Lecture #10

THERMODYNAMICS OF EQUILIBRIUM

At every stage of a reversible transformation, the system departs from equilibrium only infinitesimally. The system remains at equilibrium. Therefore, to be at equilibrium can be assumed to be reversible. The condition of equilibrium is;

$$TdS = dQ_{rev}$$

The condition of spontaneity can be written by Clausius inequality as;

$$TdS > dQ_{irr}$$

By combining the above expressions, the conditions of equilibrium and spontaneity can be written as;

$$TdS \geq dQ$$

By using the first law;

$$TdS \geq dE + dW$$

$$- dE - dW + TdS \geq 0$$

The work includes all kinds, pressure-volume work P'dV and all others dU;

$$-dE - P'dV - dU + TdS \geq 0$$

For an isolated system:

$$dE = dW = dQ = 0$$

TdS $\geq$ 0

In an isolated system, the entropy increases and reaches a maximum at equilibrium.

At constant temperature:

-dE – dW + d(TS) $\geq$ 0

-d(E-TS) $\geq$ dW

All the terms in parantheses depend upon the properties of the system. So, the sum is a state function called "***Work function or Helmholtz function***" and designated as **A;**

A = E – TS

-dA $\geq$ dW

-ΔA $\geq$ W

The work produced in an isothermal process is less than or equal to the decrease in work function.

At constant temperature and pressure:

At constant pressure P' = P, so the conditions of equilibrium and spontaneity can be written as;

-dE – d(PV) + d(TS) $\geq$ dU

-d(E + PV − TS) ≥ dU

-d(H − TS) ≥ dU

The terms in parantheses define another state function, **_Gibbs Free Energy_** designated by **G:**

G = H − TS

-dG ≥ dU

-ΔG ≥ U

The decrease in free energy in a transformation at constant T and P is greater than or equal to the work over and above expansion work. There are three possibilities for a transformation proceeding at constant T and P;

ΔG < 0 …………. the transformation can occur spontaneously

ΔG = 0 …………. the system is at equilibrium

ΔG > 0 …………. the natural direction is opposite to the direction considered

Natural Changes

At constant T and P, the change in G can be written as;

ΔG = ΔH - TΔS

According to the above equation, there are two contributions to ΔG. One is **_energetic_** ΔH, the other is **_entropy_** ΔS. To make ΔG negative, it is best if ΔH is

negative and if ΔS is positive. In nature, in all natural changes the systems attempt to achieve the lowest enthalpy and the highest entropy, in other words the lowest energy and the highest disorder.

Fundamental Equations of Thermodynamics

There are mainly 4 fundamental equations of thermodynamics. These equations give relations between the properties of the systems and the thermodynamic functions.

The 1st Equation:

The first equation gives the change in internal energy. The derivation can be started by the general condition of equilibrium;

TdS = dQ

TdS = dE + PdV

dE = TdS - PdV

The 2nd Equation:

The derivation of the second equation can be started by the definition of enthalpy. Then by differentiating the equation and substituting the first equation, the second fundamental equation is obtained;

H = E + PV

dH = dE + PdV + VdP

   = TdS − PdV + PdV + VdP

dH = TdS + VdP

The 3rd Equation:

By using the definition of the work function, differentiating and substituting the first equation, the third fundamental equation is obtained;

A = E − TS

dA = dE − TdS − SdT

    = TdS − PdV − TdS − SdT

dA = -SdT − PdV

The 4th Equation:

The fourth fundamental equation is obtained by using the definition of Gibbs free energy, differentiating and substituting the first equation;
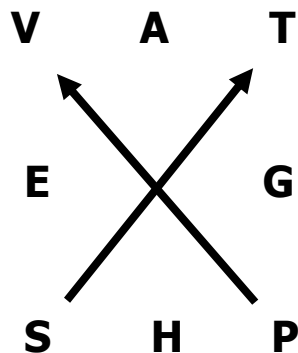
G = H − TS

  = E + PV − TS

dG = dE + PdV + VdP − TdS − SdT

    = TdS − PdV + PdV + VdP − TdS − SdT

dG = -SdT + VdP

The fundamental equations can be written directly by using the **thermodynamic cycle;**

$$
\begin{array}{ccc}
\textbf{V} & \textbf{A} & \textbf{T} \\
 & & \\
\textbf{E} & & \textbf{G} \\
 & & \\
\textbf{S} & \textbf{H} & \textbf{P}
\end{array}
$$

To draw the thermodynamic cycle, first write VAT horizontally, and then write VES vertically. Place P in the empty corner, H on the lowest edge and G right edge. Draw two arrows diagonally upward. The symbols in the middle of the edges show the functions on the left-hand side of the fundamental equations. The changes in these functions depend upon the neighboring symbols. The coefficients on the right-hand sides of the equations are obtained by going along the arrows. If you are going in the same direction as the arrow use a positive sign, if in the opposite direction use a negative sign.

Maxwell Relations

The right-hand sides of the fundamental equations are exact differential expressions. For an exact differential expression of the form;

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

the cross-derivatives are equal.

$$\left[\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right)_y\right]_x = \left[\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right)_x\right]_y$$

By appling this rule to the 4 fundamental equations of thermodynamics, 4 Maxwell relations are obtained as follows;

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

Properties of A

The fundamental equation giving dA is;

dA = -SdT - PdV

According to this equation A is a function of T and V. The change in A with respect to T at constant volume is;

$$\left(\frac{\partial A}{\partial T}\right)_V = -S$$

Since entropy is always positive, A decreases with an increase in T. The rate of this decrease is greater, the greater the entropy. The order for entropy is;

$$S_{gas} > S_{liq} > S_{solid}$$

Therefore, the rate of this decrease is larger for gases than liquids which have larger entropies than solids. On the other hand; the change in A with respect to volume at constant temperature is;

$$\left(\frac{\partial A}{\partial V}\right)_T = -P$$

An increase in volume decreases A. The rate of this decrease is greater the higher the pressure.

The Properties of G

The fundamental equation giving dG is;

dG = -SdT + VdP

According to this equation G is a function of T and P. The change in G with respect to T at constant pressure is;

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

Since entropy is always positive, G decreases with an increase in T. The rate of this decrease is greater, the greater the entropy. The order for entropy is;

$$S_{gas} > S_{liq} > S_{solid}$$

Therefore, the rate of this decrease is larger for gases than liquids which have larger entropies than solids. On the other hand; the change in G with respect to pressure at constant temperature is;

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

An increase in pressure increases G. The rate of this increase is greater the higher the volume. Therefore, the rate of this increase is larger for gases than liquids which have larger volumes than solids.

For a pure substance at a certain T;

$$dG = VdP$$

$$\int_{1}^{P} dG = \int_{1}^{P} VdP$$

$$G = G^{o}(T) + \int_{1}^{P} VdP$$

For solids and liquids, volume is assumed to be independent of pressure;

$$G(T) = G^{o}(T) + V(P-1)$$

Since V is very small for solids and liquids, the second term on the right is negligible;

$$G = G^{o}(T)$$

On the other hand, volume is dependent upon pressure for gases and for an ideal gas;

$$G(T) = G^{o}(T) + \int_{1}^{P} \frac{nRT}{P} dP$$

$$= G^{o}(T) + nRT \ln \frac{P}{1}$$

$$\frac{G}{n} = \frac{G^{o}(T)}{n} + RT \ln P$$

$$\mu = \mu^{o} + RT \ln P$$

For real gases;

$$\mu = \mu^{o} + RT \ln f$$