

# Free Study Material from All Lab Experiments



**Thermodynamics Notes  
for NET/GATE Physical Sciences  
# Born-Hyber & Other Topics #**

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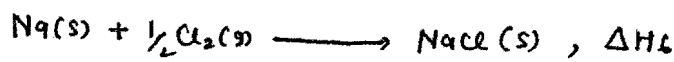
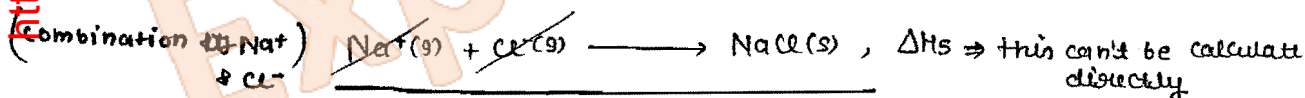
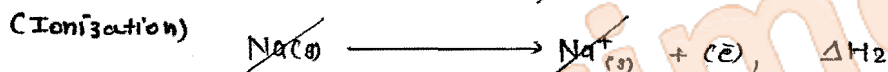
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## Bohr-Haber Cycle ⇒

Bohr-Haber cycle is used to calculate lattice energy. Lattice energy can't be calculated experimentally but with the application of B.H. cycle we are able to calculate lattice energy.

↓  
 "Lattice Energy is defined as the energy required to separate one mole of solid ionic compound into gaseous ions"

Formation of NaCl crystals from Na(s) + Cl<sub>2</sub>(g)



[Practically impossible]

from Hess's law -

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

By the appl<sup>n</sup> of Hess's law & Bohr-Haber's cycle ⇒

we know,  $\Delta H_1, \Delta H_2, \Delta H_3, \Delta H_4, \Delta H_6$  then,

$$\Delta H_5 = \Delta H_6 - (\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4)$$

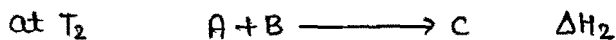
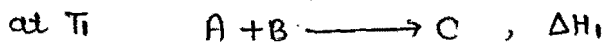
↓  
(Lattice Energy)

⇒  $\Delta H_f^\circ(\text{NaCl}) = -410.87 \text{ kJ mol}^{-1}$

←: Kirchhoff's Equation : ⇒

(Variation of temp.,  $\Delta H$ )

→) For Rxn at  $\Delta H$  given at diff. temp.  $T_1$   
↓  
Kirchhoff Eq<sup>n</sup> -



$$\Delta H = H_2 - H_1$$

$$\left( \frac{\partial(\Delta H)}{\partial T} \right)_P = \left( \frac{\partial(H_2)}{\partial T} \right)_P - \left( \frac{\partial(H_1)}{\partial T} \right)_P$$

$$= (C_p)_{Prod} - (C_p)_{React}$$

$$\left( \frac{\partial(\Delta H)}{\partial T} \right)_P = \Delta C_p$$

$$\partial(\Delta H) = \Delta C_p \cdot \partial T$$

Inte. both side

$$\int_{H_1}^{H_2} \partial(\Delta H) = \Delta C_p \int_{T_1}^{T_2} \partial T$$

$$\boxed{\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)}$$

Variation of heat of reaction with temp.

Mathematical form of this statement is  
Kirchhoff Eq<sup>n</sup>.

Kirchhoff Eq<sup>n</sup> can be expressed either in terms of  $\Delta H$  or  $\Delta E$

Kirchoff's Equation in term of  $\Delta E$ .

$$\therefore \Delta E = E_2 - E_1$$

$$\left( \frac{\partial (\Delta E)}{\partial T} \right)_V = \left( \frac{\partial E_2}{\partial T} \right)_V - \left( \frac{\partial E_1}{\partial T} \right)_V$$

$$\left( \frac{\partial (\Delta E)}{\partial T} \right)_V = (C_V)_{P_2} - (C_V)_{P_1}$$

$$\left[ \frac{\partial (\Delta E)}{\partial T} \right]_V = \Delta C_V$$

$$\partial (\Delta E) = \Delta C_V \cdot \partial T$$

Int on both side

$$\int_{\Delta E_1}^{\Delta E_2} \partial (\Delta E) = \Delta C_V \int_{T_1}^{T_2} \partial T$$

$$\Delta E_2 - \Delta E_1 = \Delta C_V (T_2 - T_1)$$

Numerical  $\Rightarrow$



where  $C_p$  of (C  $\Rightarrow$  product)  $\Rightarrow 5$

$$(C_p)_B = 3$$

$$(C_p)_A = 1$$

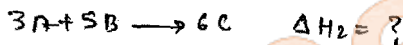
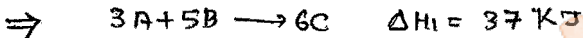
$$\Delta H_2 - 37 = \cancel{(5-3)} \times (500 - 298)$$

$$\Delta H_2 - 37 = 1 \times (202)$$

$$\Delta H_2 = 202 + 37$$

$$\Delta H_2 = 239 \text{ kJ}$$

$$= 23900 \text{ kJ}$$



$$(C_p)_A = 3$$

$$(C_p)_B = 5$$

$$(C_p)_C = 1$$

$$\Delta H_2 - \Delta H_1 = [3 \times 6 - 3 \times 3 - 5 \times 5] [500 - 298]$$

$$\Delta H_2 - 37000 = [18 - 28] \times 202$$

$$\Delta H_2 - 37000 = -2020$$

$$\Delta H_2 = 37000 - 2020$$

$$\Delta H_2 = 34980 \text{ J}$$

(Rxn Higher temp  $\mu$  is Endothermic)

Q4.6

$$\Delta H_1 = -922 \text{ kJ}$$

$$\Delta H_2 = ?$$

$$T_2 = 373$$

$$T_1 = 298$$

$$\begin{array}{r} 106.7 \\ 70.2 \\ \hline 36.5 \end{array}$$

$$\Delta H_2 - \Delta H_1 = (2 \times 35.1 - 3 \times 28.8 - 1 \times 29.1) (373 - 298)$$

$$\Delta H_2 + 92.2 = (70.2 - 77.6 - 29.1) (75)$$

$$\Delta H_2 + 92.2 = (70.2 - 106.7) 75$$

$$\Delta H_2 + 92.2 = -35.3 \times 75$$

$$\Delta H_2 = -35.3 \times 75 - 92.2 \times 1000$$

~~$$\Delta H_2 = -35.3 \times 75 - 92.2 \times 1000$$~~

~~$$\Delta H_2 = -35.3 \times 75 - 92.2 \times 1000$$~~

$$\Delta H_2 = -45.3 \times 75 - 92200$$

$$\Delta H_2 > \Delta H_1$$

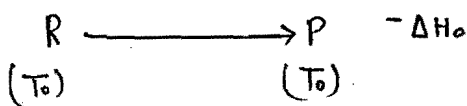
more exothermic

Adiabatic flame temp.

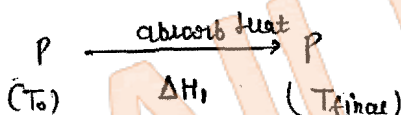
and

Adiabatic - Explosion temp.

Ist step



IInd step



at a const. pressure  $\Rightarrow$  Adiabatic flame  
at a const. volume  $\Rightarrow$  Explosion

$$-\Delta H_0 = \Delta H_1$$

(defn)  
complete  
Combustion  
 $\downarrow$   
 $\text{CO}_2(g) + \text{H}_2\text{O}(l)$   
(Only product)  
(No Rct)

<https://alllabexperiments.com>

Ist step me product ke temp ke product final temp  
achive karega ke temp ke Ist step me  $-\Delta H_0$  release  
hoga iske heat kega agar me complete combustion  
agar const. pressure par hoga to adiabatic flame temp.  
agar const. volume par hoga to adiabatic explosion temp.

$$-\Delta H_0 = \sum n C_p \int_{T_0}^{T_f} dT$$

$$-\Delta H_0 = \sum n C_p (T_f - T_0)$$

$$\frac{-\Delta H_0}{\sum n C_p (\text{product})} + T_0 = T_f$$

$$-\frac{\Delta E^{\circ}}{\Delta C_v} + T_0 = T_f$$

$\downarrow$   
 (Product)  
 at constt volume

Adiabatic flame temp.

⇒

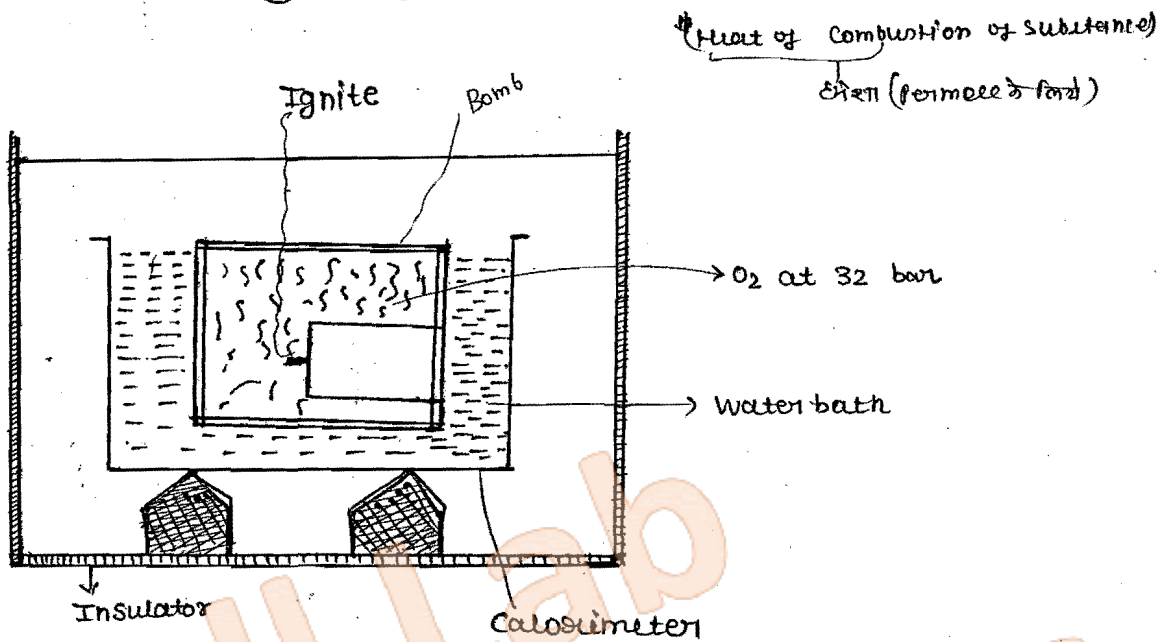
When a complete combustion of a substance take place, the final temp. which is achieved by product at const. pressure condition is called A.F.T.

Adiabatic explosion temp.

⇒ When a complete combustion of a substance take place the final temp. which is achieved by product at const. volume condition is called A.E.T. Close



# BOMB - CALORIMETER



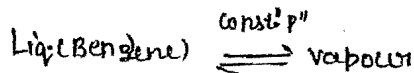
$$q_{\text{water}} = m C_{\text{water}} \Delta T$$

$$q_{\text{Bomb}} = m \times C_{\text{bomb}} \Delta T$$

$$q_{\text{combustion}} = q_{\text{water}} + q_{\text{Bomb}}$$

(Failed)  
 ⇒ Trouton's Rule: ⇒ [which under go association or dissociation]

$$\Delta S = \frac{\Delta H_{\text{vap}}}{T_b}$$



⇒ "For Molt of the liquid at a respective b.p.t.,  
 molar entropy of vapourization is fixed.  
 which is 88 JK<sup>-1</sup>mol<sup>-1</sup> or 21 cal K<sup>-1</sup>mol<sup>-1</sup>."

$$88 \text{ JK}^{-1} \text{ mol}^{-1}$$

or

$$21 \text{ cal K}^{-1} \text{ mol}^{-1}$$

[Statement of Trouton's Rule]

This law is failed which liquid is association or dissociation.

[like - CH<sub>3</sub>COOH]

This law is also failed which having <sup>very</sup> high + very low b.p.t.

Gibbs - Chemem Equation: -

$$G = f(T, P, n_1, n_2, n_3, \dots, n_i)$$

$$\frac{dG}{d} = \left( \frac{\partial G}{\partial T} \right)_{P, n_1, n_2, n_3, \dots, n_i} dT + \left( \frac{\partial G}{\partial P} \right)_{T, n_1, n_2, \dots} dP + \left( \frac{\partial G}{\partial n_1} \right)_{T, P, n_2} dn_1 + \dots$$

at const - T, P

$$dG = dn_1 \mu_1 + dn_2 \mu_2 + dn_3 \mu_3 + dn_4 \mu_4 + \dots$$

Integrate both side

$$G = \mu_1 n_1 + \mu_2 n_2 + \mu_3 n_3 + \dots \quad \text{--- (2)}$$

Differentiate both side

$$dG = n_1 d\mu_1 + \mu_1 dn_1 + n_2 d\mu_2 + \mu_2 dn_2 + \dots \quad \text{--- (3)}$$

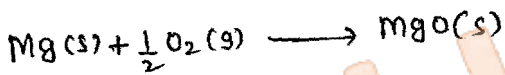
Substrate (3) - (2)

$$0 = n_1 d\mu_1 + n_2 d\mu_2 + n_3 d\mu_3 + n_4 d\mu_4 + \dots$$

$$\sum n_i d\mu_i = 0$$

↓  
Gibb's Dheem Equation

TIFR Assignment



$$\Delta H_{\text{M}}^{\circ} = -602 \text{ kJ/mol}$$

$$\Delta S_{\text{M}}^{\circ} = -108 \text{ kJ/mol}$$

$$\Delta G_{\text{M}}^{\circ} = \Delta H_{\text{M}}^{\circ} - T \Delta S_{\text{M}}^{\circ}$$

$$= -602 \text{ kJ/mol} - 273 \times (-108)$$

$$= -602 \text{ kJ/mol} + 29484 \text{ kJ/mol}$$

$$= 28882$$

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

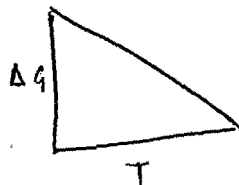
$$y = mc + mx$$

Qn. 3

$$\text{slope} \left\{ \tan \theta = \frac{1}{\text{Base}} \right\} =$$

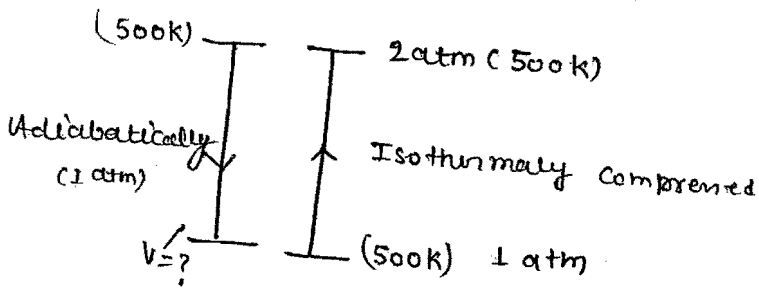
$$\frac{3600 \text{ J (P)}}{40 \text{ (W)}}$$

$$\Rightarrow 75 \text{ J mol}^{-1} \text{ K}^{-1}$$



All Lab Experiments

Q.20



[∵ ideal gas]

$PV = nRT$

$2 \times 10^5 = 1 \times 0.082 \times 500$

$V = \frac{0.082 \times 500}{2} = 20.5 \text{ dm}^3$

$V_1 = 20.5 \text{ dm}^3$

$T_1 = 500 \text{ K}, T_2 = ?$

$\left(\frac{T_1}{T_2}\right)^\gamma = \left(\frac{P_2}{P_1}\right)^{1-\gamma}$

$\left(\frac{500}{T_2}\right)^{1.66} = \left(\frac{1}{2}\right)^{(1-1.66)}$

$\left(\frac{500}{T_2}\right)^{1.66} = \left(\frac{1}{2}\right)^{-0.66}$

$\left(\frac{500}{T_2}\right)^{1.66} = 1.58$

$\frac{500}{T_2} = (1.58)^{1/1.66}$   
 $\frac{500}{T_2} = 1.33$

$T_2 = \frac{500}{1.33} = 375.9$

$(PV)^\gamma = \text{constant}$

$P_1 V_1^\gamma = P_2 V_2^\gamma$

$\left(\frac{V_1}{V_2}\right)^\gamma = \frac{P_2}{P_1}$

$\left(\frac{20.5}{V_2}\right)^2 = \frac{2}{1}$

$\left(\frac{20.5}{V_2}\right)^2 = 2$

$\frac{20.5}{V_2} = 1.5$

$C_V = 1.5R$

$C_P - C_V = R$

$C_P - 1.5R = R$

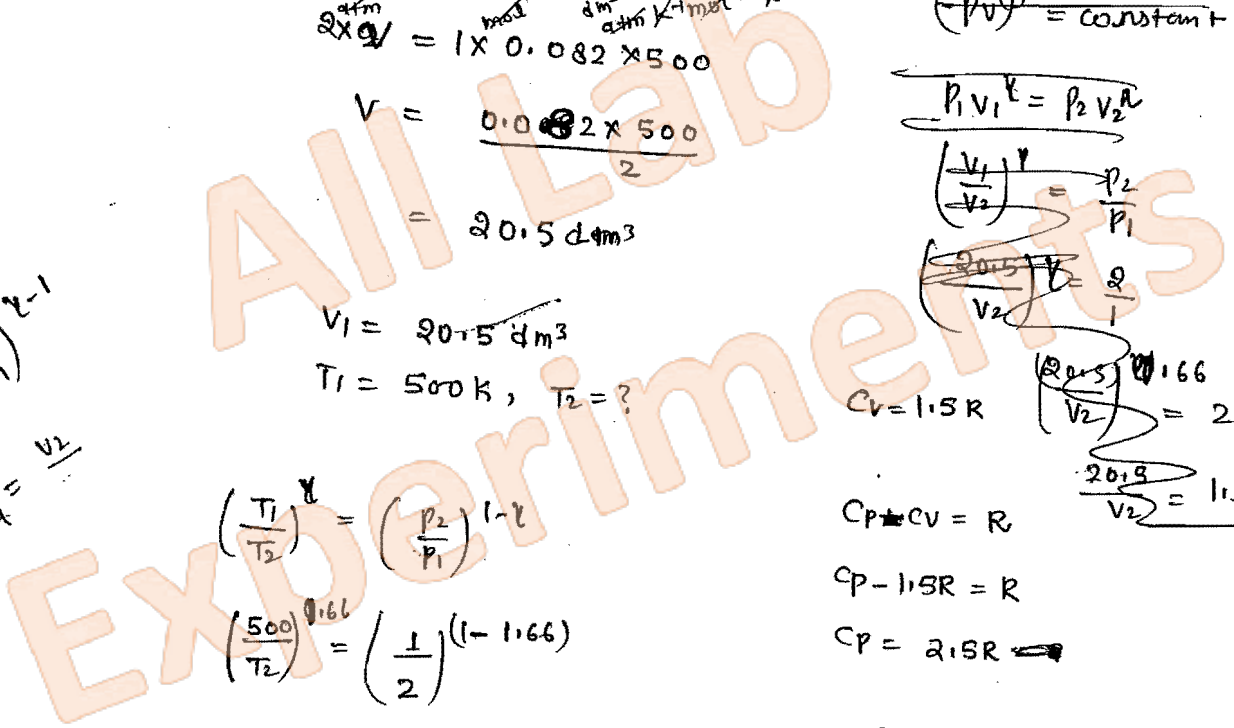
$C_P = 2.5R$

$\frac{C_P}{C_V} = \gamma$

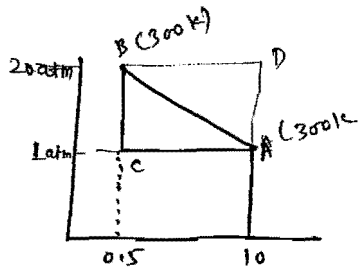
$\frac{2.5}{1.5} = \gamma$

$\gamma = \frac{5}{3} = 1.66$

https://alllabexperiments.com



(27)



$$V_1 = 10L$$

$$V_2 = 0.5L$$

Expansion:  
Isothermal (rev. work done)

$$W = -nRT \ln \frac{V_2}{V_1}$$

$$= -nR \times 300 \times \ln \frac{0.5}{10}$$

$$= -\frac{10}{200} \times 300 \times \ln \frac{0.5}{10}$$

$$= -10 \ln \frac{5}{100} = (-) -10 \ln \frac{100}{5}$$

$$= \underline{\underline{10 \ln 20}}$$

$$PV = nRT$$

$$\frac{1 \times 10}{300} = nR$$

Q4.30 →

$$T_1 = 15^\circ C$$

$$T_2 = 75^\circ C$$

$$C_p \text{ of water} = 75 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\frac{\Delta H}{\Delta T} = n c_p$$

$$n = \frac{W}{m} = \frac{54}{18} = 3 \text{ mol}$$

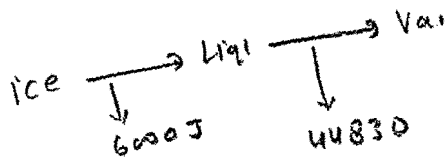
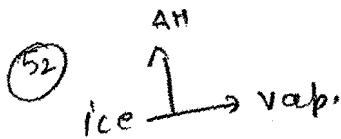
$$\frac{\Delta H}{\Delta T} = 3 \times 75$$

$$\underline{\underline{348 - 288}}$$

$$\frac{\Delta H}{348 - 288} = 3 \times 75$$

$$\frac{\Delta H}{+60} = 3 \times 75$$

$$\Delta H = 13.5 \text{ KJ}$$



53

$$\ln \frac{P_2}{P_1} = \frac{\Delta H}{R} \left( \frac{T_2 - T_1}{T_1 \cdot T_2} \right)$$

variation of temp. with pressure  
 → Clausius - Clapeyron Eq<sup>n</sup>

$$P_1 = 2.02 \times 10^3 \text{ N m}^{-2}$$

$$P_2 = 1 \text{ atm} = 1 \times 10^5 \text{ N m}^{-2}$$

$$\Delta H = 41 \text{ KJ mol}^{-1}$$

Solve Yourself

$$\ln \frac{1 \times 10^5}{2.02 \times 10^3} = \frac{41000}{8.314} \left( \frac{T_2 - 293}{293 T_1} \right)$$

$$\ln \left( \frac{100}{2.02} \right) =$$

$$\ln 49.50 = 4931.44 \left( \frac{T_2 - 293}{293 T_1} \right)$$

$$3.902 = 4931.44 \left( \frac{T_2 - 293}{293 T_1} \right)$$

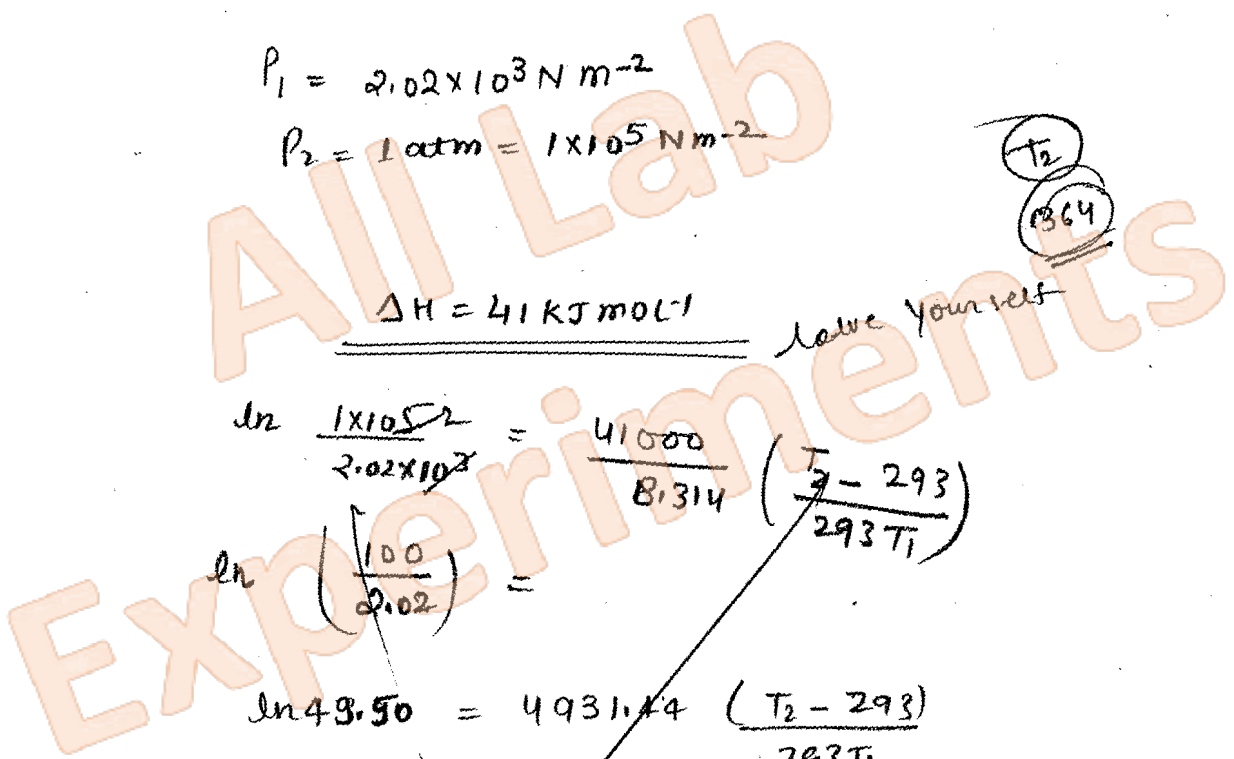
$$\frac{3.902 \times 293}{4931.44} = \frac{(T_1 - 293)}{T_1}$$

$$0.22 = 1 - \frac{293}{T_1}$$

$$1 - 0.22 = \frac{293}{T_1}$$

$$T_1 = \frac{293}{0.78}$$

T<sub>2</sub>  
 1364



- 293 / 1e

Q4.57  $U = 3.5 PV + K$

$$V_1 = 0.25 \text{ m}^3$$

$$V_2 = 0.86 \text{ m}^3$$

$$P_1 = 5 \text{ Nm}^{-2}$$

$$PV^{1.3} = \text{constant}$$

where  $\gamma = 1.3$

$$5 = \left( \frac{0.86}{0.25} \right)$$

Note  $\Rightarrow$

(Water),  $\Delta H_{\text{fusion}} = 324 \text{ kJ/kg}$  or  $\text{J/kg}$

$$\Delta H_{\text{vaporization}} = 2264.76 \text{ kJ/kg}$$

$$c_p = \text{specific heat of water} = 4.18 \text{ J/g}$$

$$c_p = \text{specific heat of ice} = 2.023 \text{ J/g}$$

(Net previous)

Q.2 ②  $\Rightarrow PV^{\alpha} = \text{constant}$

$$T_1 V_1^{\alpha-1} = T_2 V_2^{\alpha-1} = K$$

$$\therefore T_2 > T_1$$

$$\frac{T_1 V_1^{\alpha-1}}{V_2^{\alpha-1}} = T_2$$

$$\frac{T_1 V_1^{\alpha-1}}{V_2^{\alpha-1}} > T_1$$

$$\left(\frac{V_1}{V_2}\right)^{\alpha-1} > 1$$

$$\left(\frac{V_1}{V_2}\right)^{\alpha-1} > \left(\frac{V_1}{V_2}\right)^0$$

$$\alpha - 1 < 0$$

$$\boxed{\alpha < 1}$$

Q.28

$$q = -(q_{\text{water}} + q_{\text{can}})$$

$$q = -2500 \text{ J K}^{-1} \times 4$$

$$q = -2500 \times (\Delta T)$$

$$q = -2500 \times 4$$

$$q_{\text{com.}} = -10000$$

$$n = \frac{6 \text{ g}}{505} = \frac{1}{100} = 0.01$$

$$q_{\text{com.}} / \text{mole} = \frac{-10000}{0.01}$$

$$= -1000000$$

$$q_{\text{combun.}} \text{ per mol} = -1000 \text{ kJ}$$

Q.4.6

$$\frac{dp}{dT} = \frac{\Delta H}{T(V_{\text{vap.}} - V_L)}$$



# Degree of freedom

Tr, Rot, Vib

Linear

$$\downarrow$$

$$T_r = 3$$

$$R_{ot} = 2$$

CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>

Non linear

$$T = 3$$

$$R = 3$$

(NH<sub>3</sub>, SO<sub>2</sub>)

$$\underline{\underline{(3N-6)}}$$

$$T + R + V = 3N \quad (\text{No. of atom})$$

$$V = 3N - 5$$

$$V = 3 \times 2 - 5$$

$$= 6 - 5$$

$$= 1$$

(Contribution)

⊕

$$C_v \Rightarrow R/2$$

$$C_v \Rightarrow \textcircled{R} \rightarrow R/2$$

$$C_v \Rightarrow \textcircled{V} \rightarrow R \text{ at High}$$

0.2R at R/T

0 at low temp.

Monatomic

⊕

He, Ne, Ar, Kr, Xe, ...

$$T = 3$$

$$R_{otational} = 0$$

$$V_{ibrational} = 0$$

$$C_v = 3R/2$$

$$R_{otat} = 0$$

$$V_{ibrat} = 0$$

$$\text{Total } C_v = 3R/2 + 0 + 0$$

$$\boxed{C_v = 3R/2}$$

$$C_p = C_v + R$$

$$\left( C_p = \frac{5R}{2} \right)$$

$$\frac{C_p}{C_v} = \frac{5}{3} = 1.66$$

(monatomic)

The ratio of  $\frac{C_p}{C_v}$  for diatomic gas  $\Rightarrow$   
 $[O_2]$

$$\text{Transl} = 3$$

$$\text{Rotat} = 2$$

$$\begin{aligned} V &= 3N - 5 \Rightarrow L \\ &= 3 \times 2 - 5 \Rightarrow \\ &= 1 \end{aligned}$$

at high temp,

$$\begin{aligned} \text{Total } C_v &= 3 \times R/2 + 2 \times R/2 + 1 \times R \\ &= 1.5R + R + R \\ &= 3.5R \\ &= \frac{7R}{2} \end{aligned}$$

$$C_p = C_v + R \Rightarrow \frac{7R}{2} + R = \frac{9R}{2}$$

$$\frac{C_p}{C_v} = \frac{9}{7} = 1.28$$

$$C_v = 20 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{Con. Volume, } T_2 = 2T_1$$

$$\underline{W + q}$$

$$\Delta E = q + W$$

$$\Delta E = q + 0$$

$$C_v(T_2 - T_1) = q$$

$$20(2 \times 298 - 298) = q$$

$$q = 20 \times 298$$

$$q = 5960 \text{ J}$$

$$\boxed{q = 5.96 \text{ J}}$$