Lecture 7
Clausius Inequality
Assume reversible and irreversible paths between two states. Reversible path produces more work. 
\( dU \) is the same for both the paths.

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

\[
dq_{\text{rev}} - dq = dw - dw_{\text{rev}} \geq 0
\]

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

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

System is isolated.

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

Entropy

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
\[ \Delta S \geq 0, \text{ > sign for a spontaneous process and } = \text{ for equilibrium}. \]

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.

\[ dS_{\text{total}} = dS_{\text{system}} + dS_{\text{surroundings}} \]

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

Consider constant volume:

\[ dS - dU/T \geq 0 \]

\[ TdS \geq dU \] (constant V 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. Entropy is unchanged, for sponteneity, entropy of the surroundings must increase for which U of the system as to decrease.
At constant pressure,
$T \Delta S \geq \Delta H$

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

Interpretations are the same.

The inequalities mean,
$dU - T \Delta S \leq 0$
$dH - T \Delta S \leq 0$

We define,
$A = U - TS$  Helmoltz energy
$G = H - TS$  Gibbs energy
Hermann von Helmholtz
Born: 31 Aug 1821 in Potsdam, Germany
Died: 8 Sept 1894 in Berlin, Germany
\[ dA = dU - TdS \]
\[ dG = dH - TdS \]
\[ (dA)_{T,V} \leq 0 \]
\[ (dG)_{T,P} \leq 0 \]
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,
\[ = TdS + dw_{rev} + d(PV) - TdS = dw_{rev} + d(PV) \]
\[ dw_{rev} = -PdV + dw_{additional} \]
\[ dG = dw_{rev} + d(PV) = -PdV + dw_{additional} + PdV - VdP \]

\[ dG = dw_{additional} - VdP \]

At constant P and T,
\[ dG = dw_{additional} \]

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

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

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

1

\[ G = H - TS \]

\[ = U + PV - TS \]

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

\[ dU = TdS - PdV \]

\[ dG = VdP - SdT \]  

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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 $P$ 

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

\[ \int_{P_1}^{P_2} dG = \int_{P_1}^{P_2} VdP \]

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.

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

\[ = \frac{nRT}{P_1} \ln \frac{P_2}{P_1} \]

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.

\[ G_m(P) = G^0_m + RT \ln P/P^0 \]
Standard free energies

As in the case of H, S etc., only difference in G is significant. Since G is a state function, arithmetic operations can be performed with it. In other words, type of operations performed with H can be performed with G. Hess’s law is valid here too. \( \Delta G \) values can be obtained by knowing standard free energy of formation. Standard free energy is defined as the free energy change accompanying the formation of a compound from the elements; all the reactants and products in their standard states. Any element in the standard state at 298 K has zero free energy.

For a spontaneous reaction, \( \Delta G_f^\circ < 0 \) or for equilibrium \( \Delta G_f^\circ = 0 \) and \( > 0 \) for non-spontaneous process.
Considering the relation, \( \Delta G = \Delta H - T\Delta S \),
For \( \Delta G \) to be negative, both \( \Delta H \) and \( \Delta S \) make significant contribution. Let us consider the four possibilities:

<table>
<thead>
<tr>
<th></th>
<th>( \Delta H )</th>
<th>( \Delta S )</th>
<th>( \Delta G )</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>–ve</td>
<td>+ve</td>
<td>–ve</td>
<td>Spontaneous</td>
</tr>
<tr>
<td>2</td>
<td>+ve</td>
<td>–ve</td>
<td>+ve</td>
<td>Non Spontaneous</td>
</tr>
<tr>
<td>3</td>
<td>–ve</td>
<td>–ve</td>
<td></td>
<td>At low temperature ( T\Delta S ) may be below ( \Delta H ) so that reaction may occur at low temperature.</td>
</tr>
<tr>
<td>4</td>
<td>+ve</td>
<td>+ve</td>
<td></td>
<td>At high temperature, ( T\Delta S ) may be high so that ( \Delta G ) may become negative and the reaction may occur.</td>
</tr>
</tbody>
</table>
Gibb’s 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.

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

$$(\partial G/\partial T)_P = -S$$

$$(\partial \Delta G/\partial T)_P = -\Delta S$$

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

(1)

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

Where $n = \text{number of electrons evaluated}$, $F = \text{Faraday}$, $E = \text{potential of the cell}$. $F = 96500 \text{ Coulombs/gm. equiv.}$
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:

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