

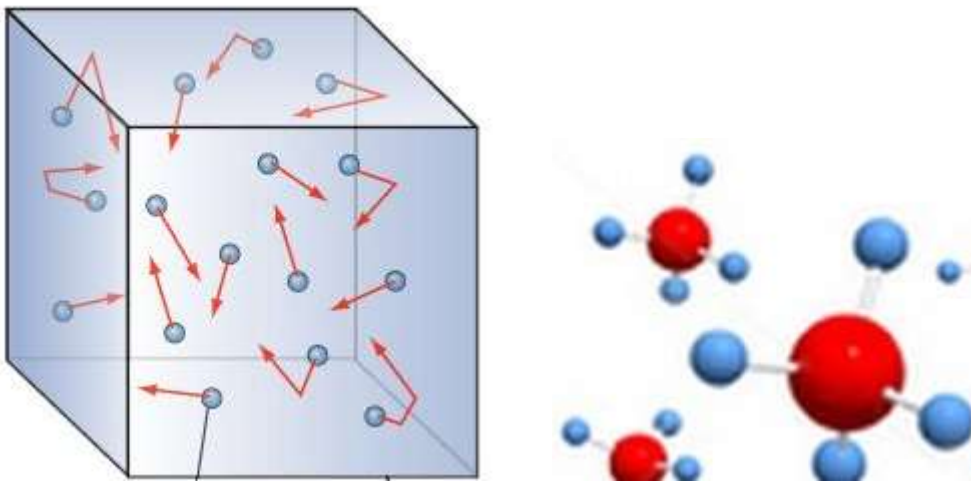


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Topic:

Second law and Entropy, Carnot's cycle & theorem, Entropy changes in reversible & irreversible processes, Entropy-temperature diagrams, Enthalpy, Gibbs, Helmholtz and Internal Energy functions.

2nd Law of Thermodynamics



Frequently Asked Questions & Numerical:

Solved Problems and Problems in exercise of Heat & Thermodynamics, Author A. B. Gupta, H.P Roy, Published by: Books & Allied Pvt. Ltd. (2018)

References:

i. *Heat & Thermodynamics, Author A. B. Gupta, H.P Roy, Published by: Books & Allied Pvt. Ltd. (2018)*

Link to Audio visual Lectures (e-Lectures) given by Distinguish Professors of Foreign Universities:

- i. https://www.youtube.com/watch?time_continue=2&v=i-bo0DoWqgA&feature=emb_title
- ii. <https://www.youtube.com/watch?v=RXo9SShMHvE>
- iii. https://www.youtube.com/watch?v=aDXBo0FtALA&list=PLwdnzlV3ogoVnCnIfjDHng_8biZSUEYtK



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Change in Entropy of 1 mole of ideal gas from (P_1, V_1, T_1) to (P_2, V_2, T_2)

① In terms of volume (V) and Temperature (T)

⇒ we have, $dQ = Tds$ &

$$dQ = du + p dv$$

$$dQ = C_v dT + p dv$$

∴ $Tds = C_v dT + p dv$

$$\Rightarrow ds = \frac{C_v dT}{T} + \frac{p}{T} dv$$

$PV = RT$
 $\frac{p}{T} = \frac{R}{V}$

$$\Rightarrow ds = C_v \frac{dT}{T} + R \frac{dv}{V}$$

Integrating,

$$\int_{S_1}^{S_2} ds = C_v \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{V_1}^{V_2} \frac{dv}{V}$$

$$\Rightarrow \Delta S = S_2 - S_1 = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

For isothermal changes, $dT = 0 \therefore T_1 = T_2$

$$\therefore S_2 - S_1 = \Delta S = R \ln \frac{V_2}{V_1}$$

Also for isochoric changes, $dv = 0 \therefore V_1 = V_2$

$$\therefore \Delta S = C_v \ln \frac{T_2}{T_1}$$

② In terms of pressure (P) & temperature (T)

$$ds = \frac{dq}{T} = \frac{du + p dv}{T}$$

$$\Rightarrow ds = C_v \frac{dT}{T} + \frac{p dv}{T}$$

$$\Rightarrow ds = C_v \frac{dT}{T} + \frac{RdT - v dp}{T}$$

$$\Rightarrow ds = (C_v + R) \frac{dT}{T} - R \frac{dp}{p}$$

We have,
 $PV = RT$
 $Pdv + v dp = R dT$
 $Pdv = R dT - v dp$
Since $PV = RT$
 $V/T = R/P$
& $C_p - C_v = R$
 $C_v + R = C_p$



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Integrating.

$$\int_{S_1}^{S_2} dS = C_p \int_{T_1}^{T_2} \frac{dT}{T} - R \int_{P_1}^{P_2} \frac{dP}{P}$$

$$\Rightarrow \Delta S = S_2 - S_1 = C_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

for isothermal changes $\Delta S = -R \ln \frac{P_2}{P_1} = R \ln \frac{P_1}{P_2}$

for isobaric changes $\Delta S = C_p \ln \frac{T_2}{T_1}$

(3) In terms of volume and pressure.

we know that $\Delta S = S_2 - S_1 = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$

$$= C_v \ln \frac{T_2}{T_1} + (C_p - C_v) \ln \frac{V_2}{V_1}$$

$$= C_p \ln \frac{V_2}{V_1} + C_v \ln \left(\frac{T_2}{T_1} \cdot \frac{V_1}{V_2} \right)$$

$$= C_p \ln \frac{V_2}{V_1} + C_v \ln \frac{P_2}{P_1}$$

$$\therefore \boxed{S_2 - S_1 = C_p \ln \frac{V_2}{V_1} + C_v \ln \frac{P_2}{P_1}}$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\frac{P_2}{P_1} = \frac{T_2 V_1}{T_1 V_2}$$

for isobaric process $\Delta S = C_p \ln \frac{V_2}{V_1}$

for isochoric process $\Delta S = C_v \ln \frac{P_2}{P_1}$



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Change in Entropy of Vanderwall's gas

We have to consider 1 mole of Vander wall's gas from state (T_1, V_1, T_1) to (T_2, V_2, T_2)

$$\text{we have. } dq = T ds$$

$$dq = du + pdv \\ = C_v dT + P dv$$

$$\therefore ds = C_v \frac{dT}{T} + \frac{P}{T} dv$$

$$\Rightarrow ds = C_v \frac{dT}{T} + R \frac{dv}{v-b}$$

$P(v-b) = RT$
from 1st approximation

Integrating we get,

$$\int_{s_1}^{s_2} ds = C_v \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{V_1}^{V_2} \frac{dv}{v-b}$$

$$\Rightarrow \boxed{\Delta S = (S_2 - S_1) = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2 - b}{V_1 - b}}$$

Entropy of a gas mixture:

We have, $dq = C_v dT + P dv$ — from 1st law

$dq = T ds$ — from 2nd law.

$$ds = \frac{dq}{T} = C_v \frac{dT}{T} + \frac{P}{T} dv$$

$$\Rightarrow ds = C_v \frac{dT}{T} + R \frac{dv}{v}$$

Integrating. $S = C_v \ln T + R \ln v + K$

$$= C_v \ln T + R \ln \left(\frac{RT}{P} \right) + K$$

$$= C_v \ln T + R \ln (T/P) + C$$

Here $C = K + R \ln R = \text{Constant}$.



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Let us consider the mixture of n_1 moles of first gas with n_2 moles of second gas

Then entropy of the gas mixture

$$S = n_1 [C_{v1} \ln T + R \ln (T/p_1) + c_1] + n_2 [C_{v2} \ln T + R \ln (T/p_2) + c_2]$$

Here C_{v1} & C_{v2} are the specific heat at constant volume of the two gases.

p_1 & p_2 are the partial pressure of the two gases

$$\left. \begin{aligned} \text{where } p_1 &= \frac{n_1}{n_1+n_2} P \\ p_2 &= \frac{n_2}{n_1+n_2} P \end{aligned} \right\} p_i = \frac{n_i}{n} P$$

$$\therefore S = \sum_i n_i [C_{vi} \ln T + R \ln (T/p_i) + c_i]$$

Increase in entropy due to diffusion.

Let us consider the diffusion of n_1 moles of 1st gas with n_2 moles of 2nd gas at pressure P & temperature T .

$$\begin{aligned} \text{Total Entropy before diffusion } S_2 &= n_1 [C_{v1} \ln T + R \ln (T/P) + c_1] \\ &+ n_2 [C_{v2} \ln T + R \ln (T/P) + c_2] + \dots \\ &= \sum_i n_i [C_{vi} \ln T + R \ln (T/P) + c_i] \quad \text{--- (1)} \end{aligned}$$

If p_1, p_2 be the partial pressures of 1st and 2nd gas after diffusion



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Entropy after diffusion (S_y)

$$S_y = \sum_i n_i [C_{v,i} \ln T + R \ln (T/p_i) + C_i] - (6)$$

\therefore Increase in entropy due to diffusion

$$\Delta S = S_y - S_x = + \sum_i n_i R \ln \frac{V}{p_i}$$

$$\therefore \Delta S = + \sum_i n_i R \ln \frac{n}{n_i}$$

$$\therefore \Delta S = - \sum_i n \cdot \frac{n_i}{n} R \ln \frac{n_i}{n}$$

$$\Rightarrow \Delta S = - nR \sum_i x_i \ln x_i$$

$$\frac{p_i}{p} = \frac{n_i}{n}$$

$$x_i = \frac{n_i}{n} \\ = \text{mole fraction}$$

For two different gases.

$$\Delta S = n_1 R \ln \frac{n_1 + n_2}{n_1} + n_2 R \ln \frac{n_1 + n_2}{n_2}$$

Change in entropy for solid and liquid at same state

$$\text{we have, } T ds = da$$

$$da = mc dT$$

$m \rightarrow$ mass of solid/liquid
 $c \rightarrow$ sp heat solid/liquid

$$\therefore ds = m c \frac{dT}{T}$$

$$\text{Integrating } \int_{s_1}^{s_2} ds = mc \int_{T_1}^{T_2} \frac{dT}{T}$$

$$\Rightarrow S_2 - S_1 = mc \ln \frac{T_2}{T_1}$$



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Change in Entropy when state changes at constant temperature.

We have. $dq = T ds$

When state changes $dq = mL$

where $m = \text{mass}$

$L = \text{Latent heat}$

$T = \text{Const}^{\text{ve}} \text{ temp.}$

$$\therefore ds = \frac{mL}{T}$$

$$\Delta S = \frac{mL}{T}$$

Internal Energy

(i) from 1st law of Thermodynamics $dq = du + pdv$

$$\Rightarrow du = dq - pdv$$

$$\Rightarrow \left(\frac{\partial u}{\partial T}\right)_v = \left(\frac{\partial q}{\partial T}\right)_v = C_v$$

$$\Rightarrow \partial u = C_v dT$$

Integrating

$$u = \int C_v dT + K (\text{constant})$$

At const^{ve} volume $dv = 0$

(ii) Enthalpy (H)

$$H = U + PV$$

$$dH = du + pdv + vdp$$

$$dH = dq + vdp$$

$$\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial q}{\partial T}\right)_p = C_p$$

$$\partial H = C_p \partial T$$

Integrating $H = \int C_p dT + K (\text{const}^{\text{ve}})$

At const^{ve} pressure
 $dp = 0$



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Thermodynamic potential at constⁿ volume / free energy (F)

$$F = U - TS$$

$$\Rightarrow dF = dU - Tds - sdT$$

$$\Rightarrow dF = dU - dU - pdv - sdT$$

$$\Rightarrow \boxed{dF = -pdv - sdT}$$

we have,

$$dq = Tds$$

$$Tds = dq = du + pdv$$

Prove

$$U = -T^2 \left(\frac{\partial F}{\partial T} \right)_V$$

$$U = F - T \left(\frac{\partial F}{\partial T} \right)_V$$

We know that, $F = U - TS$ — (i)

$$dF = dU - Tds - sdT$$

$$dF = dU - dU - pdv - sdT$$

$$dF = -pdv - sdT$$

$$\Rightarrow \left(\frac{\partial F}{\partial T} \right)_V = -S \quad \text{--- (ii)}$$

from (i) & (ii)

$$F = U + T \left(\frac{\partial F}{\partial T} \right)_V$$

$$\boxed{U = F - T \left(\frac{\partial F}{\partial T} \right)_V}$$

We can write,

$$U = -T^2 \left[\frac{-F}{T^2} + \frac{1}{T} \left(\frac{\partial F}{\partial T} \right)_V \right]$$

$$\boxed{U = -T^2 \frac{\partial}{\partial T} \left(\frac{F}{T} \right)_V}$$



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Free Energy is const^{th} for an isothermal and isochoric ~~adiabatic~~ process.

$$\text{We have } F = U - TS$$

$$\Rightarrow dF = dU - Tds - SdT$$

$$\Rightarrow dF = dU - dU - pdv - SdT$$

$$\Rightarrow dF = -pdv - SdT$$

for ~~adiabatic~~ isochoric process $dv=0$ & for isothermal $dT=0$

$$\therefore dF = 0$$

$$\Rightarrow \boxed{F = \text{const}^{\text{th}}}$$

Gibbs potential or Thermodynamic potential at const^{th} pressure: (G)

$$G = H - TS$$

$$G = U + PV - TS$$

$$\text{We have, } G = U + PV - TS$$

$$dG = dU + pdv + vdp - Tds - SdT$$

$$\Rightarrow dG = Tds + vdp - Tds - SdT$$

$$\boxed{dG = vdp - SdT}$$

$$\left. \begin{aligned} dU &= Tds \\ Tds &= dU + pdv \end{aligned} \right\}$$

for isothermal process $dT=0$ & isobaric process

$$dp=0 \therefore dG=0$$

$$G = \text{const}^{\text{th}}$$

Therefore, in case of isothermal & isobaric process Gibbs potth is const^{th} .



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Prove.

$$H = G - T \left(\frac{\partial G}{\partial T} \right)_P$$
$$H = -T^2 \left[\frac{\partial}{\partial T} \left(\frac{G}{T} \right)_P \right]$$

Proof:

$$G = U + PV - TS \quad \text{--- (1)}$$
$$dG = du + vdp + volp - Tds - sdt$$
$$\Rightarrow dG = Tds + volp - Tds - sdt$$
$$\Rightarrow dG = volp - sdt$$
$$\therefore \left(\frac{\partial G}{\partial T} \right)_P = -s \quad \text{--- (2)}$$

From (1) & (2) we get,

$$G = U + Pdv + T \left(\frac{\partial G}{\partial T} \right)_P$$
$$\Rightarrow G = H + T \left(\frac{\partial G}{\partial T} \right)_P$$
$$\Rightarrow H = G - T \left(\frac{\partial G}{\partial T} \right)_P$$

We can also write,

$$H = -T^2 \left[-\frac{G}{T^2} + \frac{1}{T} \left(\frac{\partial G}{\partial T} \right)_P \right]$$
$$\therefore H = -T^2 \frac{\partial}{\partial T} \left(\frac{G}{T} \right)_P \quad \text{(Proved)}$$

Prove (i) $U = G - T \left(\frac{\partial G}{\partial T} \right)_P - P \left(\frac{\partial G}{\partial P} \right)_T$

(ii) $F = G - P \left(\frac{\partial G}{\partial P} \right)_T$ --- (1)

$$G = U + PV - TS$$
$$\Rightarrow dG = du + vdp + volp - Tds - sdt$$
$$\Rightarrow dG = volp - sdt$$
$$\Rightarrow \left(\frac{\partial G}{\partial T} \right)_P = -s \quad \text{--- (2)}$$

and $\left(\frac{\partial G}{\partial P} \right)_T = V$ --- (3)



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Putting the value of S from eqnⁿ (2) in eqnⁿ (1) we get,

$$G = U + PV + T \left(\frac{\partial G}{\partial T} \right)_P$$

$$U = G - P \left(\frac{\partial G}{\partial P} \right)_T - T \left(\frac{\partial G}{\partial T} \right)_P \quad \text{--- (3)}$$

$$(ii) \quad F = U - TS$$

$$\Rightarrow F = G - P \left(\frac{\partial G}{\partial P} \right)_T - T \left(\frac{\partial G}{\partial T} \right)_P - TS \quad \left| \begin{array}{l} \text{Putting eqn}^n (3) \\ \text{Putting eqn}^n (2) \end{array} \right.$$

$$\Rightarrow F = G - P \left(\frac{\partial G}{\partial P} \right)_T + TS - TS$$

$$\Rightarrow \boxed{F = G - P \left(\frac{\partial G}{\partial P} \right)_T}$$

Prove!

$$(i) \quad U = \left\{ \frac{\partial(F/T)}{\partial(V/T)} \right\}_V$$

$$(ii) \quad F = \left\{ \frac{\partial(G/P)}{\partial(V/P)} \right\}_T$$

We have, $F = U - TS$

$$\& \quad S = - \left(\frac{\partial F}{\partial T} \right)_V$$

Combining the

two relations

$$U = F - T \left(\frac{\partial F}{\partial T} \right)_V$$

$$= -T^2 \left\{ \frac{\partial}{\partial T} \left(\frac{F}{T} \right) \right\}_V$$

$$= \left\{ \frac{\partial(F/T)}{\partial(V/T)} \right\}_V$$

$$(ii) \quad \text{We have, } F = G - PV \quad \& \quad V = \left(\frac{\partial G}{\partial P} \right)_T$$

Combining these two equations



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$$F = G - p \left(\frac{\partial G}{\partial p} \right)_T$$
$$= -p^2 \left\{ \frac{\partial}{\partial p} \left(\frac{G}{p} \right) \right\}_T$$
$$= \left\{ \frac{\partial (G/p)}{\partial (1/p)} \right\}_T \quad \left| \text{Since } d(1/p) = -dp/p^2 \right.$$

Prove: $\Delta G = \Delta H + T \left[\frac{\partial (\Delta G)}{\partial T} \right]_P$; $G = f(T, P)$
for reversible & isothermal change

Proof: We have, $G = f(T, P)$

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

otherwise, $G = U + PV - TS$

$$\Rightarrow dG = du + pdv + vdp - Tds - SdT$$
$$\Rightarrow dG = vdp - SdT \quad \text{--- (2)}$$

From equⁿ. (1) & (2) we get.

$$v = \left(\frac{\partial G}{\partial P} \right)_T \quad \text{and } S = - \left(\frac{\partial G}{\partial T} \right)_P$$

Again $G = H - TS$

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

for reversible isothermal change $\Delta T = 0$

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

$$\Rightarrow \Delta G = \Delta H - T\Delta \left[- \left(\frac{\partial G}{\partial T} \right)_P \right]$$
$$\Rightarrow \boxed{\Delta G = \Delta H + T \left[\frac{\partial (\Delta G)}{\partial T} \right]_P}$$