Section A Suggested Solutions

Question 1 ANS C

The addition of ammonia causes the silver chloride to dissolve because $Ag^+(aq)$ is removed from the equilibrium $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$. According to Le Chatelier's Principle, this causes the equilibrium to shift to the right and the silver chloride dissolves.

Question 2 ANS B

$$HOCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OCl^-(aq)$$

When two drops of 5.0 M HCl are added, this will not significantly change the volume of the equilibrium mixture. When two drops of 5.0 M HCl are added to an equilibrium mixture of HOCl in water at constant temperature, only some (but not all) of the added H_3O^+ ions are used up as the equilibrium shifts to the left. Hence, there is an increase in the $[H_3O^+]$. The pH of the mixture will **decrease** because of the extra H_3O^+. **A** is false. The concentration of OCl^- will **decrease** as the equilibrium shifts to the left. **C** is false. The ratio given in **D** (the equilibrium constant) will not change since the temperature is constant. **D** is false.

Question 3 ANS A

In the balanced chemical equation, 2 mol of gas X produces 3 mol of gas Y. Hence, according to Le Chatelier's Principle, an increase in pressure will favour the production of the smaller number of mol of gas. The equilibrium yield of Y will **decrease**. The forward reaction is exothermic. Hence, an increase in temperature will favour the reverse reaction. The equilibrium yield of Y will **decrease**.

Question 4 ANS A

For the original equation $2X(g) \rightleftharpoons 3Y(g)$, the equilibrium constant $= K_1 = \frac{[Y]^3}{[X]^2} = 25$

For the reaction $6Y(g) \rightleftharpoons 4X(g)$, the equilibrium constant $= K_2 = \frac{[X]^4}{[Y]^6} = \frac{1}{K_1^2} = \frac{1}{25^2} = \frac{1}{625}$.

Question 5 ANS C

Strong acids are completely ionised in solution. Weak acids are partially ionised in solution. **D** is false. The concentration of an acid is the number of mol of acid per litre (M or mol L^{-1}). A strong acid such as HCl(aq) can have a very low concentration (0.0001 M) while a weak acid such as $CH_3COOH(aq)$ can have a higher concentration (5.0 M). **A** and **B** are false. A completely ionised strong acid and a partially ionised weak acid can have the same hydrogen ion concentration in solution and, therefore, the same pH.

Question 6 ANS B
The equilibrium is $C_2H_5COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2H_5COO^-(aq)$

$$\text{Hence, } K_a = \frac{\left[C_2H_5COO^-\right]\left[H_3O^+\right]}{\left[C_2H_5COOH\right]} = 1.3 \times 10^{-5}$$

$$n(C_2H_5COOH) = \frac{m}{M_r} = \frac{0.37}{74} = 0.005$$

$$c(C_6H_5COOH) = \frac{n}{V} = \frac{0.005}{0.500} = 0.01 \text{ M}$$

$$K_a = \frac{\left[C_2H_5COO^-\right]\left[H_3O^+\right]}{\left[C_2H_5COOH\right]} = 1.3 \times 10^{-5}$$

$$\text{Since } \left[C_2H_5COO^-\right] = \left[H_3O^+\right] \text{ and } \left[C_2H_5COOH\right] \approx 0.01 \text{ M}$$

$$\left[H_3O^+\right]^2 = 1.3 \times 10^{-5} \times 0.01 = 1.3 \times 10^{-7}$$

$$\left[H_3O^+\right] = 3.61 \times 10^{-4} \text{M}$$

$$\text{pH} = -\log_{10}\left[H_3O^+\right] = -\log_{10}(3.61 \times 10^{-4}) = 3.44$$

This is closest to 3.4

Question 7 ANS D
The forward reaction is endothermic. Therefore, the energy content of the products is greater than the energy content of the reactants. **A** is false. The activation energy of the forward reaction is greater than the activation energy of the reverse reaction. **B** is false. The pH is 7 only at 298 K (see Data Book). **C** is false. According to the balanced equation, 1 mol of H_3O^+ will be produced for each mol of OH^-. Hence, the concentrations are equal independent of the temperature.

Question 8 ANS A
At any given temperature, the particles in a gas have a range of velocities. When the temperature is increased, the number of particles with greater velocities increases. A chemical reaction will occur only when particles collide with sufficient energy (and the correct alignment). Hence, an increase in temperature increases the rate of a chemical reaction by making the particles more energetic overall.

Question 9 ANS A
This is an exothermic reaction in which the heat content of the products is less than the heat content of the reactants. Energy is released. **Y** is the activation energy for the forward reaction. This is the energy required to break the bonds in the reactants. **X** is the ΔH value for the reaction.
ΔH = H(products - H(reactants). This has a negative value.

Question 10 ANS A

The equilibrium constant expression is $K_c = \frac{[H_2][I_2]}{[HI]^2}$.

To determine whether or not the system is at equilibrium, calculate the value of this expression. The system is in equilibrium if the value is equal to 2.0 . It is not necessary to know the actual values of the temperature or the volume. **C** and **D** are false.

$n(\mathrm{HI}) = \frac{1.4\times10^{19}}{6.02\times10^{23}} = 2.33\times10^{-5}$ mol

$n(\mathrm{H_2}) = n(\mathrm{I_2}) = \frac{2\times10^{19}}{6.02\times10^{23}} = 3.3\times10^{-5}$ mol

Let the volume of the vessel = V L

$$\Rightarrow K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{(3.3\times10^{-5})^2 / V^2}{(2.33\times10^{-5})^2 / V^2} = \frac{(3.3\times10^{-5})^2}{(2.33\times10^{-5})^2} = 2.0$$

⇒ the system is at equilibrium.

Question 11 ANS C

n(NaOH) initially = 1.5 × 2.5 = 3.75 mol and n(HCl) initially = 1.2 × 2 = 2.4 mol
Therefore, n(NaOH) reacting = 2.4 mol since 1 mol of NaOH reacts exactly with 1 mol of HCl and HCl is the limiting reactant.
Hence, energy released = 2.4 × 56 = 134.4 kJ. This is closest to 134 kJ.

Question 12 ANS C

Use the Data Book to find that Ag^+(aq) is a stronger oxidant than Ni^{2+}(aq). In this electrochemical cell, the silver ions accept electrons and are reduced to silver metal. This is reduction and, therefore, by definition, occurs at the cathode. The silver cathode is the positive electrode since electrons are flowing towards it.

Question 13 ANS D

The anode is the electrode at which oxidation occurs.
The anode reaction is $\mathrm{Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-}$.
The cathode is the electrode at which reduction occurs.
The cathode reaction is $\mathrm{Ag^+(aq) + e^- \rightarrow Ag(s)}$.

Question 14 ANS C

At the negative electrode, the strongest oxidant will accept electrons and be reduced. From the Data Book, it can be seen the strongest oxidant is water. Reduction will occur as the water molecules accept electrons to produce hydrogen gas and hydroxide ions. $\mathrm{2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)}$.

Question 15 ANS D

The number of mole of electrons required to deposit all of the copper = 2 × 0.5 = 1.0
The number of mole of electrons required to deposit all of the silver = 1 × 1.0 = 1.0
Hence, the quantity of electricity required = 2 × 96500 C.

Question 16 ANS D

From the electrochemical series in the Data Book, it can be seen that Pb^{2+}(aq) and Ag^+(aq) are stronger oxidants than water. Lead will be deposited at the negative electrode according to the equation: $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$. Silver will be deposited at the negative electrode according to the equation: $2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$. Al^{3+}(aq) is a weaker oxidant than water. Aluminium will not be deposited from an aqueous solution.

Note that n(Pb) deposited = $\frac{1}{2} \times n(\text{Ag})$ deposited and therefore, the ratio is 1 : 2 : 0

Question 17 ANS D

P^{2+}(aq) is a stronger oxidant than H^+(aq). P^{2+}(aq) and Q^{2+}(aq) are both stronger oxidants than R^{2+}(aq) . Hence, of the alternatives, the only possibility is $P > Q > R > H_2$

Question 18 ANS D

1M nickel sulfate ($NiSO_4$) contains the ion Ni^{2+}(aq). This has a greater E^0 value (a less negative value) than both the metals Fe and Zn. Therefore, Ni^{2+}(aq) will react with both Fe and Zn but not with either of the metals Cu or Ag. Ni^{2+}(aq) will be reduced to Ni(s) by either zinc or iron.

Question 19 ANS B

The E^0 values can be used to predict the position of equilibrium in a reaction between an oxidant and a reductant. However, these E^0 values give no information about the rate of reaction. Hence, the ‘no observable’ reaction could mean a very slow reaction.

Question 20 ANS B

The cell potential under standard conditions is given by the absolute value of the difference between the E^0 values. EMF = $|-0.23 - (-0.76)| = |-0.23 + 0.76| = 0.53$ V.

Question 1

a. Ammonia - NH_3 - catalyst – porous iron pellets with Al_2O_3 and KOH
Nitric acid – HNO_3 – catalyst – Pt-Rh gauze
Sulfuric acid – H_2SO_4 – catalyst – porous pellets of vanadium (V) oxide
Ethene – C_2H_4 – catalyst – zeolite crystals (or none)

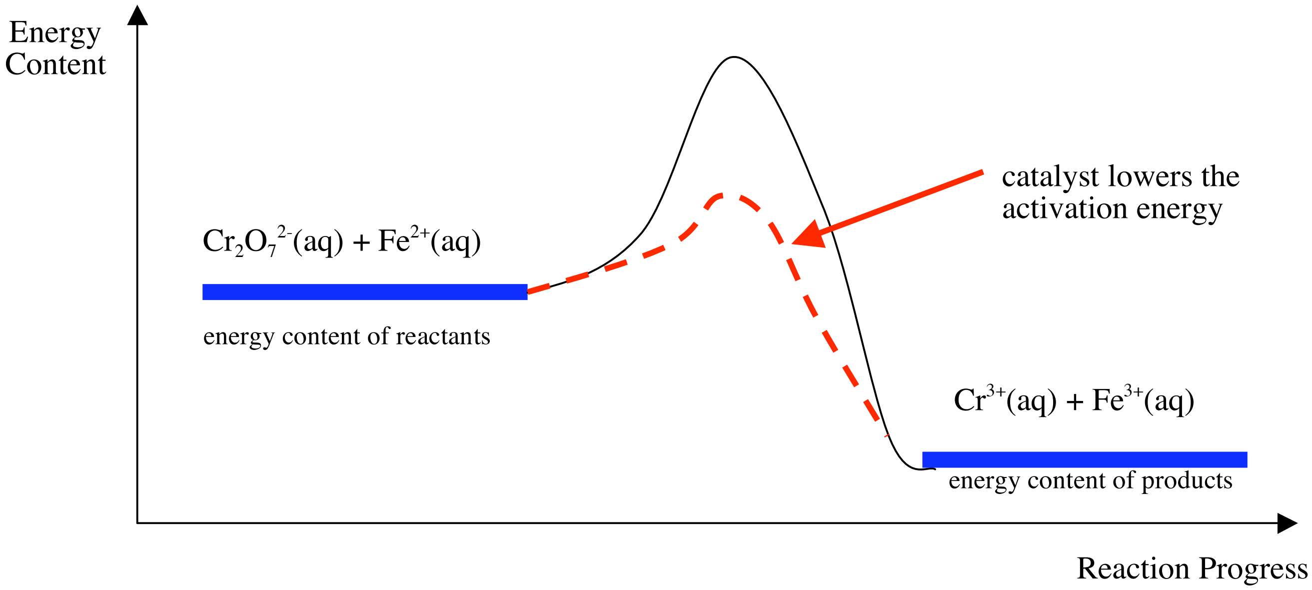
b. A catalyst lowers the activation energy of a chemical reaction by providing an alternative lower energy pathway for the reaction to proceed. Therefore, more particles with sufficient energy are able to undergo effective collisions at a fixed temperature.

c. **i.** $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$ (multiply this half equation by 6 before adding to the above)

ii. $Cr_2O_7^{2-}(aq) + 6Fe^{2+}(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 6Fe^{3+}(aq) + 7H_2O(l)$

d. The energy profiles for the non-catalysed and catalysed reactions are shown below.



Question 2

a. The reduction reaction is $Ag^+(aq) + e^- \rightarrow Ag(s)$

b. The oxidation reaction is $Ag(s) \rightarrow Ag^+(aq) + e^-$

c. The anode is the electrode at which oxidation takes place. The silver electrode.

d. There is no change in the concentration of the silver ions in solution because silver ions are produced at the silver electrode at the same rate as they are deposited on the surface of the inert electrode.

e. V(Ag) coating on the plate = 20×0.02 cm^3.

$\Rightarrow$ *m*(Ag) coating on the plate = $20 \times 0.02 \times 10.5$ g

$\Rightarrow$ *n*(Ag) coating on the plate = $(20 \times 0.02 \times 10.5)/107.9$

From the equation: $n(Ag) = n(e^-) = (20 \times 0.02 \times 10.5)/107.9$

$\Rightarrow$ Quantity of electricity = $n(e^-) \times F = (20 \times 0.02 \times 10.5) \times (96500/107.9)$

$\Rightarrow$ Current to deposit Ag $= Q/t$
$= (20 \times 0.02 \times 10.5 \times 96500)/(107.9 \times 60 \times 10)$
= 6.26 A
= 6.3 amperes

Question 3

a. The balanced equation for the reaction is $H_2SO_4(aq) + 2KOH(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$
Therefore, *n*(KOH) reacting = $2 \times n(H_2SO_4)$ reacting.
Initial $n(KOH) = 0.4 \times 0.2 = 0.08$ mol. Initial $n(H_2SO_4) = 0.4 \times 0.2 = 0.08$ mol.
KOH is the limiting reagent since 0.04 mol of H_2SO_4 reacts exactly with 0.08 mol of KOH
Hence, the reaction of 0.08 mol of KOH produces 4.56 kJ.

In the second experiment,
Initial $n(KOH) = 0.8 \times 0.2 = 0.16$ mol. Initial $n(H_2SO_4) = 0.4 \times 0.2 = 0.08$ mol.
All of the KOH and H_2SO_4 are used up since they are in the ratio of 2 : 1.
Since twice the amount of KOH reacts, the energy released = $2 \times 4.56 = 9.12$ kJ

b. The balanced ionic equation is
$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ **or** $H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(l)$

c. Since the reaction of 0.08 mol of OH^- produces 57 kJ, 1 mol of equation gives the
ΔH value for this reaction = $-\,4.56/0.08 = -\,57$ kJ mol^{-1}.

Question 3 (continued)

d. Energy released = 9.12 kJ = 9120 J
mass of water = volume × density = 1200 × 1.0 = 1200 g.
Energy released in joules = mass × specific heat of water × temperature rise
From the Data Book, the specific heat of water = 4.18 J mL^{-1} K^{-1}.
Hence, $9120 = 1200 \times 4.18 \times \Delta T$

$$\text{Therefore, } \Delta T = \frac{9120}{1200 \times 4.18} = 1.8°\text{C}$$

Question 4

a. $$K_a(\text{HCN}) = \frac{\left[H_3O^+\right]_e\left[CN^-\right]_e}{\left[HCN\right]_e}.$$

The subscript *e* indicates that the concentrations must be equilibrium concentrations.

b. Use the Data Book for the K_a value. Assuming that the concentrations of H_3O^+ and CN^- are equal and that the concentration of HCN is very close to 0.01 M,

$$K_a(\text{HCN}) = \frac{\left[H_3O^+\right]_e\left[CN^-\right]_e}{\left[HCN\right]_e} = \frac{\left[H_3O^+\right]^2}{\left[HCN\right]} = 6.3 \times 10^{-10} \text{ (Data Book)}$$

$$\Rightarrow \left[H_3O^+\right]^2 = 0.01 \times 6.3 \times 10^{-10} = 6.3 \times 10^{-12}$$

$$\Rightarrow \left[H_3O^+\right] = 2.51 \times 10^{-6} \text{ M}$$

$$\Rightarrow \text{pH} = 5.6$$

c. When sodium cyanide (NaCN) is added to the equilibrium, $CN^-(aq)$ ions are added. In accordance with Le Chatelier's Principle, this shifts the equilibrium position to the left. The hydronium ion (H_3O^+) concentration decreases and, therefore, the pH increases.

d. The change in pH will indicate whether the forward or reverse reaction has been favoured by an increase in temperature. **If** the increase in temperature increases the pH, the reverse reaction has been favoured by an increase in temperature. Hence, the reverse reaction is endothermic and the forward reaction is exothermic.

Question 5

a. $n(\text{COBr}_2)$ reacting = 4.00 – 2.56 = 1.44 mol.
Hence, at equilibrium, $n(\text{COBr}_2) = 2.56$, $n(\text{CO}) = n(\text{Br}_2) = 1.44$.
$[\text{COBr}_2]_e = 2.56/2.00 = 1.28$ M.
$[\text{CO}]_e = [\text{Br}_2]_e = 1.44/2.00 = 0.72$ M.

$$\text{Hence, } K_c = \frac{[\text{CO}][\text{Br}_2]}{[\text{COBr}_2]} = \frac{0.72 \times 0.72}{1.28} = 0.405 \text{ M} = 0.41 \text{ M}$$

b.

At the new equilibrium position	Circle the answer	Give a reason for your answer
The numerical value of the equilibrium constant, K_c, has	increased decreased [✓ not changed]	The temperature is constant.
The equilibrium **mass** of Br_2 has	increased [✓ decreased] not changed	A decrease in volume gives an increase in pressure. This shifts the equilibrium to the left – the smaller number of mol of gas.
The equilibrium **concentration** of $COBr_2$ has	[✓ increased] decreased not changed	The equilibrium shifts to the left. This gives a larger mass of $COBr_2$ in a smaller volume, This gives an increased concentration.
The equilibrium **concentration** of Br_2 has	[✓ increased] decreased not changed	The concentration of $COBr_2$ has increased. The equilibrium constant does not change. Therefore, the concentrations of Br_2 and CO must also increase.

c. The inert gas helium does not react with any of the other gases and, therefore, has no effect on the position of equilibrium. The equilibrium mass of Br_2 is unchanged.

Question 6

a. All of the energy released in the reaction in the bomb calorimeter is measured while in the simple laboratory calorimeter, some heat is lost.

b. $H_2O(l)$ has an E^0 value of +1.23 and is a stronger reductant than $Cl^-(aq)$ with an E^0 value of +1.36. However, this is under standard conditions of 1.0 M solutions. When the $Cl^-(aq)$ concentration is much higher, the potential changes and $Cl^-(aq)$ donates electrons preferentially.

c. Use the Data Book to show that the heat of combustion per gram of hydrogen $\left(\frac{-286}{2} = 143 \text{ kJg}^{-1}\right)$ is greater than the heat of combustion per gram of octane $\left(\frac{-5464}{114} = 48 \text{ kJg}^{-1}\right)$.

d. From the Data Book, it can be seen that phenolphthalein is a much weaker acid than methyl orange. The K_a value for methyl orange causes it to change colour at an acidic pH while the K_a value for phenolphthalein causes it to change colour at an alkaline pH.

Question 7

a. The anode half equation is $H_2(g) \rightarrow 2H^+(aq) + 2e^-$

b. The hydrogen ions react with the carbonate ions in the electrolyte to produce carbon dioxide and water according to the equation $2H^+(aq) + CO_3^{2-}(l) \rightarrow H_2O(g) + CO_2(g)$.
This is **not** a redox reaction.

c. The half equation for the overall reaction occurring at the anode is obtained by adding the equations in **a.** and **b.** $H_2(g) + CO_3^{2-}(l) \rightarrow H_2O(g) + CO_2(g) + 2e^-$

d. The overall cell reaction is obtained by adding the cathode half equation to twice the equation in **c.** as shown below.

$$\begin{array}{l} O_2(g) + 2\cancel{CO_2}(g) + \cancel{4e^-} \rightarrow 2\cancel{CO_3^{2-}}(l) \\ 2H_2(g) + 2\cancel{CO_3^{2-}}(l) \rightarrow 2H_2O(g) + 2\cancel{CO_2}(g) + \cancel{4e^-} \\ \hline 2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \end{array}$$

e. **i.** The cathode is the electrode at which reduction occurs. It is positive. This is the electrode on the right hand side.

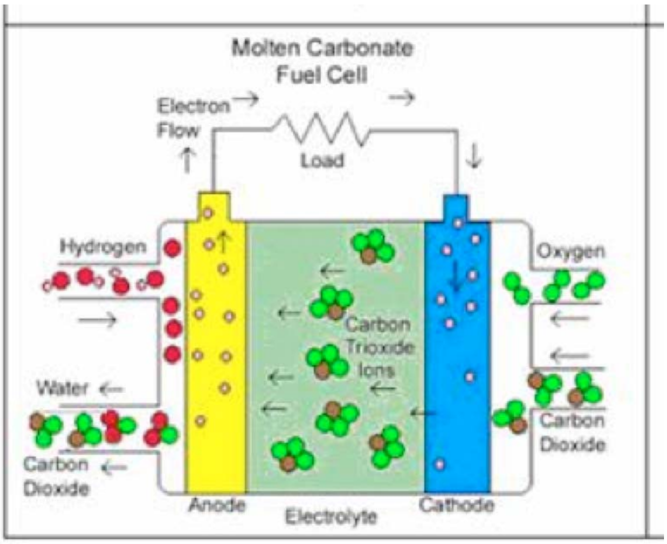
ii. The electrons flow from left to right through the external circuit (the voltmeter V)

f. There are no net carbon dioxide emissions. The overall cell reaction produces only water. Carbon dioxide is used and produced in the same amounts.

A more detailed diagram and description of a MCFC is given on the next page.

The following is not part of the solutions but is provided for the interest of teachers and students.

The internet reference is http://www.iit.edu/~smart/garrear/fuelcells.htm



MCFC: Formation of water will also occur at the anode. The hydrogen ions produced at the anode will not conduct through the electrolyte. The hydrogen gas fed to the anode ionises into $4H^+$ ion and $4e^-$. The cathode process combines oxygen O_2 and $2CO_2$ from the oxidant stream with electrons entering the cathode to produce carbonate ions $2CO_3^{2-}$ which enter the electrolyte. The free moving carbonate ions conduct through the electrolyte and combine with the hydrogen ions at the anode forming water $2H_2O$ and carbon dioxide $2CO_2$. The overall reaction shows that no extra carbon dioxide was produced since we put in $2CO_2$ at the cathode and got out $2CO_2$ at the anode.

END OF SUGGESTED SOLUTIONS

2008 VCE CHEMISTRY TRIAL WRITTEN EXAMINATION 2

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