- Briefly explain why H₂Se is a stronger Brønsted-Lowry acid than H₂O and a weaker acid than H₂Te.

In general, when comparing binary acids within the same group, the strength of the bond E-H between the element (E) and hydrogen determines the acidity:

\[
\text{H}_2\text{E}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{EH}^-(aq) + \text{H}_3\text{O}^+(aq)
\]

As the atomic size of E becomes larger, the E-H becomes longer and weaker. Thus H₃O⁺ is more readily formed in aqueous solution and acidity increases.

- Compounds of d-block elements are frequently paramagnetic. Using the box notation to represent atomic orbitals, account for this property in compounds of V³⁺.

Paramagnetism is associated with the presence of unpaired electron spins. As vanadium is in group 5, V³⁺ has two electrons in its 3d orbitals. These electrons occupy separate orbitals with the same spin to reduce the repulsion between them:

\[
\begin{array}{cccc}
\uparrow & \uparrow & & \\
\end{array} 
\quad 3d
\]

V³⁺ thus has two unpaired electrons and is paramagnetic.
Complete the following table. (en = ethylenediamine = NH₂CH₂CH₂NH₂)

<table>
<thead>
<tr>
<th>Formula</th>
<th>K₃[Fe(CN)₆]</th>
<th><a href="NO%E2%82%83">Cu(NH₃)₄(H₂O)₂</a>₂</th>
<th>cis-[CrCl₂(en)₂]Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation state of transition metal ion</td>
<td>III or +3</td>
<td>II or +2</td>
<td>III or +3</td>
</tr>
<tr>
<td>Coordination number of transition metal ion</td>
<td>6 ((6 \times \text{CN}^-))</td>
<td>6 ((4 \times \text{NH}_3 + 2 \times \text{H}_2\text{O}))</td>
<td>6 ((2 \times \text{Cl}^- + 2 \times \text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2))</td>
</tr>
<tr>
<td>Number of d-electrons in the transition metal ion</td>
<td>5</td>
<td>9</td>
<td>3</td>
</tr>
<tr>
<td>Species formed upon dissolving in water</td>
<td>3K⁺ ([\text{Fe(CN)}_6]^{3-})</td>
<td>[Cu(NH₃)₄(H₂O)₂]^{2+} (2\text{NO}_3^-)</td>
<td>cis-[CrCl₂(en)₂]⁺ (\text{Cl}^-)</td>
</tr>
</tbody>
</table>
Solution A consists of a 0.20 M aqueous solution of formic acid, HCOOH, at 25 °C. Calculate the pH of Solution A. The pKₐ of HCOOH is 3.75.

The reaction table is:

<table>
<thead>
<tr>
<th></th>
<th>HCOOH(aq)</th>
<th>H₂O(l)</th>
<th>HCOO⁻(aq)</th>
<th>H₃O⁺(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>start</td>
<td>0.20</td>
<td>large</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>-x</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>equilibrium</td>
<td>0.20-x</td>
<td>large</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

As pKₐ = -log₁₀(Kₐ) = 3.75, Kₐ = 10⁻³.₇₅ and:

\[
K_a = \frac{[HCOO^-][H_3O^+]}{[HCOOH]} = \frac{(x)(x)}{(0.20 - x)} = \frac{x^2}{(0.20 - x)} = 10^{-3.75}
\]

As Kₐ is very small, x is tiny and 0.20 – x ≈ x. Hence,

\[
K_a \approx \frac{x^2}{(0.20)} = 10^{-3.75} \quad \text{or} \quad x^2 = (0.20) \times (10^{-3.75}) \quad \text{so} \quad x = [H_3O^+] = 6.0 \times 10^{-4} \text{ M}
\]

As pH = -log₁₀([H₃O⁺(aq)]):

\[
pH = -\log_{10}(6.0 \times 10^{-4}) = 2.22
\]

Answer: 2.22

ANSWER CONTINUES ON NEXT PAGE
At 25 °C, 1.00 L of Solution B consists of 13.6 g of sodium formate, NaHCO₂, dissolved in water. Calculate the pH of Solution B.

The molar mass of NaHCO₂ is

\[
(22.99 \text{ (Na)}) + (1.008 \text{ (H)}) + (12.01 \text{ (C)}) + (2 \times 16.00 \text{ (O)}) = 68.008
\]

The solution thus contains

\[
\frac{\text{mass}}{\text{molar mass}} = \frac{13.6}{68.008} = 0.200 \text{ mol}
\]

As this is dissolved in 1.00 L, the concentration is 0.200 M. The reaction table is now:

<table>
<thead>
<tr>
<th></th>
<th>HCOO⁻(aq)</th>
<th>H₂O(l)</th>
<th>⇌</th>
<th>HCOOH(aq)</th>
<th>OH⁻(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>start</td>
<td>0.200</td>
<td>large</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>-y</td>
<td>-y</td>
<td>+y</td>
<td>+y</td>
<td></td>
</tr>
<tr>
<td>equilibrium</td>
<td>0.200-y</td>
<td>large</td>
<td>y</td>
<td>y</td>
<td></td>
</tr>
</tbody>
</table>

As \( pK_a + pK_b = 14.00 \), \( pK_b = 14.00 - 3.75 = 10.25 \), \( K_b = 10^{-10.25} \) and:

\[
K_b = \frac{[\text{HCOOH(aq)}][\text{OH}^-(aq)]}{[\text{HCOO}^-\text{(aq)}]} = \frac{(y)(y)}{(0.200 - y)} = \frac{y^2}{(0.200 - y)} = 10^{-10.25}
\]

Again \( K_b \) is very small, \( y \) is tiny and \( 0.200 - y \sim y \). Hence, \( y^2 = (0.200) \times (10^{-10.25}) \)

so \( y = [\text{OH}^-(aq)] = 3.35 \times 10^{-6} \) M and \( \text{pOH} = -\log([\text{OH}^-(aq)] = 5.47 \)

As \( \text{pH} + \text{pOH} = 14.00 \), \( \text{pH} = 14.00 - 5.47 = 8.52 \)

Solution B (1.00 L) is poured into Solution A (1.00 L) and allowed to equilibrate at 25 °C to give Solution C. Calculate the pH of Solution C.

After mixing solution A (1.00 L) and solution B (1.00 L), the total volume is 2.00 L. This halves the concentration of the both the acid and the base.

\[
\text{[acid]} = \frac{0.20}{2} = 0.10 \text{ M and [base]} = \frac{0.200}{2} = 0.100 \text{ M}
\]

Solution C contains a weak acid (HCOOH) and its conjugate base (HCOO⁻). It is a buffer and the pH can be calculated using the Henderson-Hasselbalch equation can be used:

\[
\text{pH} = pK_a + \log_{10}\left(\frac{[\text{base}]}{[\text{acid}]}\right) = 3.75 + \log_{10}\left(\frac{0.100}{0.10}\right) = 3.75
\]

If you wanted to adjust the pH of Solution C to be exactly equal to 3.00, which component in the mixture would you need to increase in concentration?

[HCOOH] would be increased (the acid)
• Define what is meant by an “allotrope”. Give an example of a pair of allotropes involving (i) phosphorus and (ii) oxygen.

Allotropes are different structural forms of the same element. Examples include:

(i) white phosphorus and red phosphorus,
(ii) O\textsubscript{2} and O\textsubscript{3}.

• The \( K_{sp} \) of Al(OH)\textsubscript{3} is \( 1.0 \times 10^{-33} \) M\textsuperscript{4}. What is the solubility of Al(OH)\textsubscript{3} in g L\textsuperscript{-1}?

The solubility equilibrium is:

\[ \text{Al(OH)}_3(s) \rightleftharpoons \text{Al}^{3+}(aq) + 3\text{OH}^-(aq) \]

If the molar solubility = \( S \) then \( [\text{Al}^{3+}(aq)] = S \) and \( [\text{OH}^-(aq)] = 3S \). Hence:

\[ K_{sp} = [\text{Al}^{3+}(aq)][\text{OH}^-(aq)] = (S)(3S)^3 = 27S^4 = 1.0 \times 10^{-33} \]

Hence, \( S = \sqrt[4]{\frac{1.0 \times 10^{-33}}{27}} = 2.5 \times 10^{-9} \) M

The formula mass of Al(OH)\textsubscript{3} is \( 26.98 \) (Al) + \( 3 \times (16.00 \) (O) + 1.008 (H)) = 78.004

As mass = number of moles × formula mass, the solubility in g L\textsuperscript{-1} is:

\[ \text{solubility} = (2.5 \times 10^{-9}) \times (78.004) = 1.9 \times 10^{-7} \text{ g L}^{-1} \]

Answer: \( 1.9 \times 10^{-7} \) g L\textsuperscript{-1}

What is the solubility of Al(OH)\textsubscript{3} in g L\textsuperscript{-1} at pH 4.00?

As pH + pOH = 14.00, pOH = 14.00 – 4.00 = 10.00.

As pOH = -log\textsubscript{10}([\text{OH}^-(aq)], [\text{OH}^-(aq)] = 10^{-10.00} \) M.

From above, \( K_{sp} = [\text{Al}^{3+}(aq)][\text{OH}^-(aq)] \). If the molar solubility is \( S \) then:

\[ K_{sp} = (S)(10^{-10.00})^3 = 1.0 \times 10^{-33} \text{ and so } S = 1.0 \times 10^{-3} \text{ M} \]

Converting the molar solubility into g L\textsuperscript{-1} gives:

\[ \text{solubility} = (1.0 \times 10^{-3}) \times (78.004) = 0.078 \text{ g L}^{-1} \]

Answer: \( 0.078 \) g L\textsuperscript{-1}
The following data were obtained for the reaction between gaseous nitric oxide and chlorine at \(-10^\circ\text{C}\).

\[
2\text{NO}(g) + \text{Cl}_2(g) \rightarrow 2\text{NOCl}(g)
\]

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Initial [NO] (mol L(^{-1}))</th>
<th>Initial [Cl(_2)] (mol L(^{-1}))</th>
<th>Initial Reaction Rate (mol L(^{-1}) min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.10</td>
<td>0.10</td>
<td>0.18</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.20</td>
<td>0.36</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.20</td>
<td>1.44</td>
</tr>
</tbody>
</table>

Deduce the rate law for this reaction and calculate the value of the rate constant.

**Rate Law**

Between experiments (1) and (2), [NO] is constant and [Cl\(_2\)] is doubled. This doubles the rate:

\[
\text{rate} \propto [\text{Cl}_2]
\]

Between experiments (2) and (3), [Cl\(_2\)] is constant and [NO] is doubled. The rate increases by a factor of 4:

\[
\text{rate} \propto [\text{NO}]^2
\]

Overall,

\[
\text{rate} \propto [\text{Cl}_2][\text{NO}]^2 = k[\text{Cl}_2][\text{NO}]^2
\]

**Rate Constant**

Using any of the three experiments,

\[
k = \frac{\text{rate}}{[\text{Cl}_2][\text{NO}]^2}
\]

For experiment 1:

\[
k = \frac{0.18}{(0.10)(0.10)^2} = 180
\]

For experiment 2:

\[
k = \frac{0.36}{(0.20)(0.10)^2} = 180
\]

For experiment 3:

\[
k = \frac{1.44}{(0.20)(0.20)^2} = 180
\]

The units of \(k\) are given by:

\[
\text{units of } k = \frac{\text{units of rate}}{(\text{concentration units})^3} = \frac{(\text{mol L}^{-1} \text{ min}^{-1})}{(\text{mol L}^{-1})^3} = \text{mol}^2 \text{L}^2 \text{ min}^{-1}
\]

Answer: \(\text{rate} = k[\text{Cl}_2][\text{NO}]^2\)

Answer: 180 mol\(^2\) L\(^2\) min\(^{-1}\)
- Draw the structure of the major organic product formed in the following reactions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Structure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. CH₃MgBr 2. H⁺ / H₂O</td>
<td><img src="image1" alt="Structure" /></td>
<td>(elimination to give more stable alkene – Zaitsev’s rule)</td>
</tr>
<tr>
<td>1. NaBH₄ 2. H⁺ / H₂O</td>
<td><img src="image2" alt="Structure" /></td>
<td></td>
</tr>
<tr>
<td>KOH ethanol solvent</td>
<td><img src="image3" alt="Structure" /></td>
<td></td>
</tr>
<tr>
<td>2 x HBr</td>
<td><img src="image4" alt="Structure" /></td>
<td>(2 × Markovnikov addition with H adding to less substituted C each time)</td>
</tr>
<tr>
<td>CH₃CH₂OH / H⁺</td>
<td><img src="image5" alt="Structure" /></td>
<td></td>
</tr>
</tbody>
</table>
Suggest reagents you could use to achieve the following transformations.

- **A**: NaOH / H₂O / heat
- **B**: H₂ / Pd catalyst
- **C**: Mg / dry ether
- **D**: 1. CO₂ 2. H⁺ / H₂O
• Add curly arrows to complete the following mechanism.

\[ \text{Br} \rightarrow \text{CN} \]

Classify this reaction as $S_N1$ or $S_N2$ and explain what the three parts of this descriptor signify.

The reaction is an $S_N1$ reaction:

- **$S$** = substitution (Br$^-$ is substituted for CN$^-$)
- **$N$** = nucleophilic (CN$^-$ is negatively charged and attacks the positively charged carbon)
- **$1$** = unimolecular (the first step, involving breaking a C-Br bond, is rate determining and involves only one molecule).

• Devise a synthesis of the product $Y$, starting from compound $X$. Note that more than one step may be required and you should indicate all necessary steps and the constitutional formulas of any intermediate compounds.

\[ \text{X} \rightarrow \text{Y} \]

\[ \text{Cr}_2\text{O}_7^{2-} \cdot \text{H}^+ \]

\[ \text{excess NH}_3 \]

\[ \text{SOCl}_2 \]

\[ \text{X} \rightarrow \text{Cl} \]
• The amino acids serine and valine are shown below.

![Amino Acids Diagram]

List the substituents attached to the stereogenic centre of *valine* in order of decreasing priority.

<table>
<thead>
<tr>
<th>highest priority</th>
<th>lowest priority</th>
</tr>
</thead>
<tbody>
<tr>
<td>-NH₂</td>
<td>-COOH</td>
</tr>
<tr>
<td>-CH(CH₃)₂</td>
<td>-H</td>
</tr>
</tbody>
</table>

Assign the absolute configuration of the stereoisomer of valine shown above.

(\(S\)) (anticlockwise)

Draw a dipeptide formed by the condensation of serine with valine.

![Dipeptide Diagram]

What are the two key elements of protein secondary structure?

The secondary structure describes the orientation of segments of the peptide chain and is defined by the H-bonding between amino acid residues. The most common secondary structures are:

- \(\alpha\)-helices, right handed coils stabilized by H-bonds between amide N-H and C=O groups four residues apart and
- \(\beta\)-pleated sheets, extended structures stabilized by H-bonds between amide N-H and C=O groups on different chains
A saturated solution of iodine in water contains 0.330 g I\textsubscript{2} per litre, but more than this amount can dissolve in a potassium iodide solution because of the following equilibrium.

\[ \text{I}^{-}(aq) + \text{I}_{2}(aq) \rightleftharpoons \text{I}_{3}^{-}(aq) \]

A 0.100 M KI solution dissolves 12.5 g of I\textsubscript{2} per litre, most of which is converted to I\textsubscript{3}\textsuperscript{-} (aq). Assuming that the concentration of I\textsubscript{2}(aq) in all saturated solutions is the same, calculate the equilibrium constant for the above reaction.

The molar mass of I\textsubscript{2} is 2 \times 126.90 = 253.8.

As 0.330 g of I\textsubscript{2} dissolves in a litre of water, the concentration of I\textsubscript{2} in the saturated solution of iodine in water is therefore:

\[ [\text{I}_{2}(aq)] = \frac{0.330}{253.8} = 0.0013 \text{ M} \]

12.5 g of I\textsubscript{2} dissolves in a litre of KI solution, corresponding to \( \frac{12.5}{253.8} = 0.0493 \text{ M} \).

For the equilibrium, the reaction table is therefore:

\[
\begin{array}{ccc}
\text{I}^{-}(aq) & \text{I}_{2}(aq) & \text{I}_{3}^{-}(aq) \\
\text{[initial]} & 0.100 & 0.0493 & 0 \\
\text{change} & -x & -x & +x \\
\text{[equilibrium]} & 0.100-x & 0.0493-x & x
\end{array}
\]

Assuming that [I\textsubscript{2}(aq)] is the same as in the saturated solution (as stated in the question), 0.0493 – x = 0.0013 so x = 0.048 giving:

\[ [\text{I}^{-}(aq)] = 0.100 - 0.048 = 0.052 \text{ M}, [\text{I}_{2}(aq)] = 0.0013 \text{ M and [I}_{3}^{-}(aq)] = 0.048 \text{ M.} \]

The equilibrium constant is therefore:

\[
K_c = \frac{[\text{I}_{3}^{-}(aq)]}{[\text{I}^{-}(aq)][\text{I}_{2}(aq)]} = \frac{(0.048)}{(0.052)(0.0013)} = 710
\]

Answer: 710