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## CHEMISTRY PHYSICAL CHEMISTRY

| Level & Board   | CIE (A-LEVEL) |
|-----------------|---------------|
|                 |               |
| TOPIC:          | EQUILIBRIA    |
|                 |               |
| PAPER TYPE:     | SOLUTION - 2  |
|                 |               |
| TOTAL QUESTIONS | 10            |
|                 |               |
| TOTAL MARKS     | 112           |

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- (a)  $2CH_3OH + 3O_2 \rightarrow 2CO_2 + 4H_2O$
- (b) Sulphur dioxide and Nitrogen dioxide
- (c) 1. Low temperature

As the forward reaction is exothermic at low temperature, the reaction will go forward to produce high yield of methanol.

2. High pressure

As the forward reaction goes to fewer gas to fewer gas molecules, the reaction will go forward at high pressure.

(d) (i) It helps to remove carbon dioxide from air which is responsible for

green – house

effect and global warming.

(ii)

|                       | 0         |                  |            |                    |
|-----------------------|-----------|------------------|------------|--------------------|
|                       | $CO_2$    | + H <sub>2</sub> | =00        | + H <sub>2</sub> U |
| Initial moles         | 0.50      | 0.50             | 0.20       | 0.20               |
|                       |           | ()               | ( )        | (                  |
| Equilibrium           | (0.5 – x) | (0.50 –x)        | (0.20 + x) | (0.20 + x)         |
|                       |           | AT UN            |            |                    |
| moles                 |           |                  |            |                    |
|                       |           |                  |            |                    |
| Equilibrium           | 0.5 – x   | 0.50 - x         | 0.20 + x   | 0.20 + x           |
|                       |           |                  | 1          | 1                  |
| concentration         | 1         | 1                | 1          | 1                  |
| concentration         |           |                  |            |                    |
| male dm <sup>-3</sup> |           |                  |            |                    |
| mole um               |           |                  |            |                    |

$$K_c = \frac{[CO][H_2O]}{[CO_2][H_2]} \implies 1.44 = \frac{(0.20+x)^2}{(0.50-x)^2} \implies x = 0.18$$

at equilibrium moles of  $(CO_2)$  = moles of  $(H_2)$  = 0.50 – 0.18 = 0.32

moles of (CO) = moles of  $(H_2O) = 0.20 + 0.18 = 0.38$ 

- (a) Acids are species that donate protons (hydrogen ions) when dissolve in water.Bases are species that accept protons when dissolve in water.
- (b) (i) When chlorine is substituted in ethanoic acid, K<sub>a</sub> value increase and acid becomes stronger. It is due to electron withdrawing effect of chlorine making
   O H bond weaker causing moles H+ ions to be free.

(i) 
$$[H^+] = \sqrt{K_a[Acid]}$$
  
=  $\sqrt{(1.3 \times 10^{-3}) \times 0.1} = 0.0114 \text{ mol dm}^{-3}$ 

$$-\log[H^+] = -\log 0.0114$$

pH = 1.94





(c) (i)  $CH_3CO_2H + OH^- \rightarrow CH_3CO_2^- + H_2O$ 

 $CH_3CO_2^- + H^+ \rightarrow CH_3CO_2HH$ 

(ii) 
$$pK_a = -\log_{10}K_a = -\log_{10}1.7 \times 10^{-5} = 4.77$$

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

$$= 4.77 + \log \frac{0.2}{0.1} = 4.77 + 0.30 = 5.07$$

3)

(i) 
$$K_{sp} = [Ca^{2+}][OH^{-}]^2$$
, units = mol<sup>3</sup> dm<sup>-9</sup>

(ii) Moles of acid (H<sup>+</sup>) = 
$$0.05 \times \frac{21}{1000} = 1.05 \times 10^{-3}$$

same moles of  $OH^{-}$  are present in 21 cm<sup>3</sup> moles I 25 cm<sup>3</sup> of Ca(OH)<sub>2</sub>.

$$[OH^{-}(aq)] = (1.05 \times 10^{-3}) \times \frac{1000}{25} = 4.2 \times 10^{-2} \text{ (mol dm}^{-3})$$

$$[Ca^{2+}(aq)] = \frac{1}{2} \times 4.2 \times 10^{-2} = 2.1 \times 10^{-2} \text{ (mol dm}^{-3)}$$

(iii)  $Ca(OH)_2$  will be less soluble in 0.1 mol dm<sup>-3</sup> NaOH because of common ion effect.

4)

(c) (i) 
$$K_{sp} = [Pb^{2+}][Cl^{-}]^2$$
 units = mol<sup>3</sup> dm<sup>-9</sup>

(ii) Suppose [Pb<sup>2+</sup>] = x

$$\implies [Pb^{2+}] \times [Cl^{-}]^{2} = (x)(2x)^{2}$$

$$\implies$$
 K<sub>sp</sub> = 4x<sup>3</sup>

$$\implies x = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{2.0 \times 10^{-5}}{4}} = 1.71 \times 10^{-2}$$

(iii) 
$$[Pb^{2+}] = \frac{2 \times 10^{-5}}{(0.5)^2} = 8.0 \times 10^{-5}$$
 mol dm<sup>-3</sup>

(iv) Solubility of  $PbCl_2$  is decreased because of common ion effect.

5)

(a) (i) order with respect to  $[CH_3CHO] = 1$ 

order with respect to  $[CH_3OH] = 1$ 

order with respect to  $[H^+] = 1$ 

## (ii) Rate of reaction = $k[CH_3CHO][CH_3OH][H^+]$

(iii) Units mol<sup>-2</sup> dm<sup>6</sup> s<sup>-1</sup>

(iv) Rate of reaction =  $\frac{0.20}{0.20} \times \frac{0.20}{0.1} \times \frac{0.20}{0.05}$ 

=  $2 \times 4 = 8$  times as fast as reaction 1.

Hence relative rate of reaction = 8.

|                | [CH₃CHO]               | [CH₃OH]                | [H <sup>+</sup> ]      | [acetal A]             | [H <sub>2</sub> O]     |
|----------------|------------------------|------------------------|------------------------|------------------------|------------------------|
|                | / mol dm <sup>-3</sup> |
| At start       | 0.20                   | 0.10                   | 0.05                   | 0.00                   | 0.00                   |
| At equilibrium | (0.20 – x)             | (0.10 – 2x)            | 0,05                   | х                      | х                      |
| At equilibrium | 0.175                  | 0.05                   | 0.05                   | 0.025                  | 0.025                  |

(iii)  $K_c = \frac{[CH_3CH(OCH_3)_2][H_2O]}{[CH_3CHO][CH_3OH]^2}$ 

units = mol<sup>-1</sup>dm<sup>3</sup>

(iv) 
$$K_c = \frac{[CH_3CH(OCH_3)_2][H_2O]}{[CH_3CHO][CH_3OH]^2}$$

 $=\frac{0.025\times0.025}{0.175\times(0.05)^2}=1.4286\ mol^{-1}dm^3$ 

6)

- (a) (i) The thermal stability decreases from HCl to Hi.
- (ii)  $2HX \rightarrow H_2 + X_2$

The thermal decomposition of HX depends on the strength of the H – X bond.

Down the Group, the atomic size of X increase and its orbital, used for

bonding, becomes more diffuse. Hence, orbital overlap between H and X

becomes smaller and less affective causing the H – X bond to become weaker.

Therefore thermal stability of these hydrides decreases down the Group.

(b) 
$$K_c = \frac{[HI]^2}{[H_2] \times (I_2)}$$
, No units.

(c) (i) As the number of moles on the right hand side and left hand side of the equation are same, increasing the pressure will have no effect on the equilibrium position.

(ii) Decreasing the temperature would favour that side of the reaction which produces more heat. As the forward reaction is exothermic, the equilibrium will move to the right hand side of the reaction

(d)

|   | H <sub>2</sub> (g) +     | l <sub>2</sub> (g) | $\rightleftharpoons$ | 2HI(g)         |
|---|--------------------------|--------------------|----------------------|----------------|
| initial moles   | 0.02                     | 0.02               |                      | 0              |
| moles at equilibrium  | 0.02 – x                 | 0.02 – x           |                      | 2x             |
| concentration (in mol/dm <sup>3</sup> )   |                          |                    |                      |                |
| at equilibrium  | $\frac{0.02-x}{1}$       | $\frac{0.02-x}{1}$ |                      | $\frac{2x}{1}$ |
| $= \frac{[HI]^2}{[H_2] \times (I_2)}$   |                          |                    |                      |                |
| $59 = \frac{(2x)^2}{(0.02 - x)(0.02 - x)}$  |                          |                    |                      |                |
| $59 = \frac{(2x)^2}{(0.02 - x)^2}$  |                          |                    |                      |                |
| $\sqrt{59} = \frac{2x}{0.02 - x}$   |                          |                    |                      |                |
| $0.02\sqrt{59} - \sqrt{59}x = 2x$   |                          |                    |                      |                |
| $2x + \sqrt{59} x = 0.02\sqrt{59} \implies x = \frac{0.02\sqrt{59}}{2+\sqrt{59}}$ | $\frac{59}{9} = 0.01587$ | ≈ 0.016            |                      |                |

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www.chemistryonlinetuition.com  $\therefore$  at equilibrium, moles of HI = 2× 0.01587

 $= 0.03174 \approx 0.032 \text{ mol}$ 

moles of  $H_2$  = moles of  $I_2$  = 0.02 – 0.01587

= 0.00413 = 0.004 mol

(a) (i)  $NH_3$  +  $HZ \rightarrow NH_4^+ + Z^ CH_3OH + HZ \rightarrow CH_3OH_2^+ + Z^-$ (ii)  $NH_3$  +  $B^- \rightarrow NH_2^- + BH$  $CH3OH + B^- \rightarrow CH_3O^- + BH$ 

- (a) (i) A reaction that can go in either direction.
  - (ii) A dynamic equilibrium occurs when the rate of the forward reaction is equal to the rate of the backward reaction.
- (b) In a buffer solution at equilibrium.

$$HZ + H_2O \rightleftharpoons Z^- + H_3O^+$$
.

When an acid is added, the reaction moves to the left as follows:

$$H^+ + Z^- \rightarrow HZ$$

Hence, the Buffer solution is able to maintain it's pH by shifting the equilibrium To the left or right.

(c) (i) 
$$K_c = \frac{[CH_3CH_2C00^-][H^+]}{[CH_3CH_2C00H]}$$
  
as  $[CH_3CH_2C00^-][H^+]$   
 $\Rightarrow [H^+] = \sqrt{K_a[CH_3CH_2C00H]}$   
 $= \sqrt{0.5 \times 1.34 \times 10^{-5}} = 2.588 \times 10^{-3} \text{ mol/dm}^3$ 

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 $pH = - \log [H^+]$ 

= 2.587 ≈ 2.59

(ii)  $CH_3CH_2CO_2H + NaOH \rightarrow CH_3CH_2CO_2Na + H_2O$ .

(iii) Total Moles of propanoic acid =  $0.5 \times \frac{100}{1000} = 0.05$ .

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Hence, the acid is in excess.

1 mole sodium hydroxide produces 1 mole of sodium propanoate.

$$\therefore$$
 concentration of propanoate =  $0.03 \div \frac{100}{1000} = 0.2 \text{ mol} / \text{dm}^3$ 

(iv) pH = - log10 K<sub>a</sub> + log<sub>10</sub>  $\left(\frac{[Salt]}{[Acid]}\right)$ 

$$= -\log_{10}(1.34 \times 10^{-5}) + \log_{10}\left(\frac{0.3}{0.2}\right)$$

= 5.049 ≈ 5.05

(d)  $G = CH_3CH_2COCI$ 

H is SOCl<sub>2</sub>

J is NaCl

8)

(c) (i)

- K<sub>a</sub> is larger than that of ethanol because the CH<sub>3</sub>CO<sub>2</sub><sup>-</sup> ion stabilized by charge delocalization.
- $K_{\mbox{\tiny a}}$  is smaller than that of chloroethanoic acid because the electronegative
  - chlorine atom in ClCH<sub>2</sub>CO<sub>2</sub>H makes the ClCH<sub>2</sub>CO<sub>2</sub><sup>-</sup> ion more stable.

(ii) 
$$[H^+] = \sqrt{K_a \times [CH_3CO_2H]}$$
  
=  $\sqrt{1.75 \times 10^{-5} \times 0.1} = 0.0013229$ 

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

 $= -\log_{10} [0.0013229] = 2.8785 \approx 2.88.$ 

(d) (i) NaOH + CH<sub>3</sub>COOH  $\rightarrow$  CH<sub>3</sub>COONa + H<sub>2</sub>O

 $\Rightarrow$  1 mol of NaOH requires 1 moles of CH<sub>3</sub>COOH.

moles of CH<sub>3</sub>COOH =  $0.100 \times \frac{10}{1000} = 0.001$  moles

moles on NaOH =  $0.100 \times \frac{20}{1000} = 0.002$  moles

 $\therefore$  remaining moles of NaOH at the end of addition = 0.002 - 0.001 = 0.001 moles

(ii) Total volume of solution =  $30 \text{ cm}^3 = 0.03 \text{ dm}^3$ 

Concentration of NaOH at the end =  $\frac{0.001}{0.03}$  = 0.03333 mol/dm<sup>3</sup>

 $NaOH \rightarrow Na^+ + OH^-$ 

:. 
$$[OH-] = 0.0333 \text{ mol/dm}^3.$$
  
(iii)  $K_w = [H^+][OH^-] \implies [H^+] = \frac{K_w}{[OH^-]}$   
 $= \frac{1 \times 10^{-14}}{0.0333} = 3.0 \times 10^{-13} \text{ mol/dm}^3$ 

 $\therefore pH = -\log_{10}[H^+]$ 

 $= -\log_{10} (3.0 \times 10^{-13}) = 12.52$ 



(v)

| Indicator       | pH at which    | Place one tick only |  |
|-----------------|----------------|---------------------|--|
|                 | colour changes | in this column      |  |
| malachite green | 0-1            |                     |  |
| thymol blue     | 1 – 2          |                     |  |
| bromophenol     | 3 – 4          |                     |  |
| thymolphthalein | 9 - 10         |                     |  |

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- (a) (i)  $4\text{FeS}_2 + 11\text{O}_2 \rightarrow 2\text{FeO}_3 + 8\text{SO}_2$
- (b) (i) The reaction of sulfur trioxide with water is very exothermic and produces

harmful acid mist.



(d) (i) Advantage: Reaction rate is high.

Explanation: More molecules have energy greater then activation energy and therefore there will be more fruitful collisions between particles. Disadvantage: As the forward reaction is exothermic, increasing the temperature will favour that side of the reaction which absorbs heat i.e. the left hand side of the reaction.

(ii) 
$$K_p = \frac{P_{SO_3^2}}{P_{SO_3^2} \times P_{O_2}}$$

(iii)

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$
Initial number of moles:  
2 2 0  
(-1.80) (-0.9)  
moles of equilibrium:  
0.2 1.1 0  
sum of moles at equilibrium = 0.2 + 1.1 + 1.80 = 3.1  
mole fraction of  $SO_2 = \frac{1.8}{3.1} = 0.581$   
mole fraction of  $SO_2 = \frac{0.2}{3.1} = 0.065$   
mole fraction of  $O_2 = \frac{1.1}{3.1} = 0.355$   
 $\therefore K_p = \frac{(0.581 \times (2 \times 10^5))^2}{(0.065 \times (2 \times 10^5))^2 \times (0.355 \times (2 \times 10^5))}$   
units = Pa<sup>-1</sup>

(d) (i) 
$$K_{sp} = [Ca^{2+}]^3 [PO_4^{3-}]^2$$

(ii) 
$$Ca_3(PO_4)_2 \longrightarrow 3Ca^{2+} + 2PO_4^{3-}$$

$$[Ca^{2+}] = 3 \times (2.50 \times 10^{-6}) = 7.6 \times 10^{-6} \text{ mol/dm}^3$$
  
 $[PO_4^{3-}] = 2 \times (2.50 \times 10^{-6}) 5 \times 10^{-6} \text{ mol/dm}^3$ 

 $K_{sp} = [Ca^{2+}]^3 [PO_4^{3-}]^2$ 

$$= [7.5 \times 10^{-6}]^3 [5 \times 10^{-6}]^2 = 1.05 \times 10^{-26} \text{ mol}^5 \text{dm}^{-15}.$$

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(e) (i) The enthalpy change when 1 mole of an ionic compound is formed from it's

gaseous ions.

(ii)  $Mg^{2+}$  has a smaller ionic radius than  $Ca^{2+}$ 





- Founder & CEO of Chemistry Online Tuition Ltd.
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