

# Statistical Mechanics

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## 1 Early points on THERMODYNAMICS

A reversible transformation is quasi-static but reverse may not be true.

An irreversible transformations can not be represented in some sort of graphs with thermodynamic parameters.

It is more efficient to heat an ideal gas by keeping the volume constant than keeping the pressure constant, as  $C_p > C_v$ . Also, intuitively, we can see that at constant volume, no work is done, thus all heat energy increases the internal energy.

Entropy :  $\int_a^b \frac{dQ}{T} \leq S(b) - S(a)$

Note: Equality holds for the reversible process!

The entropy of a thermally isolated system never decreases!

Irreversibility is generally "Wasteful", and is marked by an increase of the entropy of the total system under consideration.

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

$$TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$$

$$TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$$

$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$  - coefficient of thermal expansion

$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$  - isothermal compressibility

$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$  - adiabatic compressibility

$$C_V = \frac{TV\alpha^2\kappa_S}{(\kappa_T - \kappa_S)\kappa_T}$$

$$C_P = \frac{TV\alpha^2}{\kappa_T - \kappa_S}$$

$$A = U - TS$$

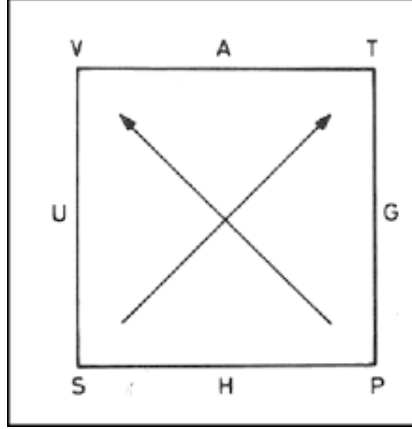
$$G = H - TS$$

For an isothermal transformation from one state to another:  $W \leq -\Delta A$ . Equality holds for reversible process.

For a mechanically isolated system kept at constant temperature, the Helmholtz energy never increases.

On Corollary, for a mechanically isolated system kept at constant temperature, the state of equilibrium is the state of minimum Helmholtz free energy

For a system kept at constant temperature and pressure, the state of equilibrium is the state of minimum Gibbs potential



$$dU = TdS - PdV \implies \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$dA = -SdT - PdV \implies \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$dH = TdS + VdP \implies \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$dG = -SdT + VdP \implies -\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

Now, the second law of thermodynamics, can not tell us about the system at  $T=0$ . It requires that in reversible process  $dQ = TdS$ . Hence at  $T=0$ ,  $dQ=0$ ; thus no reversible way to heat it to higher temperature. Thus we cannot construct Carnot engine with lower reservoir at  $T = 0$ .

Now, this brings the need of "Third Law of Thermodynamics". It states that "The entropy of a system at absolute zero is a universal constant, which at be taken to be zero".

Now, we cannot compare two different quantities or states entropy directly, as they from different sheets in PVT graph. Therefore, they must be related from their absolute zero temperature state.

Upon calculation we reach at:

$$dT = \left(\frac{V\alpha}{C_P}\right)TdP$$

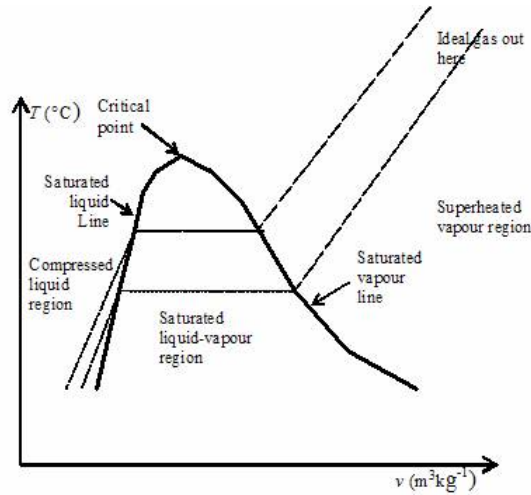
Thus, the unavailability of absolute zero can be said as an alternative of third law of thermodynamics.

## 2 Phase Transitions

When a certain mass of liquid is converted into gas, the total volume of the system expands, although P and T remain unchanged; is known as "First-Order Transition."

For first-order transition: Clapeyron-Equation is as follows:

$$\frac{dP(T)}{dT} = \frac{\Delta s}{\Delta v} = \frac{l}{T\Delta v}$$



Supersaturation:

Sometimes, while liquefying the gas, by compression keeping the temperature constant; the gas-liquid mixture gets supersaturated, instead of getting a constant vapour Pressure  $P_{infinity}$ . Pressure gets increased.

What happens is that, the state which is reached is not in stable equilibrium, but self-sustained. It contains a gas-liquid mixture, in which if there are more droplets of reduced radius, then the pressure increases. The stable form of vaporizing point is achieved when all the droplets combine to form of an infinite size. The equation of pressure is as follows:

$$P_r(T) = P_{infinity} \exp\left(\frac{2\sigma m}{\rho k T r}\right)$$

Same thing goes with super cooling of liquid.

Osmotic Pressure:

Entropy of Mixing:  $-n_1 R \log\left(\frac{n_1}{n_0}\right)$

For Boiling point of solution: Pressure reduces by  $\Delta P_{vapor} = \frac{\rho' n_1 RT}{\rho n_0 v_0}$  for the same temperature.

and temperature increases by  $\Delta T = \frac{T n_1 RT}{n_0 l}$  for same pressure.

where  $n_0$  is for the solvent and  $n_1$  is for the solute.