

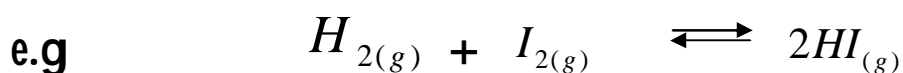
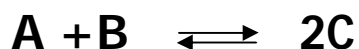
HOMOGENOUS CHEMICAL EQUILIBRUM

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



if V (in dm^3) is the total volume of the reaction mixture

then, $\frac{a-x}{V} \quad \frac{b-x}{V} \quad \frac{2x}{V}$

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

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

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.

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

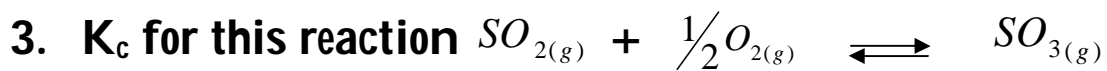
Examples:

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



Given that the partial pressures of the following substances at 45°C are $P_{H_2} = 0.065\text{atm}$, $P_{I_2} = 0.45\text{atm}$. and $P_{HI} = 0.245\text{atm}$. Calculate (a) the equilibrium constant K_p for the reaction at 45°C (b) the equilibrium constant K_p for the backward reaction



at 727°C is 16.7, calculate K_p for this reaction at 727°C.

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

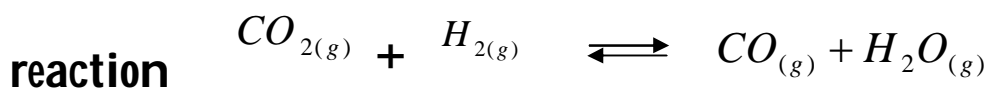
Exercises:

1. The K_p for this equilibrium reaction:



calculate K_c at this temperature.

2. The following results were obtained during analysis of a



3. At 25°C and 4 atm., PCl_5 is 10% dissociated, calculate the K_p for this reaction,

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

Case II: A \rightleftharpoons 2B

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

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

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

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,

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

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

Examples:

1. N_2O_4 at 1 atm and 25°C 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°C 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.

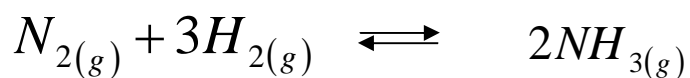
N.B- Solutions to these examples shall be treated during the lecture hours

Exercises:

- N_2O_4 is 25% dissociated at 37°C and 1 atm., calculate
(i) The K_p and (ii) the % dissociation at 0.1 atm and 37°C
- An equilibrium mixture at 27°C 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.



e.g. synthesis of Ammonia



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

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

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

Also,

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

Examples:

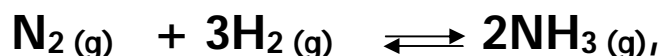
1. In an experiment, H_2 and N_2 in the mole ratio 3:1 produced 0.0735 mole fraction of NH_3 at 350°C and total pressure of 1013KNm^{-2} . Calculate K_p for the forward and reverse reactions
2. The K_p for this equilibrium reaction

$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ is 1.45×10^{-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:

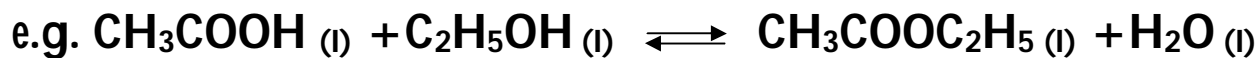
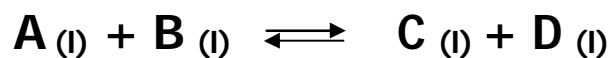
1. The dissociation pressure of CaCO_3 is 342mmHg at 840°C and at 860°C , the dissociation pressure is 420mmHg . Calculate the heat of dissociation of the carbonate. Given that $R = 8.314\text{KJmol}^{-1}$.

2. consider this reaction



The K_p is 1.64×10^{-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 , 30atm and 3atm respectively.

HOMOGENOUS (LIQUID) EQUILIBRIA



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

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

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

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

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

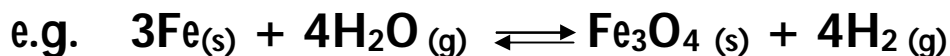
The above expression is written in term of K'_c because the concentration of water is taken to be constant, K'_c has the unit of $[Concn]^{-1}$ but K_c has no unit.

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° .
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.



$$K_c = \frac{[\text{Fe}_3\text{O}_4][\text{H}_2]^4}{[\text{Fe}]^3[\text{H}_2\text{O}]^4} = \frac{1 \times [\text{H}_2]^4}{1 \times [\text{H}_2\text{O}]^4} = \frac{[\text{H}_2]^4}{[\text{H}_2\text{O}]^4}$$

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

In term of K_p ,

$$K_p = \frac{P_{\text{H}_2}^4}{P_{\text{H}_2\text{O}}^4}$$

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

- $\text{CaCO}_{3(s)} \rightleftharpoons \text{CaO}_{(s)} + \text{CO}_{2(g)}$
- $2\text{H}_2\text{O}_{(l)} \rightleftharpoons 2\text{H}_{2(g)} + \text{O}_{2(g)}$
- $\text{NH}_4\text{Cl}_{(s)} \rightleftharpoons \text{NH}_{3(g)} + \text{HCl}_{(g)}$

Le-Chatelier's Principle

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”.