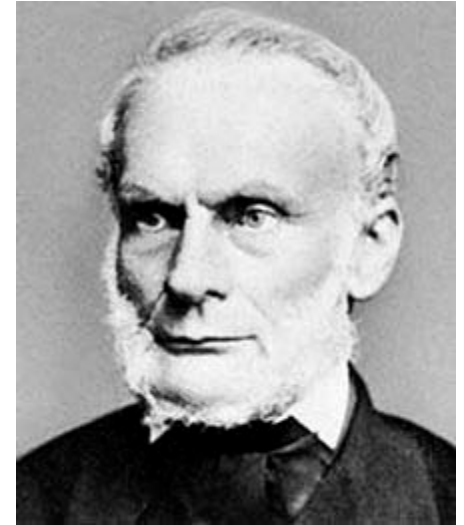


# Lecture 3

## Clausius Inequality



**Rudolf Julius Emanuel Clausius**  
2 January 1822 – 24 August 1888

Defined Entropy

Greek, en+trophein *content transformative* or *transformation content*

The energy of the universe is constant.

The entropy of the universe tends to a maximum  
1865

Assume reversible and irreversible paths between two states.

Reversible path produces more work.

$dU$  is the same for both the paths.

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

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

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

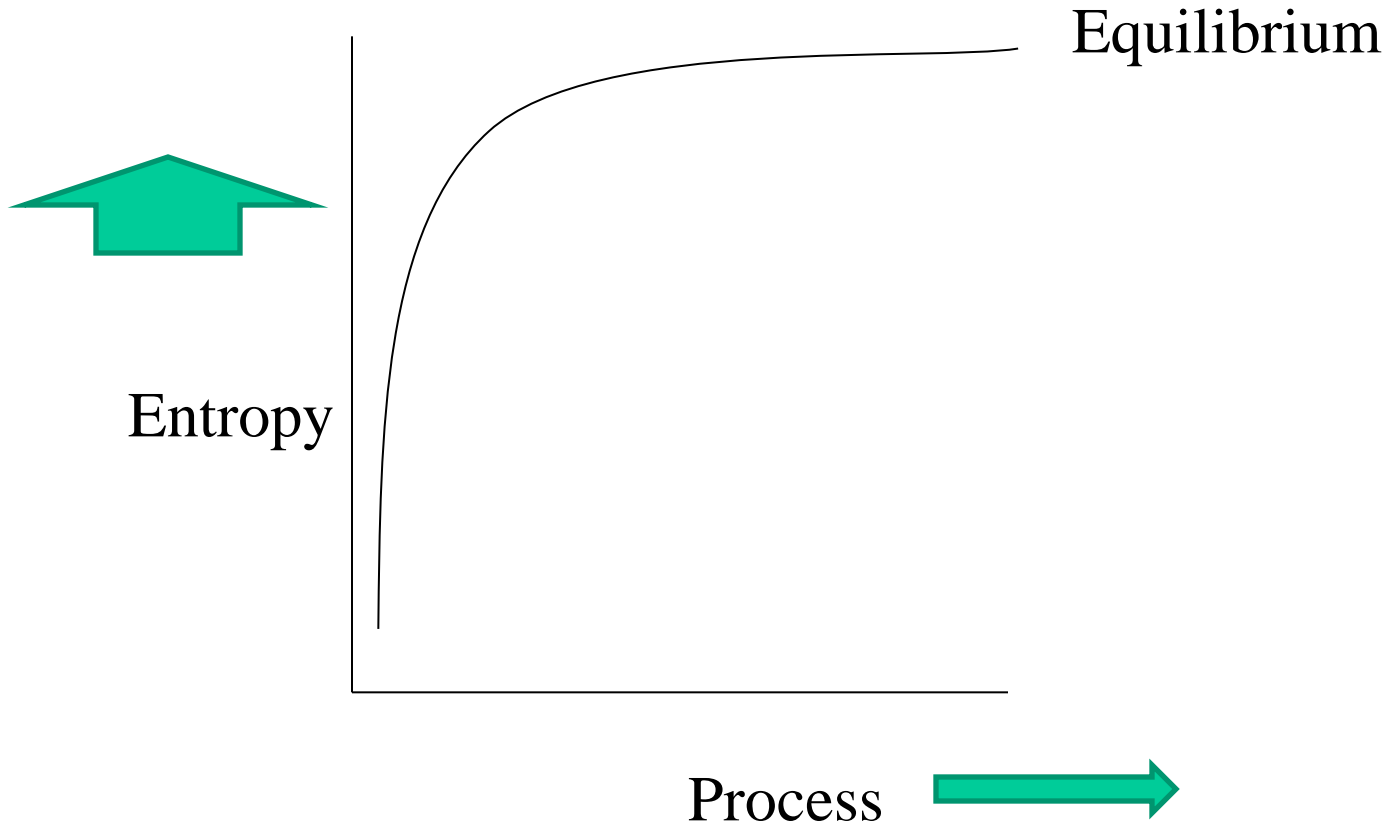
$$dS \geq dq/T$$

Clausius inequality

System is isolated.

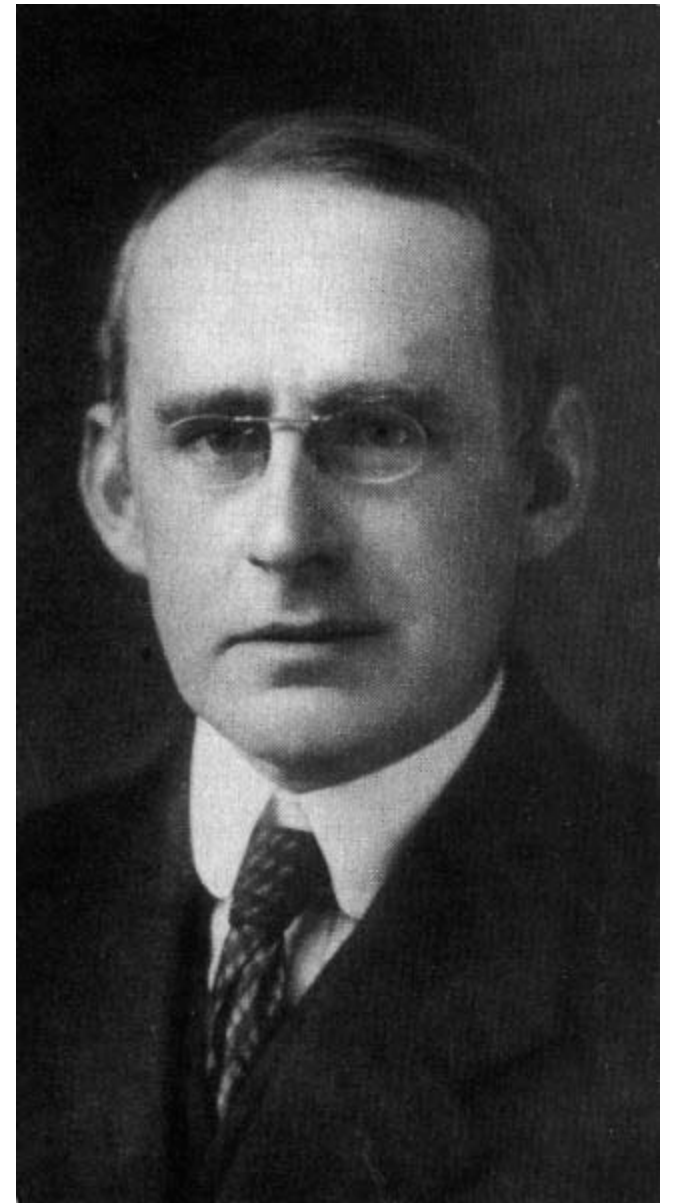
$$dS \geq 0$$

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  $\Delta S$  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:

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

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

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!!**

$$G = H - TS \qquad H = U + PV \qquad dH = dq + dw + d(PV)$$

$$= U + PV - TS$$

$$dG = dH - TdS - SdT = dq + dw + d(PV) - TdS - SdT$$

$$\text{At constant } T, dG = dq + dw + d(PV) - TdS$$

When the change is reversible,  $dw = dw_{\text{rev}}$ ,  $dq = dq_{\text{rev}} = TdS$

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

$$dw_{\text{rev}} = -PdV + dw_{\text{additional}} \quad \text{System can do work other than PdV also}$$

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

**Work function**

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

**Free energy**

Here work done by the system is taken as expansion work,  $-PdV$

$$\text{At constant } P \text{ and } T, dG = dw_{\text{additional}}$$

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.

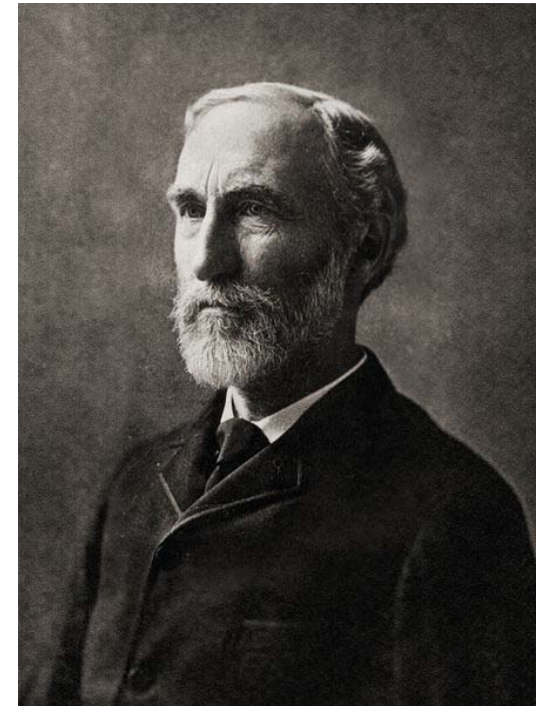
# Conditions of equilibrium

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

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

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

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



Josiah Willard Gibbs

February 11, 1839 – April 28, 1903

G is a function of P and T

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

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

$$G = H - TS$$

$$= U + PV - TS$$

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

$$dU = TdS - PdV$$

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

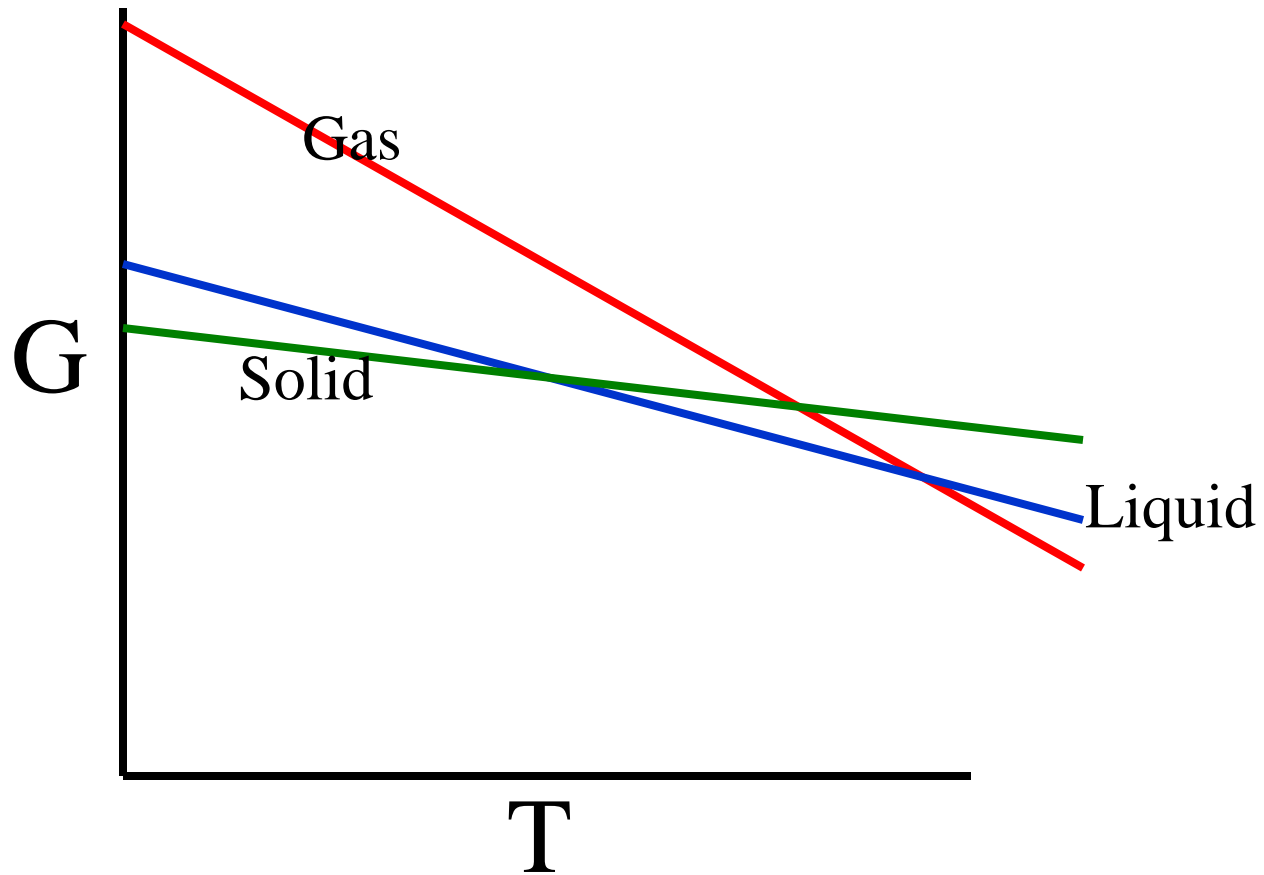
Comparing 1 and 2

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

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

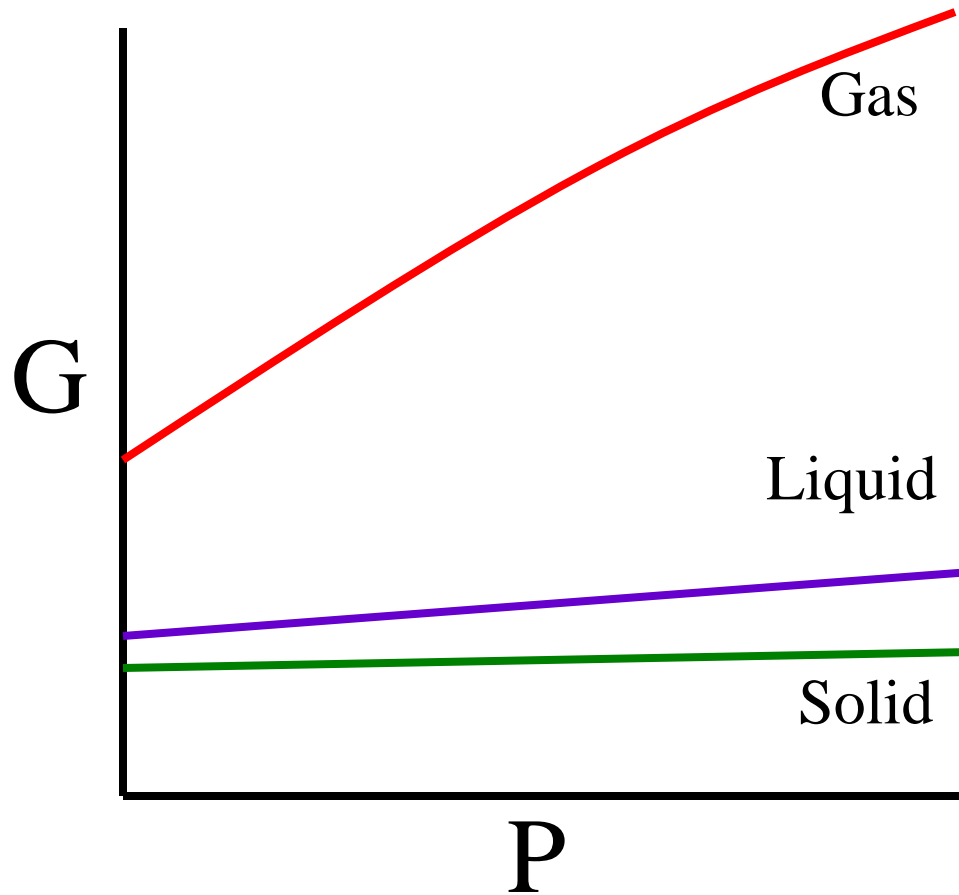
One component system

# Variation of G with T



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

# Variation of G with P



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

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

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

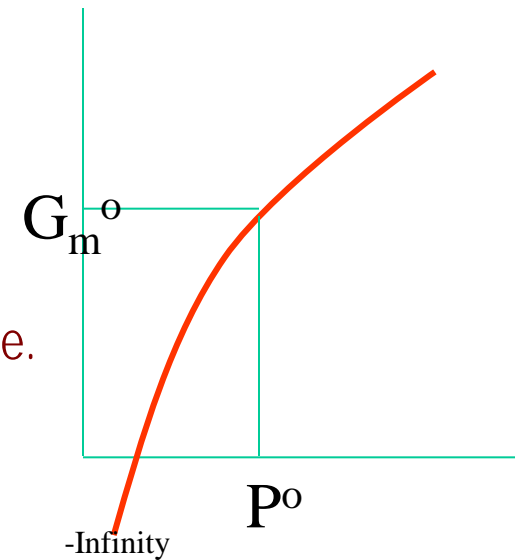
Such changes in free energy are very small.

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

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

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

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



# 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.

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

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

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

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

$\Delta G$  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  $-T^2$

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

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:

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