

CHEMICAL EQUILIBRIUM

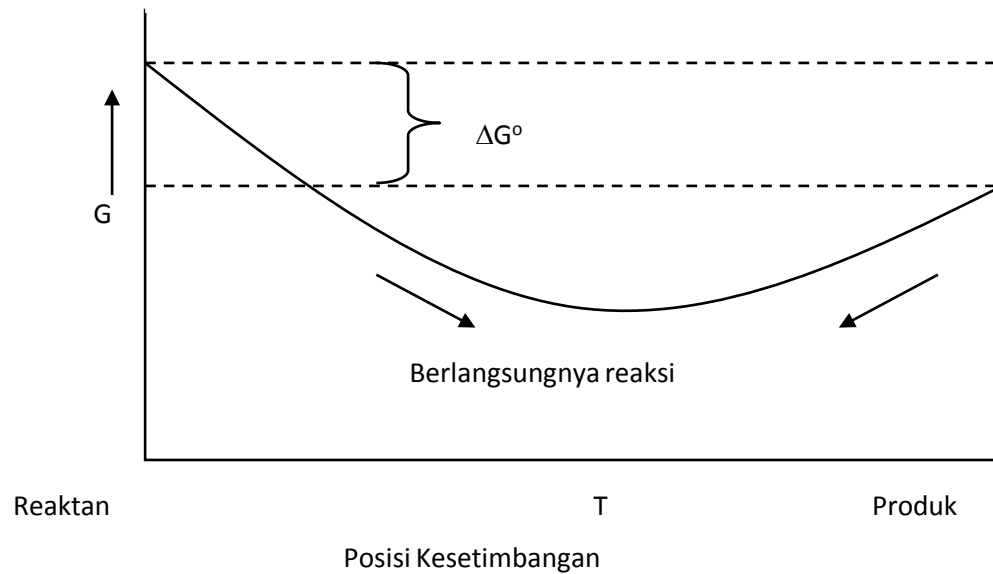
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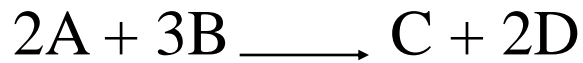
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CHEMICAL EQUILIBRIUM AND THERMODYNAMICS

Relationships ΔG° and equilibrium

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





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

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

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

Q = reaction Quotient

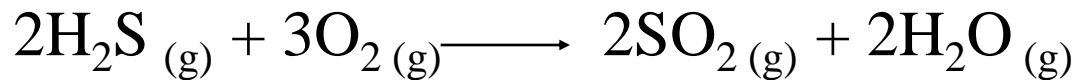
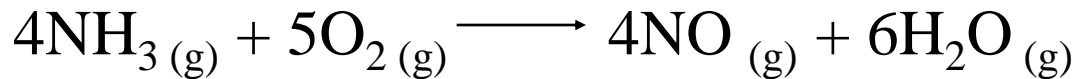
$$a = \text{activity} = \frac{f}{P^\circ}$$

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

f = Fugacities

$$Q = \frac{f(C) f(D)^2 (P^\circ)^2}{f(A)^2 f(B)^3}$$

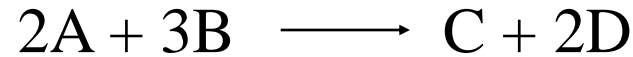
Determine reaction Quotient



EQUILIBRIUM CONDITION

$$\Delta G_r = 0$$

$$K = (Q)_{\text{equilibrium}}$$



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

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

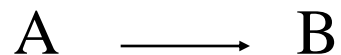
$$\Delta G^\circ = -RT \ln K_p$$

K_p = Equilibrium constante parcial presure

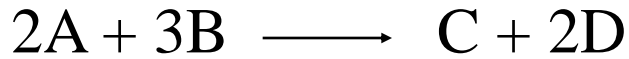
$$\Delta G_r = \Delta G^\circ + RT \ln Q$$

$$\Delta G^\circ = -RT \ln K$$

K = Thermodynamic Equilibrium constante



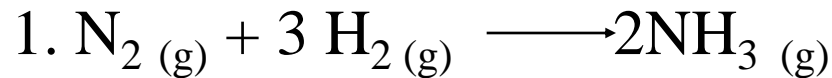
$$\Delta G^\circ = \Delta G_f^\circ(B) - \Delta G_f^\circ(A)$$



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

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

Calculate an Equilibrium constant at 25° C:



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

$$\Delta G^\circ = 2\Delta G_f^\circ (NH_3) - \Delta G_f^\circ (N_2) - \Delta G_f^\circ (H_2)$$

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

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

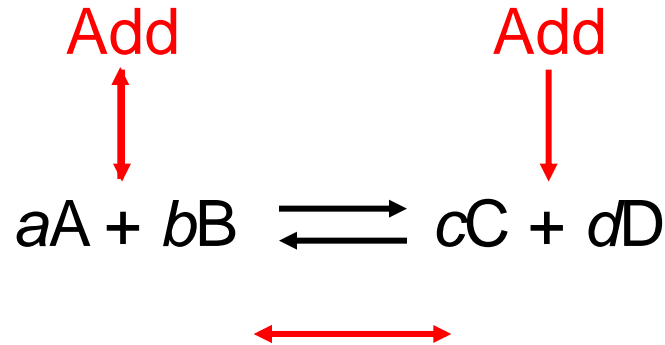
$$K_p = 6 \times 10^5$$

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



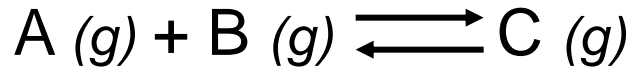
Change

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)

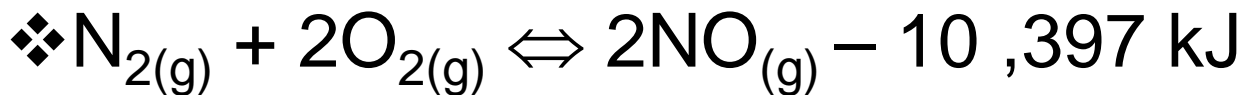


<u>Change</u>	<u>Shifts the Equilibrium</u>
Increase pressure	Side with fewest moles of gas
Decrease pressure	Side with most moles of gas
Increase volume	Side with most moles of gas
Decrease volume	Side with fewest moles of gas

Le Châtelier's Principle

- Changes in Temperature

- ❖ Only factor that can change value of K



Change

Exothermic Rx

Endothermic Rx

Increase temperature

K decreases

K increases

Decrease temperature

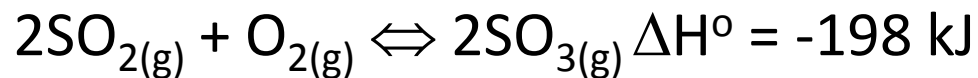
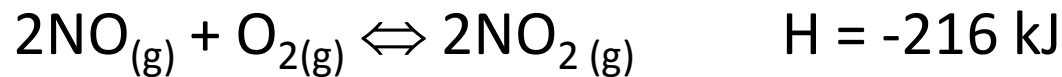
K increases

K decreases

Respon Equilibrium With Temperature



Van't Hoff ([Belanda](#)) :



$$\frac{d \ln K}{dT} = \frac{-1}{R} \frac{d (-\Delta G^\circ)}{dT} \quad \frac{d (\Delta G^\circ)}{dT} = -\frac{\Delta H^\circ}{T^2}$$

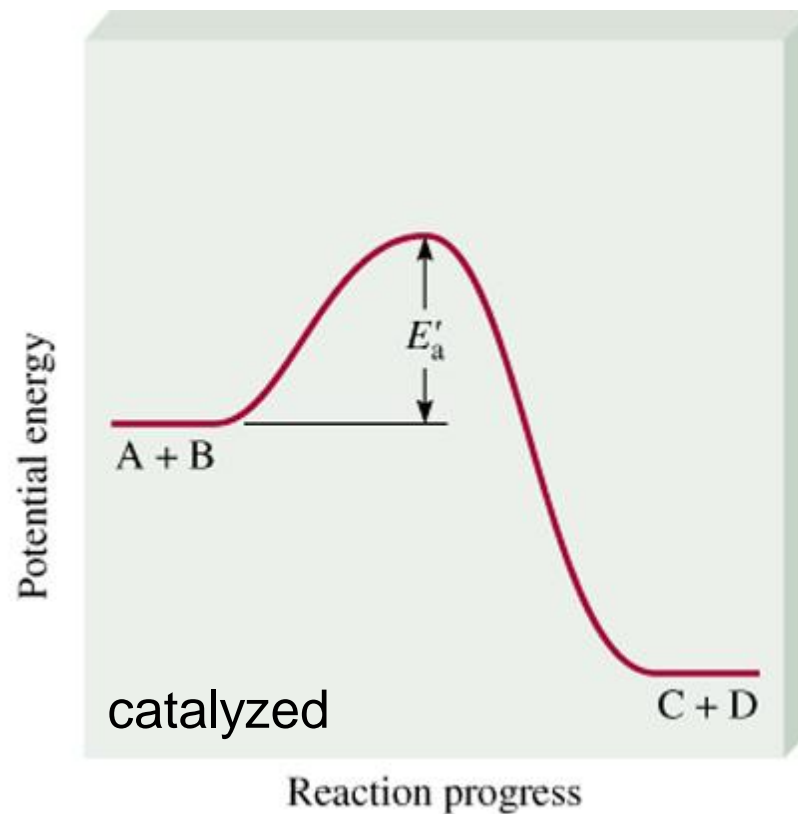
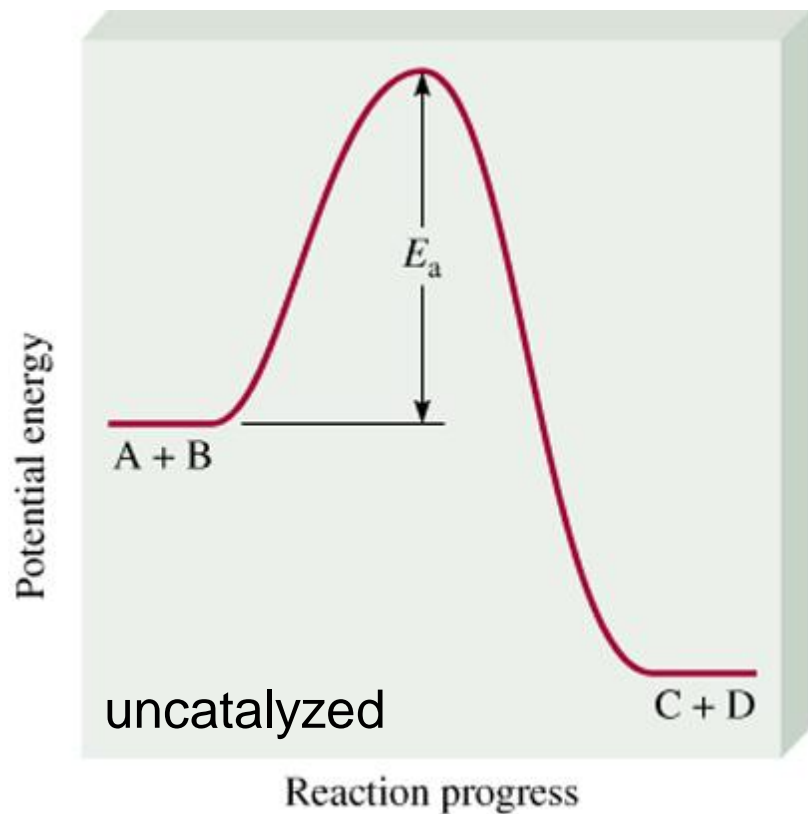
$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2}$$

Van't Hoff

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

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

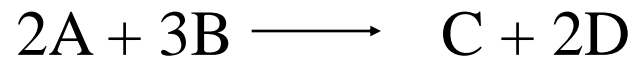


Catalyst lowers E_a for **both** forward and reverse reactions.

Catalyst does not change equilibrium constant or shift equilibrium.

Thermodynamic Properties of Ions in Solution

Enthalpy and Gibbs Energy



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

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

Table Thermodynamic standart ion at 25o C

Ion	ΔH_f° (kJ/mol)	H° (JK ⁻¹ mol ⁻¹)	ΔG_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_f° (Ag⁺, aq)

$$\text{Ag}_{(s)} + \frac{1}{2} \text{Cl}_{2(g)} \rightarrow \text{Ag}^+_{(aq)} + \text{Cl}^-_{(aq)} \quad \Delta H^\circ = -61,58 \text{ kJ/mol}$$

$$\Delta H^\circ = \Delta H_f^\circ (\text{Ag}^+, \text{aq}) + \Delta H_f^\circ (\text{Cl}^-, \text{aq}) = -61,58 \text{ kJ/mol}$$

$$\Delta H_f^\circ (\text{Ag}^+, \text{aq}) = -61,58 \text{ kJ/mol} - (-167,16 \text{ kJ/mol})$$

$$= + 105,58 \text{ kJ/mol}$$