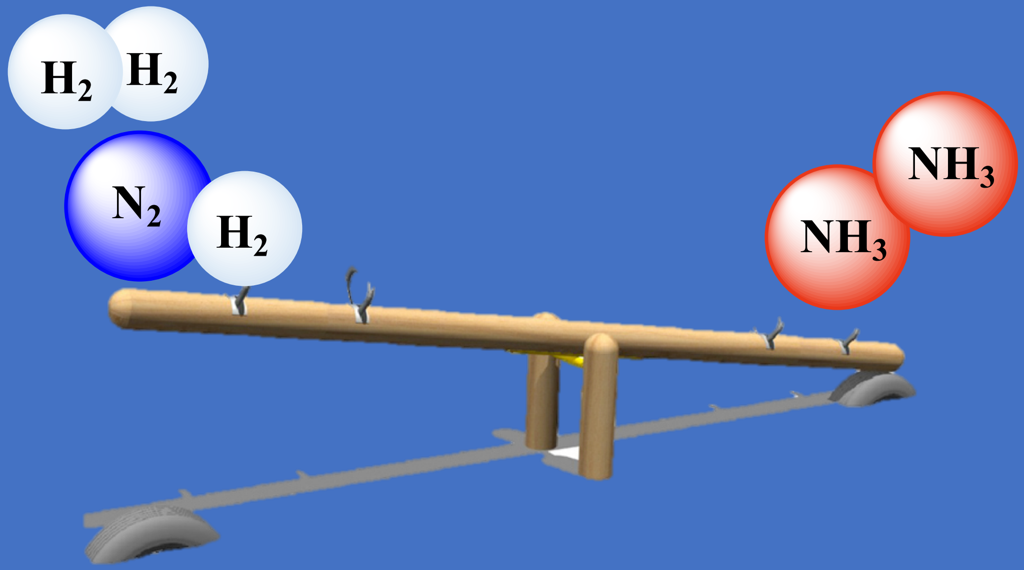
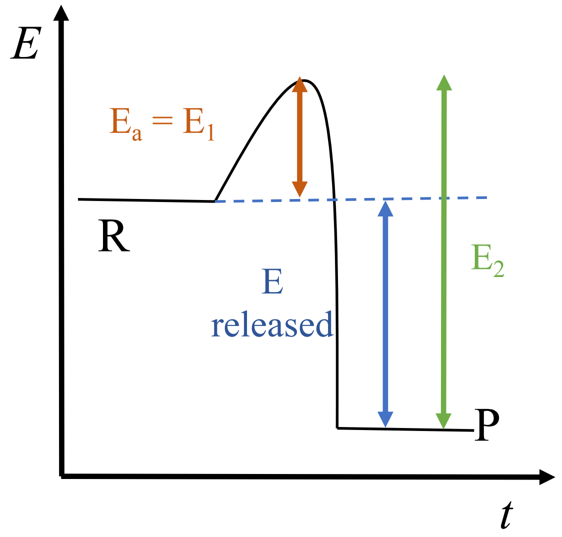
CHEMICAL EQUILIBRIUM



When Chemical Equilibrium occurs?

It depends on the Energy of chemical substances that take part in the reaction.



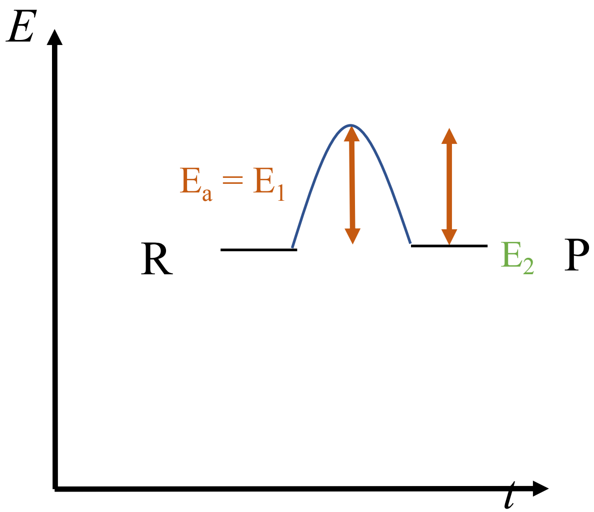
$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O$

$\Delta G = \Delta H - T\,\Delta S$

$\Delta G < 0$

- Spontaneous reaction
- No equilibrium

$E_2 >> E_1$



$H_2 + I_2 \rightleftharpoons 2\,HI$

$E_2 = E_1$

$\Delta G = 0$

Particles of products can have enough energy to react transforming again in reactants.

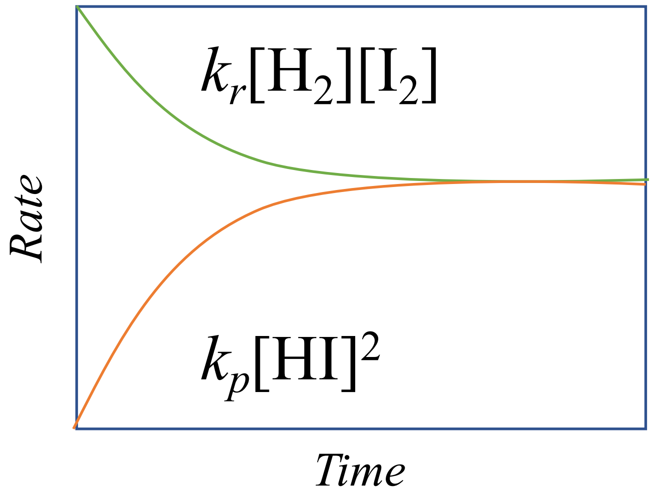
Chemical Equilibrium

$$H_{2\,(g)} + I_{2\,(g)} \underset{v_2}{\overset{v_1}{\rightleftharpoons}} 2HI_{(g)}$$

colourless gas — purple gas — colourless gas

Chemical Equilibrium occurs when a reaction and its reverse reaction proceed at the same rate.

$$v_1 = v_2$$



Once the equilibrium is achieved, the amount of each reactant and product remains constant.

Dynamic Equilibrium

Equilibrium Constant

$$aA + bB \rightleftharpoons cC + dD$$

Chemical equilibrium occurs when opposing reactions are proceeding at equal rates.

Kc depends on the rate constants which in turn depend on the reaction (Ea) and temperature.

$$Rate_R = Rate_P$$

$$k_R[A]^a[B]^b = k_P[C]^c[D]^d$$

K << 1
the reaction is reactants favoured

$$K_c = \frac{k_P}{k_R} = \frac{[C]^c\,[D]^d}{[A]^a[B]^b}$$

K >> 1
the reaction is products favoured

Equilibrium Constant

Since the pressure is proportional to the concentration of a gas in a closed system.

$$K_c = \frac{[C]^c\,[D]^d}{[A]^a[B]^b}$$

$$K_P = \frac{[P_C]^c\,[P_D]^d}{[P_A]^a[P_B]^b}$$

$$K_\chi = \frac{[\chi_C]^c\,[\chi_D]^d}{[\chi_A]^a[\chi_B]^b}$$

Relationship between Kc and K_P

$$N_2 + 3H_2 \rightleftharpoons 2\,NH_3$$

$$PV = nRT$$

$$P = \frac{nRT}{V}$$

$$P = [C]RT$$

$$K_P = \frac{[P_{NH3}]^2}{[P_{N_2}][P_{H_2}]^3} = \frac{[NH_3]^2}{[N_2][H_2]^3}\frac{RT^2}{RT^4}$$

$$K_P = Kc\,\frac{RT^2}{RT^4} = Kc\,\frac{1}{RT^2}$$

$$K_P = K_C RT^{(\Delta v)}$$

- **Homogeneous Equilibria** occurs when all reactants and all products are in the same phase.
- **Heterogeneous Equilibria** occurs when reactants or products are in different phase.
- The value used for the concentration of a pure substance is always equal to 1.

$$CaCO_{3\,(s)} \rightleftharpoons CaO_{(s)} + CO_2 \qquad K_{eq} = K_P = P_{CO_2}$$

$$HA + H_2O \rightleftharpoons A^- + H_3O^+ \qquad K_{eq} = \frac{[A^-][H_3O^+]}{[HA]}$$

Es. In un Sistema chiuso all' equilibrio inizialmente sono contenute $1x10^{-3}$ M di H_2 e $2x10^{-3}$ M di I_2 a 448°C. La concentrazione di HI è di 1.87×10^{-3} M. Calcolare K_c *a 448 °C.*

$$H_2 + I_2 \rightleftharpoons 2\,HI$$

	$[H_2]$, M	$[I_2]$, M	[HI], M
Start	1×10^{-3}	2×10^{-3}	0
Change	$- 9.35 \times 10^{-4}$	$- 9.35 \times 10^{-4}$	**$+ 1.87 \times 10^{-3}$**
Equilibrium	6.5×10^{-5}	1.065×10^{-3}	1.87×10^{-3}

$$K_c = \frac{(1.87x10^{-3})^2}{(6\,x\,10^{-5})(1.065x10^{-3})} = 51$$

The reaction Quotient, Q

Concentration ratio when reaction is not at equilibrium.

$$Q = \frac{[C]^c\,[D]^d}{[A]^a[B]^b}$$

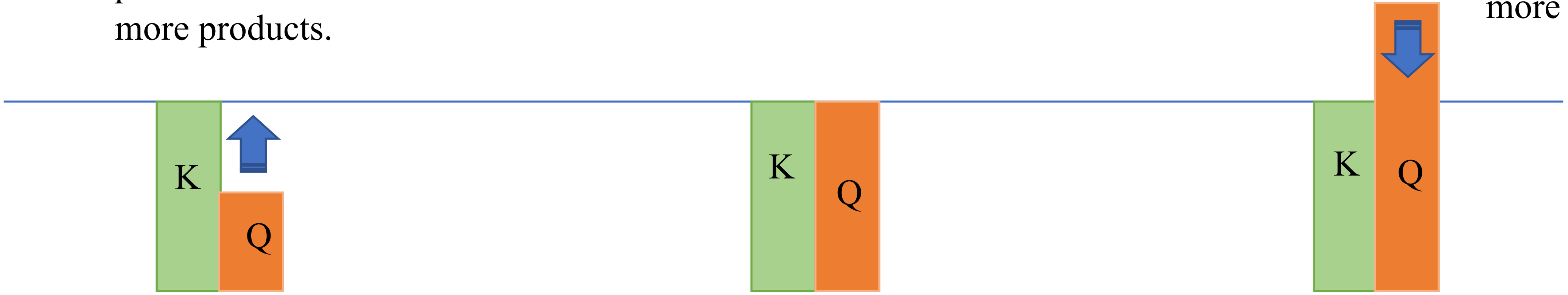
If Q < K there is too much reactants.

If Q > K there is too much products.

If Q = K there is equilibrium.

Forward reaction proceeds to form more products.

Forward reaction proceeds to form more reactants.



equilibrium

Le Châtelier's Principle

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

➢ *Concentration's Influence*

If a substance is added to a system in equilibrium, the system reacts to consume the substance and to establishes the equilibrium again.

If the concentration of a reactant is increased or the concentration of a product decreased, $Q < K$

Reaction shifts right

If the concentration of a reactant is decreased or the concentration of a product increased, $Q > K$

Reaction shifts left

➢*Pressure's Influence*

Considering PV = nRT, at T constant, reducing the volume of a gaseous equilibrium mixture causes the system to shift to the direction that reduce the number of molecules of gases. (concentration)

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

$$K_P = \frac{[P_{NH_3}]^2}{[P_{N_2}][P_{H_2}]^3} = \frac{[P\chi_{NH_3}]^2}{[P\chi_{N_2}][P\chi_{H_2}]^3}$$

$$K_P = \frac{1}{P^2}\,\frac{\chi_{NH_3}{}^2}{\chi_{N_2}[\chi_{H_2}]^3}$$

$\Delta v = -2$

If pressure value increases — Reaction shifts right

If pressure value decreases — Reaction shifts left

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

$\Delta v = 1$

If pressure value increases — Reaction shifts left

If pressure value decreases — Reaction shifts right

If the pressure increase the reaction is favoured towards the formation of a less amount of molecules.

➢ *Temperature's Influence*

Correlation between K_{eq} and kinetic constants of direct and inverse reaction.

$$K_c = \frac{k_1}{k_{-1}} = \frac{[C]^c\,[D]^d}{[A]^a[B]^b} \qquad k = Ae^{-\frac{E_a}{RT}}$$

Endothermic reaction , $\Delta H > 0$

Increase of T → Reaction shifts right

Decrease of T ← Reaction shifts left

Exothermic reaction, $\Delta H < 0$

Increase of T ← Reaction shifts left

Decrease of T → Reaction shifts right

$$aA + bB \rightleftharpoons cC + dD$$

$$\Delta G° = cG°_C + dG°_D - aG°_A - bG°_B \qquad \Delta G° = -RT \ln K = -2.30\, RT \log K$$

Van't Hoff equation

T_1

$$\Delta G_1° = -RT_1 \ln K_1 \qquad \ln K_2 = -\frac{\Delta G_1°}{RT_1}$$

T_2

$$\Delta G_2° = -RT_2 \ln K_2 \qquad \ln K_2 = -\frac{\Delta G_2°}{RT_2}$$

$$\frac{d\,(\ln K)}{dT} = \frac{\Delta H°}{RT^2}$$

$$\ln\left(\frac{K_1}{K_2}\right) = -\frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

1) Data la reazione $PBr_{5(g)} \rightleftharpoons PBr_{3(g)} + Br_{2(g)}$, dopo aver descritto la struttura delle molecole coinvolte, prevedere attraverso considerazioni qualitative il segno di $\Delta H°_{reaz}$ *e* $\Delta S°_{reaz}$ e l' andamento di $\Delta G°_{reaz}$. In quali condizioni di temperature per la reazione risulta $K_{eq} > 1$?

2) A 650°C la costante di equilibrio della reazione 4 $HCl_{(g)}$ + $O_{2(g)} \rightleftharpoons$ 2 H_2O + 2 $Cl_{2(g)}$ è sperimentalmente pari a K_c= 0,42. Calcolare il quoziente di reazione Q_p, e stabilire come evolve la reazione quando p di HCl = 1,0 bar, p O_2 = 1,0 bar, p H_2O = 1,0 bar e p Cl_2 = 2,0 bar.

3) La CO_2 si dissocia termicamente secondo l' equlibrio:

$$CO_2 \rightleftharpoons CO + \frac{1}{2} O_2$$

Supponendo di avere un recipiente chiuso del volume di 1,0 L, mantenuto alla temperature di 1000°C e contentente inizialmente CO_2 alla pressione di 10 atm, calcolare la Kp e la massa dei tre component presenti all' equilibrio, sapendo che in queste condizioni la CO_2 si dissocia per il 7%.

4) Introducendo una mole di N_2 ed 1,00 moli di O_2 in un recipiente da 10 l mantenuto a 1727 K, si trova che una volta stabilito l' equilibrio $N_2 + O_2 \rightleftharpoons 2\ NO$ si sono formate 0,26 moli di NO. Calcolare K_c.

5) Una miscela contenente il 78 % di O_2 e il 22 % di SO_2 in volume viene fatta reagire alla pressione costante 3,0 atm ad una temperatura T tale che il 90% di SO_2 venga ossidato a SO_3. Calcolare K_P per la seguente reazione all' equilibrio.

$$2\ SO_2 + O_2 \rightleftharpoons 2\ SO_3$$

6) A 25°C ed 1,00 atm il grado di dissociazione di N_2O_4 è pari a $\alpha = 0{,}170$. Calcolare il valore di $\Delta G°_{reaz}$:

$$N_2O_4 \rightleftharpoons 2\,NO_2$$

7) Alla temperature t e alla pressione P = 1, 000 atm, il triossido di zolfo, in fase gassosa, si dissocia per il 33 % e da' luogo al seguente equilibrio : $2\ SO_3 \rightleftharpoons 2\ SO_2 + O_2$

Si calcoli il valore della Kp all' equilibrio e alla temperatura t.

8) Una mole di NO_2 viene introdotta in un recipiente inizialmente vuoto, alla temperature di 25°C. Si stabilise l' equilibrio $2\ NO_2 \rightleftharpoons 2\ NO + O_2$ e ad equilibrio raggiunto la pressione totale P= 0,5 atm e le moli di O_2 presenti sono $n_{O2} = 6{,}00 \times 10^{-5}$. Si calcoli **ΔG°** della reazione.

9) Il compost CCl_2F_2 ("Freon" 12) ha un calore latente di evaporazione di 39,9 cal/g e tensione di vapore di 500 Torr a – 40°C. Calcolare la temperature di ebolizione del composto.

10) Si fanno reagire 0.80 moli di A con 0.80 moli di B e 0.80 moli di C in 0.900 litri di soluzione. Si stabilisce l'equilibrio A + B +C = D + 2E. Calcolare la concentrazione di tutte le specie al raggiungimento dell'equilibrio sapendo che la costante di equilibrio e Kc = 0.95.