

Spontaneous Process: A process that proceeds on its own, without any external help

Non-spontaneous Process: The reverse process that does not proceed on its own.

Criteria for Spontaneity:

Spontaneous change is one-way @ unidirectional.

For Spontaneous Process time is not a factor.

Spontaneous process will continue till equilibrium.

In equilibrium it will not undergo further spontaneous change, if it was left undisturbed.

Spontaneous process is accompanied by decrease in internal energy ^(or) and enthalpy (ΔH)

Reason for spontaneous change is the tendency of energy and matter to become disordered.

The measure of the disorder is called Entropy "S".

Energy loss in system = Energy gain in surrounding

[Reason 1st law of TD].

2nd Law of TD

The entropy of an Isolated System tends to increase.

$$\Delta S = \frac{q_{rev}}{T}$$

" Change in entropy of a substance = energy transferred as heat to it reversibly divided by the temp. at which the transfer takes place

(i) Reversible transfer of heat
[Smooth, uniform]

(ii) Heat and not work.

[Heat \Rightarrow disorder work \Rightarrow orderly]

(iii) Temp in denominator.

$\alpha + 1 \Rightarrow$ less significant

$1 + 1 \Rightarrow$ more significant

Entropy \Rightarrow state fn.

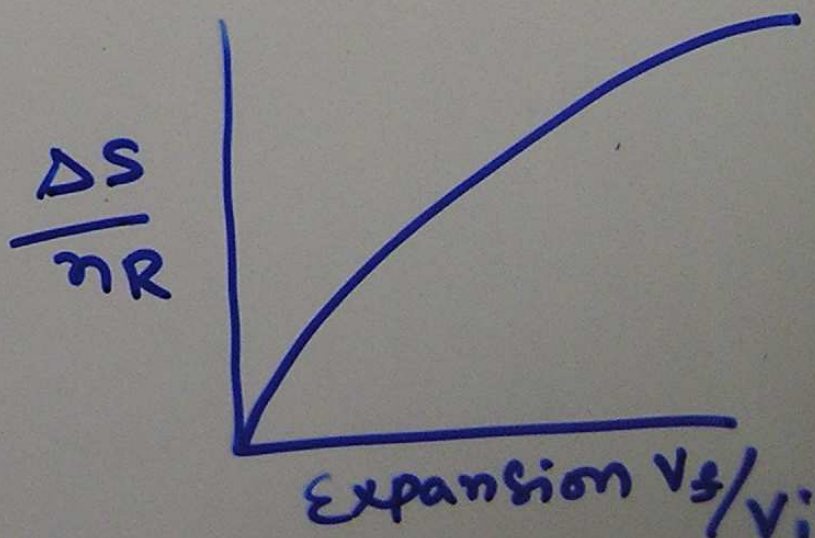
$$q_{\text{rev}} = nRT \ln \frac{V_f}{V_i} \quad [\text{Isothermal Perfect gas}]$$

$$\Delta S = \frac{nRT \ln \frac{V_f}{V_i}}{T} = nR \ln \frac{V_f}{V_i}$$

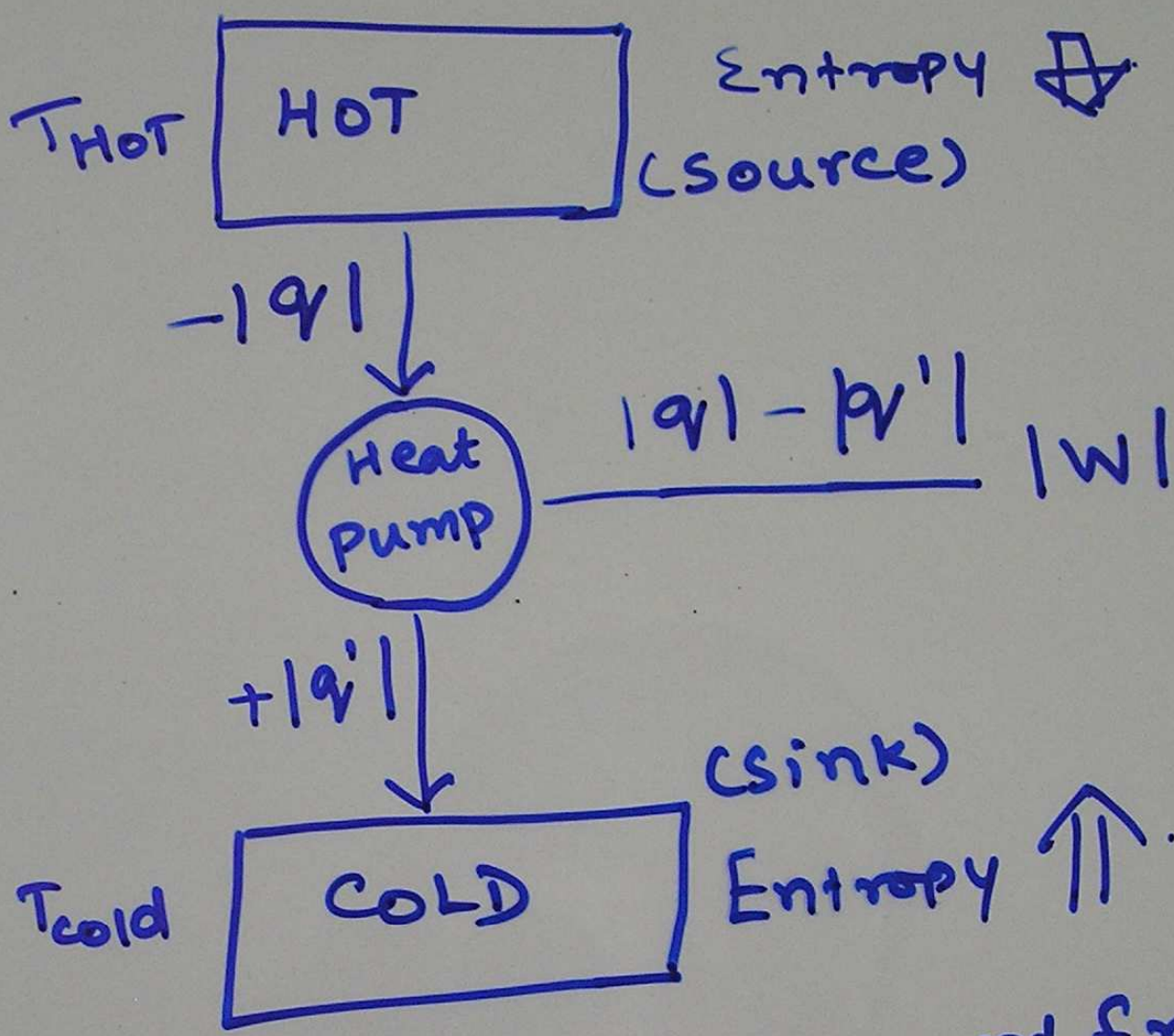
$$V_f > V_i \Rightarrow \frac{V_f}{V_i} > 1 \Rightarrow \Delta S +ve$$

[randomness increases]

Expansion \Rightarrow
higher ΔS



Heat Engine.



$-|q| \rightarrow$ heat removed from source
 $+|q'| \rightarrow$ heat supplied to sink

$$\Delta S_{total} = \frac{-|q|}{T_{HOT}} + \frac{|q'|}{T_{cold}}$$

$\Delta S = -ve$ (non-spontaneous)

when $\Delta S = 0$ when $|q'| = \frac{T_{cold}}{T_{HOT}} \times |q|$

Energy given to sink $|q'|$

$$\therefore \text{maximum work expected} = |q| - |q'|$$

$$\text{Efficiency } \Sigma = \frac{\text{work Produced}}{\text{heat absorbed}}$$

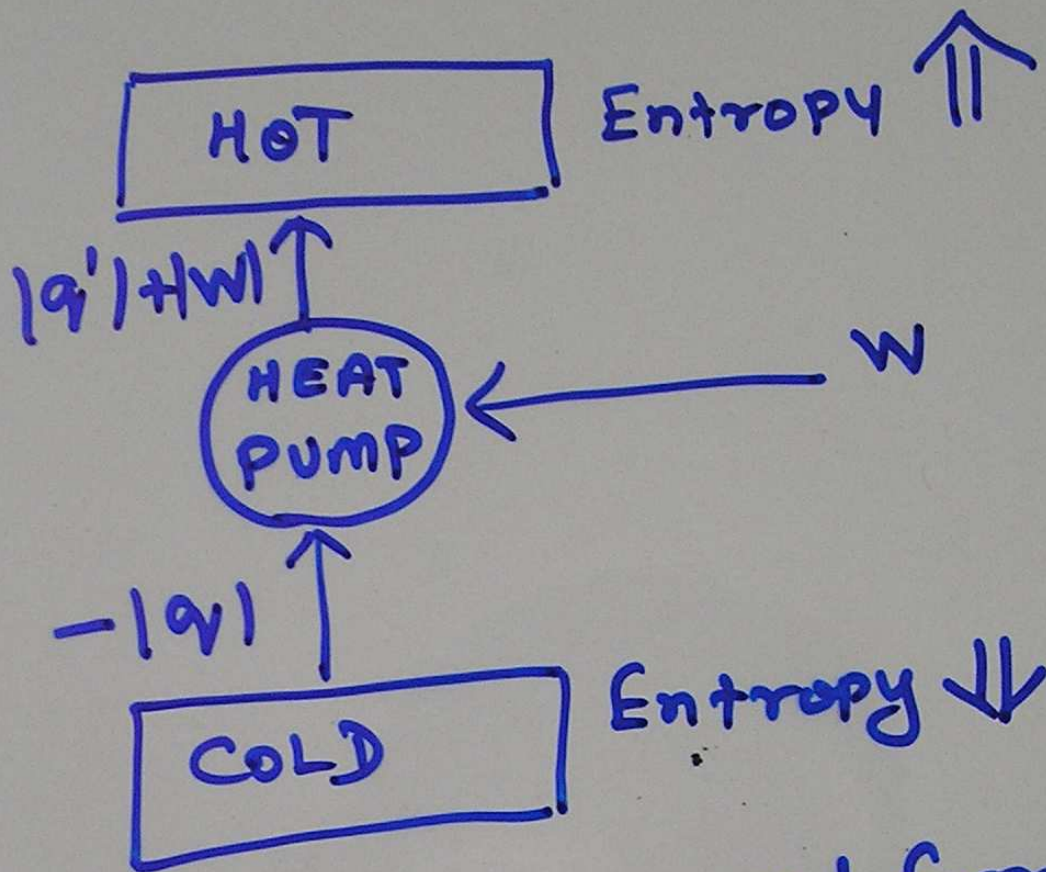
$$= \frac{|q| - |q'|}{|q|} = 1 - \frac{|q'|}{|q|}$$

$$\therefore |q'| = \frac{T_{\text{cold}} \times |q|}{T_{\text{HOT}}}$$

$$\Sigma = 1 - \frac{T_{\text{cold}} \times \frac{|q|}{|q|}}{T_{\text{HOT}}}$$

$$= 1 - \frac{T_{\text{cold}}}{T_{\text{HOT}}}$$

Refrigerator



$-|q|$ - heat removed from sink
 $|q'|$ - heat/Energy given to
outside surroundings

$\Delta S = -ve$ Engine will not
operate

So work needs to be done.

$$\Delta S = c \ln \frac{T_f}{T_i}$$

c - heat capacity of the system

Entropy of fusion

$$\Delta_{\text{fus}} S = \frac{\Delta_{\text{fus}} H(T_f)}{T_f}$$

The change of entropy per mole of substance, at the melting temp. T_f is given above

Enthalpy (H) of Entropy (S) of fusion is $\frac{\Delta_{\text{fus}} H(T_f)}{T_f}$

$$\Delta_{\text{vap}} S = \frac{\Delta_{\text{vap}} H(T_b)}{T_b}$$

T_b - boiling temp.

Trouton's Rule: " $\Delta_{\text{vap}} S$ " is approximately same for all liquids except when hydrogen bonding (or) other molecular interactions are present.

H_2O - Hydrogen bonding.

Hg - metallic bonding.

Entropy change in the surroundings

$$\Delta S_{\text{sur}} = \frac{q_{\text{sur, rev}}}{T}$$

at constant pre. [surroundings]

$$q_{\text{sur, rev}} = \Delta H_{\text{sur}}$$

∴ "H" is a state function

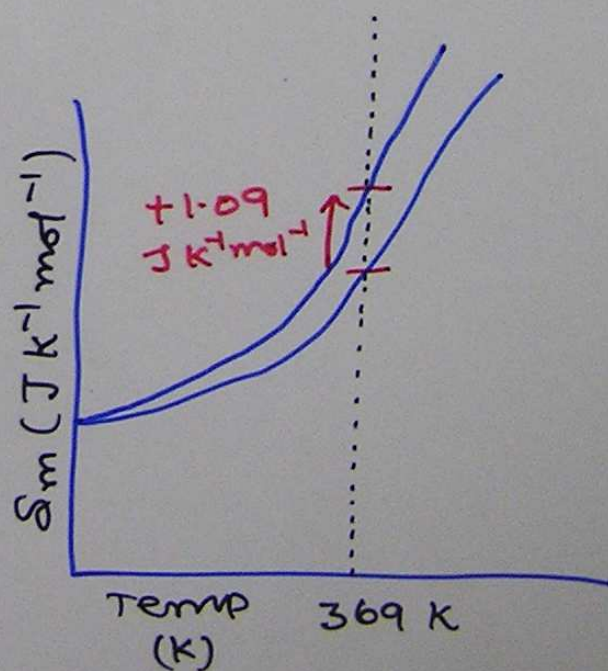
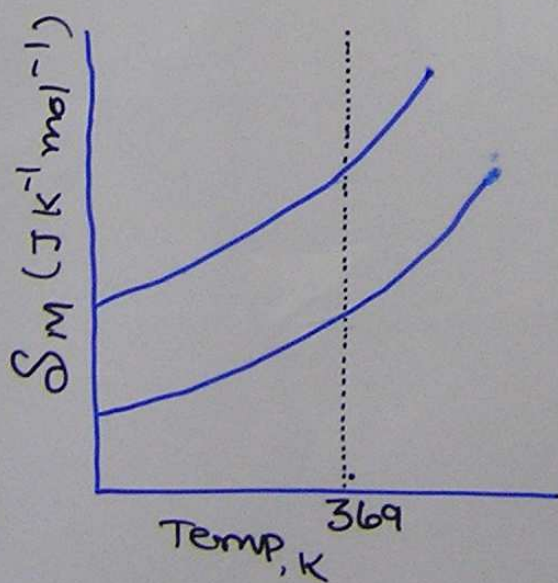
$$\Delta S_{\text{sur}} = \frac{q_{\text{sur}}}{T}$$

Energy supplied to surrounding = $-q$

$$\Delta S_{\text{sur}} = \frac{-q}{T} \quad (\text{or}) \quad \frac{-\Delta H}{T}$$

For exothermic process $\Delta H = -ve$

∴ $\Delta S = +ve$.

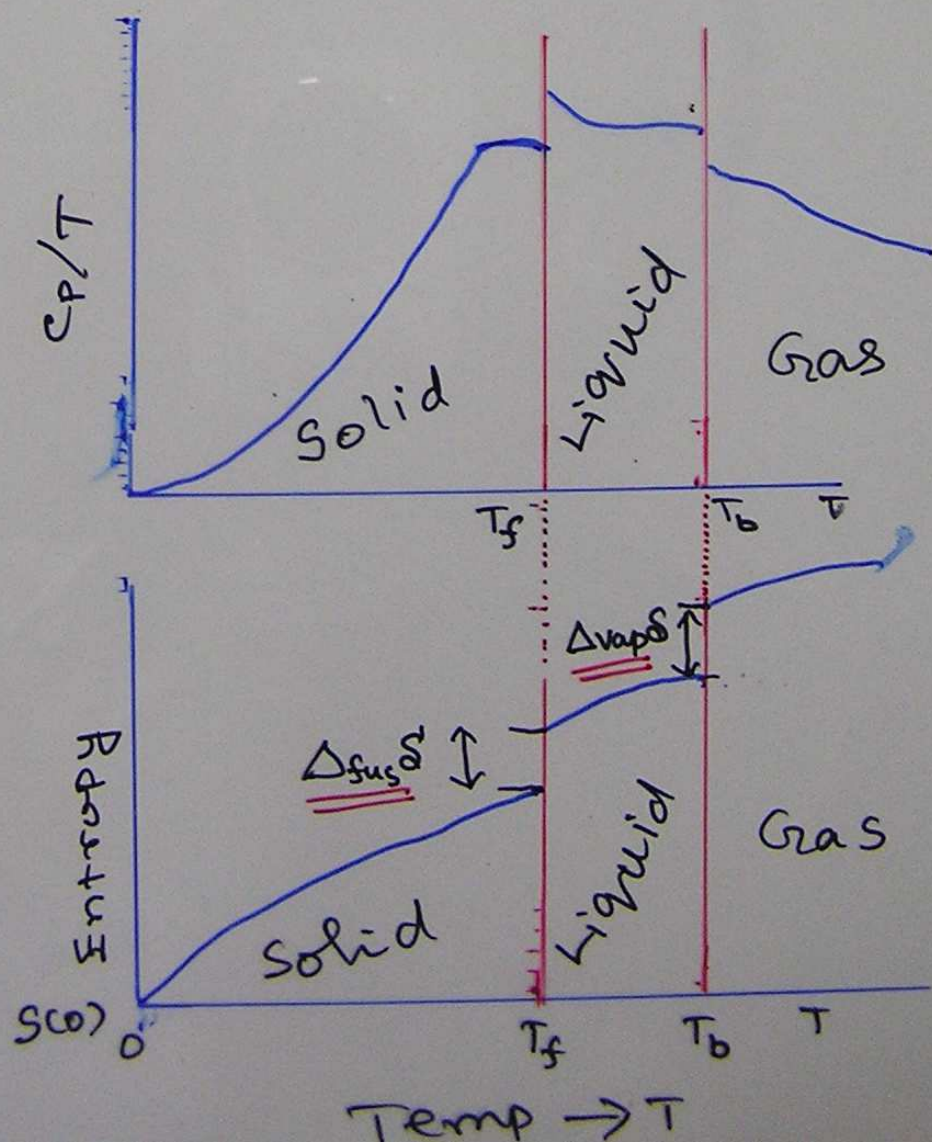


S_m of monoclinic and rhombic Sulphur

When temp is reduced molecular motion also reduces. So the disorderness also reduces. For a crystalline substance all atoms occupy defined location. In other words $S = 0$ when $T = 0$.

The entropies of all perfectly crystalline substances are the same at $T = 0$.

\Rightarrow Entropy at zero temp. is zero for all perfectly ordered crystalline material.



For non-metallic substance. Debye T^3 -law

At temp close to $T=0$

$$C_{v,m} = a T^3 \quad [a - \text{constant}]$$

$$\Rightarrow S_m(T) = \frac{1}{3} C_{v,m}(T)$$

molar entropy at temp 'T' = one third of the constant vol heat capacity at that temp.

$$\Delta S = S_m(T_f) - S_m(T_i) = \int_{T_i}^{T_f} \frac{C_{v,m}}{T} dT$$

when $T=0$ $S=0$

$$\therefore S_m(T) = \int_0^T \frac{a T^3}{T} dT = a \int_0^T T^2 dT$$

$$= a \frac{1}{3} T^3 = \frac{1}{3} a T^3$$

$$= \frac{1}{3} a [C_{v,m}(T)]$$

Standard Reaction entropy $\Delta_r S^\ominus$

$$\Delta_r S^\ominus = \sum \nu S_m^\ominus(\text{Products}) - \sum \nu S_m^\ominus(\text{reactants})$$

Spontaneity of chemical reaction.

consider "S" of both system & surroundi

$$\Delta_r S_{\text{sur}} = - \frac{\Delta_r H}{T}$$

$$\Delta_r S_{\text{total}} = \Delta_r S_{\text{system}} + \Delta_r S_{\text{sur.}}$$

Gibbs Energy.

$$\Delta_r S_{\text{total}} = \Delta_r S_{\text{sur}} + \Delta_r S_{\text{sus}}$$

$$\Delta S_{\text{total}} = \Delta S_{\text{sus}} + \Delta S_{\text{sur}}$$

For Spontaneous Process at constant
Pre. and vol. we can use "H" instead of "S"

$$\Delta S_{\text{total}} = \Delta S - \frac{\Delta H}{T} (\Rightarrow \text{Surrounding})$$

Assume

$$G = H - TS$$

G - Gibbs energy.

at constant temp

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

$$\Delta S_{\text{total}} = \frac{T \Delta S - \Delta H}{T}$$

$$T \Delta S_{\text{total}} = T \Delta S - \Delta H$$

$$T \Delta S = T \Delta S_{\text{total}} + \Delta H$$

$$\Delta G = \Delta H - [T \Delta S_{\text{total}} + \Delta H]$$

$$\Delta G = -T \Delta S_{\text{total}}$$

at constant
Pre & temp

In a spontaneous change at constant temp and pressure, the Gibbs energy decreases.

The value of ΔG for a process gives the maximum non-expansion work that can be extracted from the process at constant temp and pre.

Ex. non expansion work - electrical, mechanical, electrochemical, biological etc.

At constant temp and pre.

$$\Delta G = w'_{\max} \text{ [non-expansion work]}$$

H - enthalpy \Rightarrow measure of energy in the form of heat.

S - entropy \Rightarrow amount of energy stored in random motion.
 TS \rightarrow

$$\text{Total Energy (H)} - \text{random Energy (TS)} = \text{Gibbs energy.}$$

Gibbs energy = energy stored in orderly motion.