

CHAPTER II

THERMODYNAMIC PROPERTIES

2.1 Thermodynamic Properties at Steady State

From the second law of thermodynamics, a system at equilibrium can not undergo any spontaneous change as shown in Figure 2.1

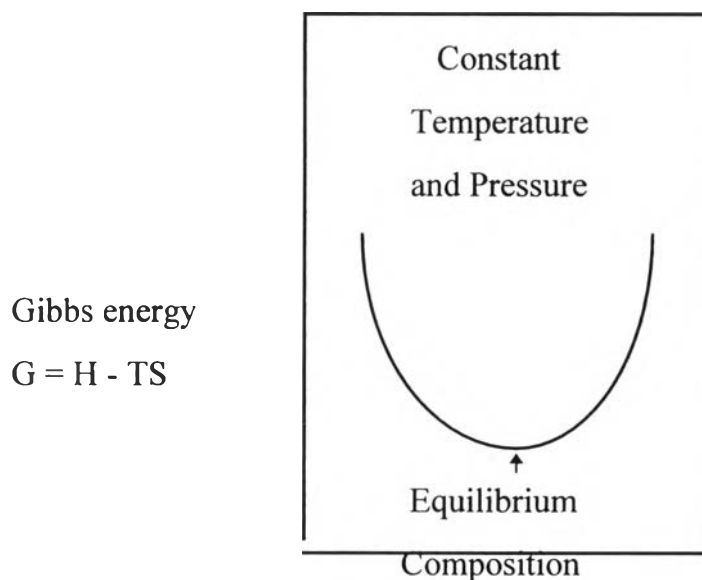


Figure 2.1 The system moves toward a state of minimum Gibbs energy at constant T and P

The condition for equilibrium is therefore

$$dS_{\text{total}} = dS_{\text{system}} + dS_{\text{surrounding}} = 0 \quad (2.1)$$

It is more convenient to define equilibrium with reference to changes in the system only, without explicitly considering the environment. Suppose that the system and the surroundings are at the same temperature,

$$T_{\text{system}} = T_{\text{surroundings}} \quad (2.2)$$

Suppose that a process occurs spontaneously in the system, and that an amount of heat dq leaves the system and enters the surroundings. This amount entering the surroundings may be written as $dq_{\text{surroundings}}$, and is equal to the heat change $-dq_{\text{system}}$ in the system :

$$dq_{\text{surroundings}} = -dq_{\text{system}} \quad (2.3)$$

The surroundings experience no volume change when heat is transferred to them, and $dq_{\text{surrounding}}$ is therefore equal to the change $dU_{\text{surrounding}}$ in the internal energy, which is a state function. It therefore does not matter whether the heat $ad_{\text{surrounding}}$ enters the surroundings reversibly or irreversibly; the heat $dq_{\text{surr};\text{irrev.}} = dq_{\text{surr. Rev.}} = dU_{\text{surr}}$ (2.4)

The entropy change in the surroundings is

$$dS_{\text{surr.}} = (dq_{\text{surr.}}) / (T_{\text{surr.}}) \quad (2.5)$$

But $T_{\text{surr}} = T_{\text{syst.}}$ and $dq_{\text{surr.}} = -dq_{\text{syst.}}$; therefore

$$dS_{\text{surr.}} = -(dq_{\text{syst.}}) / (T_{\text{syst.}}) \quad (2.6)$$

Or

$$dS_{\text{total}} = dS_{\text{syst.}} - (dq_{\text{syst.}} / T_{\text{syst.}}) = 0 \quad (2.7)$$

Dropping the superscript "system", the condition for equilibrium will be written simply as :

$$dS - (dq / T) = 0 \quad (2.8)$$

Or

$$dq - T dS = 0 \quad (2.9)$$

Constant Temperature and Pressure : The Gibbs Energy

Chemical processes commonly occur in open vessels at constant pressure, in which case dq can be equated to dH , the enthalpy change. Equation 6.9 therefore becomes

$$dH - TdS = 0 \quad (2.10)$$

From the Gibbs energy “G”

$$G = H - TS \quad (2.11)$$

At constant temperature :

$$dG = dH - T dS \quad (2.12)$$

From equation 6.10 the condition for equilibrium at constant T and P is

$$dG = 0 \quad (2.13)$$

Constant Temperature and Volume : The Helmholtz Energy

Similar to the Gibbs Energy, the quantity dq in equation 2.9 is equated to dU:

$$dU - T dS = 0 \quad (2.14)$$

The quantity $U - TS$, also a state function, is called the Helmholtz function or Helmholtz energy and is given the symbol A:

$$A = U - TS \quad (2.15)$$

Equation 2.14 therefore can be written as

$$dA = 0 \quad (2.16)$$

2.2 Enthalpy Change versus % Composition of the Products

The thermodynamic equilibrium constant K^u is related to the standard Gibbs energy change for the process by

$$\Delta G^\circ = - RT \ln K^u \quad (2.17)$$

This thermodynamic equilibrium constant K^u is a dimensionless quantity. If the standard state for ΔG° is 1 atm pressure, K^u is K^u_p , which is the dimensionless form of K_p in which pressures are in atmospheres; if the standard state is 1 mol dm⁻³ the K^u is K^u_c , which is the dimensionless form of K_c in which concentrations are expressed in mol dm⁻³.

$$\ln K^u_p = - \Delta G^\circ / RT = - (\Delta H^\circ / RT) + (\Delta S^\circ / R) \quad (2.18)$$