

Free Study Material from All Lab Experiments



**Thermodynamics Notes
for NET/GATE Physical Sciences
Fugacity & Hess's Law #**

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⇌ FUGACITY ⇌

(Latin) means
words → (figure)

(corrected pressure for a real gas) = f (fugacity)
↓
[escaping tendency]

Ankur

- * It is a corrected pressure which is used for real gas
- * Fugacity of a real gas contains all the interaction which takes place in real gas.
- * It can also be understood as an escaping tendency of a real gas.
- * ~~It is~~ This new term is given by "G.N. Lewis"
- * at low pressure when pressure tends toward zero then the real gas behaves as an ideal gas.

We know that f is a fugacity & P is pressure.

$$\therefore f/P = \gamma \text{ [fugacity coefficient]}$$

$$\lim_{P \rightarrow 0} f/P = 1$$

$$[\because \gamma = 1]$$

$$\boxed{f = P}$$

The gas behaves as an ideal gas.

Mathematical Calculation of fugacity \Rightarrow

We know that,

free Energy for an ideal gas at a particular temp. can be written as -

$$G = G^{\circ} + RT \ln P \quad \text{--- (I)}$$

this expression can be used for real gas also
By introducing a new term 'f'

$$G = G^{\circ} + RT \ln f \quad \text{--- (II)}$$

free Energy for an real gas at particular temp. can be written as above \Rightarrow

Eqn (ii) differentiate both side w.r.t to P at constant temp.

$$\left(\frac{dG}{dP}\right)_T = 0 + RT \left[\frac{d(\ln f)}{dP}\right]_T \quad \text{---}$$

$$\left(\frac{dG}{dP}\right)_T = RT \left[\frac{d(\ln f)}{dP}\right]_T \quad \text{--- (III)}$$

$$\therefore dG = v dp - S dT \quad \text{[at const. } T, dT=0]$$

$$\left(\frac{dG}{dP}\right)_T = v_m(\text{const.})$$

put the value of $\left(\frac{dG}{dP}\right)_T$ in (III)

$$V_{\text{ideal}} = RT \left(\frac{\partial \ln f}{\partial p} \right)_T$$

$$V_{\text{ideal}} \cdot dp = RT (d \ln f) \quad \text{--- (IV)}$$

$$\therefore \alpha = V_{m(\text{ideal})} - V_{m(\text{real})}$$

Multiply dp both side by dp

$$\alpha \cdot dp = V_{m(\text{ideal})} dp - V_{m(\text{real})} dp$$

$$\alpha \cdot dp = \frac{RT}{p} dp - RT d(\ln f)$$

\therefore Inte. both side \rightarrow

$$\int_0^p \alpha \cdot dp = RT \int \frac{dp}{p} - RT \int d(\ln f)$$

$$\int_0^p \alpha \cdot dp = + RT \ln p - RT \ln f$$

$$\int_0^p \alpha \cdot dp = -RT [\ln f/p]$$

$$\boxed{-\frac{1}{RT} \int_0^p \alpha \cdot dp = \ln f/p}$$

$$\ln f/p = -\frac{1}{RT} \int_0^p \alpha \cdot dP$$

$$f/p = e^{-\frac{1}{RT} \int_0^p \alpha \cdot dP}$$

$$f = p \cdot e^{-\frac{1}{RT} \int_0^p \alpha \cdot dP}$$

$$\gamma = f/p = e^{-\frac{1}{RT} \int_0^p \alpha \cdot dP}$$

$\gamma \Rightarrow$ fugacity coefficient

Fugacity can also be terms of compressibility factor -

$$Z = \frac{P(V_{\text{real}})}{RT}$$

$[1 < z > 1]$ - real Gas

for an Ideal Gas $[z=1]$

$$\ln f/p = -\frac{1}{RT} \int_0^p [V_{m(\text{Ideal})} - V_{m(\text{real})}] dP$$

$$\ln f/p = -\frac{1}{RT} \int_0^p \left[\frac{RT}{P} - \frac{zRT}{P} \right] dP$$

$$\ln f/p = -\frac{1}{RT} \int_0^p \alpha \cdot dP$$

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$$\ln f/p = \int_0^p \frac{1}{p} (Z-1) dp$$

$$\ln \gamma = \int_0^p \frac{(Z-1) dp}{p}$$

fugacity at low pressure \Rightarrow

$$\ln f/p = \frac{-1}{RT} \int_0^p \alpha \cdot dp$$

$$\ln f/p = - \frac{\alpha p}{RT}$$

$$\ln x = x-1 \text{ [Stirling's formula]}$$

$$\therefore \ln f/p = f/p - 1$$

from (i)

$$- \frac{\alpha p}{RT} = f/p - 1$$

$$1 - \frac{\alpha p}{RT} = f/p$$

$$1 - \frac{[\frac{RT}{p} - V_{\text{real}}] p}{RT} = f/p$$

[beoz No change
in pressure
 \therefore Initial = final]

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$$1 - \frac{[RT - PV_{\text{real}}]}{RT} = f/p$$

$$\frac{\cancel{RT} - \cancel{RT} + PV_{\text{real}}}{RT} = f/p$$

$$\frac{PV_{\text{real}}}{RT} = f/p$$

$$f = \frac{P^2 V_{\text{real}}}{RT}$$

↓
This is fugacity at low pressure

$$P(V_m - b) = RT$$

$$PV - Pb = RT$$

$$\frac{PV}{RT} - \frac{Pb}{RT} = 1$$

$$Z = \frac{PV}{RT} = 1 + \frac{Pb}{RT}$$

$$\ln f/p = \int_0^P \frac{(1 + \frac{Pb}{RT})}{P} dp$$

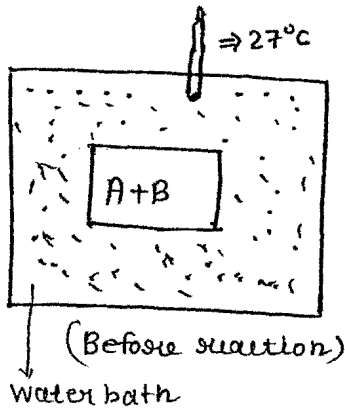
$$= \int_0^P \frac{Pb}{RT P} dP$$

$$= \int_0^P \frac{b}{RT} dP$$

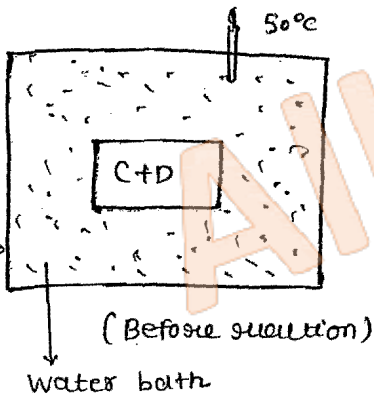
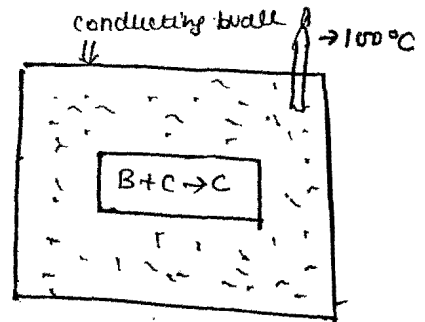
$$\ln f/p = \left(\frac{bP}{RT} \right)$$

$$f/p = e^{bP/RT}$$

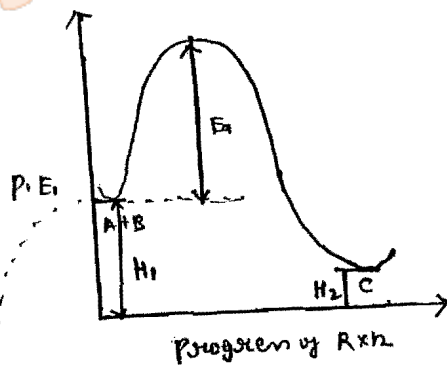
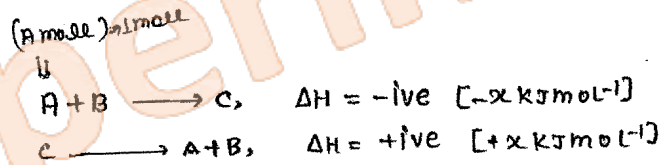
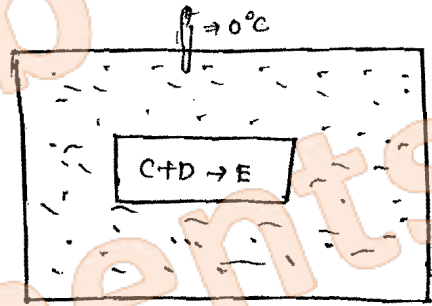
$$f = p e^{bP/RT}$$



Exothermic Rxn



Endothermic Rxn



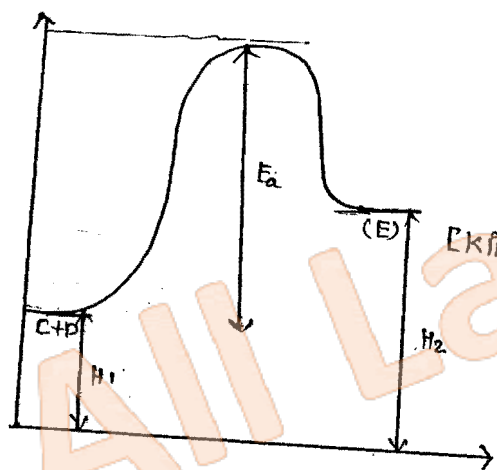
[Threshold Energy - average P.E.] = Activation Energy

→ Average - Potential Energy of Reactant.

⇒ **Activation Energy = Threshold Energy - Average P.E. of Reactant**

⇒ The product form in Exothermic Rxn is thermodynamically stable

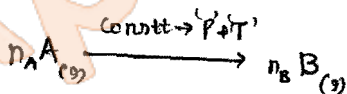
⇒ Temp only change when Heat is Evolved or absorb



$$\Delta H = H_2 - H_1 = +ive$$

↓
form very easily and unstable but it change into reactant bcoz Ea of product is very less. [most of the pressure is comtt. so that change in ΔH]

Relation b/w ΔH and ΔE in the case of Ideal Gas ⇒



$$P V_A = n_A R T \quad \text{[Reactant]} \quad \text{--- (i)}$$

$$P V_B = n_B R T \quad \text{[Product]} \quad \text{--- (ii)}$$

$$(ii) - (i)$$

$$P(V_B - V_A) = (n_B - n_A) R T$$

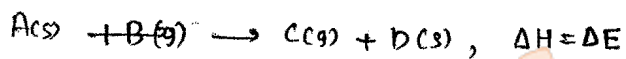
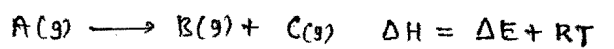
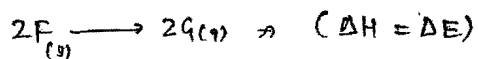
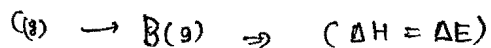
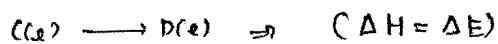
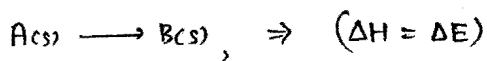
$$P \Delta V = \Delta n_g R T \quad \text{--- (3)}$$

$$H = E + PV$$

$$\partial H = \partial E + \partial(PV) \quad \text{--- from [3]}$$

$$\partial H = \partial E + P \partial V + V \partial P$$

most of the Rxn which is happen in the nature in comtt. temp. & pressure.

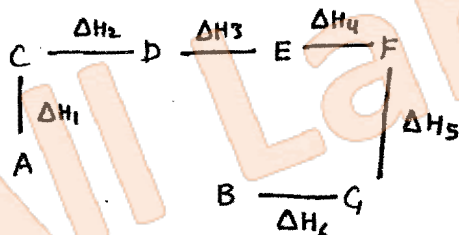
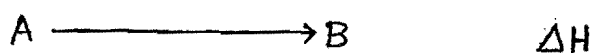


Heat Change in consti-volume (ΔE)

$$q_p = q_v + \Delta n_g RT$$

Heat Change in consti-pressure (ΔH)

⇐ Hess's Law ⇒



$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6$$

Conservation of Energy

Heat may be absorbed or evolved

“According to Hess's law ⇒ the Enthalpy change during the reaction is same whether reaction complete one step or several step.”

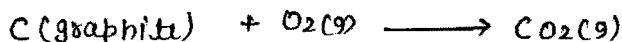
Numerical Question on Hess's Law: \Rightarrow
 Ques:- Compute the standard heat of formation of methane



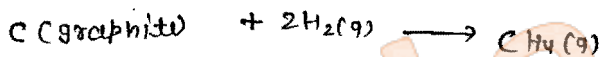
$$\Delta H^\circ(298\text{K}) = -890.35 \text{ kJ}$$



$$\Delta H^\circ(298\text{K}) = -285.84 \text{ kJ}$$



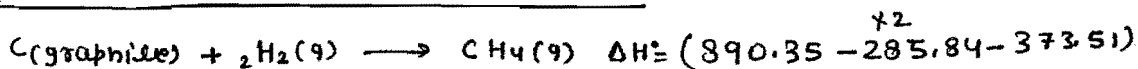
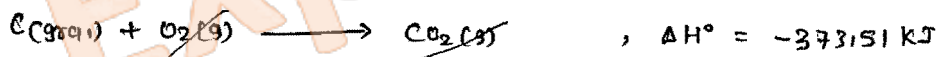
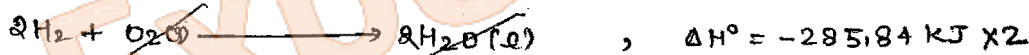
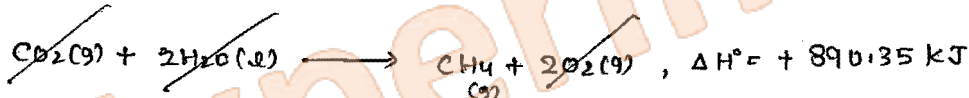
$$\Delta H^\circ(298\text{K}) = -373.51 \text{ kJ}$$



$$\Delta H^\circ(298\text{K}) = ?$$

\Rightarrow Calculate the enthalpy change for above reaction.

B40



~~$$= 890.35 - 571.68 - 373.51$$~~

~~$$= 131.68 - 285.84$$~~

~~$$= -$$~~

$$= 890.35 - 2 \times 285.84 - 373.51$$

$$= 890.35 - 571.68 - 373.51$$

$$= 890.35 - 945.19$$

$$= -54.84 \text{ kJ}$$

Standard- State

Solid State (Pure Crystalline)

Substance at 1 atm or 1 bar at particular temp.

Liquid- State (Pure / molar)

1 atm pressure or 1 bar at particular temp.

$P_{\text{white}} > P_{\text{black}}$ [Phosphorus]

$S_R > S_M$ [Sulphur]
Rhombic (monoclinic)

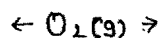
$C_{\text{graphite}} > C_{\text{diamond}}$ [Carbon]

Gas \Rightarrow 1 bar, pure
or 1 atm

$\Delta H^\circ \Rightarrow$ Standard Enthalpy change

Enthalpy of formation for an Element

⇒ The standard enthalpy of formation for any element in its stable state of aggregation at 1 bar pressure and specified temp. is assigned as zero



$$\Delta H_f^\circ [\text{O}_2(\text{g})] = 0$$

$$\Delta H_f^\circ [\text{C}_{\text{graphite}}] = 0 \text{ [Stable]}$$

But $\Delta H_f^\circ [\text{C}_{\text{diamond}}] \neq 0$ [diamond is not stable state]

$$\Delta H_f^\circ [\text{Br}_2, \text{1 atm}] = 0$$

$$\Delta H_f^\circ [\text{S}_{\text{rhombic}}] = 0 \text{ [Rhombic is stable state]}$$

$$\Delta H_f^\circ [\text{S}_{\text{monoclinic}}] \neq 0$$

$$\Delta H_f^\circ [\text{P}_{\text{white}}] = 0$$

$$\Delta H_f^\circ [\text{P}_{\text{black}}] \neq 0$$