

Chapter 5

Spontaneity and Equilibrium: Free Energy

5.1 Spontaneity and Equilibrium

Let us consider that a system is at a constant temperature, T and a constant pressure (P). Note, even at constant T and P , many reversible and irreversible changes of thermodynamic state may occur because the volume V and number of moles of individual species may change. The reversible and irreversible changes at constant temperature and pressure are defined as follows.

a) An irreversible change occurring at constant temperature and pressure is called a spontaneous process.

b) A reversible change occurring at constant temperature and pressure is called an equilibrium process.



James Clark Maxwell (1831-1879) a Scottish physicist, is considered to be the third most influential physicist after Newton and Einstein. He developed the *electromagnetic theory* (in 1865), the *kinetic theory of gases* and *Maxwell-Boltzmann distribution* (1859-65). In 1871, he derived the *Maxwell's thermodynamic relations*. He and Gibbs mutually inspired each other. After his early death at the age of 48, it was said that, "only one man lived who could understand Gibbs's papers. That was Maxwell and now he is dead."



Willard Gibbs (1839-1903), the first American doctorate in engineering, introduced *Gibbs' free energy* ($G=H-TS$) and *chemical potential* and many new concepts. His monograph, *On the Equilibrium of Heterogeneous Substances*, (published in 1875 and 1878) is often referred to as the "*Principia of Thermodynamics*." According to Ostwald, Gibbs was the "*father of chemical energetics*." Einstein called him "*the greatest mind in American history*."



Hermann von Helmholtz (1821 – 1894), a German physician and physicist, made significant contributions to many apparently unconnected areas of science such as physics, physiology and psychology,. He introduced the concept of *Helmholtz free energy* ($A = E-TS$).

From Clausius inequality, equation (2.20)

For an irreversible process $dS > dQ/T$

For a reversible process $dS = dQ/T$

We will now derive the corresponding relations under constant T and P, i.e. for spontaneous and equilibrium processes.

2.15 Gibbs Free Energy

Willard Gibbs introduced the free energy as

$$G = H - TS \quad (2.33)$$

Evidently, G is composite state function which depends on three other state functions.

$$dG = dH - TdS - SdT$$

Or, $dG = dE + PdV + VdP - TdS - SdT \quad (2.34)$

From first law (1.3)

$$dE = dQ - dW \quad (2.35)$$

Let us now assume that the system does both mechanical work and non-mechanical work.

Thus, $W = W_{\text{mech}} + W_{\text{non-mech}} \quad (2.36)$

The mechanical work refers to that due to the volume change and is given by $P_{\text{ext}}dV$. The non-mechanical work ($W_{\text{non-mech}}$) involves other types of work such as, electrical, magnetic and so on.

For a reversible process, $dQ = TdS$ and at constant pressure $P_{\text{ext}} = P$.

Thus from (2.34)

$$dG = -W_{\text{non-mech}} + VdP - SdT \quad (2.37)$$

2.16 Free Energy is a measure of non-mechanical work **in Reversible process**

From 2.37, at constant temperature and pressure,

$$dG_{T,P} = -W_{\text{non-mech}} \quad (2.38)$$

Thus, the free energy change at constant temperature and pressure is equal to negative of non-mechanical work done. We will show later this conclusion and equation (2.5) plays a fundamental role in electrochemical cells.

2.17 Free Energy change at constant T and P: Condition for spontaneity and equilibrium

At constant T and P, (2.34) becomes

$$dG_{T,P} = dE + PdV - TdS \quad (2.39)$$

In the absence of non-mechanical work, $dE + PdV = dQ$

$$\text{Thus } dG_{T,P} = dQ - TdS \quad (2.40)$$

From Clausius inequality (2.20)

$$dS \geq dQ/T$$

$$\text{or, } TdS \geq dQ$$

$$\text{or, } dQ - TdS \leq 0 \quad (2.41)$$

In this relation, the less than sign corresponds to irreversible process and the equal to sign to reversible process. From (2.40 and 2.41)

$$\text{For a spontaneous process, } dG_{T,P} < 0$$

$$\text{For equilibrium } dG_{T,P} = 0 \quad (2.42)$$

The two relations given under (2.42) are, perhaps, the most important conclusions derived from thermodynamics.

2.18 Work Function

The work function or Helmholtz free energy, A is defined as,

$$A = E - TS \quad (2.43)$$

So that $dA = dE - TdS - SdT$

Or, at constant T, $dA_T = dE - TdS$

$$\text{Or, } dA_T = -dW + dQ - TdS$$

$$\text{Or, } dA_T + dW = dQ - TdS$$

Using equation (2.41)

$$dA_T + dW \leq 0$$

$$\text{Or, } dW \leq (-dA_T) \quad (2.44)$$

The less than sign corresponds to irreversible work and the equal sign to reversible process. Thus the maximum work is equal $(-dA_T)$ and hence, work function is a measure of maximum work done by the system.

2.19 Maxwell's relations

The Maxwell's relations refer to derivatives of various thermodynamics variables and their inter-relations. To derive this let us consider reversible processes with zero-non-mechanical work.

Under this condition

$$dE = dQ - dW = TdS - PdV \quad (2.45)$$

$$dH = dE + PdV - VdP = TdS - VdP \quad (2.46)$$

$$dG = VdP - SdT \quad (2.47)$$

$$dA = dE - TdS - SdT = -PdV - SdT \quad (2.48)$$

From (2.45) $(\partial E/\partial S)_V = -T$ and $(\partial E/\partial V)_S = -P$. Thus

$$(\partial T/\partial V)_S = -(\partial P/\partial S)_V \quad (\text{both equal to } \partial^2 E/\partial S\partial V) \quad (2.49)$$

$$\text{From (2.46)} \quad (\partial T/\partial P)_S = -(\partial V/\partial S)_P \quad (\text{both equal to } \partial^2 H/\partial S\partial P) \quad (2.50)$$

$$\text{From (2.47)} \quad (\partial S/\partial P)_T = -(\partial V/\partial T)_P \quad (\text{both equal to } \partial^2 G/\partial T\partial P) \quad (2.51)$$

$$\text{From (2.48)} \quad (\partial P/\partial T)_V = (\partial S/\partial V)_T \quad (\text{both equal to } -\partial^2 A/\partial V\partial T) \quad (2.52)$$