

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.

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

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

$$dq_{\text{rev}}/T \geq dq/T$$

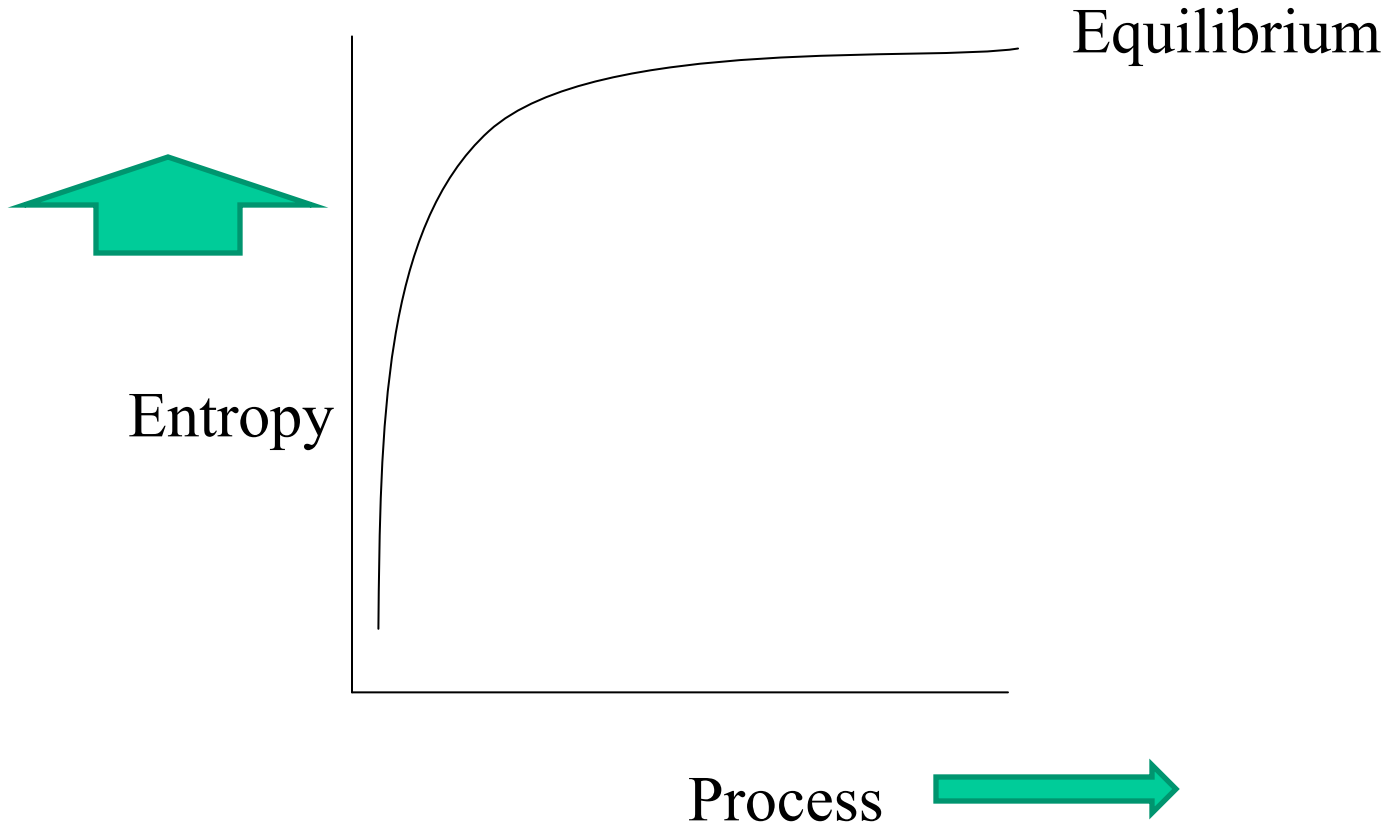
$$dS \geq dq/T$$

Clausius inequality

System is isolated.

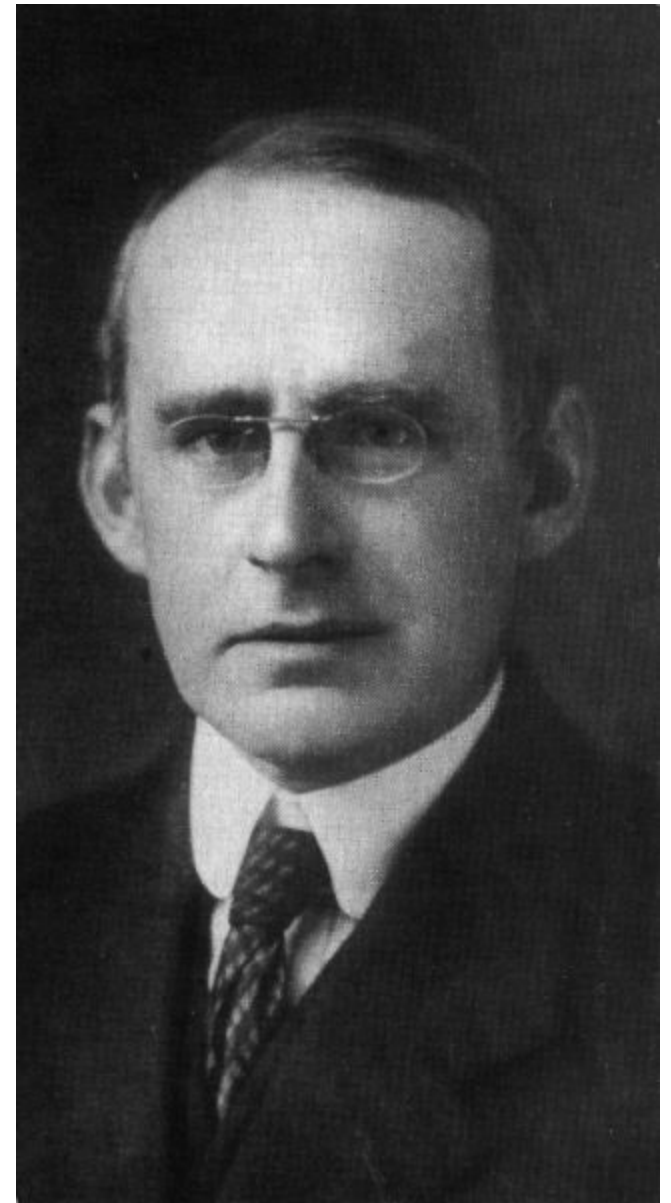
$$dS \geq 0$$

Clausius inequality



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 ΔS 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:

$$dS - dU/T \geq 0$$

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

At constant U or at constant S, the expression is:

$$1. dS_{U,V} \geq 0 \quad 2. dU_{S,V} \leq 0$$

Criterion of spontaneity 1. is the common statement of second law.

2. Entropy is unchanged, for spontaneity, entropy of the surroundings must increase for which U of the system as to decrease.

At constant pressure,
 $TdS \geq dH$

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

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

$$dA = dU - TdS$$

$$dG = dH - TdS$$

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

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

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_{\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,

$$dG = dw_{additional}$$

Work function

Free energy

Decrease in free energy, ΔG , 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

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

$$dG = \left(\frac{\partial G}{\partial P}\right)_T dp + \left(\frac{\partial G}{\partial T}\right)_P dT \quad 1$$

$$G = H - TS$$

$$= U + PV - TS$$

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

$$dU = TdS - PdV$$

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

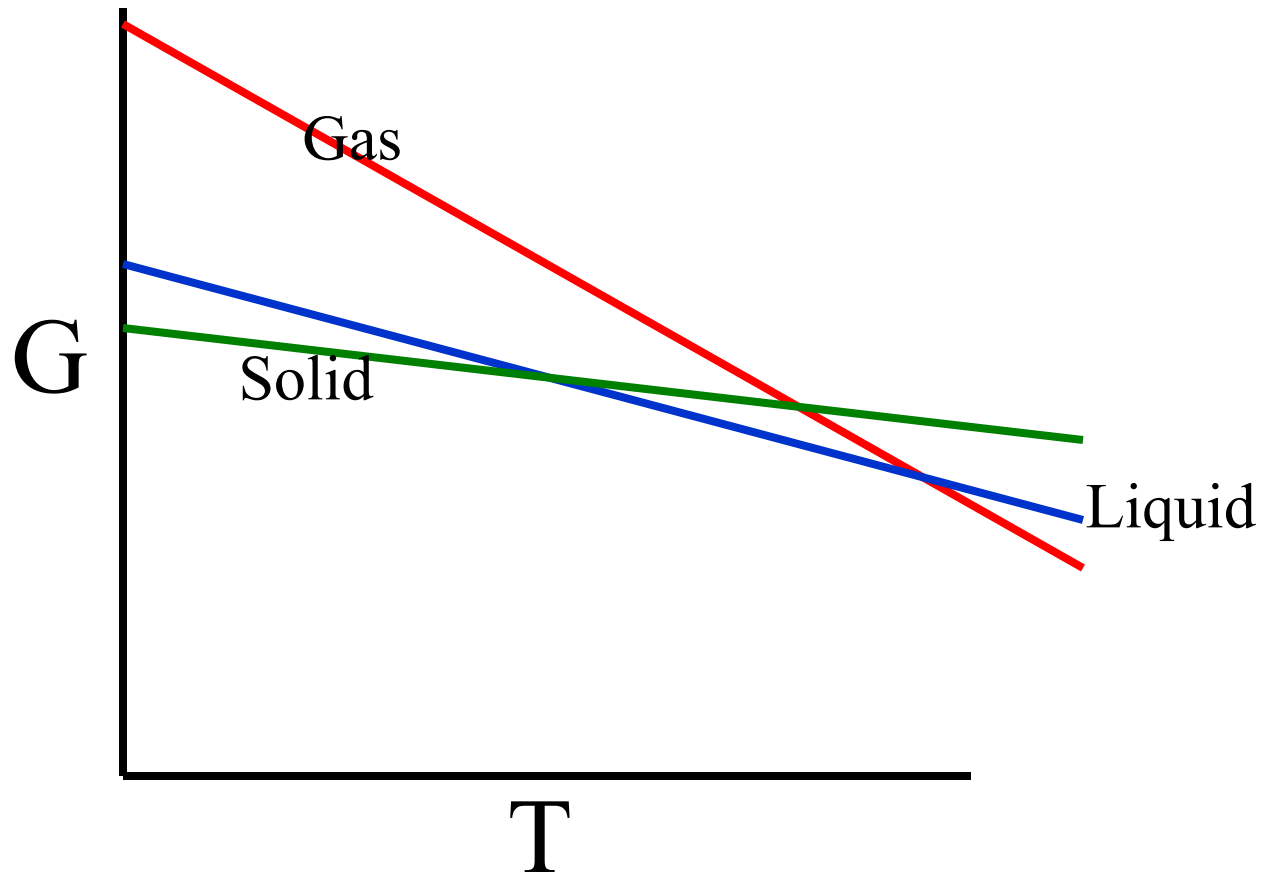
Comparing 1 and 2

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

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

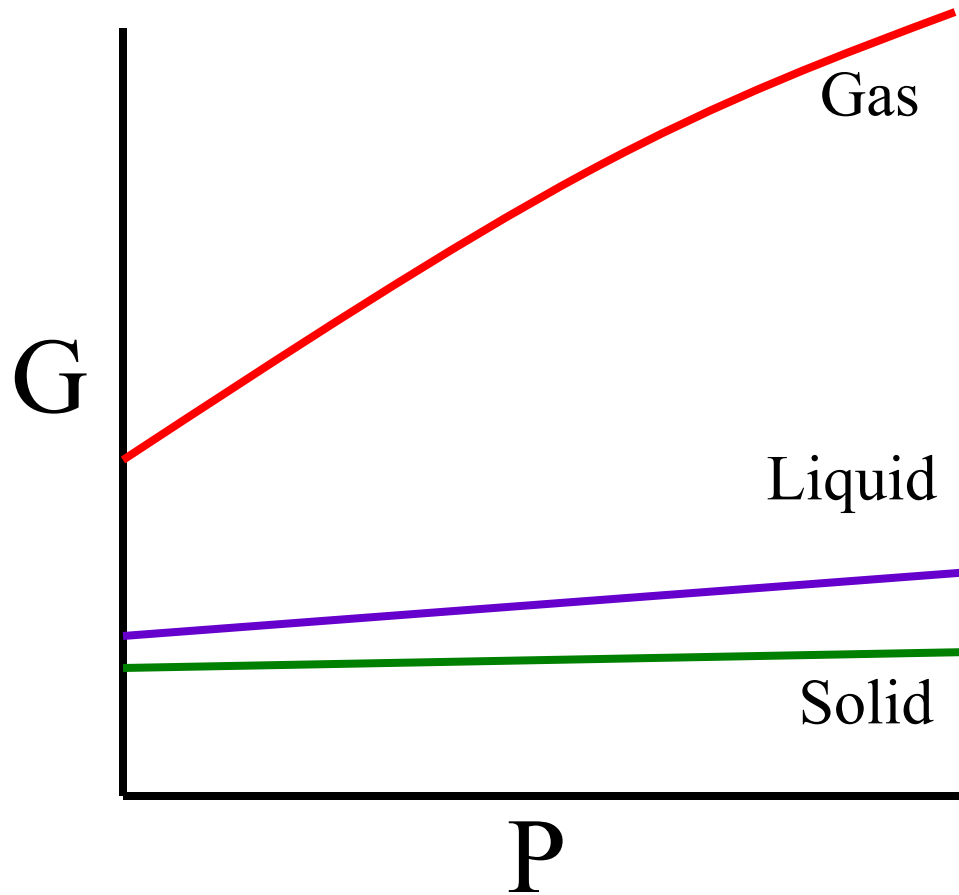
One component system

Variation of G with T



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

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,

$$\int_{P_1}^{P_2} dG = \int_{P_1}^{P_2} V dP$$

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

$$\Delta G = V\Delta P$$

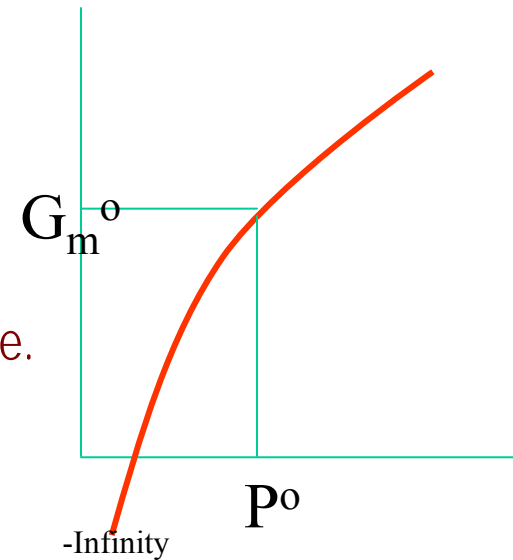
Such changes in free energy are very small.

For gases, since volume change is large, ΔG is large.

$$\begin{aligned} \int_1^2 dG &= \int_1^2 nRT/P dP \\ &= nRT \ln P_2/P_1 \end{aligned}$$

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.

$$G_m(P) = G_m^0 + RT \ln P/P^0$$



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. 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 Helmholtz 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.

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

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

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

$$\Delta G = \Delta H + T (\partial \Delta G/\partial T)_p \quad (1)$$

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:

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