

Lecture 27

Thermodynamics of Reactive Systems

The Equilibrium Constant



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Today's Topics

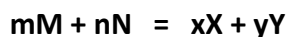
- The Equilibrium Constant
- Free Energy and Equilibrium Constant
- Temperature Dependency of Equilibrium Constant
- The Uses of Equilibrium Constant

The Equilibrium Constant

The law of mass action

“The rate of any chemical reaction is proportional to the active masses of the reacting substances”

- By active masses, it means the activities of the solid or liquid reacting substances, or partial pressures in the case of gaseous substances.
- If pure solids and liquids are involved in a reaction, their active masses, or activities, can be regarded as unity.



$$\text{Rate of forward reaction} = k_1 \cdot (a'_M)^m \cdot (a'_N)^n$$

$$\text{Rate of reverse reaction} = k_2 \cdot (a'_X)^x \cdot (a'_Y)^y$$

where a'_j etc. are the activities of element j at any state of the reaction, and k_1 and k_2 are proportionality constants.

- At equilibrium, the rates of forward and reverse reactions are equal.

$$k_1 \cdot (a_M)^m \cdot (a_N)^n = k_2 \cdot (a_X)^x \cdot (a_Y)^y$$

where a_j is the concentration of element at equilibrium.

$$K = \frac{k_1}{k_2} = \frac{(a_X)^x \cdot (a_Y)^y}{(a_M)^m \cdot (a_N)^n}$$

where K is the equilibrium constant of the reaction.

$$K_a = \left(\frac{(a_X)^x \cdot (a_Y)^y}{(a_M)^m \cdot (a_N)^n} \right)_e$$

The suffice e used in the above equation indicates that the activities are of equilibrium values.

The Relationship Among Equilibrium Constants

$$K_a = \frac{(a_X)^x \cdot (a_Y)^y}{(a_M)^m \cdot (a_N)^n}$$

- For gaseous components,

$$K_p = \frac{(p_X)^x \cdot (p_Y)^y}{(p_M)^m \cdot (p_N)^n} ; \quad K_c = \frac{(c_X)^x \cdot (c_Y)^y}{(c_M)^m \cdot (c_N)^n}$$

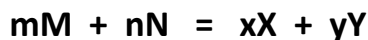
p_k = partial pressure of component k

c_k = molar concentration of component k

- For ideal gas, $p_k = (n_k/V) RT = c_k RT$

$$K_p = K_c (RT)^{\Delta n} \quad \Delta n = (x+y)-(m+n)$$

Free Energy and Equilibrium Constant



$$\Delta G = (x\mu_X + y\mu_Y) - (m\mu_M + n\mu_N)$$

$$\mu_k = \mu_k^\circ + RT \ln a_k$$

$$\Delta G = \left\{ (x\mu_X^\circ + y\mu_Y^\circ) - (m\mu_M^\circ + n\mu_N^\circ) \right\} + RT \left\{ (x \ln a_X + y \ln a_Y) - (m \ln a_M + n \ln a_N) \right\}$$

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{(a_X)^x \cdot (a_Y)^y}{(a_M)^m \cdot (a_N)^n} \right)_{ne}$$

ΔG = **Chemical Affinity** or Gibbs free energy change of a reaction

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{(a_X)^x \cdot (a_Y)^y}{(a_M)^m \cdot (a_N)^n} \right)_{ne}$$

$$Q = \text{Activity Quotient} = \left(\frac{(a_X)^x \cdot (a_Y)^y}{(a_M)^m \cdot (a_N)^n} \right)_{ne}$$

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

- If the reactants and products are in equilibrium with each other, $\Delta G = 0$, and

$$0 = \Delta G^\circ + RT \ln \left(\frac{(a_X)^x \cdot (a_Y)^y}{(a_M)^m \cdot (a_N)^n} \right)_e$$

$$\Delta G^\circ = -RT \ln K_a \quad \text{and} \quad K_a = \exp \left(\frac{-\Delta G^\circ}{RT} \right)$$

Example 8.6

Calculate the equilibrium constant for the reaction $\langle \text{NiO} \rangle + (\text{H}_2) = \langle \text{Ni} \rangle + (\text{H}_2\text{O})$ at 750 C from the following data:

$$\langle \text{Ni} \rangle + 1/2(\text{O}_2) = \langle \text{NiO} \rangle; \quad \Delta G^\circ = -58450 + 23.55 T \text{ cal}$$

$$(\text{H}_2) + 1/2(\text{O}_2) = (\text{H}_2\text{O}); \quad \Delta G^\circ = -58900 + 13.10 T \text{ cal}$$

ANSWER

$$\langle \text{NiO} \rangle = \langle \text{Ni} \rangle + 1/2(\text{O}_2); \quad \Delta G^\circ = +58450 - 23.55 T \text{ cal}$$

$$(+)\ (\text{H}_2) + 1/2(\text{O}_2) = (\text{H}_2\text{O}); \quad \Delta G^\circ = -58900 + 13.10 T \text{ cal}$$

$$\langle \text{NiO} \rangle + (\text{H}_2) = \langle \text{Ni} \rangle + (\text{H}_2\text{O}); \quad \Delta G^\circ = -450 - 10.45 T \text{ cal}$$

At 750 C (or, 1023 K), $\Delta G^\circ = -450 - 10.45 (1023) = -11140.35 \text{ cal/mol}$

$$K_a = \exp \left(\frac{-(-11140.35 \text{ cal/mol})}{(1.987 \text{ cal/deg/mol}) \times (1023 \text{ K})} \right) = 239.98$$

$$\Delta G = \Delta G^\circ + RT \ln Q \quad \text{and} \quad \Delta G^\circ = -RT \ln K_a$$

$$\Delta G = RT \ln (Q/K_a) \quad \text{van't Hoff Isotherm}$$

Knowing the value of ΔG° and the activities of reactants and products at any given condition, the free energy change for the equation at that condition, ΔG , can be calculated, and the **thermodynamics feasibility** of the reaction can be predicted.

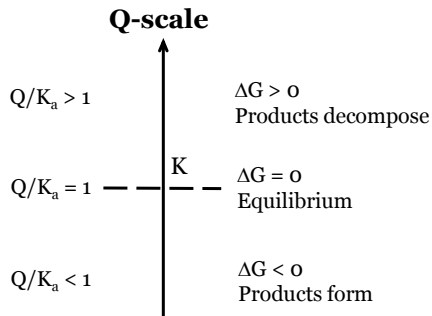
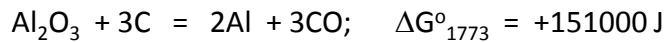


FIGURE 8.1
Sketch of the scale for the ΔG and (Q/K_a) showing the spontaneous change of a chemical reaction.

The importance of **van't Hoff isotherm** can be understood by considering the thermodynamic possibility of the reduction of alumina by carbon at 1500 C:



$$\Delta G_{1773} = \Delta G^\circ_{1773} + RT \ln \frac{(a_{\text{Al}})^2 \cdot (p_{\text{CO}})^3}{(a_{\text{Al}_2\text{O}_3}) \cdot (a_{\text{C}})^3}$$

$$\Delta G_{1773} = 151000 + 14740.72 \ln (p_{\text{CO}})^3$$

So it is seen that if $p_{\text{CO}} > 1$, clearly there is no possibility of a spontaneous change because ΔG_{1773} is positive.

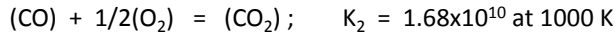
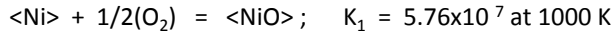
However, if the partial pressure of CO gas can be reduced, for example, by placing the system in a vacuum, the value of ΔG will decrease.

$p_{\text{CO}}, \text{ atm}$	$\Delta G_{1773}, \text{ J/mol}$
1	+151000
10^{-1}	+49000
10^{-2}	-52700
10^{-3}	-154400

Thus, reaction becomes thermodynamically possible if p_{CO} is lowered sufficiently.

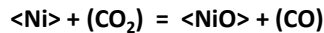
Example 8.7

Would an atmosphere containing 15 % CO₂, 5 % CO and 80 % N₂ oxidise nickel at 1000 K? Given data:



ANSWER

In the given atmosphere the following oxidation reaction of nickel could occur:



Nickel would be oxidised if $\Delta G = RT \ln (Q/K)$ for the above oxidation reaction is negative. In the equation, ΔG is negative if Q/K is less than one.

Now, given that, $K = (p_{\text{CO}} / p_{\text{CO}_2})_e = K_1/K_2 = 3.43 \times 10^{-3}$ at 1000 K

and $Q = (p_{\text{CO}} / p_{\text{CO}_2})_{\text{actual}} = (0.05/0.15) = 0.333$ at 1000 K

Hence, $Q/K = 96.21$. Now, since $Q/K > 1$, ΔG will be positive for the reaction. Thus, the reaction would not occur, that is, nickel would not be oxidised.

Example 8.8

Calculate the equilibrium extent of decomposition of nitrogen tetroxide due to the chemical reaction $(\text{N}_2\text{O}_4) = 2(\text{NO}_2)$ at 25 C and 1 atm. What will be the equilibrium composition of the gas mixture? Given data: $\Delta G_{298}^\circ = 4644 \text{ J/mol}$.

ANSWER

The equilibrium constant for the reaction

$$K = (p_{\text{NO}_2})^2 / p_{\text{N}_2\text{O}_4} = \exp (-\Delta G_{298}^\circ / RT)$$

$$(p_{\text{NO}_2})^2 / p_{\text{N}_2\text{O}_4} = 0.153$$

Considering that all the gases are in their ideal conditions, changing the partial pressure to mole fraction,

$$(X_{\text{NO}_2})^2 / X_{\text{N}_2\text{O}_4} = 0.153$$

Let **a** be the equilibrium extent of the decomposition of N_2O_4 according to the reaction $(N_2O_4) = 2(NO_2)$

	No. of moles before reaction	No. of moles at equilibrium	Equilibrium mole fraction, X
N_2O_4	1	(1-a)	$X_{N_2O_4} = (1-a) / (1+a)$
NO_2	0	2a	$X_{NO_2} = 2a / (1+a)$
Total moles	1	(1+a)	

$$(X_{NO_2})^2 / X_{N_2O_4} = 0.153$$

$$4a^2 / (1 - a^2) = 0.153 ; \quad a = 0.19$$

Hence, about 19 % decomposition of N_2O_4 would occur and the equilibrium composition of the gas mixture would be:

$$X_{N_2O_4} = (1-a) / (1+a) = \mathbf{0.68, \text{ or } 68\%}$$

$$X_{NO_2} = 2a / (1+a) = \mathbf{0.32, \text{ or } 32\%}$$

Temperature Dependence of Equilibrium Constant

$$\Delta G^\circ = - R T \ln K$$

- Upon differentiation with respect to temperature at constant P

$$\left(\frac{\partial(\Delta G^\circ)}{\partial T} \right)_P = - R \ln K - RT \left(\frac{\partial \ln K}{\partial T} \right)_P$$

- Now multiplying both side of the equation with T

$$T \left(\frac{\partial(\Delta G^\circ)}{\partial T} \right)_P = - RT \ln K - RT^2 \left(\frac{\partial \ln K}{\partial T} \right)_P$$

$$T \left(\frac{\partial(\Delta G^\circ)}{\partial T} \right)_P = \Delta G^\circ - RT^2 \left(\frac{\partial \ln K}{\partial T} \right)_P$$

- Now, the **Gibbs-Helmholtz equation** states that

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = \Delta H^\circ + T \left(\frac{\partial(\Delta G^\circ)}{\partial T} \right)_P$$

$$\begin{aligned} dG &= -SdT + VdP \\ -S &= (\partial G/\partial T)_P \end{aligned}$$

$$\Delta G^\circ - \Delta H^\circ = T \left(\frac{\partial(\Delta G^\circ)}{\partial T} \right)_P$$

- Now since $T \left(\frac{\partial(\Delta G^\circ)}{\partial T} \right)_P = \Delta G^\circ - RT^2 \left(\frac{\partial \ln K}{\partial T} \right)_P$

$$\Delta G^\circ - \Delta H^\circ = \Delta G^\circ - RT^2 \left(\frac{\partial \ln K}{\partial T} \right)_P$$

$$\left(\frac{\partial \ln K}{\partial T} \right)_P = \frac{\Delta H^\circ}{RT^2} \quad \text{or,} \quad d \ln K = \frac{\Delta H^\circ}{RT^2} dT$$

This equation is known as **van't Hoff isochore**, and it shows the relationship between the equilibrium constant and temperature of the reaction.

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

- K grows with increasing temperature in processes attended by the absorption of heat ($\Delta H^\circ > 0$).
- If the standard reaction is exothermic, $\Delta H^\circ < 0$, then K grows with diminishing temperature.
- Assuming that ΔH° is constant over the temperature range, integration of the equation will result

$$\ln K = - \frac{\Delta H^\circ}{RT} + \text{constant}$$

- So if the standard enthalpy change for a reaction and the equilibrium constant at one particular temperature is known, calculation of equilibrium constant for the reaction at some other temperature can be calculated by using this equation.

Next Class

Lecture 28

Thermodynamics of Reactive Systems

Applications of the Ellingham Diagram