

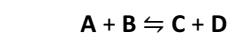
CHEMICAL EQUILIBRIUM

Reversible Reactions: (denoted by \rightleftharpoons)

→ proceed in both forward and backward directions

→ reach **equilibrium state** w/ both rxn and pdt

e.g. Contact Process: $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$



$$\text{Rate}_f = k_f$$

$$\text{Rate}_b = k_b = 0$$

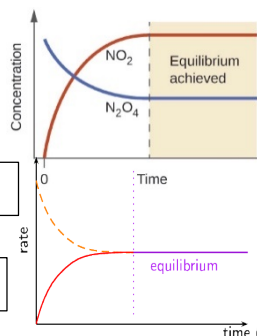
At $t = 0$,

$[\text{A}] + [\text{B}]$, $\text{rate}_f \downarrow$
 $[\text{C}] + [\text{D}]$, $\text{rate}_b \uparrow$

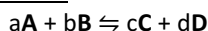
Rxn proceeds

$[\text{A}][\text{B}][\text{C}][\text{D}]$ constant

At t_{eqm}



Equilibrium Law + Constants:



At any given time, rxn quotient, $Q_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$

→ Q_c changes as rxn.

proceeds towards equilibrium as conc. change until equilibrium is reached

→ K_c is when Q_c becomes **constant** at a given temperature

Value of K_c is **NOT** affected by:

→ change in **concentrations** of rxn. and pdt.

→ change in **total pressure** of reaction system

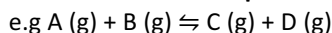
→ presence/absence of **catalyst**

Magnitude of $K_c \Rightarrow$ **extent of rxn.** **NOT** rate of reaction (larger

$K_c \Rightarrow$ position of equilibrium lies to the right)

Homogenous Equilibrium:

→ substances involved are in the **same phase**



Heterogenous Equilibrium:

→ substances involved are not in the **same phase**

- $K_c \neq$ concentration/partial pressure of pure solids and pure liquids **OR** conc. of pure water as solvent

\Rightarrow **CONSTANT** at a given temperature

I.C.E Table

	SO_2Cl_2	SO_2	Cl_2	Total
Initial amt.	a	0	a	a
Change in amt.	-0.2a	+0.2a	+0.2a	+0.2a
Equilibrium amt.	0.8a	0.2a	0.2a	1.2a

→ When pressures are involved, degree of dissociation involved

Mole fraction	2/3	1/6	1/6	1
Equilibrium PP	2p/3	p/6	p/6	p

→ As long as temperature is constant, K_c is also constant.

Dynamic Equilibrium:

→ **state in a reversible system** in which $\text{Rate}_f = \text{Rate}_b \neq 0$ and **no net change** in macroscopic properties occurs

- No net change** through particles continue reacting
- Equilibrium can only be achieved in a **closed system**
- Equilibrium can be attained **from either direction**

Same equilibrium state attained from any amount of rxn., pdt.

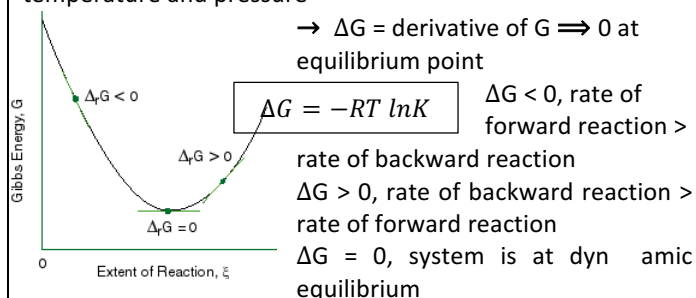
→ if temperature remains constant

Gibbs Free Energy + Position of Equilibrium:

→ ΔG^\ominus predicts **thermodynamic feasibility** of a reaction

- Mixing of substances \Rightarrow increase in entropy \Rightarrow decrease in overall G

\therefore G is at **minimum at dynamic equilibrium** under constant temperature and pressure



→ Side with lower G = more proportion at equilibrium position
 e.g. if $G_{\text{rxn}} < G_{\text{pdt}}$, equilibrium has more rxn. than pdt.

\therefore **position of equilibrium depends ONLY on ΔG**

→ $\Delta G < 0$, $K > 1$ = equilibrium position lies more to the **right**

(If $K \gg 1$, reaction goes to completion)

→ $\Delta G > 0$, $K < 1$ = equilibrium position lies more to the **left**

(If $K \ll 1$, reaction never happens)

Le Chatelier's Principle:

- when a system in **equilibrium** is subject to a **change**, the system will **counteract the change to re-establish equilibrium**