HOMOGENOUS CHEMICAL EQUILIBRUM

Homogenous equilibrium is an equilibrium in which the reactants and the products are in the same phase.

-Homogenous gaseous equilibria

Case I: **The Hydrogen-Iodide system**

Consider a reaction

$$A + B \rightleftharpoons 2C$$

e.g	$H_{2(g)}$ + $I_{2(g)}$	$\rightleftharpoons$	$2HI_{(g)}$
t=0	a b		
t=t	a-x b-x		2x

if V (in dm³) is the total volume of the reaction mixture

then, $\dfrac{a-x}{V} \qquad \dfrac{b-x}{V} \qquad \dfrac{2x}{V}$

Hence,

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(2x/V\right)^2}{\left(\dfrac{a-x}{V}\right)\left(\dfrac{b-x}{V}\right)}$$

$$K_c = \frac{4x^2}{(a-x)(a-b)}$$

K_c **is independent of the volume**

In term of partial pressure,

$$K_p = \frac{P_C^2}{P_A \times P_B}$$

But $P_A = \frac{n_A}{N} \times P$, $P_B = \frac{n_B}{N} \times P$ **and** $P_C = \frac{n_C}{N} \times P$

Where $N = n_A + n_B + n_C =$ **total number of moles,**

$P =$ **total (external) pressures** $P_A, P_B \,\&\, P_C$ **are partial pressures of A, B and C respectively.**

$$\therefore \quad K_p = \frac{\left(\frac{n_C}{N} \times P\right)^2}{\left(\frac{n_A}{N} \times P\right) \times \left(\frac{n_B}{N} \times P\right)} = \frac{n_C^2}{n_A + n_B}$$

Examples:

1. **A mixture of 1 mole of H_2 and 1 mole of I_2 in a flask was heated until the equilibrium is reached. On analysis, the**

equilibrium mixture is found to contain 0.7mole of HI. Calculate the K_c

2. **Consider this reaction** $H_{2(g)}$ **+** $I_{2(g)} \rightleftharpoons 2HI_{(g)}$ **Given that the partial pressures of the following substances at 45°C are** P_{H_2} **= 0.065atm,** P_{I_2} **=0.45 atm. and** P_{HI} **=0.245 atm. Calculate (a) the equilibrium constant K_p for the reaction at 45°C (b) the equilibrium constant K_p for the backward reaction**

3. **K_c for this reaction** $SO_{2(g)}$ **+** $\frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$ **at 727°C is16.7, calculate K_p for this reaction at 727°C.**

N.B- Solutions to these examples shall be treated during the lecture hours

Exercises:

1. **The K_p for this equilibrium reaction:** $NH_4Cl_{(s)} \rightleftharpoons NH_{3(g)}$ **+** $HCl_{(g)}$ **is 0.11 at 25°C, calculate K_c at this temperature.**
2. **The following results were obtained during analysis of a reaction** $CO_{2(g)}$ **+** $H_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$

3. At 25°C and 4 atm., PCl_5 is 10% dissociated, calculate the K_p for this reaction, $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

<u>Case II:</u> **A $\rightleftharpoons$ 2B**

e.g. Decomposition of N_2O_4**, i.e** $N_2O_4 \rightleftharpoons 2NO_2$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{\left(2x/V\right)^2}{\left(\frac{a-x}{V}\right)}$$

$$\therefore \quad K_c = \frac{4x^2}{(a-x)V}$$

In term of K_p,

$$K_p = \frac{[NO_2]^2}{[N_2O_4]} = \frac{P_{NO_2}^2}{P_{N_2O_4}}$$

Also, while considering the equation, if *x* represent the degree of dissociation, then 2x of NO_2 will be produced, then 1-x of N_2O_4 will be left. then, the total number of moles present at equilibrium = (1-x) +2x=1+x.

$$\therefore P_{N_2O_4} = \left(\frac{1-x}{1+x}\right)P \quad \& \quad P_{NO_2} = \left(\frac{2x}{1+x}\right)P$$

So,

$$K_p = \frac{P_{NO_2}^2}{P_{N_2O_4}} = \frac{\left[\left(\frac{2x}{1+x}\right)P\right]^2}{\left(\frac{1-x}{1+x}\right)P}$$

$$\therefore \quad K_p = \frac{4x^2P}{1-x^2}$$

Examples:

1. N_2O_4 at 1 atm and 25^oC dissociated by 18.5%, calculate its K_p at this temperature. If the atmospheric temperature was reduced to half its original value at the same temperature, calculate the degree of dissociation of the gas.

2. N_2O_4 is 25% dissociated at 30$_oC$ and 1 atm., calculate
(a) The equilibrium constant for the decomposition
(b) The amount of NO_2 that would be attained if there had been 4 moles of N_2O_4 at the same temperature and pressure.

N.B- Solutions to these examples shall be treated during the lecture hours

Exercises:

1. N_2O_4 is 25% dissociated at 37^0C and 1 atm., calculate
   (i) The K_p and (ii) the % dissociation at 0.1 atm and 37^oC
2. An equilibrium mixture at 27^oC contains N_2O_4 and NO_2 having 0.28 atm. and 1.1 atm. pressures respectively. If the volume of the container is doubled, calculate the new equilibrium pressure of the gases.

Case III: **A + 3B $\rightleftarrows$ 2C**

e.g. synthesis of Ammonia

$$N_{2(g)} + 3H_{2(g)} \rightleftarrows 2NH_{3(g)}$$

$$\frac{a-x}{V} \qquad \frac{b-x}{V} \qquad \frac{2x}{V}$$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{\left(2x/V\right)^2}{\left(\frac{a-x}{V}\right)\times\left(\frac{b-x}{V}\right)^3}$$

$$\therefore \quad K_c = \frac{4x^2V^2}{(a-x)(b-x)^3}$$

Also,

$$K_p = \frac{P_{NH_3}^2}{P_{N_2} \times P_{H_2}^3}$$

Examples:

1. In an experiment, H_2 and N_2 in the mole ratio 3:1 produced 0.0735mole fraction of NH_3 at 350°C and total pressure of 1013KNm^{-2}. Calculate Kp for the forward and reverse reactions
2. The K_p for this equilibrium reaction

   $$N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2NH_{3\,(g)}$$ is 1.45 x 10^{-5} at 500°C. Calculate the partial pressure of NH_3 when the partial pressure of H_2 is 0.928atm and that of N_2 is 0.432atm.

Exercise:

1. The dissociation pressure of $CaCO_3$ is 342mmHg at 840°C and at 860°C, the dissociation pressure is 420mmHg. Calculate the heat of dissociation of the carbonate. Given that R=8.314KJmol^{-1}.

2. consider this reaction

   $$N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2NH_{3\,(g)},$$

   The K_p is 1.64x10^{-4} at 400°C. calculate (i) the ΔG of the reaction (ii) ΔG when the partial pressure of N_2, H_2 and NH_3 are 10atm, 30 atm and 3 atm respectively.

HOMOGENOUS (LIQUID) EQUILIBRIA

$A_{(l)} + B_{(l)} \rightleftharpoons C_{(l)} + D_{(l)}$

e.g. $CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_5{}_{(l)} + H_2O_{(l)}$

t=0	a	b	0	0
t=t	a-x	b-x	x	x

$$K_c = \frac{\left(\frac{x}{V}\right) \times \left(\frac{x}{V}\right)}{\left(\frac{a-x}{V}\right) \times \left(\frac{b-x}{V}\right)}$$

$$\therefore \quad K_c = \frac{x^2}{(a-x)(b-x)}$$

The equation above is the general expression for the liquid equilibria. However, in the example above where water molecule is involved, the expression can be written as

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

$$\frac{K_c}{[H_2O]} = K_c^{'} = \frac{[CH_3COOC_2H_5]}{[CH_3COOH][C_2H_5OH]}$$

The above expression is written in term of $K_c^{'}$ because the concentration of water is taken to be constant, $K_c^{'}$ has the unit of $[Concn]^{-1}$ but K_c has no unit.

Example:

1. **In an esterification process between 1 mole of ethanoic acid and 1 mole of ethanol at 25°C, 66.7% of the acid is** esterified calculate the equilibrium constant and ΔG^0.
2. **When 1 mole of ethanoic acid and 1 mole of ethanol were heated together at a temperature of 25°C until the equilibrium is reached. Titration of the reaction mixture shows that 2/3 of the acid have been used up. Calculate the equilibrium constant.**

HETEROGENEOUS EQUILIBRIA SYSTEM

Heterogeneous equilibrium is an equilibrium in which the reactants and the products are not in the same phase.

e.g. $3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_4{}_{(s)} + 4H_2{}_{(g)}$

$$K_c = \frac{[Fe_3O_4][H_2]^4}{[Fe]^3[H_2O]^4} = \frac{1\times[H_2]^4}{1\times[H_2O]^4} = \frac{[H_2]^4}{[H_2O]^4}$$

N.B: **the concentration of substances in solid phase is taken to be unity.**

In term of K_p,

$$K_p = \frac{P_{H_2}^4}{P_{H_2O}^4}$$

Exercises: Express the equilibrium constants K_p, for the following reactions.

1. $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$
2. $2H_2O_{(l)} \rightleftharpoons 2H_{2(g)} + O_{2(g)}$
3. $NH_4Cl_{(s)} \rightleftharpoons NH_{3(g)} + HCl_{(g)}$

<u>Le-Chatelier's Principle</u>

It states that "if a chemical system is in equilibrium and one of the factors involved in the equilibrium is altered, the

equilibrium will shift, so as to neutralize the effect of the change".