Lecture 2
Clausius Inequality
Assume reversible and irreversible paths between two states. Reversible path produces more work. 
\(dU\) is the same for both the paths.

\[
dU = dq + dw = dq_{\text{rev}} + dw_{\text{rev}}
\]

\[
dq_{\text{rev}}/T \geq dq/T
\]

\[
dS \geq dq/T \quad \text{Clausius inequality}
\]

System is isolated.

\[
dS \geq 0 \quad \text{Clausius inequality}
\]
Equilibrium Process

Entropy

Equilibrium

Process
Spontaneous processes entropy increases.

“Entropy is Time’s Arrow”

Arthur Stanley Eddington (1882-1944)
How do we derive conditions for equilibrium and spontaneity?

For an isolated system
\[ \Delta S \geq 0, \] > sign for a spontaneous process and = for equilibrium.

In the case of open or closed system, there are two ways

1. Evaluate \( \Delta S \) for systems and surroundings.
\[ \Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \]

\[ \Delta S \geq 0 \]
2. Other way is to define entropy change of the **system** alone.

\[ dS_{\text{Total}} = dS_{\text{System}} + dS_{\text{Surroundings}} \]

\[ dS - \frac{dq}{T} \geq 0 \quad \text{Clausius inequality} \]

Consider constant volume:

\[ dS - \frac{dU}{T} \geq 0 \]

\[ TdS \geq dU \quad \text{(constant } V \text{ and so no work due to expansion)} \]

At constant \( U \) or at constant \( S \), the expression is:

1. \( dS_{U,V} \geq 0 \)
2. \( dU_{S,V} \leq 0 \)

Criterion of spontaneity 1. is the common statement of second law.
2. For spontaneity, entropy of the surroundings must increase for which \( U \) of the system has to decrease.
3. At constant pressure, 
\( TdS \geq dH \)

1. \( dS_{H,P} \geq 0 \)  
2. \( dH_{S,P} \leq 0 \)

Interpretations are the same.

The inequalities mean, 
\( dU - TdS \leq 0 \) 
\( dH - TdS \leq 0 \)

We define, 
A = \( U - TS \) Helmholtz energy 
G = \( H - TS \) Gibbs energy
Hermann von Helmholtz
Born: 31 Aug 1821 in Potsdam, Germany
Died: 8 Sept 1894 in Berlin, Germany
What is $A$?

\[ dU = dq + dW \quad - \text{First law} \]
\[ TdS \geq dq \]

\[ dU \leq TdS + dW \]

\[ dW \geq dU - TdS = dA \]

Most negative value of $W$ is $W_{\text{max}}$ and that is equal to $dA$.

Under constant $T$ and $V$ can the system do work?

$A$ is not defined only for this condition!!
\[ G = H - TS \quad H = U + PV \quad dH = dq + dw + d(PV) \]
\[ = U + PV - TS \]
\[ dG = dH + - TdS - SdT \]
\[ = dq + dw + d(PV) - TdS - SdT \]

At constant temperature,
\[ = TdS + dw_{rev} + d(PV) - TdS = dw_{rev} + d(PV) \]
\[ dw_{rev} = -PdV + dw_{\text{additional}} \]
\[ dG = dw_{rev} + d(PV) = -PdV + dw_{\text{additional}} + PdV - VdP \]

\[ dG = dw_{\text{additional}} - VdP \quad \text{Work function} \]

At constant P and T,
\[ dG = dw_{\text{additional}} \quad \text{Carnot limitation} \]

Decrease in free energy, \( \Delta G \), at constant temperature and pressure corresponds to the maximum work other than the P – V work that the system is capable of doing under reversible conditions.
Conditions of equilibrium

\[
(dS)_U, q \geq 0 \\
(TdS)_U, V \geq 0 \\
(dA)_T, V \leq 0 \\
(dG)_T, P \leq 0
\]
If there is other work in addition to P – V work, 

\[ TdS_{\text{system}} - [dU_{\text{system}} + PdV_{\text{system}} + dw_{\text{other}}] \geq 0 \]

**Combined law**

Now conditions for spontaneity and equilibrium can be found out by subjecting it to various conditions.
G is a function of P and T

\[ G = f(P, T) \]

\[ dG = \left( \frac{\partial G}{\partial P} \right)_T \, dp + \left( \frac{\partial G}{\partial T} \right)_P \, dT \tag{1} \]

\[ G = H - TS \]

\[ = U + PV - TS \]

\[ dG = dU + PdV + VdP - TdS - SdT \]

\[ dU = TdS - PdV \]

\[ dG = VdP - SdT \tag{2} \]

Comparing 1 and 2

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

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

One component system
Variation of $G$ with $T$

\[ (\partial G / \partial T)_P = -S \]
Variation of $G$ with $P$

\[ (\frac{\partial G}{\partial P})_T = V \]
S and V are always positive quantities. G should increase with P at constant temperature and decrease with temperature at constant pressure. For a finite change in free energy at constant temperature,

\[ \int_{P_1}^{P_2} dG = \int_{P_1}^{P_2} V dP \]

For solids and liquids, the volume change will be small and

\[ \Delta G = V \Delta P \]

Such changes in free energy are very small.

For gases, since volume change is large, \( \Delta G \) is large.

\[ \int_{P_1}^{P_2} dG = \int_{P_1}^{P_2} nRT/P \ dP = nRT \ln P_2/P_1 \]

This relation shows that G is (1) extensive and (2) a state function. \( \Delta G \) for a change \( 1 \rightarrow 2 \) is the same whether the change of state is carried out reversibly or irreversibly.

\[ G_m(P) = G^o_m + RT \ln P/P^o \]
Gibbs-Helmholtz equation

$\Delta G_f^\circ$ values predict the feasibility of a reaction at 298 K. $\Delta G$ values at any temperature can be calculated by Gibbs - Helmholtz equation.

$$\Delta G = \Delta H - T\Delta S$$

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

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

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

(1)

$\Delta G$ can be evaluated from emf measurement since $\Delta G = -nFE$

Where $n$ = number of electrons evaluated, $F = $ Faraday, $E = $ potential of the cell. $F= 96500$ Coulombs/gm. equiv.
Divide eqn. 1 by $-T^2$

$$-\Delta G/T^2 + 1/T \left( \partial \Delta G/\partial T \right)_P = -\Delta H/T^2$$

Write $-1/T^2$ as $\partial/\partial T (1/T)$

$$\Delta G \left[ \partial/\partial T (1/T) \right]_P + 1/T \left( \partial \Delta G/\partial T \right)_P = -\Delta H/T^2$$

$$\{UdV + VdU = d(UV)\}$$

$$\left[ \partial/\partial T (\Delta G/T) \right]_P = -\Delta H/T^2$$

Helmholtz equation:

$$\left[ \partial/\partial T (\Delta A/T) \right]_P = -\Delta U/T^2$$