RAFFLES INSTITUTION
Year 5 H2 CHEMISTRY 2025
Tutorial 7 – Chemical Equilibria

(Suggested answers for Practice Questions)

Question 7

(a) Initial amt of CH_3OH = 20/1000 x 0.50 = 0.01 mol
Initial $[CH_3OH]_{mix}$ = 0.01 ÷ 50/1000 = 0.200 mol dm^{-3}

Initial amt of ethanedioic acid = 30/1000 x 0.40 = 0.012 mol
Initial [ethanedioic acid]$_{mix}$ = 0.012 ÷ 50/1000 = 0.240 mol dm^{-3}

$(COOH)_2(aq) + 2NaOH(aq) \longrightarrow (COONa)_2(aq) + 2H_2O(l)$

Amt of ethanedioic acid reacted with NaOH = 1/2 x (30/1000 x 0.10) = 0.00150 mol

At eqm, [ethanedioic acid] = 0.0015 ÷ 10/1000 = 0.150 mol dm^{-3}

	$2CH_3OH(aq)$	+	$(COOH)_2(aq)$	⇌	$(COOCH_3)_2(aq)$	+	$2H_2O(l)$
Initial conc / mol dm^{-3}	0.200		0.240		0		–
Change in conc / mol dm^{-3}	**–0.180**		**–0.0900**		**+0.0900**		–
Eqm conc / mol dm^{-3}	**0.0200**		0.150		**0.0900**		–

$[CH_3OH]_{eqm}$ = 0.0200 mol dm^{-3}

$$K_c = \frac{[(COOCH_3)_2]}{[CH_3OH]^2[(COOH)_2]} = \frac{(0.0900)}{(0.0200)^2(0.150)} = 1500 \text{ mol}^{-2} \text{ dm}^6$$

(b) The titration must be done quickly to **minimise the shift in the position of equilibrium during titration** as the acid $(COOH)_2$ is continually being neutralised by NaOH(aq). If the titration was done too slowly, the shift in the position of equilibrium will cause the equilibrium concentrations of all species to differ from the actual values. As a result, K_c determined **would not be accurate** for that temperature.

Question 8

(a) (i) $$K_C = \frac{[Hb(O_2)_4]}{[O_2]^4[Hb]} \text{ mol}^{-4} \text{ dm}^{12}$$

(ii) $$K_C = \frac{[Hb(O_2)_4]}{[O_2]^4[Hb]} = \frac{y}{(7.6\times10^{-6})^4(y)} = 3.00 \times 10^{20} \text{ mol}^{-4} \text{ dm}^{12}$$

(iii) Let x mol dm^{-3} be the initial [Hb]

$$\frac{0.99x}{[O_2]^4(0.01x)} = 3.00 \times 10^{20} \text{ mol}^{-4} \text{ dm}^{12}$$

$[O_2] = 2.40 \times 10^{-5}$ mol dm^{-3}

(b) Let the total eqm conc of MbO_2 & Mb in the mixture be **x** mol dm^{-3}, fraction of MbO_2 be **y** and fraction of Mb be 1 – **y**.

$[MbO_2]_{eqm}$ = **xy** mol dm^{-3}
$[Mb]_{eqm}$ = (1 – **y**)**x** mol dm^{-3}

$$K_C = \frac{[MbO_2]}{[O_2][Mb]} = \frac{xy}{(7.6\times10^{-6})(1-y)x} = 1 \times 10^6 \text{ mol}^{-1} \text{ dm}^3$$

Solving the equation, y = 0.884

Therefore, the % of MbO_2 in the Mb-MbO_2 equilibrium mixture is **88.4%.**

Alternative method:

$$\frac{[MbO_2]}{[Mb][O_2]} = 1 \times 10^6$$

Since $[O_2] = 7.6 \times 10^{-6}$

$$\frac{[MbO_2]}{[Mb]} = 7.6$$

$[MbO_2] = 7.6[Mb]$

$$\% \ MbO_2 = \frac{7.6}{7.6+1} \times 100\%$$

= 88.4%

Question 9
Let the initial pressure of N_2O_4 be **a** & the equilibrium partial pressure of O_2 be **y**.

	$2NO_2(g)$	$\rightleftharpoons$	$2NO(g)$	+	$O_2(g)$
Initial p	**a**		0		0
Change in p	– 2**y**		+2**y**		+**y**
Eqm p	**a** – 2**y**		2**y**		**y**

Total pressure at eqm = **a** + **y**
Since the equilibrium total pressure is 20% greater than initial pressure,
a + y = 1.2**a**
y = 0.2**a**

Mole fraction of O_2 at equilibrium = equilibrium partial pressure of O_2 / total equilibrium pressure
= **y / (a+y)** = 0.2**a** / 1.2**a** = **0.167**

Question 10
Assuming ideal gas behaviour,

$$\text{amt of } (HCOOH)_2 \text{ before reaction} = \frac{(101325)(\frac{0.40}{1000})}{(8.31)(300+273)} = 8.512 \times 10^{-3} \text{ mol}$$

$$\text{amt of gases after eqm is reached} = \frac{(101325)(\frac{0.60}{1000})}{(8.31)(300+273)} = 1.277 \times 10^{-2} \text{ mol}$$

	$(HCOOH)_2(g)$	$\rightleftharpoons$	$2HCOOH(g)$
Initial amt / mol	8.512×10^{-3}		0

Change in amt / mol	–x	+2x
Eqm amt / mol	$8.512 \times 10^{-3} - x$	2x

$8.512 \times 10^{-3} - x + 2x = 1.277 \times 10^{-2}$
$x = 4.256 \times 10^{-3}$ mol

Amt of $(HCOOH)_2$ at eqm = $8.512 \times 10^{-3} - 4.256 \times 10^{-3} = 4.256 \times 10^{-3}$ mol

Partial pressure of $(HCOOH)_2$ = $(4.256 \times 10^{-3}/1.277 \times 10^{-2}) \times 1$ atm = 0.3333 atm

Partial pressure of HCOOH(g) = 1 – 0.3333 = 0.6667 atm

$$K_p = \frac{p_{HCOOH}^2}{p_{(HCOOH)2}} = \frac{0.6667^2}{0.3333} = 1.33 \text{ atm}$$

Alternative method:

Under constant P and T, V α n
Hence by Avogadro's law, reacting volumes of gases are proportional to reacting amounts, and we construct ICE to track stoichiometric changes using reacting volumes.

	$(HCOOH)_2(g)$	$\rightleftharpoons$	$2HCOOH(g)$
Initial volume / dm^3	0.40		0
Eqm volume / dm^3	0.40 – x		2x

At eqm, total volume = 0.60 dm^3
0.40 – x + 2x = 0.40 + x = 0.60
x = 0.2

Since V α n,
relative eqm amount of HCOOH = 0.4 (no units)
relative eqm amount of $(HCOOH)_2$ = 0.2 (no units)

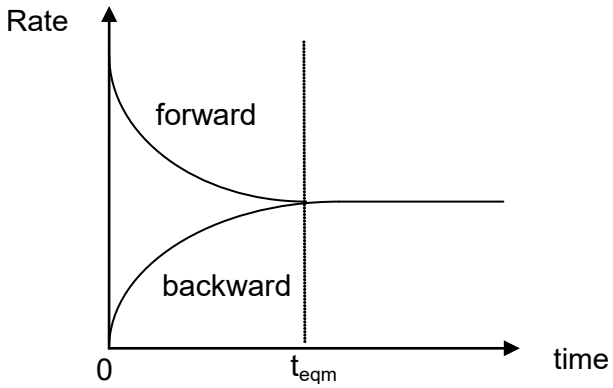
At eqm, total pressure = 1 atm
Partial pressure of HCOOH = $\frac{0.2}{0.6} \times 1$ atm = $\frac{1}{3}$ atm
Partial pressure of $(HCOOH)_2$ = $\frac{0.4}{0.6} \times 1$ atm = $\frac{2}{3}$ atm

$K_p = \frac{p_{HCOOH}^2}{p_{(HCOOH)2}} = \frac{{}^2/_3{}^2}{{}^1/_3} = 1.33$ atm

** For teachers to note in discussions: Please note that this method is based on Avogadro's law, where reacting volume is proportional to reacting amount. The ICE table is a method which tracks the stoichiometry of the reaction.
"Eqm volume need not be taken as partial volume", but rather, the result together with reacting volumes.

Question 11

(a)



(b) $K_p = \frac{p_{SO_3}^2}{p_{SO_2}^2 p_{O_2}}$ atm^{-1}

(c) At equilibrium, p_{SO_3} = 4.7 atm

p_{SO_2} = 2/3 x (5.0 – 4.7) = 0.2 atm;
p_{O2} = 1/3 x (5.0 – 4.7) = 0.1 atm

Substituting into expression in **(b)**,

$K_p = \frac{4.7^2}{(0.2)^2\ 0.1}$ = **5.52 x 10^3 atm^{-1}**

(d) When the temperature is decreased, the position of equilibrium will shift to the right to favour the forward exothermic reaction that releases heat.
More SO_3 will be produced. Since P_{SO3} increase, and P_{SO2} and P_{O2} decrease, equilibrium constant is larger at 300 K.

(e) Although the yield of SO_3 is higher at 300 K, the rate of production of SO_3 may be too slow at 300 K. Thus, a compromise is needed and a moderately high temperature of 800 K is preferred to ensure a reasonable rate of production and yield of SO_3.

Question 12

(a) Dynamic equilibrium refers to a state in a reversible reaction within a closed system where the forward and backward reactions are continuing at the same rate, resulting in no net change in the macroscopic properties (e.g. concentrations or partial pressures) of the reactants and products.

(b) **(i)** The same amount of carbon used in the form of lumps has a smaller surface area than in powder form. Hence, the rate of reaction is slower, and it will take a longer time to reach equilibrium.

(ii) The position of equilibrium remains the same as the vapour pressure and concentration of a solid is a constant at a given temperature.

(iii) The numerical value of K_p remains the same as K_p is only dependent on temperature.

Question 13

(a)

	$H_2O(g)$	+	$CO(g)$	$\rightleftharpoons$	$CO_2(g)$	+	$H_2(g)$
Initial amt / mol	4		4		0		0
Change in amt / mol	–x		–x		+x		+x
Equilibrium amt / mol	4 – x		4 – x		x		x

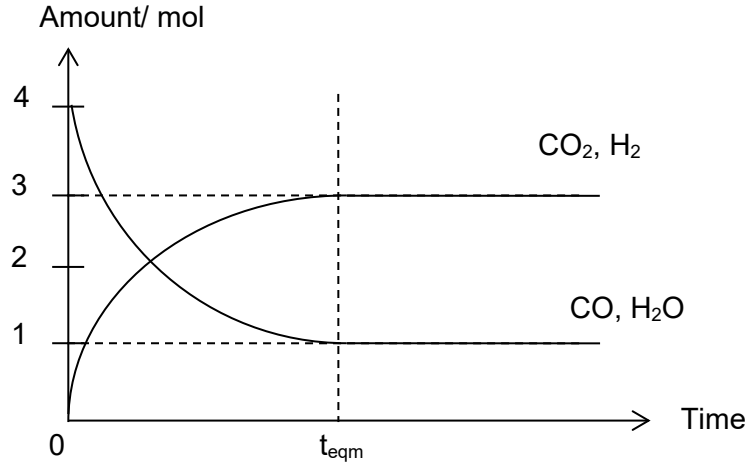
Let the volume of the vessel be V dm^3.

$$K_c = \frac{[CO_2][H_2]}{[H_2O][CO]} = \frac{(\frac{x}{V})(\frac{x}{V})}{(\frac{4-x}{V})(\frac{4-x}{V})} = 9.0 \Rightarrow x = 3 \text{ mol}$$

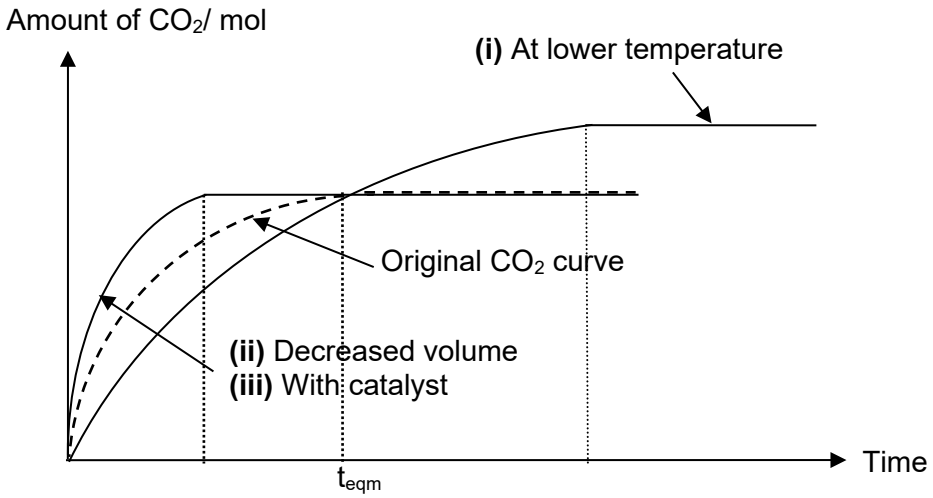
Hence, equilibrium amt of CO = 4 – 3 = 1 mol

(b) Amount of H_2 = amount of CO_2 = x = 3 mol
Amount of CO = amount of H_2O = 1 mol

(c)



(d)



(i) When temperature is lowered, equilibrium position shifts right to **favour the forward exothermic** reaction, so the equilibrium amount of CO_2 is higher. As temperature is lowered, **rate is lower**.

(ii) When volume of vessel is decreased, equilibrium position **does not shift** as the total amount of gases on each side of the equilibrium is **equal**. As initial pressure is higher, initial **rate is higher**.

(iii) A catalyst **does not change** the equilibrium position, but it **speeds up** the reaction. The **same amount of CO_2 is obtained**, but the rate at which this amount is obtained is higher.

Question 14 (Answer: A)

A is an incorrect statement. When solid $K_2Cr_2O_7$ is added, it dissolves in the aqueous solution and $[Cr_2O_7^{2-}(aq)]$ increases. The equilibrium system will counteract the increase in $[Cr_2O_7^{2-}(aq)]$ by favouring the backward reaction which removes $Cr_2O_7^{2-}(aq)$ ⇒ equilibrium position shifts to the left.

B is a correct statement. Solid NaOH dissolves to give $OH^-(aq)$ which reacts with $H^+(aq)$ to form water. The decrease of $[H^+]$ causes the equilibrium position to shift left, forming more yellow CrO_4^{2-}.

C is a correct statement. Water is a solvent in this equilibrium and hence present in large excess. This means that the $[H_2O]$ is approximately constant and hence, excluded from the K_c expression.

D is a correct statement. Diluting the solution with water will cause the concentration of all ions in solution to decrease. The equilibrium system will counteract this by favouring the backward reaction which produces more ions, increasing the concentration of ions in solution. The solution thus turns more yellow due to formation of more CrO_4^{2-}.

Note: D is a correct statement but the following reasoning is **incorrect**:
Adding water causes the $[H_2O]$ to increase, thus favouring the backward reaction to decrease the concentration of water.

The above reasoning is not correct as water is a solvent in this equilibrium and hence present in large excess and $[H_2O]$ is approximately constant (as explained in option C).

Question 15

The mixture is kept within a movable syringe, so internal pressure is equal to external pressure at equilibrium.

Change #**1** is correct. When the plunger is pulled, the total volume of the system increases. As the number of moles of gases remains constant, all the concentrations of gases are simultaneously decreased, accounting for the sudden dip in concentration of H_2.

The system restores equilibrium by favouring the backward reaction which produces more gaseous particles. Thus, $[H_2]$ gradually increases until the new equilibrium position is established.

Change #**2** is incorrect. As the forward reaction is endothermic ($\Delta H > 0$), lowering the temperature would cause the backward exothermic reaction to be favoured, producing more H_2. However, there is no sudden change in number of moles of gases and in volume. Thus, there will not be a sudden dip in concentration of H_2.

Change #**3** is correct. At constant temperature, in order for the pressure inside the syringe to be the same as that of the surroundings, the volume of the system must increase when a small amount of Ar(g) is added. The effect on the equilibrium will be similar to that in option **1** where total volume of the system increases.

Question 16

At 273 K, ice and water are in **equilibrium** and the process of ice melting into water is reversible, so $\Delta G = 0$.

Hence $\Delta S = \frac{\Delta H}{T} = \frac{+6000}{273} = +21.98 \text{ J mol}^{-1} \text{ K}^{-1}$

At 298 K, using $\Delta G = \Delta H - T\Delta S$

$\Delta G = +6000 - (298)(+21.98) = -549.45 \text{ J mol}^{-1} = -0.549 \text{ kJ mol}^{-1}$

Since $\Delta G < 0$ (negative), ice spontaneously changes into water at 298 K.

Question 17

(a) $\Delta G^{\ominus} = -RT \ln K_p$ [Note: This formula is not required in the 'A' Level syllabus.]

$\Delta G^{\ominus} = -(8.31)(298) \times \ln(1 \times 10^{-30}) \div 2 = 8.55 \times 10^4$

The value of ΔG is very large and positive, the reaction is non-spontaneous

(b) $\Delta G^{\ominus} = -RT \ln K_c$

$-16.6 \times 10^3 = -(8.31)(298) \times \ln K$

$K = 815$ (3 sf)

Since K is larger than 1, the equilibrium position lies to the right, favouring the formation of products.

Question 18

(a)

	$2CH_3CO_2H$	$\rightleftharpoons$	$(CH_3CO_2H)_2$
Initial conc / mol dm^{-3}	0.100		0
Change in conc / mol dm^{-3}	– 2(0.0417)		+0.0417
Eqm conc / mol dm^{-3}	0.0166		0.0417

$[(CH_3CO_2H)_2]/[CH_3CO_2H] = 0.0417/0.0166 = 2.51$

(b) In an aqueous solution, the <u>equilibrium position will lie further left</u> as the system <u>favours the formation of the monomer</u>, which can form more extensive hydrogen bonding with surrounding water molecules. As a result, the ratio of [products]/[reactants] at equilibrium in an aqueous solution will be smaller than that as compared to that in a non-polar solvent.