• Often pH is used to characterise acidic solutions. Give a brief definition of pH.

\[
pH = -\log_{10}[^{\text{aq}}\text{H}^+]\]

Describe the difference between a strong acid and a weak acid.

**A strong acid dissociates completely in water. For example:**

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

**A weak acid dissociates only slightly in water. For example:**

\[
\text{HF(aq)} \rightleftharpoons \text{H}^+(aq) + \text{F}^-(aq)
\]

The pH of a solution of a strong acid depends on its concentration and a strong acid can give a high pH (corresponding to low \[^{\text{aq}}\text{H}^+\]) if the acid is present in a low concentration.

In general, can pH be used to define the strength of an acid? Explain your answer.

No.

The pH of a solution of a strong acid depends on its concentration. Thus, the pH of a 0.1 M solution of HCl is 1.0 and the pH of a solution of \(10^{-6}\) M HCl is 6.0.

A low pH can arise from a solution of a strong acid or a more concentrated solution of a weak acid.

A high pH can arise from a weak solution of a strong acid or from a stronger solution of a weak acid.
• Rank H₂O(l), H₂S(aq) and HF(aq) in order of their Brønsted acid strengths. Explain your reasoning.

\[
\text{HF(aq)} > \text{H₂S(aq)} > \text{H₂O(l)}
\]

The H–F bond is more polar than H–O so is easier to break HF into H⁺ and F⁻ than to break H₂O into H⁺ and OH⁻. Hence HF is stronger acid than H₂O.

S is much larger atom than O, so the H–S bond is much longer and weaker than H–O; hence H₂O is weaker acid than H₂S.

HF is stronger than H₂S because the small F⁻ ion bonds more strongly to the water molecules than does the larger HS⁻ ion.

• Buffer systems are frequently used in chemistry. Briefly describe a buffer system and how it functions? Use equations where appropriate.

Buffer systems resist changes in pH. They consist of a weak acid (HA) and its conjugate base (A⁻) in high concentrations.

If H⁺ is added, it is consumed by the A⁻ ions:

\[
\text{H}^+(aq) + \text{A}^-(aq) \rightarrow \text{HA}(aq)
\]

If OH⁻ is added, it is consumed by the acid present:

\[
\text{OH}^-(aq) + \text{HA}(aq) \rightarrow \text{H₂O} + \text{A}^-(aq)
\]

If the amount of H⁺ or OH⁻ added is too great, there may be insufficient HA or A⁻ present and so the buffer may not work.

What ratio of concentrations of acetic acid to sodium acetate would you require to prepare a buffer with pH = 4.00? The \(K_a\) of acetic acid is \(1.8 \times 10^{-5}\) M.

The pH of a buffer can be calculated using the Henderson-Hasselbalch equation can be used:

\[
\text{pH} = \text{pK}_a + \log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right)
\]

For acetic acid, \(K_a = -\log_{10}K_a = -\log_{10}(1.8 \times 10^{-5}) = 4.74\). Thus to achieve pH 4.00, the ratio of base to acid must be:

\[
4.00 = 4.74 + \log_{10} \left( \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \right)
\]

\[
\log_{10} \left( \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \right) = -0.74 \quad \text{or} \quad \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = 5.6
\]

Answer: \(\text{CH}_3\text{COOH} : \text{CH}_3\text{COO}^- = 5.6\)
Barium sulfate is used as a contrast agent for X-ray images of intestines. What is the solubility product constant, \( K_{sp} \), for \( \text{BaSO}_4 \), given that a maximum of \( 1.167 \times 10^{-8} \) g will dissolve in 500 mL of water?

The formula mass of \( \text{BaSO}_4 \) is \( 137.34 \) (Ba) + \( 32.07 \) (S) + \( 4 \times 16.00 = 233.41 \) g mol\(^{-1}\). 1.167 \times 10^{-8} \) g therefore corresponds to:

\[
\text{number of moles} = \frac{\text{mass}}{\text{formula mass}} = \frac{1.167 \times 10^{-8}}{233.41} = 5.000 \times 10^{-11}
\]

Barium sulfate dissolves according to the equilibrium:

\[
\text{BaSO}_4(s) \rightleftharpoons \text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq) \quad K_{sp} = [\text{Ba}^{2+}(aq)][\text{SO}_4^{2-}(aq)]
\]

As \( 5.000 \times 10^{-11} \) mol dissolves in 500 mL,

\[
[\text{Ba}^{2+}(aq)] = [\text{SO}_4^{2-}(aq)] = \frac{\text{number of moles}}{\text{volume}} = \frac{5.000 \times 10^{-11}}{0.500} = 1.00 \times 10^{-10} \text{ M}
\]

Hence,

\[
K_{sp} = (1.00 \times 10^{-10}) \times (1.00 \times 10^{-10}) = 1.00 \times 10^{-20}
\]

Answer: \( 1.00 \times 10^{-20} \)

What advantage would there be in administering \( \text{BaSO}_4 \) as a slurry that also contains 0.5 M \( \text{Na}_2\text{SO}_4 \)?

As indicated by the very small solubility above, the equilibrium

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

lies far to the left. Adding more \( \text{SO}_4^{2-}(aq) \) ions pushes it further to the left.

This acts to remove \( \text{Ba}^{2+}(aq) \) ions from solution. This is advantageous as barium ions are highly toxic.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.
• What is a chelate ligand?

A chelate is a ligand with more than one donor atom that can bond to the same metal ion.

Draw all possible isomers of \([\text{CoCl}_2(\text{en})_2]\). \(\text{en} = \text{ethylenediamine} = \text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2\)

* cis and trans geometric isomers are possible. The cis-isomer can exist as non-superimposable mirror images (enantiomers).

\[
\begin{align*}
\text{cis-} & \\
\text{trans-} & \\
\text{cis-} & 
\end{align*}
\]

• Explain briefly why the \([\text{Fe(H}_2\text{O)}_6]^{3+}\) cation has a \(K_a\) of \(6 \times 10^{-3}\) M, whilst the \([\text{Fe(H}_2\text{O)}_6]^{2+}\) cation has a \(K_a\) of \(4 \times 10^{-9}\) M.

The \(\text{Fe}^{3+}\) ion has a higher charge and is smaller than the \(\text{Fe}^{2+}\) ion – it has a higher charge density. The higher charge density withdraws electron density from the oxygen and leading to a more polarised O–H bonds that are more easily broken.
- You may recall from a lecture demonstration or your laboratory work that solid CO$_2$ sublimes under ambient conditions while ice melts. Define the terms sublimation and melting.

**Sublimation** is a phase change from solid to gas without passing through the liquid phase.

**Melting** is a phase change from solid to liquid.

What is a triple point (e.g. in the phase diagram of CO$_2$ or H$_2$O)?

The triple point is the temperature and pressure at which all three phases (solid, liquid and gas) coexist in equilibrium.

What does the different behaviour of ice and solid CO$_2$ indicate about the relative positions of their respective triple points?

- The triple point of CO$_2$ is above ambient pressure.
- The triple point of H$_2$O is below ambient pressure.

- Carbon has a number of allotropes, the two major ones being graphite and diamond. The phase diagram of carbon shows that diamond is not the stable allotrope under normal conditions. Why then does diamond exist under normal conditions?

Graphite is more stable at room temperature and pressure. Diamond has a more compact structure than graphite and becomes more stable than graphite at very high pressures. Under very high pressures, graphite can be converted into diamond.

When the pressure is released, the reverse process is favourable. However, the structural rearrangement required is considerable and the activation energy is very high. Thus, at low temperatures, the diamond → graphite conversion is extremely slow and diamonds can exist for many thousands of years.
Hydrogenation of nitric oxide to nitrogen and water is a potential means of reducing smog-forming NO\(_x\) gases:

\[ 2\text{NO}(g) + 2\text{H}_2(g) \rightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(g) \]

The initial rates of this reaction at constant temperature were determined at the following combination of initial pressures \((P_0)\).

<table>
<thead>
<tr>
<th>Run</th>
<th>(P_0) ((\text{H}_2)) / kPa</th>
<th>(P_0) ((\text{NO})) / kPa</th>
<th>Rate / kPa s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>53.3</td>
<td>40.0</td>
<td>0.137</td>
</tr>
<tr>
<td>2</td>
<td>53.3</td>
<td>20.3</td>
<td>0.033</td>
</tr>
<tr>
<td>3</td>
<td>38.5</td>
<td>53.3</td>
<td>0.213</td>
</tr>
<tr>
<td>4</td>
<td>19.6</td>
<td>53.3</td>
<td>0.105</td>
</tr>
</tbody>
</table>

Derive an expression for the rate law for this reaction.

Between Run 1 and 2, \(P_0\) (\(\text{H}_2\)) is constant and \(P_0\) (\(\text{NO}\)) is halved. This causes the rate to be reduced by a factor of four. The rate is second order with respect to \(\text{NO}\).

Between Run 3 and 4, \(P_0\) (\(\text{H}_2\)) is halved and \(P_0\) (\(\text{NO}\)) is constant. This causes the rate to be reduced by a factor of two. The rate is first order with respect to \(\text{H}_2\).

Overall,

\[ \text{rate} = k \times P(\text{H}_2) \times P^2(\text{NO}) \]

Answer: \( \text{rate} = k \times P(\text{H}_2) \times P^2(\text{NO}) \)

Calculate the value of the rate constant.

Using Run 1, \( \text{rate} = 0.137 \text{ kPa s}^{-1} \) when \( P(\text{H}_2) = 53.3 \text{ kPa} \) and \( P(\text{NO}) = 40.0 \text{ kPa} \):

\[ 0.137 \text{ kPa s}^{-1} = k \times 53.3 \text{ kPa} \times (40.0 \text{ kPa})^2 \]

\[ k = 1.61 \times 10^{-6} \text{ kPa}^{-2} \text{ s}^{-1} \]

Answer: \( k = 1.61 \times 10^{-6} \text{ kPa}^{-2} \text{ s}^{-1} \)

What is the order of the reaction? \( \text{1 (H}_2\text{) + 2 (NO) = 3 (third order)} \)
Hemochromatosis or “iron overload” is a potentially fatal disorder in which excess iron is deposited in the bodily organs as insoluble hydrated iron(III) oxide. It can be treated by administration of desferioxamine B (Desferal), a natural substance isolated from fungi.

Desferal is taken over 8-12 hour periods up to six times per week. A value of \( \log K = 30.6 \) is associated with the following equilibrium:

\[
Fe^{3+} + LH_3^+ \rightleftharpoons FeL^+ + 3H^+ \text{ where } LH_3^+ = \text{Desferal}
\]

Briefly describe the chemical basis for the use of Desferal in iron overload therapy.

The solubility of \( Fe_2O_3 \) is very small - the equilibrium for the reaction below lies far to the left:

\[
Fe_2O_3(s) + \text{excess } H_2O \rightleftharpoons 2Fe^{3+}(aq) + 6OH^-(aq)
\]

Complexation of \( Fe^{3+} \) ions with Desferal is very favourable – the equilibrium for the reaction below lies far to the right (as \( K \) for this reaction is \( 10^{30.6} \)):

\[
Fe^{3+} + LH_3^+ \rightleftharpoons FeL^+ + 3H^+ \text{ where } LH_3^+ = \text{Desferal}
\]

The Desferal complexes all free \( Fe^{3+}(aq) \) ions, so more \( Fe_2O_3 \) must dissolve to re-establish the first equilibrium (le Chatelier's principle). Eventually all the \( Fe_2O_3 \) will dissolve.
• The structure of salbutamol, a drug used to treat bronchospasms, is given below.

![Structure of Salbutamol]

Give the molecular formula of salbutamol. **C₁₃H₂₁O₃N**

Calculate the \( m/z \) value for the major peak you would expect to see for the molecular ion in the high resolution mass spectrum.

[Atomic masses: \(^1\text{H} = 1.0078; \; ^{12}\text{C} = 12.0000; \; ^{16}\text{O} = 15.9949; \; ^{14}\text{N} = 14.0031\)]

**The molar mass of C₁₃H₂₁O₃N is**

\[
13 \times 12.0000 \text{ (C)} + 21 \times 1.0078 \text{ (H)} + 3 \times 15.9949 \text{ (O)} + 1 \times 14.0031 \text{ (N)}
\]

Answer: **239.1516**

Give the structure(s) of the major organic products formed when salbutamol is treated with the following reagents.

- **cold HCl (1 M)**
  ![Structure of Product from cold HCl]

- **NaOH (1 M)**
  ![Structure of Product from NaOH]

- **Cr₂O₇²⁻ / H⁺**
  ![Structure of Product from Cr₂O₇²⁻ / H⁺]
Complete the following table.

<table>
<thead>
<tr>
<th>Starting material</th>
<th>Reagents / Conditions</th>
<th>Major organic product(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="https://example.com/image1" alt="Image" /></td>
<td>SOCl₂</td>
<td><img src="https://example.com/image2" alt="Image" /></td>
</tr>
<tr>
<td><img src="https://example.com/image3" alt="Image" /></td>
<td>HCl</td>
<td><img src="https://example.com/image4" alt="Image" /></td>
</tr>
</tbody>
</table>
| ![Image](https://example.com/image5) | 1. NaBH₄  
2. H⁺ / H₂O | ![Image](https://example.com/image6) |
| ![Image](https://example.com/image7) | hot conc. KOH  
ethanol (solvent) | ![Image](https://example.com/image8) |
| ![Image](https://example.com/image9) | CN⁻ | ![Image](https://example.com/image10) |

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.
A mixture of concentrated nitric and sulfuric acids generates the nitronium ion, \( \text{NO}_2^+ \). Benzene will react with such a mixture to give nitrobenzene.

\[
\text{C}_6\text{H}_6 + \text{conc. HNO}_3 / \text{conc. H}_2\text{SO}_4 \rightarrow \text{C}_6\text{H}_5\text{NO}_2
\]

What 3-part name is given to the mechanism of this nitration reaction?

**electrophilic aromatic substitution**

- Consider the reaction sequence below.

\[
\text{C}_6\text{H}_5\text{OH} + \text{H}^+ \rightarrow \text{A} + \text{B}
\]

Draw the structures of products A and B.

- Draw the structure of the product, C, from the following reaction.

\[
\text{CH}_3\text{COCH}_3 + \text{H}_2 / \text{Pd/C catalyst} \rightarrow \text{C}
\]

Product C undergoes hydrolysis when heated with 4 M NaOH. Give the structures of the products (in their correct ionic states) formed in this reaction.
The incomplete proposed mechanism for the reaction of acetyl chloride with ammonia is shown below. Complete the mechanism by adding curly arrows to illustrate the bonding changes that take place.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.
• Sketch the $^1$H NMR spectrum of bromoethane, CH$_3$CH$_2$Br. The signals appear at 1.7 and 3.3 ppm. Clearly indicate the splitting patterns of both signals and show their relative intensities.
• Devise a synthesis of 3-methylheptan-3-ol using the two starting materials shown. Show the structures of any intermediate products involved, as well as the reagents required for each step. More than one step is required.

Would the product be isolated as a racemic mixture or a single enantiomer or is the product achiral? racemic mixture