CHEMICAL EQUILIBRIUM

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Chemical equilibrium is achieved when:

- the rates of the forward and reverse reactions are equal and

they are <u>not</u> zero.

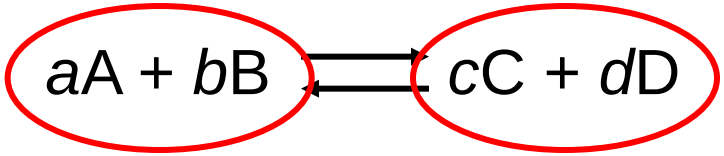
- the concentrations of the reactants and products remain constant

Chemical equilibrium

$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$

$$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$$

$$K = \frac{[NO_2]^2}{[N_2O_4]} = 4.63 \times 10^{-3}$$



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

Equilibrium Will

$K >> 1$	Lie to the right	Favor products
$K << 1$	Lie to the left	Favor reactants

Homogenous equilibrium applies to reactions in which all reacting species **are in the same phase.**

$$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} \qquad K_p = \frac{P_{NO_2}^2}{P_{N_2O_4}}$$

In most cases

$$K_c \neq K_p$$

$$a\text{A}\,(g) + b\text{B}\,(g) \rightleftharpoons c\text{C}\,(g) + d\text{D}\,(g)$$

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

Δn = moles of gaseous products – moles of gaseous reactants

= (c + d) – (a + b)

Heterogenous equilibrium applies to reactions in which reactants and products **are in different phases.**

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$$K_c' = \frac{[CaO][CO_2]}{[CaCO_3]}$$

$[CaCO_3]$ = constant
$[CaO]$ = constant

$$K_c = [CO_2] = K_c' \times \frac{[CaCO_3]}{[CaO]}$$

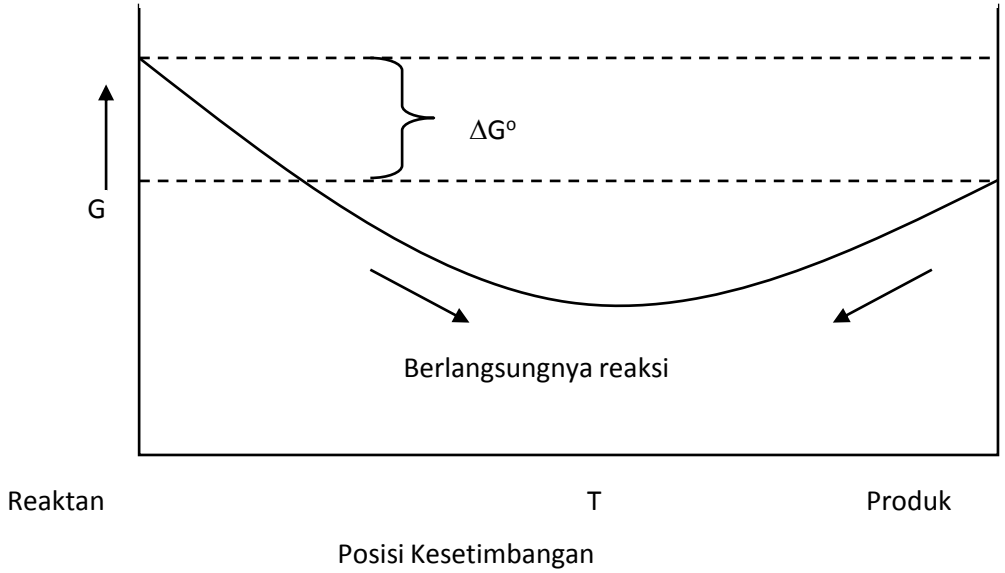
$$K_p = P_{CO_2}$$

The concentration of **solids** and **pure liquids** are not included in the expression for the equilibrium constant.

CHEMICAL EQUILIBRIUM AND TERMODYNAMICS

Relationships **ΔG^o and equilibrium**

$$\Delta G = \Delta G^o + RT \ln Q$$



$2A + 3B \longrightarrow C + 2D$

$\Delta G_r = \Delta G^o + RT \ln Q$

$\Delta G^o = - RT \ln Q$

$Q = \dfrac{(a_C)(a_D)^2}{(a_A)^2 (a_B)^3}$

Q = reaction Quotient

a = activity = $\dfrac{f}{P^o}$

$Q = \dfrac{\left(\dfrac{f(C)}{P^o}\right)\left(\dfrac{f(D)}{P^o}\right)^2}{\left(\dfrac{f(A)}{P^o}\right)^2\left(\dfrac{f(B)}{P^o}\right)^3}$

f = Fugacities

$Q = \dfrac{f(C)\, f(D)^2 (P^o)^2}{f(A)^2 f(B)^3}$

Determine reaction Quotient

$4NH_{3\,(g)} + 5O_{2\,(g)} \longrightarrow 4NO_{(g)} + 6H_2O_{(g)}$

$2H_2S_{(g)} + 3O_{2\,(g)} \longrightarrow 2SO_{2\,(g)} + 2H_2O_{(g)}$

EQUILIBRIUM CONDITION

$\Delta G_r = 0$

$K = (Q)_{equilibrium}$ $\qquad 2A + 3B \longrightarrow C + 2D$

$$K = Q = \frac{(a_C)\,(a_D)^2}{(a_A)^2\,(a_B)^3}$$

$\Delta G_r = \Delta G^o + RT \ln Q_p$

$\Delta G^o = - RT \ln K_p$ $\qquad K_p$ = Equilibrium **c**onstante parcial presure

$\Delta G_r = \Delta G^o + RT \ln Q$

$\Delta G^o = - RT \ln K$ $\qquad$ K= Thermodynamic Equilibrium **c**onstante

$A \longrightarrow B$

$\Delta G^o = \Delta G_f{}^o (B) - \Delta G_f{}^o (A)$

$2A + 3B \longrightarrow C + 2D$

$$K = \frac{(a_C)(a_D)^2}{(a_A)^2 (a_B)^3}$$

$$\Delta G^o = \Delta G_f{}^o(C) + 2\Delta G_f{}^o(D) - 2\Delta G_f{}^o(A) - 3\Delta G_f{}^o(B)$$

Calculate an Equilibrium **c**onstant at 25^o C:

1. $N_{2\,(g)} + 3\,H_{2\,(g)} \longrightarrow 2NH_{3\,(g)}$

$\Delta G_f{}^o(N_2) = 0 \qquad \Delta G_f{}^o(H_2) = 0 \quad \Delta G_f{}^o(NH_3) = -16{,}5$ kJ/mol

$$\Delta G^o = 2\Delta G_f{}^o(NH_3) - \Delta G_f{}^o(N_2) - \Delta G_f{}^o(H_2)$$

$$\Delta G^o = -RT \ln K_p$$

$$\ln K_p = -\frac{2 \times 16{,}5 \text{ kJ/mol}}{2{,}48 \text{ kJ/mol}} \qquad K_p = 6 \times 10^5$$

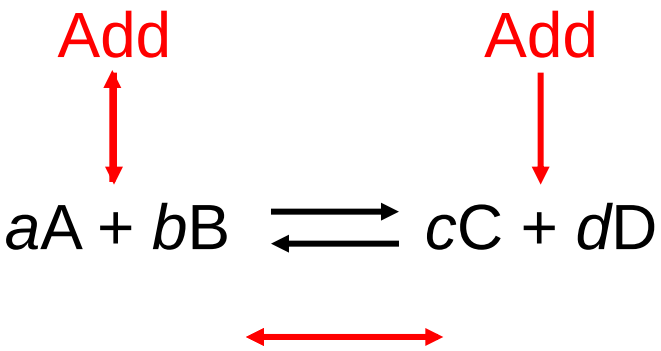
2. $N_2O_{4\,(g)} \longrightarrow 2NO_{2\,(g)}$

Le Châtelier's Principle

1. System **starts** at equilibrium.
2. A change/stress is then made to system at equilibrium.
    - Change in concentration
    - Change in volume
    - Change in pressure
    - Change in Temperature
    - Add Catalyst
3. System responds by shifting to reactant or product side to **restore** equilibrium.

Le Châtelier's Principle

- Changes in Concentration continued



Change	**Shifts the Equilibrium**
Increase concentration of product(s)	left
Decrease concentration of product(s)	right
Increase concentration of reactant(s)	right
Decrease concentration of reactant(s)	left

Le Châtelier's Principle

- Changes in Volume and Pressure
  (Only a factor with gases)

$$A\,(g) + B\,(g) \rightleftharpoons C\,(g)$$

Change	**Shifts the Equilibrium**
Increase pressure	Side with fewest moles of gas
Decrease pressure	Side with most moles of gas
Increase volume	Side with most moles of gas
Decrease volume	Side with fewest moles of gas

Le Châtelier's Principle

- Changes in Temperature
  - ❖Only factor that can change value of K
  - ❖$N_{2(g)} + 2O_{2(g)} \Leftrightarrow 2NO_{(g)} - 10,397\ kJ$

Change	**Exothermic Rx**	**Endothermic Rx**
Increase temperature	*K* decreases	*K* increases
Decrease temperature	*K* increases	*K* decreases

Respons Equilibrium WithTemperature

Van't Hoff (Belanda) :

$N_{2(g)} + 2O_{2(g)} \Leftrightarrow 2NO_{(g)} - 10,397$ kJ

$2NO_{(g)} + O_{2(g)} \Leftrightarrow 2NO_{2\,(g)}$ H = -216 kJ

$2SO_{2(g)} + O_{2(g)} \Leftrightarrow 2SO_{3(g)}$ ΔH^o = -198 kJ

$$\frac{d \ln K}{dT} = \frac{-1}{R} \frac{d}{dT}\left(-\frac{\Delta G^o}{T}\right) \qquad \frac{d}{dT}\left(\frac{\Delta G^o}{T}\right) = -\frac{\Delta H^o}{T^2}$$

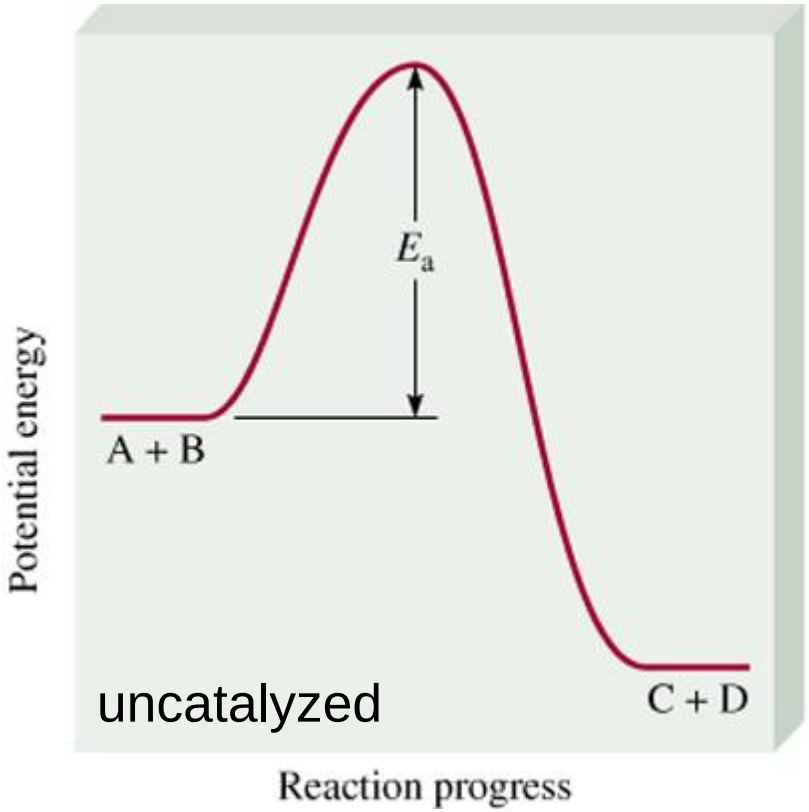
$$\frac{d \ln K}{dT} = \frac{\Delta H^o}{RT^2}$$

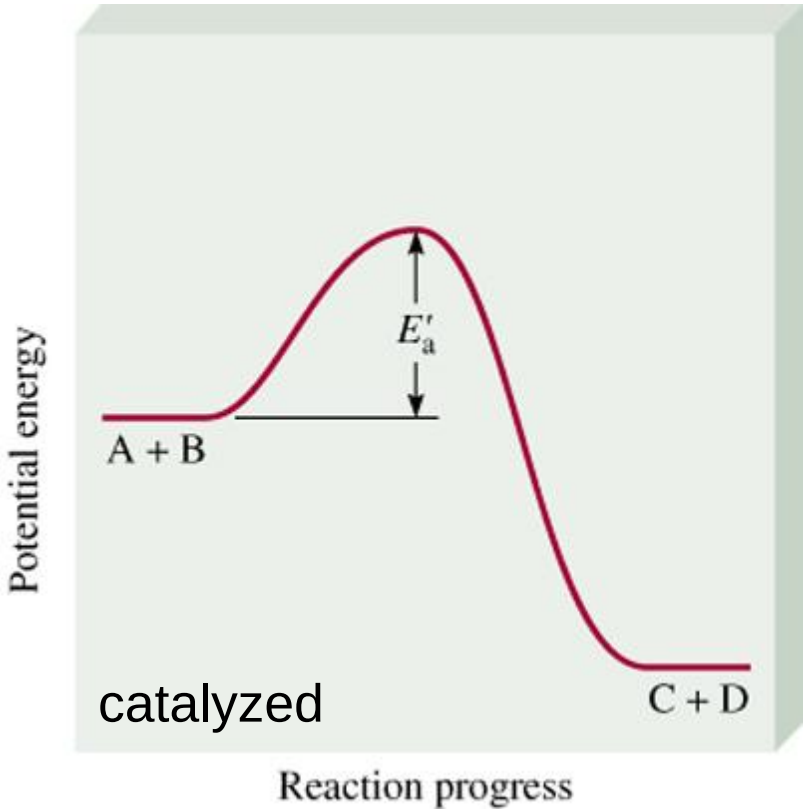
Van't Hoff

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

Le Châtelier's Principle

- Adding a Catalyst
  - does not change *K*
  - does not shift the position of an equilibrium system
  - system will reach equilibrium sooner





Catalyst lowers E_a for **both** forward and reverse reactions.

Catalyst does not change equilibrium constant or shift equilibrium.

Thermodynamic Properties of Ions in Solution
Enthalpy and Gibbs Energy

$$2A + 3B \longrightarrow C + 2D$$

$$K = \frac{(a_C)\,(a_D)^2}{(a_A)^2\,(a_B)^3}$$

$$\Delta G^o = \Delta G_f{}^o(C) + 2\Delta G_f{}^o(D) - 2\Delta G_f{}^o(A) - 3\Delta G_f{}^o(B)$$

Table Termodynamic standart ion at 25o C

Ion	ΔH^o_f (kJ/mol)	H^o ($JK^{-1}\ mol^{-1}$)	ΔG^o_f (kJ/mol)
Cl^-	-167,2	+56,5	-131,2
Cu^{2+}	+64,8	-99,6	+65,5
H^+	0	0	0
K^+	-252,4	+102,5	-283,3
Na^+	-240,1	+59,0	-261,9
PO_4^{3-}	-1277	-221,8	-1019

Determine ΔH^o_f **(Ag+, aq)**

$Ag_{(s)} + ½\ Cl_{2(g)} \rightarrow Ag^+_{(aq)} + Cl^-_{(aq)}$ ΔH^o = -61,58 kJ/mol

$\Delta H^o = \Delta H^o_f\ (Ag^+, aq) + \Delta H^o_f\ (Cl^-, aq)$ = -61,58 kJ/mol

$\Delta H^o_f\ (Ag^+, aq)$ = -61,58 kJ/mol – (-167,16 kJ/mol)

= + 105,58 kJ/mol