Lecture 4

Clausius Inequality

Entropy distinguishes between irreversible and reversible processes.

$$\underset{\text{rev}}{\overset{\text{irrev}}{\Delta S \geq 0}}$$

In a spontaneous process, there should be a net increase in the entropy of the system and the surroundings.

How is this?

For a process to be spontaneous, total entropy change, ΔS_{tot} has to be greater than zero.

$$\Delta S_{tot} = \Delta S + \Delta S_{surr} \geq 0$$

The entropy change of the system is ΔS

To make this change surroundings lost $-q_{irr}$

$$\Delta S - q_{irr} /T > 0$$
$$T\Delta S > q_{irr}$$

For a reversible process $\Delta S - qrev/T = 0$

$$T\Delta S = qrev$$

For an infinitesimal process,

$$TdS \underset{\text{rev}}{\overset{\text{irr}}{\geq}} dq$$

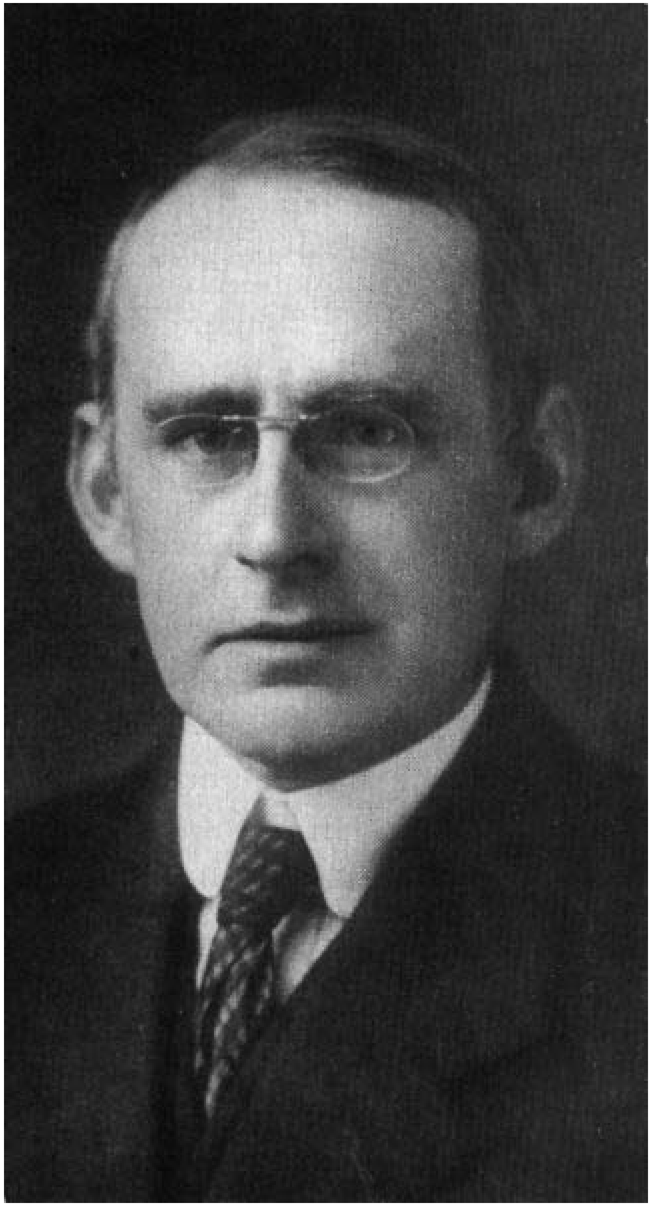
This statement is called the Clausius inequality.

If the system is isolated, $dS \geq 0$

Entropy of an isolated system increases with time

Spontaneous processes entropy increases.

“Entropy is Time’s Arrow”



Arthur Stanley Eddington (1882-1944)

Entropy of the universe increases as a result of every spontaneous process. When the entropy reaches a maximum, an equilibrium state is reached and no further change occurs. Thus Clausius put forward the first and second laws as,

1. Energy of the universe is constant (First Law)
2. Entropy of the universe tends to a maximum (Second Law)

$w_{rev} > w_{irr}$ $T\Delta S\text{system} > q\text{irr}$

$q_{rev} > q_{irr}$ $\Delta S\text{system} > q\text{irr}/T$

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 ΔS for systems and surroundings.

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$$

$$\Delta S \geq 0$$
$$<$$

> Refers to spontaneous = refers to reversible or equilibrium < refers to non-spontaneous processes.

2. Other way is to define entropy change of the system alone.

dStotal = dSsystem + dSsurroundings

dq_{rev} represents heat absorbed by the system and $-dq_{rev}$ is the heat lost by the surroundings.

$dS_{surroundings} = -dq_{rev}/T$

Since entropy of the universe increases,

$$dS_{system} - dq_{rev}/T \geq 0$$

$$TdS_{system} - dq_{rev} \geq 0$$

We know from first law

$$dU_{system} = dq_{rev} - dw_{rev}$$

For P – V work, $dw_{rev} = PdV$

$$dq_{rev} = dU_{system} + PdV_{system}$$

$$TdS_{system} - [dU_{system} + PdV_{system}] \geq 0$$

This relation is in terms of the system variables alone.

If there is other work in addition to P – V work,

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

Combined law

Now conditions for spontaneity and equilibrium can be found out by subjecting it to various conditions.

Conditions:

$TdS_{system} – [dU_{system} + PdV_{system} + dw_{other}] \geq 0$

$TdS_{system} – dq_{rev} \geq 0$

a). Transformation of an isolated system

$$dU = 0,\ dq = 0,\ dS \geq 0$$

b). System at constant U and V

$$dU = 0,\ dV = 0 \quad TdS \geq 0$$

For spontaneous transformation, $TdS > 0$ and for equilibrium, $TdS = 0$.

It is important to note that it is U not T that is constant. When T is kept constant not U, it is possible that $dS \neq 0$ at equilibrium.

Let us consider vaporization of a liquid at a temperature. At equilibrium, ΔS will not be zero since vapour at a given temperature will have more entropy than the liquid since it uses latent heat of vaporization upon evaporation.

Thus it is important to mention $(\Delta S)_{U, V} = 0$ for equilibrium.

c). Constant T and V, dV = 0, dT = 0

$$TdS - dU \geq 0$$

$$d(TS - U) \geq 0 \text{ since } dT = 0$$

$$-d(U-TS) \geq 0$$

Decrease in A has to be positive

$$(dA)_{T, V} \leq 0$$

What is A?

For a thermodynamic reversible isothermal process, $\Delta S = q_{rev}/T$

$$\Delta A = \Delta U - q_{rev}$$

From first law, $\Delta U = q_{rev} - W_{rev}$

$$-W_{rev} = \Delta U - q_{rev}$$

$$\Delta A = -W_{rev} \text{ or } -\Delta A = W_{rev}$$

Decrease in A is equal to the work done by the system.

Since $W_{rev} = W_{max}$, decrease in A is the maximum isothermal work that can be done by the system.

Under constant T and V can the system do work?

A is not defined only for this condition!!

Hermann von Helmholtz

Born: 31 Aug 1821 in Potsdam, Germany

Died: 8 Sept 1894 in Berlin, Germany

Most transformations do not occur at constant volume and

dA is not used as a good criterion.

$$A_1 = U_1 - T_1S_1$$

$$A_2 = U_2 - T_2S_2$$

$$\Delta A = \Delta U - \Delta(TS)$$

Constant T,

$$\Delta A = \Delta U - T\Delta S$$

d). Constant temperature and pressure

$$dT = 0,\ dP = 0$$

$$d(PV) = PdV;\ d(TS) = TdS$$

$$TdS - (dU + PdV) \geq 0$$

$$d(TS) - d\,(U + PV) \geq 0$$

$$U + PV = H$$

$$d(TS) - dH \geq 0$$

$$-d(H - TS) \geq 0$$

$$d(H - TS) \leq 0$$

$H - TS$ is another state function

called Gibbs function or free energy, G

$dG_{T,P} \leq 0$ or $\Delta G_{T,P} \leq 0$

For an irreversible change at constant T and P, $\Delta G < 0$.
For equilibrium, $\Delta G = 0$. Since most of the transformations occur at constant T and P, ΔG is the most useful quantity in defining equilibrium.

$\Delta G = \Delta H - \Delta(TS)$

At constant temperature and pressure,

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

$\Delta G = \Delta U + P\Delta V - T\Delta S$

$\Delta U - T\Delta S = \Delta A$

$\Delta G = \Delta A + P\Delta V$

$-\Delta A = Wmax$

$-\Delta G = -\Delta A - P\Delta V$

$= Wmax - P\Delta V$

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

$$(dS)_{U,\ q} \geq 0$$

$$(TdS)_{U,\ V} \geq 0$$

$$(dA)_{T,\ V} \leq 0$$

$$(dG)_{T,\ P} \leq 0$$

G is a function of P and T

$$G = f(P, T)$$

$$dG = (\partial G/\partial P)_T\, dp + (\partial G/\partial T)_P\, dT \qquad 1$$

$$G = H - TS$$

$$= U + PV - TS$$

$$dG = dU + PdV + VdP - TdS - SdT$$

$$dU = TdS - PdV$$

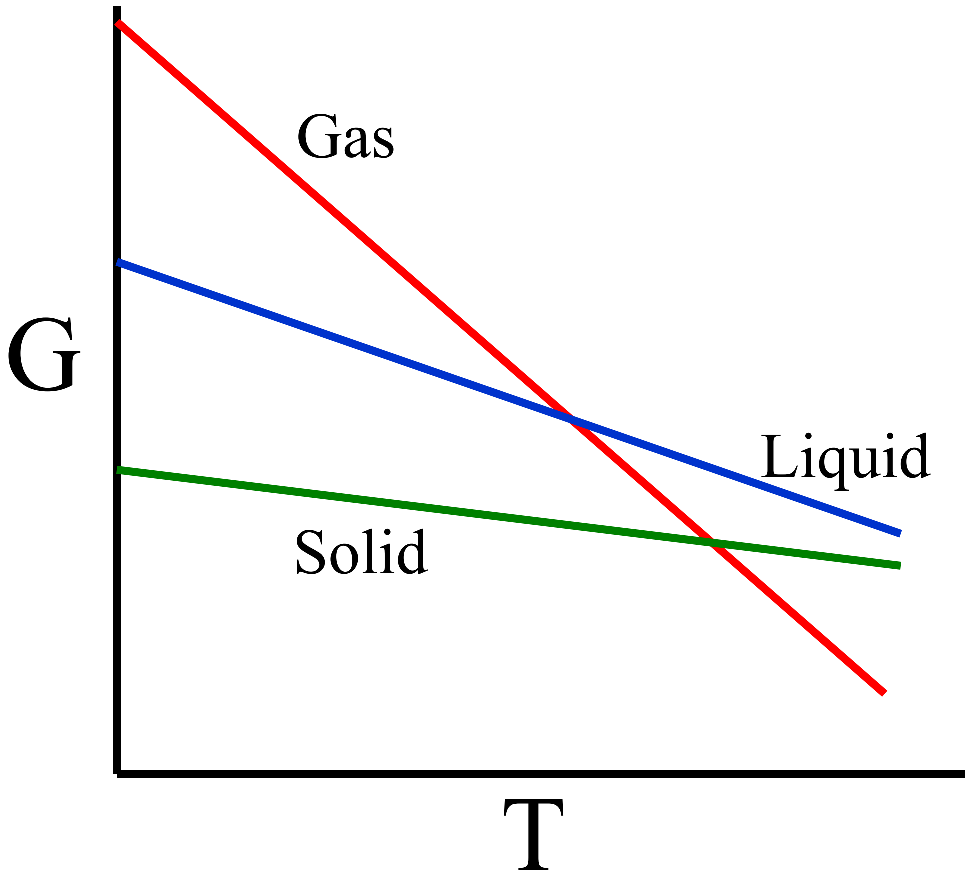
$$dG = VdP - SdT \qquad 2$$

Comparing 1 and 2

$$(\partial G/\partial P)_T = V$$

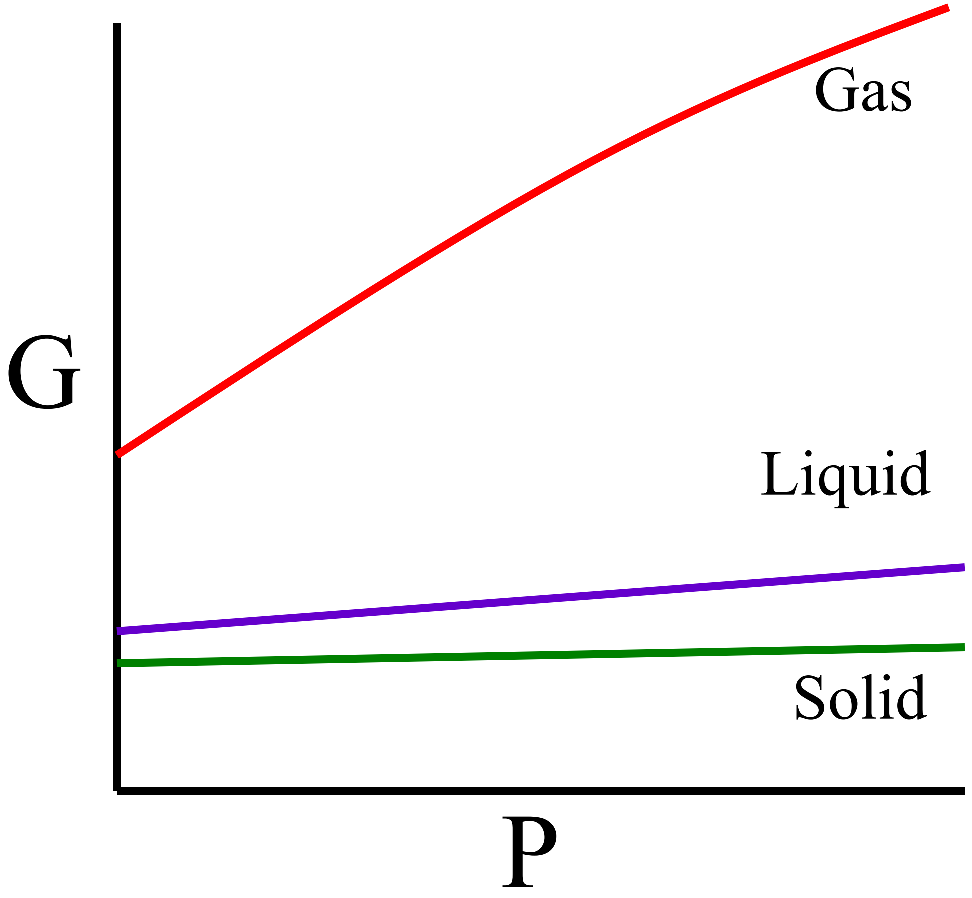
$$(\partial G/\partial T)_P = -S$$

Variation of G with T



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

Variation of G with P



$$\left(\partial G / \partial P\right)_T = V$$

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,

$$\int_{P1}^{P2} dG = \int_{P1}^{P2} VdP$$

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, ΔG is large.

$$\int_1^2 dG = \int_1^2 nRT/P\, dP$$

$$= nRT \ln P_2/P_1$$

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

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. ΔG 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 ΔG to be negative, both ΔH and ΔS make significant contribution. Let us consider the four possibilities:

	ΔH	ΔS	ΔG	Comment
1	–ve	+ve	–ve	Spontaneous
2	+ve	–ve	+ve	Non Spontaneous
3	–ve	–ve		At low temperature $T\Delta S$ may be below ΔH so that reaction may occur at low temperature.
4	+ve	+ve		At high temperature, $T\Delta S$ may be high so that ΔG may become negative and the reaction may occur.

Gibb’s Helmoholtz equation

ΔG_f° values predict the feasibility of a reaction at 298 K.
ΔG values at any temperature can be calculated by
Gibbs - Helmholtz equation.

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

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

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

$$\Delta G = \Delta H + T\,(\partial \Delta G/\partial T)_P \qquad (1)$$

ΔG 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 $-T^2$

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

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

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

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

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

Helmholtz equation:

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