Chemical Equilibrium

Chemical equilibrium – occurs when **opposing reactions are proceeding at equal rates** i.e. the forward and reverse reactions are proceeding at the same rate.

The rate at which the products are being formed from reactants is equal to the rate at which the reactants are being re-formed from the products.

At equilibrium therefore, a mixture of the products and reactants have reached concentrations that will not change any more with time.

Equilibrium reactions are said to be **reversible**. **Double half arrows** are used to denote a reversible reaction.

e.g. For: $A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B$

k_f = rate constant for $A \longrightarrow B$

k_r = rate constant for $B \longrightarrow A$

Using rate laws:

$$k_f[A] = k_r[B]$$

$\frac{[B]}{[A]} = \frac{k_f}{k_r}$ = a constant called **K**, the **equilibrium constant**

For reactions involving reactants and products at certain **concentrations**:

e.g. $aA + bB \rightleftharpoons dD + eE$ [a, b, d & e = no. of mols.]

The equilibrium constant, $\mathbf{K_c}$ can be calculated:

$$\mathbf{K_c} = \frac{[D]^d[E]^e}{[A]^a[B]^b} \quad \begin{array}{l} \longrightarrow \text{concentrations of products} \\ \longrightarrow \text{concentrations of reactants} \end{array}$$

Note that, unlike in Kinetics (Rates), **the number of moles of each product and reactant must be considered when writing Equilibrium constants.**

e.g. For the reaction: $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$

$$\mathbf{K_c} = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

e.g. **(1)** Calculate K_c for the reaction: $N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$

Given that at equilibrium, 0.0014M of N_2O_4 and 0.0172 M of NO_2 are produced.

$$\mathbf{K_c} = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.0172\ M)^2}{0.0014\ M} = 0.211\ M$$

Calculating K from Initial and Equilibrium concentrations

e.g. **(2)** 0.1 M of H_2 and 0.2 M of I_2 at 448°C were allowed to reach equilibrium. Analysis of the equilibrium mixture showed the concentration of HI to be 0.02 M. Calculate K_c at 448°C for the reaction: $H_2\ (g) + I_2\ (g) \rightleftharpoons 2HI\ (g)$

Step 1: Fill in the data given in the question:

	H_2	**I_2**	**HI**
Initial conc./ M	0.1	0.2	0
Change in conc./ M			
Equil. Conc./ M			0.02

Since 0.02 mols. of HI are produced at equilibrium, (0.02 ÷ 2 = 0.01) mols. each of H_2 and I_2 must have reacted (Check the **mole ratios** from the reaction: H_2 : HI = **1 : 2** & I_2 : HI = **1 : 2**).

So we deduct the number of mols. of H_2 and I_2 that reacted from the initial number of mols. used in the reaction to calculate the number of mols. of H_2 and I_2 remaining at equilibrium.

Step 2:

Calculate and fill in the rest of the values:

	H_2	**I_2**	**HI**
Initial conc./ M	0.1	0.2	0
Change in conc./ M	- 0.01	- 0.01	+ 0.02
Equil. Conc./ M	0.09	0.19	0.02

Step 3:

Write the K_c expression for the reaction and substitute the **equilibrium concentration values**:

$$\mathbf{K_c = \frac{[HI]^2}{[H_2][I_2]}} = \frac{(0.02\ \text{M})^2}{(0.09\ \text{M})(0.19\ \text{M})} = 1.2$$

For reactions involving gases, at certain **pressures**:

e.g. $aA_{(g)} + bB_{(g)} \rightleftharpoons dD_{(g)} + eE_{(g)}$ [a, b, d & e = no. of mols.]

The equilibrium constant, $\mathbf{K_p}$ can be calculated:

$$\mathbf{K_p} = \frac{(P_D)^d(P_E)^e}{(P_A)^a(P_B)^b} \begin{array}{l} \longrightarrow \text{products} \\ \longrightarrow \text{reactants} \end{array}$$

[where $\mathbf{P_D}$, $\mathbf{P_E}$, $\mathbf{P_A}$ & $\mathbf{P_B}$ are the **partial pressures** of D, E, A & B resp.]

e.g. **(3)** A mixture of hydrogen and nitrogen is allowed to attain equilibrium. The equilibrium mixture was analyzed and found to contain 7.38 atm. of H_2, 2.46 atm. of N_2 and 0.166 atm. of NH_3. From these data, calculate K_p for the reaction.

$$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g)$$

$$\mathbf{K_p} = \frac{P(NH_3)^2}{P(N_2)\ P(H_2)^3} = \frac{(0.166\ \text{atm.})^2}{(2.46\ \text{atm.})(7.38\ \text{atm.})^3} = 2.79 \times 10^{-5}\ \text{atm.}^{-2}$$

NB: Always use the <u>concentrations at equilibrium</u> to work out K_c or K_p.

N.B.: The ICE (Initial, Change, Equilibrium) table (from e.g. 2) can also be used to calculate equilibrium partial pressures if initial partial pressures are given.

❖ Converting between K_c & K_p

Use the relationship: $\mathbf{K_p = K_c(RT)^{\Delta n}}$

Where: **R** = molar gas constant (0.0821 L atm. mol^{-1} K^{-1})

T = absolute temperature (K)

Δ**n** = change in number of moles (i.e. mols. of products – mols. of reactants)

e.g. **(4)** The K_c for the production of ammonia at 300°C is 9.60 L^2 mol^{-2}. Calculate K_p.

$N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g)$

T = 300 + 273 = 573 K

Δ**n** = mols. of products – mols. of reactants = 2 – 4 = -2

Therefore: $\mathbf{K_p = K_c(RT)^{\Delta n}}$

$= 9.60\ L^2\ mol^{-2}\ (0.0821\ L\ atm.\ mol^{-1}\ K^{-1} \times 573\ K)^{-2}$

$= 4.23 \times 10^{-7}\ atm.^{-2}$

❖ Le Chatelier's Principle

If a system at equilibrium is disturbed by a change in temperature, pressure or concentration of one of its components, the system will shift its equilibrium position so as to counteract the effect of the disturbance.

➢ Change in concentration:

If the concentration of a component increases, the system shifts its equilibrium position so as to decrease the concentration of that component, and vice-versa.

e.g. Consider: $N_2 + 3H_2 \rightleftharpoons 2NH_3$

Increasing the concentration of H_2 shifts the equilibrium position to the right (in order to decrease the concentration of H_2) which in turn increases the concentration of NH_3

Increasing the concentration of NH_3 shifts the equilibrium position to the left (in order to decrease the concentration of NH_3) which increases the concentration of both N_2 and H_2

Decreasing the concentration of H_2 shifts the equilibrium position to the left (in order to increase the concentration of H_2) thereby decreasing the concentration of NH_3

Removing NH_3 from the reaction shifts the equilibrium position to the right (in order to increase the concentration of NH_3) which decreases the concentration of both N_2 and H_2

NB: The value of the equilibrium constant, i.e. K_c or K_p, is <u>NOT affected</u> by changes in concentration.

- **Change in volume and pressure** (for gaseous systems):

Reducing the volume in which a system exists increases the pressure of the system (Recall the Gas Laws), so the system must shift its equilibrium position so as to reduce pressure. It does this by producing the **lower number of moles** of either the reactants or products.

Increasing the volume in which a system exists reduces the pressure of the system, so the system must shift its equilibrium position so as to increase pressure. It does this by producing the **higher number of moles** of either the reactants or products.

e.g. (1) Consider: $N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$

If volume is reduced, equilibrium position shifts to the left, producing more N_2O_4 (this is because pressure has been increased so the system produces less moles of components in order to reduce the added pressure being exerted).

If volume is increased, equilibrium position shifts to the right, producing more NO_2 (this is because pressure has been reduced so the system produces more moles of components in order to increase pressure).

For reactions that have multiple reactants and products, find the total number of mols. of reactants and the total number of mols. of products, then compare to find the greatest or least number of mols. being produced.

e.g. (2) Consider: $N_2 + 3H_2 \rightleftharpoons 2NH_3$

Reducing volume increases pressure so equilibrium position shifts to the right (less mols. produced, i.e. 2 mols.).

Increasing volume decreases pressure so equilibrium position shifts to the left (more mols. produced, i.e. 4 mols.).

NB: The value of the equilibrium constant, i.e. K_c or K_p, is NOT affected by changes in volume and/ or pressure.

- **Change in temperature:**

Exothermic reactions favor low temperatures.

Endothermic reactions favor high temperatures.

e.g. (1) Consider: $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ $\Delta H = 87.9$ kJ

An increase in temperature shifts equilibrium position to the right, producing more PCl_3 and Cl_2 (this is because the forward reaction is endothermic and proceeding in this direction will use up the heat being added to the reaction and decrease temperature; Recall: endothermic reactions require energy).

A decrease in temperature shifts equilibrium position to the left, producing more PCl_5 (this is because the reverse reaction is exothermic and proceeding in this direction will produce heat and increase temperature; Recall: exothermic reactions produce energy).

e.g. (2) Consider: $2NO_2 \rightleftharpoons N_2O_4$ $\Delta H = -58$ kJ

Increasing temperature shifts equilibrium position to the left, producing more NO_2.

Decreasing temperature shifts equilibrium position to the right, producing more N_2O_4.

NB: The value of the equilibrium constant, i.e. K_c or K_p, IS ALWAYS affected by changes in temperature (refer to the Summary table below).

- **Addition of a catalyst**

Adding a catalyst to the equilibrium reaction affects BOTH the forward and reverse reactions, therefore there is **<u>NO change</u>** either in the position of equilibrium of in the value of K_c or K_p.

Summary:

Change		**Effect on equilibrium position**	**Effect on equilibrium constant (K_c or K_p)**
Concentration/ Amount	Increase in conc. of reactants or decrease in conc. of products	Shifts to the right	No change
	Decrease in conc. of reactants or increase in conc. of products	Shifts to the left	No change
Pressure/ Volume	Decrease in volume or increase in pressure	Shifts to the side that produces the lower no. of moles of gas	No change
	Increase in volume or decrease in pressure	Shifts to the side that produces the higher no. of moles of gas	No change
Temperature	For **exothermic** rxns.:		
	If temp. increases	Shifts to the left	K_c or K_p decreases
	If temp. decreases	Shifts to the right	K_c or K_p increases
	For **endothermic** rxns.:		
	If temp. increases	Shifts to the right	K_c or K_p increases
	If temp. decreases	Shifts to the left	K_c or K_p decreases
Catalyst		No change	No change

Practice questions:

1. For the following reaction:

$N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g)$

It was found that at equilibrium: $[NH_3] = 0.015$ M

$[N_2] = 0.07$ M

$[H_2] = 0.20$ M

Calculate the value of K_p for the reaction at 25°C.

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.015\ M)^2}{(0.07\ M)(0.20\ M)^3} = 0.40\ M^{-2}\ (\text{or } 0.40\ mol^{-2}\ L^2)$$

$K_p = K_c(RT)^{\Delta n}$

T = 25 + 273 = 298 K

Δn = mols. of product – mols. of reactant = 2 – 4 = -2

$K_p = K_c(RT)^{\Delta n} = 0.40\ mol^{-2}\ L^2\ (0.0821\ L\ atm.\ mol^{-1}\ K^{-1} \times 298\ K)^{-2} = 6.7 \times 10^{-4}\ atm.^{-2}$

2. When equimolar proportions of hydrogen and iodine are heated together at a certain temperature, the system at equilibrium was found to contain 0.0017 $moldm^{-3}$ of hydrogen, 0.0017 $moldm^{-3}$ of iodine and 0.0018 $moldm^{-3}$ of hydrogen iodide.

$$H_2 (g) + I_2 (g) \rightleftharpoons 2HI (g)$$

Calculate the equilibrium constant for the reaction at this temperature, and hence the K_p for the reaction.

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.0018\ M)^2}{(0.0017\ M)(0.0017\ M)} = 1.12$$

$K_p = K_c(RT)^{\Delta n}$

Δn = mols. of product – mols. of reactant = 2 – 2 = 0

$K_p = K_c(RT)^{\Delta n}$

$= 1.12\ (0.0821\ \text{L atm. mol}^{-1}\ \text{K}^{-1} \times 298\ \text{K})^0$

$= 1.12\ (1)$

$= 1.12$

[That is, $K_p = K_c$ when: no. of mols of product = no. of mols. of reactant]

3. A sample of nitrosyl bromide is heated to 100°C in a 10.00 L container in order to decompose it partially according to the equation:

$$2NOBr\ (g) \rightleftharpoons 2NO\ (g) + Br_2\ (g)$$

The container is found to contain 6.44 g of NOBr, 3.15 g of NO and 8.38 g of Br_2 at equilibrium.

(i) Find the value of K_c at 100°C.

(ii) Find the total pressure exerted by the mixture of gases.

(iii) Calculate K_p for the reaction at 100°C.

[R.A.M.: N = 14; O = 16; Br = 79.9]

(i) M_r of NOBr = 109.9 g

No. of mols. NOBr = 6.44 g/ 109.9 g = 0.059 mols.

[NOBr] = 0.059/ 10.00 = 0.0059 molL^{-1}

M_r of NO = 30 g

No. of mols. NO = 3.15 g/ 30 g = 0.105 mols.

[NO] = 0.105/ 10.00 = 0.0105 molL^{-1}

M_r of Br_2 = 159.8 g

No. of mols. Br_2 = 8.38 g/ 159.8 g = 0.052 mols.

$[Br_2]$ = 0.052/ 10.00 = 0.0052 $molL^{-1}$

$$K_c = \frac{[NO]^2[Br_2]}{[NOBr]^2} = \frac{(0.0105\ molL^{-1})^2\,(0.0052\ molL^{-1})}{(0.0059\ molL^{-1})^2} = 0.016\ molL^{-1}$$

(ii) Total mols. of gas in 10 L = 0.059 mols. + 0.105 mols. + 0.052 mols. = 0.216 mols.

PV = nRT (This is the Ideal Gas Equation)

P(10 L) = 0.216 mols.(0.0821 L atm. mol^{-1} K^{-1})(373 K)

P = 0.66 atm.

(iii) T = 100 + 273 = 373 K

Δn = mols. of product – mols. of reactant = 3 – 2 = 1

$K_p = K_c(RT)^{\Delta n}$ = 0.016 mol L^{-1}(0.0821 L atm. mol^{-1} K^{-1} x 373 K$)^1$ = 0.49 atm.

4. Consider the following equilibrium at 460°C:

$$SO_2\,(g) + NO_2\,(g) \rightleftharpoons NO\,(g) + SO_3\,(g) \qquad \Delta H = +\,640\ kJ\ mol^{-1}$$

Predict and explain the effect on concentration of SO_3 (g) when the changes indicated below are carried out:

(i) The pressure is increased.

(ii) The reaction vessel is cooled to 200°C.

(iii) NO (g) is removed.

(iv) A catalyst is added.

(i) The concentration of SO_3 remains the same. Since there are equal number of moles of gas on both sides, pressure has no effect on the equilibrium position or on the concentration of SO_3.

(ii) The concentration of SO_3 decreases. Since temperature is being reduced, heat must now be produced. Therefore the reverse reaction, which is exothermic, must occur. NO (g) & SO_3 (g) are thus being used up.

(iii) The concentration of SO_3 increases. Since a product's concentration (NO) is decreasing, equilibrium shifts to the right and more NO and SO_3 are produced.

(iv) The concentration of SO_3 remains the same. A catalyst has no effect on the equilibrium position or on the concentration of SO_3.

5. Consider an equilibrium mixture of nitrogen, hydrogen and ammonia, in which the reaction is:

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g) \qquad \Delta H = -\,92.2 \text{ kJ at } 25^{o}C$$

For each of the changes listed below, determine whether the value of K_c increases, decreases or stays the same and determine whether more or less NH_3 is present at the new equilibrium established after the change.

(i) More H_2 is added (at a constant temperature of $25^{o}C$ and constant volume).

(ii) The temperature is increased.

(iii) The volume of the container is doubled (at constant temperature).

(iv) Some more N_2 is pumped into the equilibrium mixture from an external source.

(i) No change in K_c; more NH_3 present (equilibrium shifts to the right)

(ii) K_c decreases; less NH_3 present (equilibrium shifts to the left)

(iii) No change in K_c; less NH_3 present (equilibrium shifts to the left)

(iv) No change in K_c; more NH_3 present (equilibrium shifts to the right)