons \text{H}_2\text{SO}_3 (aq) & \rightleftharpoons \text{H}^+(aq) + \text{HSO}_3^-(aq)
\end{align*}
\]

in air in solution sulphurous acid dissociated ions

\[ K_a = 1.4 \times 10^{-2} \]

**Strong & Weak Bases**

*Sodium hydroxide*, along with *potassium hydroxide* and *lithium hydroxide*, were our ‘main 3 alkalis’. From now on, they are our ‘main 3 strong bases’. So what does the word ‘strong’ tell you about a base? Most bases start off as ionic substances, (oxides or hydroxides)

\[ \text{Na}^+\text{OH}^-(s) + \text{water} \longrightarrow \text{Na}^+(aq) + \text{OH}^-(aq) \]

When dissolved in water, the bases dissociate (dissolve) into separate ions. With strong bases this conversion is 100% and a single arrow \( \longrightarrow \) is correct.

**A strong base is completely dissociated to form \( \text{OH}^- \) ions in solution**

*Less soluble* hydroxides (*Data Book*) are unlikely to dissociate completely (except at very low concentrations) and will be considered weak bases:

- Group 1 metal hydroxides - very soluble
- Group II metal hydroxides - slightly soluble
- Transition metal hydroxides - insoluble

Again, *calculation* of \( \text{pH} \) of solutions of strong bases is made *easier* by the ability to assume 100% dissociation.

The most important weak base that you should know about is ammonia, \( \text{NH}_3 \). Similar to weak acids, ammonia is a *polar covalent molecule* that dissolves readily in water (*fountain experiment*). Most of the ammonia (99.6%) remains as molecules, but a small amount reacts with water to produce hydroxide ions. This reaction is reversible.

\[
\begin{align*}
\text{NH}_3(g) + \text{water} & \longrightarrow \text{NH}_3(aq) + \text{H}_2\text{O}(l) & \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq)
\end{align*}
\]

ammonia ammonia solution ammonium hydroxide solution

\[ K_b = 1.8 \times 10^{-5} \]
Other weak acids include the organic 'ammonia derivatives' - the amines. 

$K_b$ values can be read like $K_a$ values, so we can deduce that increasing the carbon chain makes the weak base stronger, while a benzene ring (aniline) makes the base even weaker.

However, as will be dealt with in more detail later in this Topic, this course will use the $K_a$ values of the 'conjugate acid' where the stronger the conjugate acid, the weaker the base will be the rule.

### Properties of Strong & Weak Acids

<table>
<thead>
<tr>
<th>Comparison</th>
<th>0.1 M HCl</th>
<th>0.1 M CH$_3$COOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>1</td>
<td>2.9</td>
</tr>
<tr>
<td>Conductivity</td>
<td>100 mA</td>
<td>15 mA</td>
</tr>
<tr>
<td>Reaction Rate</td>
<td>fast</td>
<td>slow</td>
</tr>
</tbody>
</table>

Both acids are equimolar - they contain exactly the same number of moles (same number of molecules) per litre of solution.

Both acids are monoprotic (meaning that they are capable of releasing one hydrogen ion per molecule).

**Discussion of Results**

**pH**  
there were equal numbers of molecules of acid dissolved in both solutions and 100% of the HCl molecules dissociated to produce many H$^+$ ions - very low pH

Less than 1% of the CH$_3$COOH molecules dissociated so there were much fewer H$^+$ ions present - pH still < 7, but higher than HCl.

**Conductivity**  
there were equal numbers of molecules of acid dissolved in both solutions and 100% of the HCl molecules dissociated to produce many H$^+$ ions - very high conductivity

Less than 1% of the CH$_3$COOH molecules dissociated so there were much fewer H$^+$ ions present - conducts, but not as good as HCl.

**Reaction Rate**  
there were equal numbers of molecules of acid dissolved in both solutions and 100% of the HCl molecules dissociated to produce many H$^+$ ions - very fast reaction

Less than 1% of the CH$_3$COOH molecules dissociated so there were much fewer H$^+$ ions present - fewer collisions with magnesium ribbon so rate of reaction is slower.

**Conclusion**  
Weak acids produce less H$^+$ ions than strong acids and, therefore, are less acidic than strong acids of equal concentration.
**Stoichiometry**

Stoichiometry is the word used to describe the numerical proportions (usually expressed in moles) of substances involved in reactions.

Vol. needed to neutralise 10 cm$^3$ 0.1M HCl = 10 cm$^3$

Vol. needed to neutralise 10 cm$^3$ 0.1M CH$_3$COOH = 10 cm$^3$

Perhaps surprisingly, it takes *exactly the same amount* of NaOH to neutralise a strong acid and a weak acid.

Both acids were the same concentration so they both contained the same number of molecules to begin with.

The strong acid will have dissociated completely meaning that all the H$^+$ ions were available to react with the OH$^-$ ions added from the burette.

The weak acid is only partially dissociated so less than 1% of the H$^+$ ions are available at the beginning.

\[
\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^- \text{ (ethanoate ions)}
\]

However, as the H$^+$ ions react with OH$^-$ they are effectively removed from the equilibrium mixture. This slows down or even stops the reverse reaction, but the forward reaction continues:

\[
\text{CH}_3\text{COOH} \rightarrow \text{H}^+ + \text{CH}_3\text{COO}^- 
\]

More H$^+$ ions will be produced which will then react with the OH$^-$ ions and so on until every single CH$_3$COOH molecule dissociates to form H$^+$ ions.

Overall, a weak acid can supply exactly the same number of H$^+$ as an equal quantity of a strong acid.

\[
\begin{align*}
\text{HCl (aq)} & \quad + \quad \text{NaOH (aq)} & \rightarrow & \quad \text{H}_2\text{O (l)} & \quad + \quad \text{NaCl (aq)} \\
1 \text{ mole} & \quad + \quad 1 \text{ mole} & \rightarrow & \quad \text{1 mole} & \quad + \quad \text{1 mole} \\
\text{CH}_3\text{COOH (aq)} & \quad + \quad \text{NaOH (aq)} & \rightarrow & \quad \text{H}_2\text{O (l)} & \quad + \quad \text{NaCH}_3\text{COO (aq)} \\
1 \text{ mole} & \quad + \quad 1 \text{ mole} & \rightarrow & \quad \text{1 mole} & \quad + \quad \text{1 mole}
\end{align*}
\]

Strong and weak acids have **different properties**, but they have the *same stoichiometry*.

Strong and weak bases have an equivalent relationship.

<table>
<thead>
<tr>
<th>Comparison</th>
<th>0.1 M NaOH</th>
<th>0.1 M NH$_4$OH</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>13</td>
<td>10</td>
</tr>
<tr>
<td>Conductivity</td>
<td>75 mA</td>
<td>5 mA</td>
</tr>
</tbody>
</table>

**Weak bases** produce less OH$^-$ ions than strong bases and, therefore, are less alkaline than strong bases of equal concentration but react with the *same stoichiometry*.

\[
\begin{align*}
\text{Fe}^{3+}\text{(NO}_3^-)\text{}_3 \quad + \quad 3 \text{ Na}^+\text{OH}^-(aq) & \rightarrow \quad \text{Fe}^{3+}\text{(OH}^-\text{)}_3 \quad + \quad 3 \text{ Na}^+\text{NO}_3^- (aq) \\
\text{Fe}^{3+}\text{(NO}_3^-)\text{}_3 \quad + \quad 3 \text{ NH}_4^+\text{OH}^-(aq) & \rightarrow \quad \text{Fe}^{3+}\text{(OH}^-\text{)}_3 \quad + \quad 3 \text{ NH}_4^+\text{NO}_3^- (aq)
\end{align*}
\]
Salt Solutions

Salts are ionic compounds derived from an acid and a base. Though we describe the reaction between an acid and a base as neutralisation, it would be wrong to assume that the final salt solution is always neutral.

It depends on the strength of the parent acid and the parent base.

<table>
<thead>
<tr>
<th>Salt</th>
<th>Formula</th>
<th>Parent Base &amp; Strength</th>
<th>Parent Acid &amp; Strength</th>
<th>pH and type of solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>sodium chloride</td>
<td>NaCl⁻</td>
<td>sodium hydroxide STRONG</td>
<td>hydrochloric acid STRONG</td>
<td>pH = 7 NEUTRAL</td>
</tr>
<tr>
<td>sodium sulphite</td>
<td>(Na)₂SO₃²⁻</td>
<td>sodium hydroxide STRONG</td>
<td>sulphurous acid WEAK</td>
<td>pH = &gt; 7 ALKALI</td>
</tr>
<tr>
<td>ammonium nitrate</td>
<td>NH₄⁺NO₃⁻</td>
<td>ammonia WEAK</td>
<td>nitric acid STRONG</td>
<td>pH = &lt; 7 ACID</td>
</tr>
<tr>
<td>magnesium sulphate</td>
<td>Mg²⁺SO₄²⁻</td>
<td>magnesium hydroxide WEAK</td>
<td>sulphuric acid STRONG</td>
<td>pH = &lt; 7 ACID</td>
</tr>
<tr>
<td>sodium stearate</td>
<td>Na⁺C₁₇H₃₅COO⁻</td>
<td>sodium hydroxide STRONG</td>
<td>stearic acid WEAK</td>
<td>pH = &gt; 7 ALKALI</td>
</tr>
<tr>
<td>ammonium sulphate</td>
<td>NH₄⁺SO₄²⁻</td>
<td>ammonia WEAK</td>
<td>sulphuric acid STRONG</td>
<td>pH = &lt; 7 ACID</td>
</tr>
</tbody>
</table>

'Rule of Thumb'

❶ ACIDIC solutions
parent ACID STRONG, parent BASE WEAK

❷ ALKALI solutions
parent ACID WEAK, parent BASE STRONG

❸ NEUTRAL solutions
parent ACID STRONG, parent BASE STRONG

Full explanations will require the consideration of multiple equilibria. For example, sodium ethanoate is the salt made from sodium hydroxide (strong base) and ethanoic acid (weak acid) and you would predict that it would produce an alkaline solution

\[
\text{CH}_3\text{COONa}(s) + \text{water} \rightarrow \text{CH}_3\text{COO}^- \text{(aq)} + \text{Na}^+(aq)
\]

Sodium ethanoate is soluble, and dissolves to release ions into the water;

There are, however, already two reactions taking place in the water;

\[
\text{H}_2\text{O} \rightleftharpoons \text{H}^+ \text{(aq)} + \text{OH}^- \text{(aq)}
\]

Secondary reactions between the salt ions and the water ions are possible;

\[
\text{CH}_3\text{COOH}(s) + \text{water} \rightarrow \text{CH}_3\text{COO}^- \text{(aq)} + \text{Na}^+(aq)
\]

\[
\text{H}_2\text{O} \rightleftharpoons \text{H}^+ \text{(aq)} + \text{OH}^- \text{(aq)}
\]

Ethanoate ions (\(\text{CH}_3\text{COO}^-\text{(aq)}\)) will react with hydrogen ions (\(\text{H}^+\text{(aq)}\)) to produce covalent molecules of ethanoic acid (\(\text{CH}_3\text{COOH}\text{(aq)}\)). Being a weak acid, only a small proportion of these molecules will dissociate to reform \(\text{H}^+\) ions. As a result \(\text{H}^+\) ion concentrations will drop. This will slow down the backward reaction so for a while;

\[
\text{H}_2\text{O} \rightleftharpoons \text{H}^+ \text{(aq)} + \text{OH}^- \text{(aq)}
\]

The extra \(\text{H}^+\text{(aq)}\) ions produced will be mopped up by the ethanoate ions (\(\text{CH}_3\text{COO}^-\text{(aq)}\)) but the extra \(\text{OH}^-\text{(aq)}\) ions build up so,

\(\text{OH}^- > \text{H}^+\) and \(\text{pH} > 7\), alkaline solution
1.3.4 Using K values - 'Special K's'

**Solubility Products**

When low solubility ionic substances dissolve in water the 'reverse' reaction will eventually result in an equilibrium mixture in which ions rejoin the solid (associate) at the same rate at which the solid **dissociates**. For example,

\[
\text{Ba}^{2+}\text{SO}_4^{2-} \rightleftharpoons \text{Ba}^{2+}\text{(aq)} + \text{SO}_4^{2-}\text{(aq)}
\]

\[K = \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{[\text{Ba}^{2+}\text{(aq)}][\text{SO}_4^{2-}\text{(aq)}]}{[\text{Ba}^{2+}\text{SO}_4^{2-}\text{(s)}]}\]

As previously mentioned, solids are assumed to have an activity = 1, so the constant can be simplified to

\[K_{sp} = [\text{Ba}^{2+}\text{(aq)}][\text{SO}_4^{2-}\text{(aq)}] = 1.08 \times 10^{-10}\]

**Solubility Product Constants (at 25°C)**

<table>
<thead>
<tr>
<th>Substance</th>
<th>(K_{sp})</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgBr</td>
<td>(7.70 \times 10^{-13})</td>
</tr>
<tr>
<td>AgBrO₃</td>
<td>(5.77 \times 10^{-6})</td>
</tr>
<tr>
<td>Ag₂CO₃</td>
<td>(6.15 \times 10^{-12})</td>
</tr>
<tr>
<td>AgCl</td>
<td>(1.56 \times 10^{-10})</td>
</tr>
<tr>
<td>Ag₂CrO₄</td>
<td>(9.00 \times 10^{-12})</td>
</tr>
<tr>
<td>Ag₂Cr₂O₇</td>
<td>(2.00 \times 10^{-7})</td>
</tr>
<tr>
<td>AgI</td>
<td>(1.50 \times 10^{-16})</td>
</tr>
<tr>
<td>AgSCN</td>
<td>(1.16 \times 10^{-12})</td>
</tr>
<tr>
<td>Al(OH)₃</td>
<td>(1.26 \times 10^{-30})</td>
</tr>
<tr>
<td>BaCO₃</td>
<td>(8.10 \times 10^{-8})</td>
</tr>
</tbody>
</table>

**Water Dissociation Constant**

Similarly, the dissociation of water

\[\text{H}_2\text{O}(l) \rightleftharpoons \text{H}^+(aq) + \text{OH}^-(aq)\]

Strictly, \[K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}\] but instead we use

\[K_w = [\text{H}^+][\text{OH}^-] = 10^{-14} \text{ mol}^2\text{ l}^{-2}\]

This is a very significant and very useful relationship which allows very quick and easy conversion from (usually) \([\text{OH}^-]\) to \([\text{H}^+](=10^{14}/[\text{OH}^-])\) or from pOH to pH since pH + pOH = 14 for all solutions at 25°C.
Solvent Extraction

Almost any reversible process can be treated as an equilibrium and an equilibrium constant derived which can provide the basis for useful calculations.

Iodine is soluble in 'water' (KI\(_{\text{(aq)}}\)) and in cyclohexane. These solvents, however, are immiscible and will form separate layers.

If an aqueous iodine solution is shaken with cyclohexane, the following equilibrium will be set up.

\[ \text{I}_2\text{(aq)} \rightleftharpoons \text{I}_2\text{(C}_6\text{H}_{12}) \]

\[ K = \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{[\text{I}_2\text{(C}_6\text{H}_{12})]}{[\text{I}_2\text{(aq)}]} \]

One direction is 'favoured' due to the greater solubility of the iodine in this solvent. The concentrations can be determined by titration with thiosulphate using starch as an 'indicator'. For example,

A 25 cm\(^3\) sample was taken from each layer and analysed by titration with standard 0.250 mol l\(^{-1}\) sodium thiosulphate solution, Na\(_2\text{S}_2\text{O}_3\text{(aq)}\) using starch as an indicator. (At the endpoint of the titration the blue/black colour of the iodine-starch complex disappears).

The equation for the titration is:

\[ 2\text{S}_2\text{O}_3^{2-} + \text{I}_2 \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{I}^- \]

The titres were: aqueous layer = 12.4 cm\(^3\) cyclohexane layer = 18.6 cm\(^3\)

**Calculation of \(K\):**

**aqueous:**
moles of \(\text{S}_2\text{O}_3^{2-}\), \(n = C \times V = 0.25 \times 0.0124 = 0.0031\) moles
moles of \(\text{I}_2\) = moles of \(\text{S}_2\text{O}_3^{2-}\) \(\div 2 = 0.0031 \div 2 = 0.00155\) moles

\([\text{I}_2\text{(aq)}], C = \frac{n}{V} = 0.00155 \div 0.025 = 0.062\) mol l\(^{-1}\)

**\(C_6\text{H}_{12}\):**
moles of \(\text{S}_2\text{O}_3^{2-}\), \(n = C \times V = 0.25 \times 0.0186 = 0.00465\) moles
moles of \(\text{I}_2\) = moles of \(\text{S}_2\text{O}_3^{2-}\) \(\div 2 = 0.00465 \div 2 = 0.002325\) moles

\([\text{I}_2\text{(aq)}], C = \frac{n}{V} = 0.002325 \div 0.025 = 0.093\) mol l\(^{-1}\)

**\(K\) (partition coefficient):**
\[ K = \frac{[\text{I}_2\text{(C}_6\text{H}_{12})]}{[\text{I}_2\text{(aq)}]} = \frac{0.093}{0.062} = 1.5 \]

Notice that both calculations of \([\text{I}_2]\) are identical due to the fact that equal volumes of each solution was extracted and they were titrated against a Na\(_2\text{S}_2\text{O}_3\) solution of equal concentration. Therefore, the volumes of Na\(_2\text{S}_2\text{O}_3\) could have been used directly to calculate \(K\),

\[ K = \frac{18.6}{12.4} = 1.5 \]
Chromatography

Chromatography is the general name for a wide range of techniques that are used to separate and identify molecules based on their properties. In general, chromatography involves two phases:

- A Stationary Phase. This is typically a solid e.g. paper, silica gel or powder filled tube.
- A Mobile Phase. This is typically a liquid or mixture of liquids. It can be a gas.

Solute molecules will be constantly moving backwards and forwards between the different solvents and this is a special type of reversible reaction called Partition.

Like most reversible reaction, one direction will be ‘favoured’ but eventually the concentrations will become constant and the rates at which solute molecules move will become equal.

\[
\text{Solute} \text{ (polar solvent)} \rightleftharpoons \text{Solute} \text{ (non-polar solvent)}
\]

The equilibrium constant, $K$, is termed the distribution constant; defined as the molar concentration of solute in the stationary phase divided by the molar concentration of the solute in the mobile phase.

\[
K = \frac{[\text{Solute} \text{ (stationary)}]}{[\text{Solute} \text{ (mobile)}]}
\]

The distribution constant, $K$, (along with the volume of the two solvents) can be used to calculate the Retention Factor which measures how fast a particular molecule will travel.
Questions

Q1 Iodide ions are oxidised by acidified nitrite ions according to the equation

$$2\text{NO}_2^- + 2\text{I}^- + 4\text{H}^+ \rightleftharpoons 2\text{NO} + \text{I}_2 + 2\text{H}_2\text{O}$$

Addition of sodium ethanoate to the reaction mixture slows down the formation of iodine.

The most likely explanation for this effect is that ethanoate ions:

A remove iodine
B reduce the concentration of iodide ions
C react with nitrite ions
D react with hydrogen ions.

Q2 Caffeine can be extracted from coffee dissolved in water using the solvent dichloromethane (CH$_2$Cl$_2$).

$$\text{caffeine} \text{(aq)} \rightleftharpoons \text{caffeine} \text{(CH}_2\text{Cl}_2)$$

Which of the following, when increased, will change the value of the equilibrium constant for this process?

A temperature
B mass of coffee
C volume of water
D volume of dichloromethane.

Q3 Substance X is distributed between equal volumes of two immiscible liquids as shown in the diagram.

The number of dots represents the relative distribution of X in the two liquids at equilibrium.

The value of the equilibrium constant for this system is

A 0.46
B 0.50
C 2.00
D 2.17

Q4 Phosphoric acid is a weak acid and undergoes partial dissociation according to the equation

$$\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}_2\text{PO}_4^- + \text{H}^+$$

The position of equilibrium would be shifted to the right by the addition of

A a catalyst
B sulfuric acid
C sodium hydroxide
D sodium dihydrogenphosphate.

Q5 Which of the following decreases when an aqueous solution of ethanoic acid is diluted?

A pH
B $K_a$
C [H$^+$]
D the degree of dissociation.

Q6 Iodine was added to 50 cm$^3$ of two immiscible solvents X and Y as shown. After shaking, the following equilibrium was established.

$$\text{I}_2 \text{(Y)} \rightleftharpoons \text{I}_2 \text{(X)}$$

An extra 10 cm$^3$ of solvent X was added, the mixture shaken and equilibrium re-established.

Which of the following statements is correct?

A The concentration of I$_2$ in Y increases.
B The concentration of I$_2$ in Y decreases.
C The equilibrium constant increases.
D The equilibrium constant decreases.
**Q7** Consider this equilibrium:

\[ \text{PCl}_3(g) + \text{Cl}_2(g) \rightleftharpoons \text{PCl}_5(g) \]

The equilibrium concentrations of the reagents involved, under certain conditions are:

\[ [\text{PCl}_3(g)] = 0.04 \text{ mol l}^{-1} \]
\[ [\text{Cl}_2(g)] = 0.06 \text{ mol l}^{-1} \]
\[ [\text{PCl}_5(g)] = 0.12 \text{ mol l}^{-1} \]

Calculate the equilibrium constant, \( K \), under these conditions.

**Q8** In the equilibrium:

\[ 2 \text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g) \]

The concentrations of the gases are:

\[ [\text{NO}_2(g)] = 0.05 \text{ mol l}^{-1} \]
\[ [\text{N}_2\text{O}_4(g)] = 0.4 \text{ mol l}^{-1} \]

Calculate the equilibrium constant, \( K \), under these conditions.

**Q9** The esterification of methanol and ethanoic acid to form methyl ethanoate and water is represented by the equation:

\[ \text{CH}_3\text{OH}(l) + \text{CH}_3\text{COOH}(l) \rightleftharpoons \text{CH}_3\text{COOCH}_3(l) + \text{H}_2\text{O}(l) \]

At equilibrium, the concentrations of the substances present are:

\[ [\text{CH}_3\text{OH}(l)] = 0.2 \text{ mol l}^{-1} \]
\[ [\text{CH}_3\text{COOH}(l)] = 0.5 \text{ mol l}^{-1} \]
\[ [\text{H}_2\text{O}(l)] = 0.8 \text{ mol l}^{-1} \]

Calculate the equilibrium constant, \( K \), under these conditions.

**Q10** 0.2 mol of ethanol and 0.2 mol of methanoic acid are mixed with a few drops of concentrated sulphuric acid catalyst in an empty reaction vessel. After equilibrium is established, it is determined that 0.15 mol of the ester, ethyl methanoate, has been formed.

\[ \text{CH}_3\text{CH}_2\text{OH}(l) + \text{HCOOH}(l) \rightleftharpoons \text{HCOOCH}_2\text{CH}_3(l) + \text{H}_2\text{O}(l) \]

Calculate the equilibrium constant, \( K \), under these conditions.

**Q11** 0.5 mol of \( \text{CH}_4(g) \) and 0.5 mol of \( \text{H}_2\text{O}(g) \) are introduced into an empty, 1 litre, reaction chamber and the following reaction takes place:

\[ \text{CH}_4(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + 3 \text{H}_2(g) \]

When equilibrium is established, it is determined that 0.15 mol of \( \text{CO}(g) \) is present. Calculate the equilibrium constant, \( K \), under these conditions.

**Q12** The industrial production of 'freon', \( \text{CCl}_2\text{F}_2(g) \), is represented by the following equation.

\[ \text{CCl}_4(g) + 2 \text{HF}(g) \rightleftharpoons \text{CCl}_2\text{F}_2(g) + 2 \text{HCl}(g) \]

1 mol of \( \text{CCl}_4(g) \) and 2 mol of \( \text{HF}(g) \) are introduced into an empty reaction chamber. When equilibrium is established, it is found that 0.75 mol of 'freon' has been formed. Calculate the equilibrium constant, \( K \), for the reaction under these conditions.

**Q13** Toluene is an organic liquid which is immiscible in water. A different organic substance, \( \text{X} \), is soluble in both liquids. A sample of \( \text{X} \) is shaken up with toluene and water and given time for the equilibrium shown below to stabilise.

\[ \text{X} (\text{toluene}) \rightleftharpoons \text{X} (\text{aq}) \]

Samples of substance \( \text{X} \) in each of the layers were analysed. The concentration of \( \text{X} \) in the toluene layer was found to be 0.253 mol l\(^{-1}\). The concentration of \( \text{X} \) in the aqueous layer was 0.201 mol l\(^{-1}\). Calculate the partition coefficient: \( [\text{X} (\text{aq})] / [\text{X} (\text{toluene})] \).
Q14 A monoprotic acid organic acid, A, is soluble in both ethoxyethane and water. Ethoxyethane and water are immiscible.

\[
A_{(\text{ethoxyethane})} \rightleftharpoons A_{(aq)}
\]

A 10 cm\(^3\) sample of each solution was extracted by pipette and titrated with standard 0.10 mol l\(^{-1}\) sodium hydroxide, NaOH\(_{(aq)}\). The titre of the ethoxyethane layer was 22.3 cm\(^3\). The titre of the aqueous layer was 14.8 cm\(^3\).

Calculate

\(a\) the concentration of the organic acid in each of the two layers.

\(b\) the partition coefficient for this equilibrium, \([A_{(aq)}]/[A_{(\text{ethoxyethane})}]\).

Q15 An organic acid substance, X, of molecular mass 60, can dissolve both in water and in hexane. The two solvents are immiscible.

\[
X_{(\text{hexane})} \rightleftharpoons X_{(aq)}
\]

The partition coefficient for this equilibrium, the ratio \([X_{(aq)}]/[X_{(\text{hexane})}]\), is 1.42.

A quantity of of substance X is shaken up with 50 cm\(^3\) of water and 50 cm\(^3\) of hexane and left until equilibrium is established. The concentration of X in the hexane layer is found to be 0.40 mol l\(^{-1}\).

Calculate

\(a\) the concentration of X in the aqueous layer.

\(b\) the mass of X in the aqueous layer.

Q16 An organic substance, A, of molecular mass 65, is soluble in both toluene and water. The solvents are immiscible. A quantity of substance A was shaken with 100 cm\(^3\) of each solvent until the following equilibrium was established.

\[
A_{(aq)} \rightleftharpoons A_{(\text{toluene})}
\]

The partition coefficient for this equilibrium, in the ratio \([A_{(\text{toluene})}]/[A_{(aq)}]\), is 1.50.

The aqueous leyer was analysed and the concentration of A in this layer was found to be 0.24 mol l\(^{-1}\).

Calculate

\(a\) the concentration of A in the toluene layer.

\(b\) the mass of A in the toluene layer.

Q17 The salt sodium propanoate, C\(_2\)H\(_5\)COO Na\(^+\), is produced when sodium hydroxide reacts with propanoic acid. When sodium propanoate is dissolved in water an alkaline solution is formed.

\(a\) Write the formula for the conjugate base of propanoic acid.

\(b\) Explain why a solution of sodium propanoate is alkaline.

Q18 The balanced equation for the principle reaction in the contact process is:

\[
2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g) \quad \Delta H = -\text{ve}
\]

\(a\) Write an expression for K, the equilibrium constant for this reaction, when the system has reached equilibrium.

\(b\) Predict how an increase in temperature would affect the position of equilibrium.

\(c\) Explain the effect this increase in temperature would have on the value of K.
Q19 The value for the equilibrium constant, K, for a specific example of the following reaction is equal to 1:

\[ \text{acid} + \text{alcohol} \rightleftharpoons \text{ester} + \text{water} \]

a) i) Predict the maximum yield of ester, given this value of K.

ii) Give one reason why this yield might not be achieved in practice.

b) A student suggested that a careful choice of catalyst could increase the yield of ester. Comment on this suggestion.

c) Another student suggested that increasing the concentration of the alcohol in the reaction mixture would increase the yield of ester by altering the value of K. Comment on this suggestion.

Q20 In the Data Booklet, the solubility of barium sulphate, shown by the equation:

\[ \text{BaSO}_4(s) + \text{water} \rightleftharpoons \text{Ba}^{2+}_{(aq)} + \text{SO}_{4}^{2-}_{(aq)} \]

is given as less than 1 g l\(^{-1}\). In a more advanced text book, it is noticed that an equilibrium constant, known as the solubility product \( K_{sp} \), can be written to represent the dissolving process.

\[ K_{sp} = [\text{Ba}^{2+}] \times [\text{SO}_{4}^{2-}] \]

a) At 298K, \( K_{sp} \) for barium sulphate is equal to \( 1 \times 10^{-10} \) mol\(^2\) l\(^{-2}\). For a saturated solution of barium sulphate at 298K, calculate

i) the concentration of barium ions dissolved in the solution.

ii) the mass of barium sulphate dissolved in 1 litre of solution.

b) A small quantity of very soluble sodium sulphate is now added to the saturated solution of barium sulphate.

i) What will happen to the value of \( K_{sp} \)?

ii) What will happen to the concentration of barium ions?

Q21 The ionic product of water (\( Kw \)) is usually taken to be \( 10^{-14} \), but it varies with temperature. The following table shows this variation.

<table>
<thead>
<tr>
<th>Temperature / K</th>
<th>( Kw )</th>
</tr>
</thead>
<tbody>
<tr>
<td>273</td>
<td>( 0.114 \times 10^{-14} )</td>
</tr>
<tr>
<td>283</td>
<td>( 0.293 \times 10^{-14} )</td>
</tr>
<tr>
<td>298</td>
<td>( 1.008 \times 10^{-14} )</td>
</tr>
<tr>
<td>323</td>
<td>( 5.476 \times 10^{-14} )</td>
</tr>
<tr>
<td>373</td>
<td>( 51.3 \times 10^{-14} )</td>
</tr>
</tbody>
</table>

a) What is meant by the term ‘ionic product of water’?

b) Since Kw varies with temperature, the pH of pure water is not always 7. Calculate the pH of pure water at 373K.

c) The ionisation of water is endothermic. Explain how the information in the table supports this statement.
Q22 An organic acid can be extracted from a reaction mixture using ethoxyethane. Ethoxyethane belongs to a family called the ethers in which there is a central oxygen atom with a hydrocarbon chain either side. 100 cm$^3$ of ethoxyethane were added to 500 cm$^3$ of an aqueous organic acid and the mixture shaken. After being allowed to settle, two immiscible layers formed.

a) Draw a structural formula for ethoxyethane.

b) What piece of apparatus would be used to separate both layers?

c) The following equilibrium was established.

$$\text{organic acid (aqueous)} \rightleftharpoons \text{organic acid (ethoxyethane)}$$

25·0 cm$^3$ of the ethoxyethane layer required 22·7 cm$^3$ of 1·10 mol l$^{-1}$ NaOH solution to neutralise it. 25·0 cm$^3$ of the aqueous layer was neutralised by 8·25 cm$^3$ of 0·10 mol l$^{-1}$ NaOH solution.

Calculate the equilibrium constant for the system.

Q23 A student measured the pH of water at various temperatures using a pH meter and obtained the following results.

<table>
<thead>
<tr>
<th>Temperature $^\circ$C</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>7·08</td>
</tr>
<tr>
<td>30</td>
<td>6·92</td>
</tr>
<tr>
<td>50</td>
<td>6·63</td>
</tr>
</tbody>
</table>

The student was unsure whether the results were accurate or if the pH meter was faulty. Using your knowledge of chemistry, discuss possible reasons for the results obtained.