

Lecture 3

Clausius Inequality

Assume reversible and irreversible paths between two states.
Reversible path produces more work.
 dU is the same for both the paths.

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

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

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

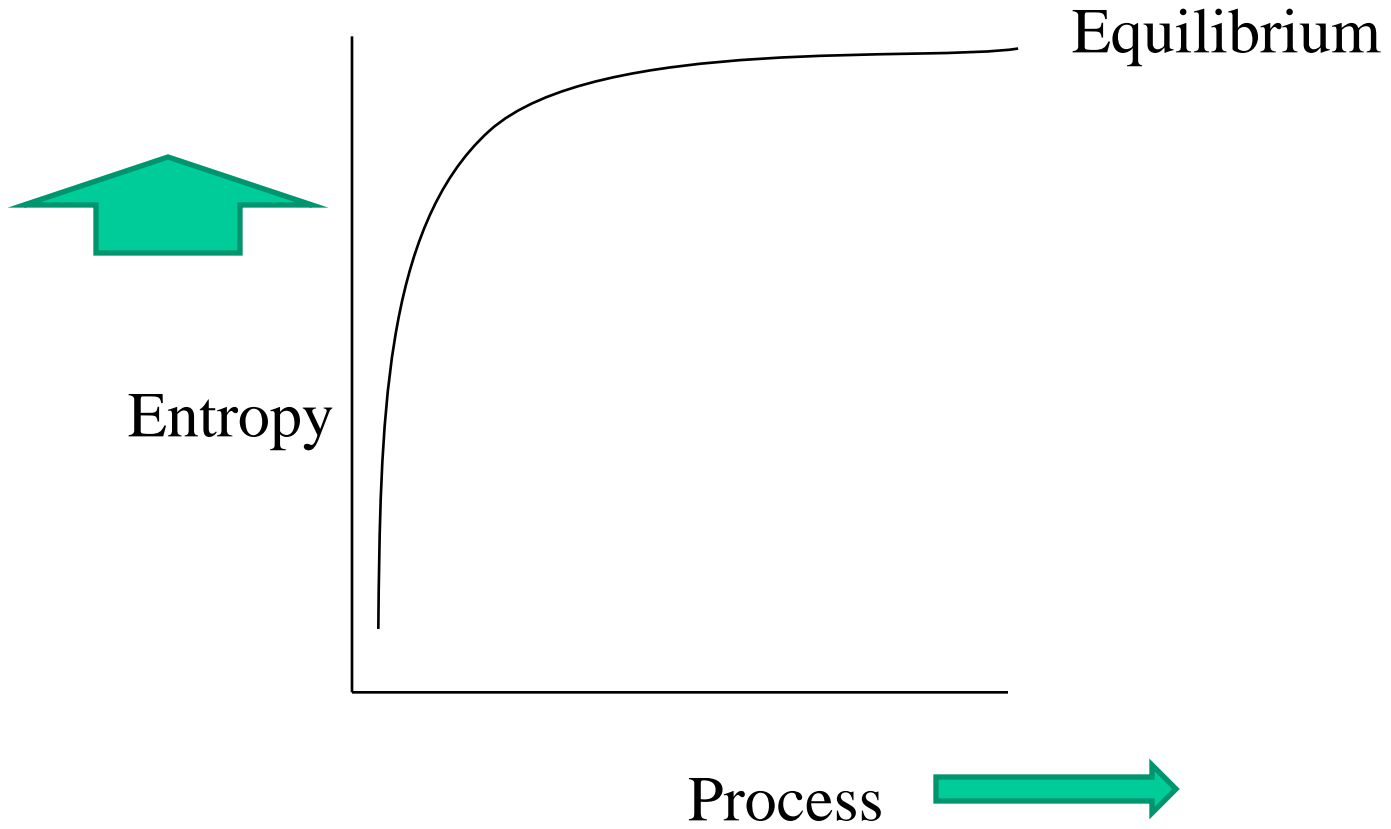
$$dS \geq dq/T$$

Clausius inequality

System is isolated.

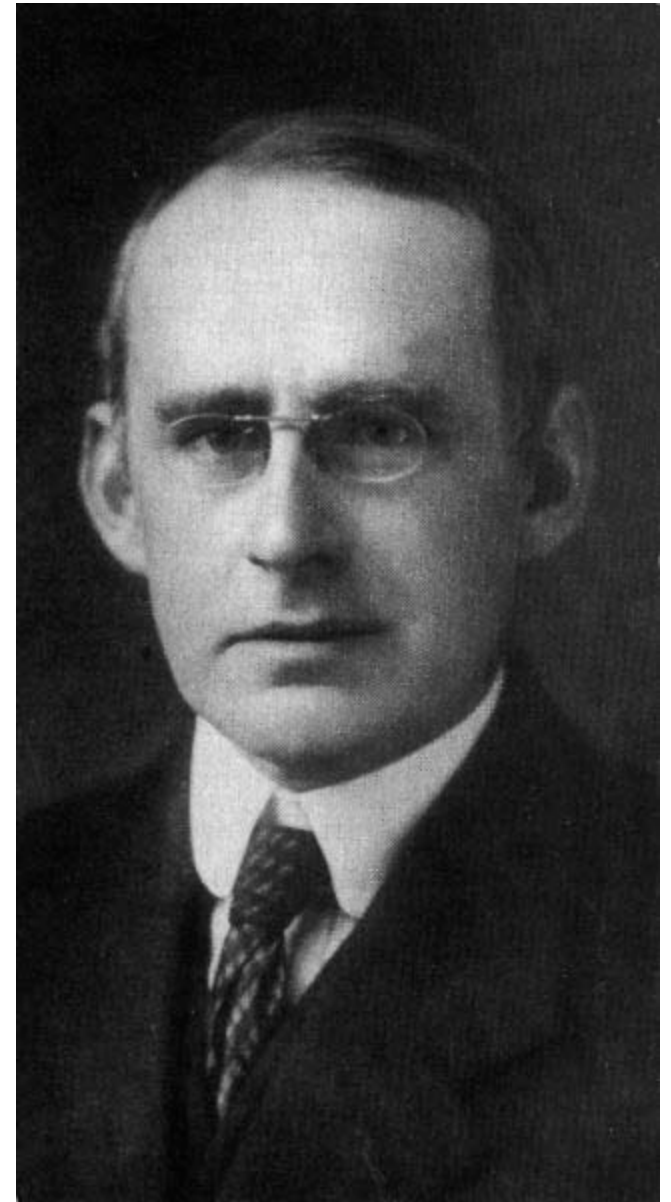
$$dS \geq 0$$

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

$$dA = dU - TdS$$
$$dG = dH - TdS$$

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



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_{\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,

$$= TdS + dw_{\text{rev}} + d(PV) - TdS = dw_{\text{rev}} + d(PV)$$

$$dw_{\text{rev}} = -PdV + dw_{\text{additional}}$$

$$dG = dw_{\text{rev}} + d(PV) = -PdV + dw_{\text{additional}} + PdV - VdP$$

$$dG = dw_{\text{additional}} - VdP$$

At constant P and T,

$$dG = dw_{\text{additional}}$$

Carnot limitation

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

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

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

$$G = H - TS$$

$$= U + PV - TS$$

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

$$dU = TdS - PdV$$

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

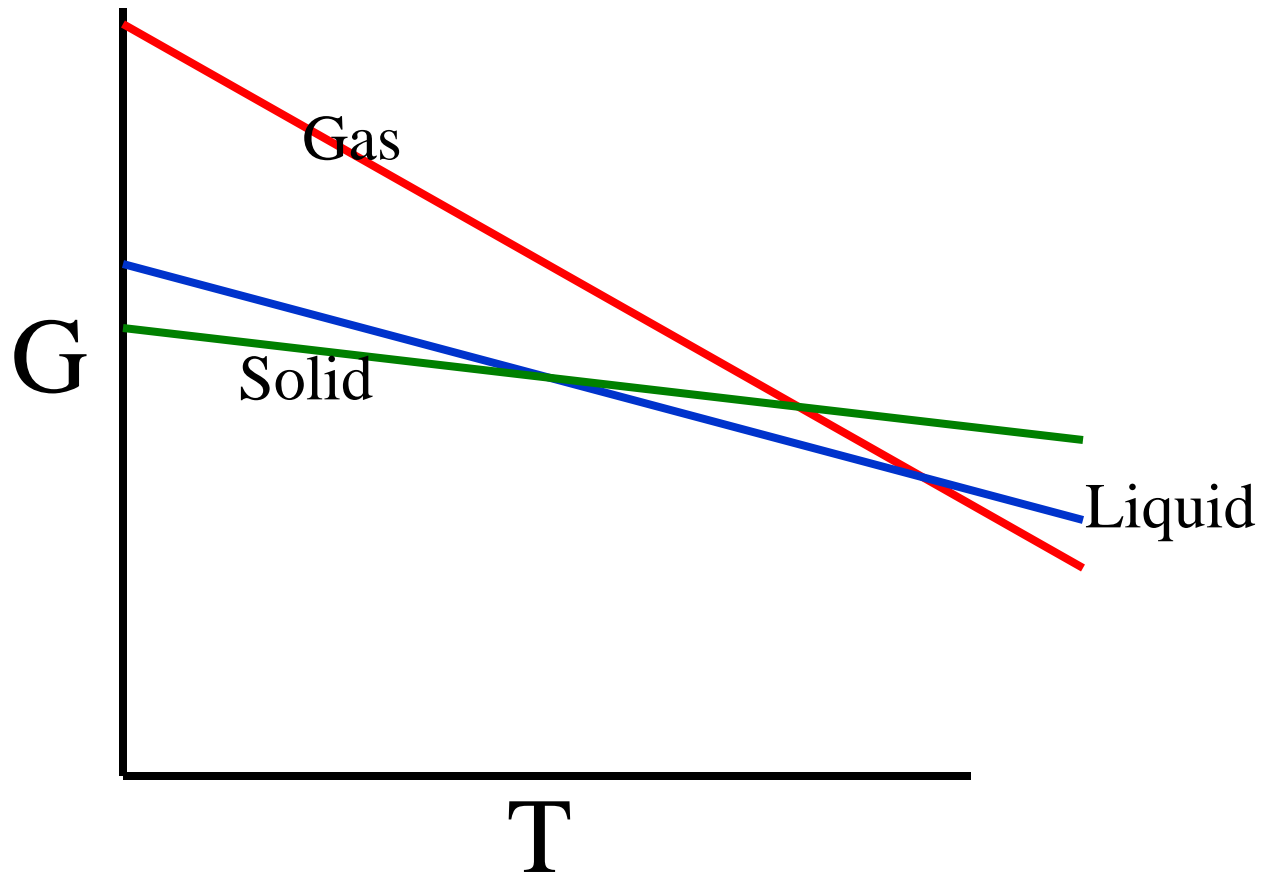
Comparing 1 and 2

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

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

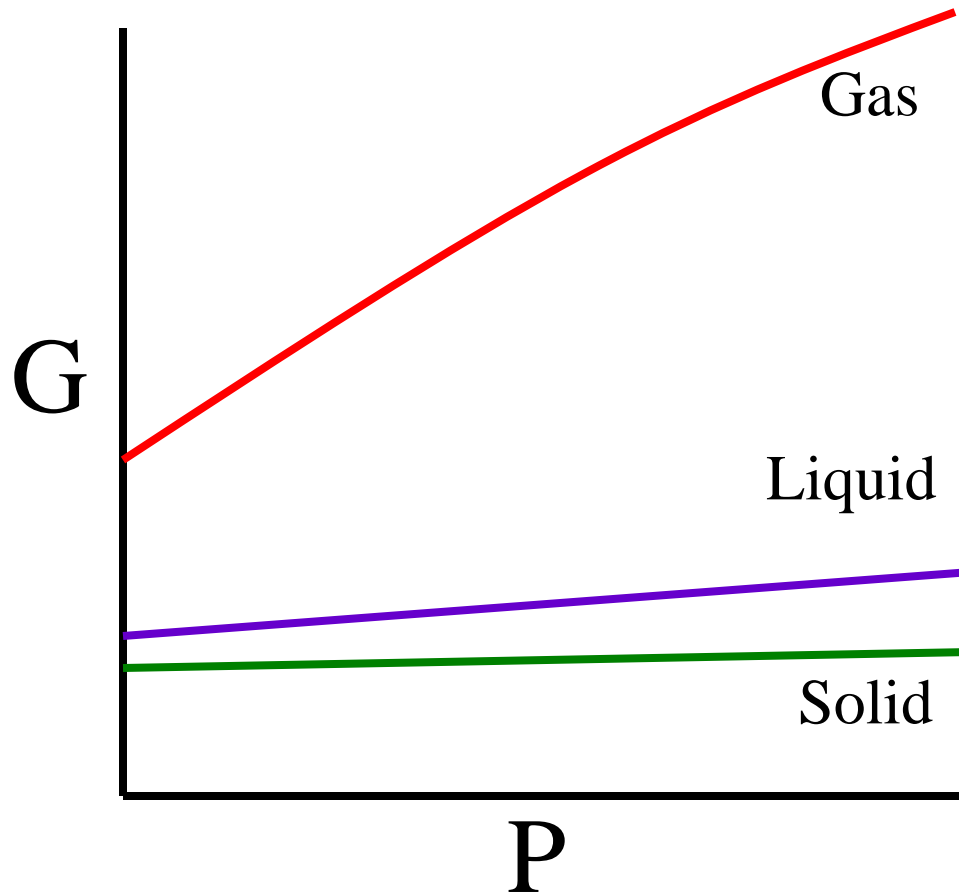
One component system

Variation of G with T



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

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

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

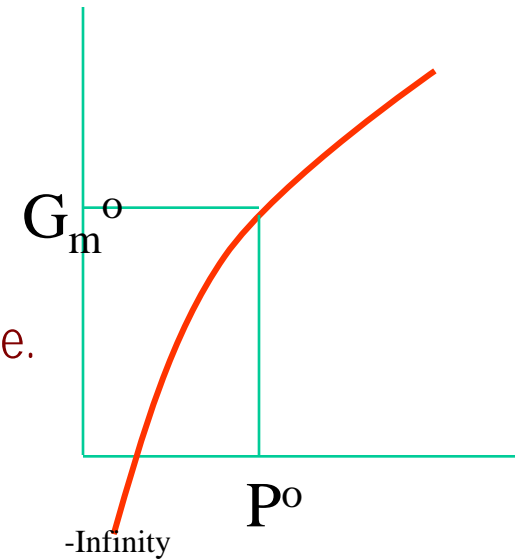
Such changes in free energy are very small.

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.

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



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:

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