

EQUILIBRIA

10

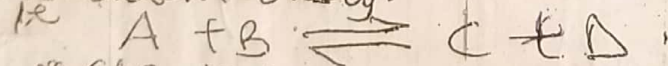
There are different types of equilibria. These include Chemical Equilibrium^{and} physical equilibrium. Our discussion will however be centred on chemical equilibrium.

Chemical Equilibrium

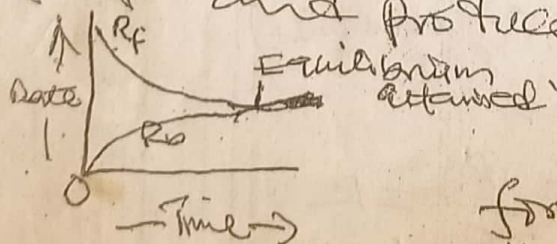
Equilibrium means balance between two things. In this case between the rate of forward and the backward reactions. Chemical equilibrium can only be discussed properly by considering reversible reactions.

Reversible reactions (1)

These are reactions that can be made to go either side by changing the reaction conditions. Reversible reactions are usually represented by two half arrows, one pointing to the right (\rightarrow) indicating forward reaction and one pointing to the left (\leftarrow) indicating the backward or reverse reaction. These reactions occur simultaneously.



Chemical equilibrium may be defined as the state of a reversible reaction when the two opposing reactions occurring at the same time rate and the concentration of reactants and products do not change with time.



At equilibrium the forward reaction equals the backward reaction.

Characteristics of Chemical Equilibrium

- i) constancy of concentrations: When an equilibrium is established, the concentrations of all the species are constant.
- ii) Equilibrium can be initiated from either side: The state of an equilibrium of a reversible reaction can be initiated from the reactants or the products.
- iii) Equilibrium cannot be attained in an open vessel. Equilibrium can only be obtained in a closed vessel where no part of the reactants & products is allowed to escape.
- iv) A catalyst cannot change the equilibrium position. A catalyst will speed up the attainment of equilibrium by speeding up the forward and the backward reactions.
- v) Value of Equilibrium Constant does not ~~depend~~ on the initial concentration of reactants.
- vi) At Equilibrium, $\Delta G = 0$.

(2)

Law of Mass Action

The law states that the rate of a chemical reaction is proportional to the active masses of the reactants (where the active masses refer to molar concentrations).

For the reaction $A + B \rightarrow \text{Products}$ and $A + B + C \rightarrow \text{Products}$

$$\text{i.e. Rate} \propto [A][B] \quad \text{and} \quad \text{Rate} \propto [A][B][C]$$

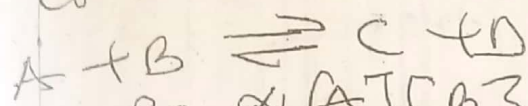
$$\text{or Rate} = k[A][B]$$

$$\text{Rate} = k[A][B][C]$$

Therefore, the rate of reaction is proportional to molar concentrations of the reactants.

Equilibrium Constant

Consider the following hypothetical reaction,



$$R_f \propto [A][B] \text{ or } R_f = k_f [A][B]$$

$$R_b \propto [C][D] \text{ or } R_b = k_b [C][D]$$

where k_f and k_b are rate constants for forward and backward (reverse) reactions respectively.

At eqm, rate of forward rxn = rate of backward rxn.

$$\text{i.e. } k_f [A][B] = k_b [C][D]$$

$$\frac{k_f}{k_b} = \frac{[C][D]}{[A][B]}$$

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

$$k_b = [C][D]$$

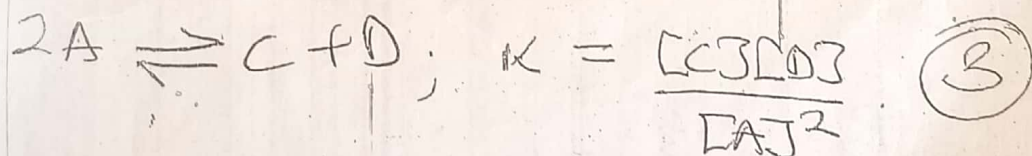
Cross multiply

$$k_f [C][D]$$

$$k_b [A][B]$$

The ratio of k_f/k_b is referred to as an Equilibrium Constant, K_c or K .

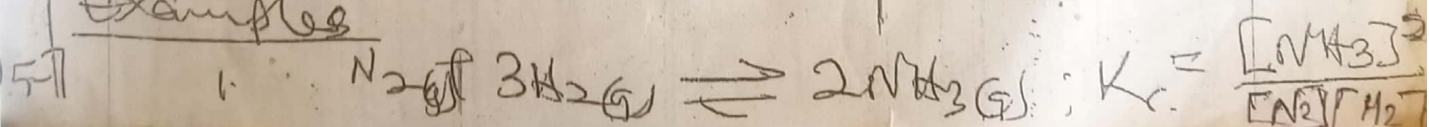
$$\therefore K = \frac{[C][D]}{[A][B]} \text{ — Equilibrium constant, expression or equilibrium law.}$$

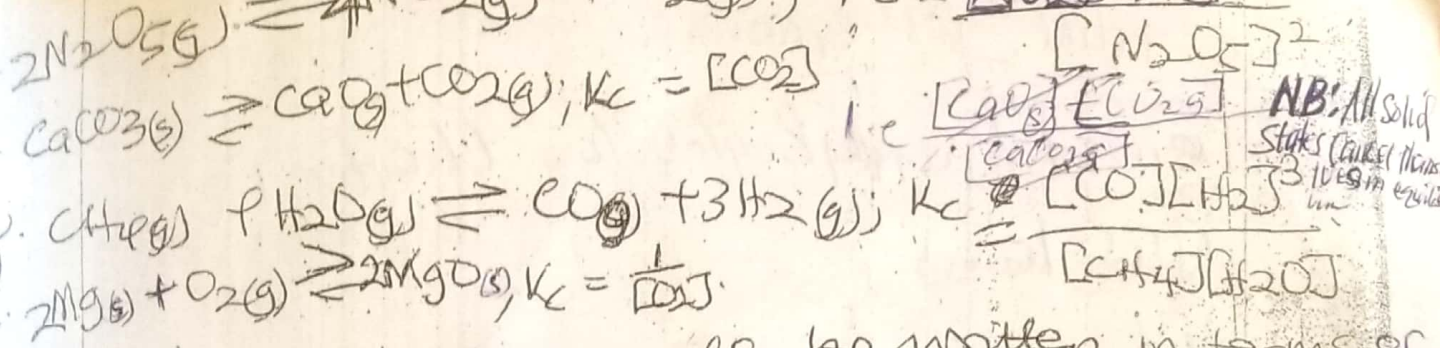


$$\text{i.e. } aA + bB \rightleftharpoons cC + dD; K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

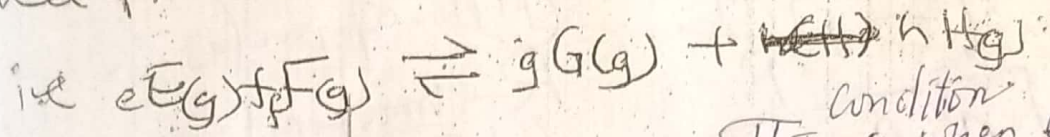
Therefore the equilibrium constant may be defined as the product of the equilibrium conc. of the products divided by the product of the equilibrium concs of the reactants, with each concentration term raised to a power equal to the coefficient of the substance in the balanced equation.

Examples





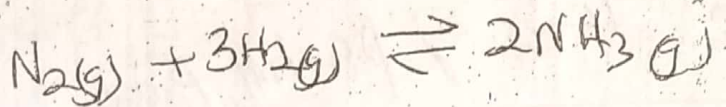
Equilibrium constant can also be written in terms of partial pressures.



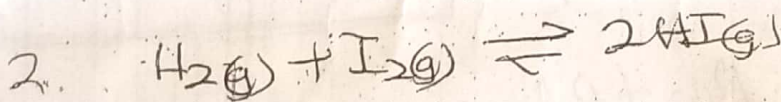
$$K_p = \frac{(P_G)^g (P_H)^h}{(P_E)^e (P_F)^f}$$

Condition
This is when equilibrium is written in terms of partial pressures by adding P as the subscript to each compound

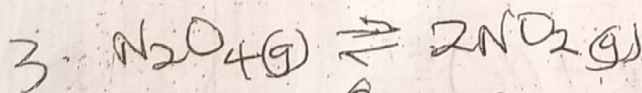
Examples



$$K_p = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3}$$



$$K_p = \frac{(P_{\text{HI}})^2}{(P_{\text{H}_2})(P_{\text{I}_2})} \quad \text{atm} \quad \text{atm}$$



$$K_p = \frac{(P_{\text{NO}_2})^2}{(P_{\text{N}_2\text{O}_4})}$$

(4)

Equilibrium constants are measured in moles for K_c and in atmospheres, or Pa , mmHg or N m^{-2} for K_p .

Unit of $K_c = \text{mol dm}^{-3}$ & $K_p = \text{atm}$

Eg, for the reaction: $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$

$$K_c = [\text{CO}_2], \therefore \text{unit} = \text{mol dm}^{-3}$$

$$K_p = (P_{\text{CO}_2}), \therefore \text{unit} = \text{atm}$$

2. For the reaction: $2\text{Mg}(s) + \text{O}_2(g) \rightleftharpoons 2\text{MgO}(s)$

$$K_c = \frac{1}{[\text{O}_2]}, \therefore \text{unit} = \frac{1}{\text{mol dm}^{-3}} = \text{mol}^{-1} \text{dm}^3$$

$$K_p = \frac{1}{(P_{\text{O}_2})}, \therefore \text{unit} = \text{atm}^{-1}$$

3. For the reaction: $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}, \therefore \text{unit} = \frac{(\text{mol dm}^{-3})^2}{(\text{mol dm}^{-3})(\text{mol dm}^{-3})} = 1$$

No unit

$$K_p = \frac{(P_{\text{HI}})^2}{(P_{\text{H}_2})(P_{\text{I}_2})}$$

$$\therefore \text{unit} = \frac{(\text{atm})^2}{(\text{atm})(\text{atm})} = 1$$

No unit

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4. For the reaction: $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$

$$K_c = \frac{[\text{NH}_3]^2}{[\text{H}_2]^3[\text{N}_2]}, \therefore \text{unit} = \frac{(\text{mol dm}^{-3})^2}{(\text{mol dm}^{-3})^3(\text{mol dm}^{-3})}$$

$$= \frac{1}{(\text{mol dm}^{-3})^2} \text{ or } \text{mol}^2 \text{dm}^{-6}$$

$$K_p = \frac{(P_{\text{NH}_3})^2}{(P_{\text{H}_2})^3(P_{\text{N}_2})}$$

$$\therefore \text{unit} = \frac{(\text{atm})^2}{(\text{atm})^3(\text{atm})}$$

$$= \frac{1}{(\text{atm})^2} \text{ or } \text{atm}^{-2}$$

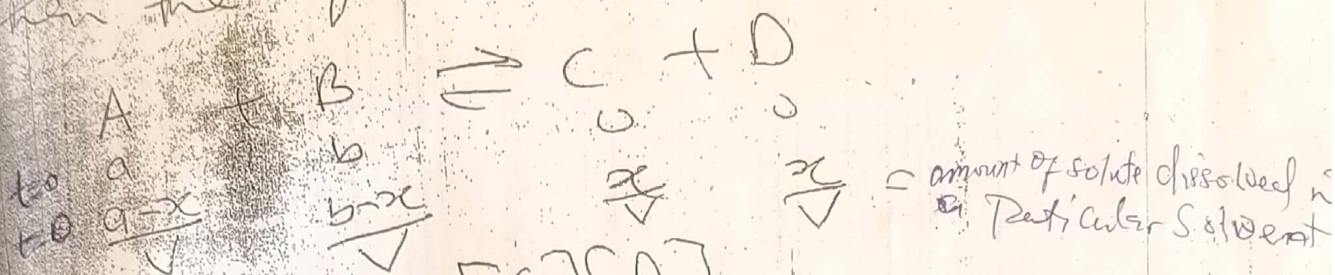
Relationship Between K_c and K_p is given as

$$K_p = K_c \times (RT)^{\Delta n} \text{ or } K_c = K_p \times (RT)^{-\Delta n}$$

Note: When $K_c, K_p = 1$, the unit is added to the unit.

Calculation of Equilibrium Constants

Consider the reaction $A + B \rightleftharpoons C + D$.
 If a and b are initial amounts of A and B respectively,
 and x is the amount that has reacted at time,
 then the equilibrium mixture will contain



$$K_c = \frac{[C][D]}{[A][B]}$$

$$= \frac{(x)(x)}{(a-x)(b-x)}$$

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

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

⑥

Examples

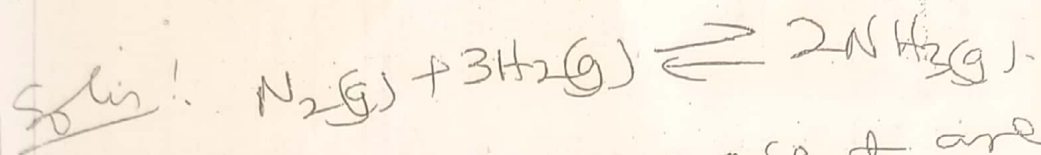
1. The concns of the reactants and products for the reaction: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ are
 $SO_2 = 0.27 \text{ mol dm}^{-3}$, $O_2 = 0.40 \text{ mol dm}^{-3}$ and $SO_3 = 0.33 \text{ mol dm}^{-3}$

Calculate the K_c for this reaction.

Ans: $K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$

$$= \frac{(0.33)^2}{(0.27)^2(0.40)} = \frac{3.7 \text{ mol} \cdot 0.1089}{0.029 \times 0.40}$$

2. Some N_2 and H_2 gases were pumped into an empty five-dm³ vessel at 500°C. When equilibrium is established, 3 mol of N_2 , 2.10 mol of H_2 and 0.298 mol of NH_3 were found to be present. What is the value of K_c ?



At eqm, mols present are

$$[N_2] = \frac{3.00 \text{ mol}}{5 \text{ dm}^3} = 0.600 \text{ mol dm}^{-3}$$

$$[H_2] = \frac{2.10 \text{ mol}}{5 \text{ dm}^3} = 0.420 \text{ mol dm}^{-3}$$

$$[NH_3] = \frac{0.298 \text{ mol}}{5 \text{ dm}^3} = 0.0596 \text{ mol dm}^{-3}$$

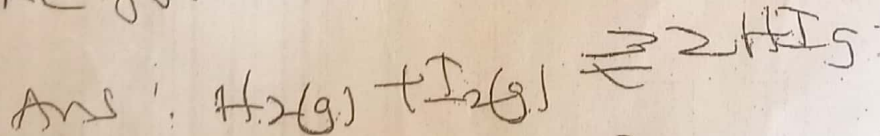
$$\text{But } K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$= \frac{(0.0596)^2}{(0.600)(0.420)^3}$$

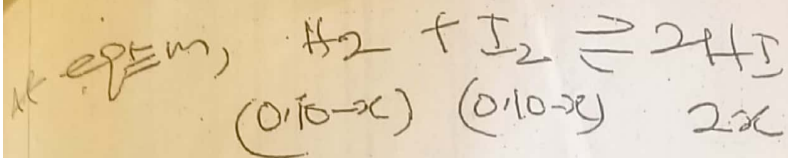
$$\frac{0.00355216}{0.600 \times 0.074088} = \frac{0.000355}{0.0444528} = 0.080$$

(8)

3. At a certain temp, 0.100 mol of H_2 and 0.02 mol of I_2 were placed in a 1 dm³ flask. The purple colour of iodine vapour was used to monitor the reaction. After some time, an equilibrium was established and the conc of I_2 was found to decrease to 0.02 mol dm⁻³. Calculate the equilibrium constant K_c for this reaction.



$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$



$$[I_2] = 0.100 - x = 0.020 \text{ (given)}$$

$$x = 0.100 - 0.020$$

$$= 0.080$$

$$[H_2] = 0.100 - x = 0.100 - 0.080 = 0.020$$

$$[I_2] = 0.020 \text{ (given)}$$

$$[HI] = 2x = 2 \times 0.080 = 0.160$$

$$\therefore K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.160)^2}{(0.02)(0.02)}$$

$$= 64$$

4. At $500^\circ C$, the reaction between N_2 and H_2 to form NH_3 has $K_c = 6.0 \times 10^{-2}$. What is the value of K_p for this reaction?

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

$$\Delta n = 2 - 4 = -2$$

$$T = 500 + 273 = 773 K$$

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$K_c = 6.0 \times 10^{-2}$$

$$\therefore K_p = (6.0 \times 10^{-2})(8.314 \times 773)^{-2}$$

$$=$$

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