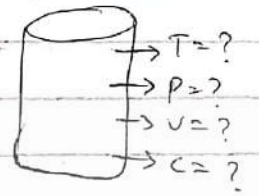
New Lec

State of System

means

* Condition of a System
* defined by parameters
* Macroscopic property
* define at equilibrium condition.
* state can be change by changing



state function

Initial state → Final.

(#) State Function → they are part of System

* parameter which define state of a system.
* Macroscopic property
* independant of path.
* defined at equilibrium state
* depend on initial & final position.

e.g

P, T, V, con, enthalpy, entropy.

Not State function:

ΔT, ΔP, ΔV, Δcon, ΔS,

except:

internal energy ← ΔU, ΔH/H

Not part of System

Path Function

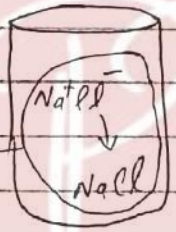
* Work = Show way of transfer of energy.
* heat = Non-mechanical way " " " .

Show transfer of energy

System

which undergo physical or chemical change.

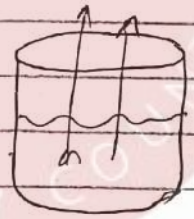
* Macroscopic * My be stable or unstable
* Real or ideal.



System

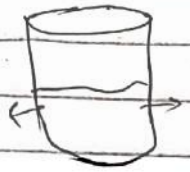
open System:

* exchange matter & energy
* Diathermic boundry.
  ↳ heat exchange.
* Real & imaginary



Close System:

* Real
* exchange heat only.
* ~~Adiabatic~~ Diathermic boundry.



Isolated or Ideal System:

↓

Nor matter nor energy transfer.

Surrounding

* No physical & chemical change occur.

* Macroscopic

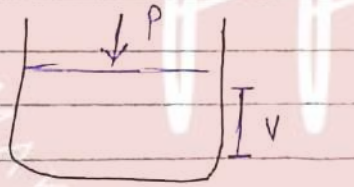
Boundry → Real / ideal

Separate boundry and Surrounding.

Adiabatic → No exchange of heat

Diathermic → heat exchange

⊕ Pressure – Volume Work



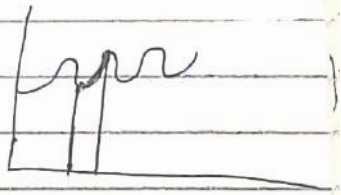
$W = P\Delta V$

const Pressure:

$$|W| = P\Delta V$$

not const pressure:

$$w = -\int_{V_1}^{V_2} P\,dV$$



At const Volume:

$\Delta V = 0$ in solid & liquid

$$w = 0$$

At const Temp:

$$w = -nRT \log \frac{V_1}{V_2}$$

$P \propto V$ $\quad \boxed{w = -nRT \log \frac{P_2}{P_1}}$

(#) For ideal gas:

$PV = nRT$

$w = P\Delta V \quad \boxed{w = \Delta nRT}$

$\Delta n = n_p - n_R$

(#) Work in a Rxn:

=> volume ⇑ = $-w$ (

=> volume ⇓ = w (work done on system)

MCQs: In the gaseous rxn in which case work is done on system?

$A + 2B \longrightarrow C + D$

Sign & symptom

work on system = $+w$

work by system = $-w$

Q#: $A + B \longrightarrow 2C + D$

For gaseous Rxn how much work is done at 27°C

a) 300R b) −300R c) −150R

$\Delta n = 3 - 2 = 1$

$T = 300K$

$w = 1 \times 300 = -300R$

Q# $2SO_2 + O_2 \longrightarrow 2SO_3$

when 1 mole of SO_2 react with O_2 at 10K, the amount of work is?

(1.5) (1)

$1\,SO_2 + 0.5\,O_2 \longrightarrow 1\,SO_3$

$\Delta n = 1 - 1.5 = 0.5$

$w = 0.5 \times 10 \times R = \boxed{5R}$

(#) Internal energy → which can change the temperature

=> Total energy of a system.

* Heat of a system at Constant Volume.

Facts:

* extensive property.
* absolute value cannot be measured.
* change can be measured.
* state function (ΔU)

M. Form:

$\boxed{q_V = \Delta U}$

$\boxed{\Delta U = U_f - U_i}$ $\boxed{\Delta U = q + w}$

$\boxed{\Delta U = \frac{n_f RT}{2}}$ ($\Delta U \propto$ degree of freedom)

$\boxed{\Delta U = K.E + P.E}$ ($\Delta U(f) \propto$ atomicity)

Q# Which one has max internal energy?

(a) O_3 O_2 O_2 Same

KJ/mol → ΔU

For Ideal gas

$\Delta U = K.E$ $\quad P.E = 0$

ΔU → for ideal gas ⇓ depend on Temperature

~~$\Delta U = \frac{3}{2} K.E_{(av)}$~~ $\quad \Delta U = \frac{3}{2} nRT$

For Real gas:

$\Delta U = K.E + P.E$ or $\Delta U = q_v + \Delta n RT$

↓

depend on T, P, V

In Thermodynamic process

Isochoric process: $(\Delta V = 0)$

$\Delta U = q_v + P\Delta V$ ($\Delta V = 0$)

$\Delta U = q_v$

Isobaric process: $P = \text{const}$ $\quad \Delta P \neq 0$

$\Delta U = q_v + P\Delta V$

↓

(in this case some work can be done)

Adiabatic process: $q_v = 0$

$\Delta U = W$

$+w \Rightarrow \Delta U\uparrow$ $\quad -w \Rightarrow \Delta U\downarrow$

* Isothermal process:

$\Delta U \propto T$ $\quad T=0$ $\quad \Delta U = 0$

$0 = q + w$

$\boxed{q = w}$ → Not change totaly used I. Energy in work done

* Cyclic process:

$\boxed{\Delta U = 0}$

(#) effect of Internal Energy

when $\Delta U \uparrow\uparrow$

* Rxn occurs * state change
* Temperature change * work done
* volume change * pressure change.

Q# when 40J heat is given to a system, it undergoes 10J work the internal energy is.

Sol:

$\Delta U = q + w$

$\Delta U = q - w$ $\quad \Delta U = 40 - 10$

$\boxed{\Delta U = 30J}$

Q# when 50J heat is given to a System, internal energy ~~changes~~ increase 30J, the work done is:

$\Delta U = q + w$

$w = \Delta U - q$

$= 30 - 50$

$\boxed{w = -20J}$

(#) Factors affecting ΔU:

* ΔU α Temperature
* ΔU α Amount — 5 KJ H_2O < 10 KJ H_2O
* ΔU α solid > liquid > solid
* ΔU α stoichemetry of rxn
* ΔU α external pressure
* ΔU α +ve work
* ΔU α $\frac{1}{\text{internal volume}}$

MCQs:

$2H_2 + O_2 \longrightarrow 2H_2O_{(l)}$ (18g)

$4H_2 + 2O_2 \longrightarrow 4H_2O_{(l)}$ ✓ (36g)

⇓ more enthalpy

Q#

graph ← $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$

diamond ← $C_{(s)} + O_{(g)} \longrightarrow CO_2$ ✓

ΔU α stable allotrophic form

New Lec

Enthalpy

* Heat at Constant pressure
* Combination of internal energy & work
* State function (H, ΔH)
* extensive property

$q_p = \Delta H$

$\Delta U = q + w$ $\quad$ $\boxed{q_p = \pm \Delta U \pm W}$

$\boxed{\Delta H = \Delta U \pm W}$ $\quad$ $\boxed{\Delta H = H_2 - H_1}$

Comparision b/w ΔH & ΔU:

* **Constant Volume:**

$\Delta H = \Delta U$ $\quad$ $\Delta V = 0$ $\quad$ $w = 0$

$\downarrow (q_p = q_v)$

$\Rightarrow$ Solid & Liquid

For Gases $\rightarrow$ $\Delta H = \Delta U + \Delta nRT$

MCQs

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $\quad$ $\Delta n = 0$

$\Delta n = 2 - 2 = 0$ then $\boxed{q_p = q_v}$

* **Constant pressure:**

$\Delta H = \Delta U \pm W$

ΔH & ΔU different by w

if w = +ve:

$\boxed{\Delta H > \Delta U \text{ by } w}$ $\quad$ $q_p > q_v$

$\Delta H + \Delta U = w$

100 = 60 + 40

if w = -ve:

$\Delta H = 50$, $\Delta U = 70$, $w = 20$

$\Delta H = \Delta U - W$

50 $\quad$ 70 $\quad$ 20

$\boxed{\Delta H < \Delta U \text{ by } -w}$ $\quad$ $q_p < q_v$

Factors

* $\Delta H \propto T$
* $\Delta H \propto$ gas > liquid > Solid
* $\Delta H \propto$ mass or mole
* $\Delta H \propto$ stoichemetry
* $\Delta H \propto$ Expressure
*

(#) Standard State

* original state of a system.
* Find by observation.
* May be stable or unstable
* May be Real or imaginary
* May achieve or may not achieve
* $T = 25^\circ C$ $P = 1$ atm.

For Gases:

Gas obey gas Law

Liq & solid:

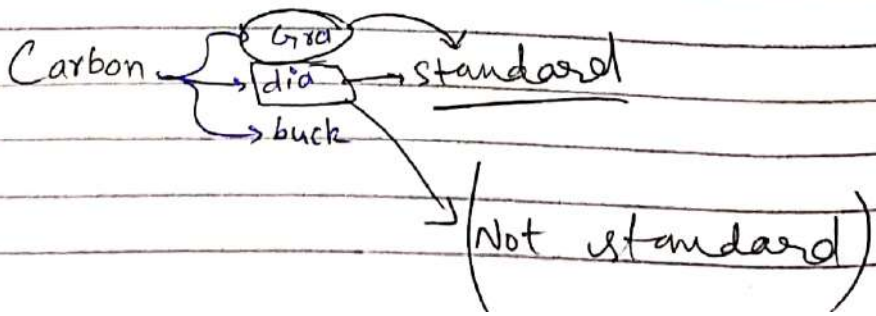
$T = 25^\circ C$, $P = 1$ atm.

Solution:

1 M Concent.

element:

stable allotropic form



exception:

phosphorus stable allotrope ⟶ Black phosphorus

* standard state ⟶ white phosphorus

Standard Enthalpy Change

change in ~~Enthalpy~~ enthalpy at 25°C & 1 atm.

Rxn Condition = T = 25°C p = 1 atm.

(1) Standard enthalpy of Formation

- product = 1 mole
- Reactant = elemental form → e.g. Na, Mg, Ca
  - (For gase) → Homoatomic molecule
    O_2, Cl_2

* State = standard state

Q# Which represent standard enthalpy of formation?

$3H_{2(g)} + N_{2(g)} \longrightarrow 2NH_{3(g)}$ ~~X~~ → 2 moles. → ΔH_r

✓ (b) $C_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)}$ → ΔH_f

c) $CO_{(g)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)}$ → ΔH_r

$$\Delta H_f = \frac{\Delta H_r^\circ}{\text{moles of product}}$$

$3H_2 + N_2 \longrightarrow 2NH_3$ $\quad \Delta H_r^\circ = -20$

$$\Delta H_f^\circ = \frac{\Delta H_r}{2} = \frac{-20}{2} = -10$$

$$\Delta H_r^\circ = \Delta H_f \times \text{moles of product}$$

MCQs

$$A_{(g)} + B_{(g)} \longrightarrow 3C_{(g)} \qquad \Delta H_f^\circ = -7\ KJ$$

what is ΔH_r° for given reaction.

$$\Delta H_r^\circ = -7 \times 3$$
$$= \boxed{-21\ KJ}$$

(2) Standard Enthalpy of Combustion:

Reactants = Organic Compound = 1 Mole

O_2 → excess

State → standard state

product → No condition

MCQs:

W.O represent ΔH_c°

(a) $CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)}$ ✗

(b) $CO_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)}$ ✓

(c) $CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)}$ ✓

$$\Delta H_c^\circ = \frac{\Delta H_r^\circ}{\text{Moles of combustible compound}}$$

$$2CH_4 + 4O_2 \longrightarrow 2CO_2 + 4H_2O$$

$$= \frac{\Delta H_r^\circ}{2}$$

MCQ

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

The ΔH_c° for the rxn is -15J then ΔH_c for the rxn for 4g of CH_4 is:

0rg.C : heat (ΔH)

1 CH_4 : -15

16g = -15J

4 : x

$16x = 60 \quad x = \frac{60}{16} = \boxed{x = -3.75J}$

Q#

$2CH_4 + 4O_2 \longrightarrow 2CO_2 + 4H_2O$

The ΔH_c° for the rxn is -40J then ΔH for 8g of CH_4 is:

$\Delta H = \Delta H_c^\circ \times 2$

$= -40 \times 2 = \boxed{-80J}$

2mole = -80J

0.5n : x

$2x = 40 \quad \boxed{x = 20J}$

(3) Standard Enthalpy of Neutralization

H_2O = 1mole

Acid & Base = standard state

$H^+ + OH^- \longrightarrow H_2O$

$\boxed{\Delta H_f^\circ = -57.8 KJ/mole \quad \Delta H_r^\circ = -14.3 KJ/mole}$

Q#

$HCl_{(l)} + NaOH_{(l)} \longrightarrow NaCl + H_2O$

~~HCl (g) +~~

$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O \quad \Delta H_x$

$$\Delta H_n^\circ = \frac{\Delta H_r^\circ}{\text{moles of } H_2O}$$

$$\Delta H_r = -57.8 \times \text{moles of } H_2O$$

Q#:

$HCl + NaOH \longrightarrow NaCl + H_2O$

when 0.5 moles of HCl reacted with 2 moles of NaOH then ΔH_r is:

HCl : H_2O

1 : 1

0.5 : x

$x = 0.5$

$\Delta H_r = -57.8 \times 0.5$

$\Delta H_r = -28.9$ kJ

Q#:

$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$

when 0.5 moles of NaOH react with 2 mole of H_2SO_4 then ΔH_r of the rxn is:

NaOH : H_2O

2 : 2

0.5 : x

$2x = 1$ $(x = 0.5)$ -28.9 kJ

New Lec

Enthalpy of Solution:

The heat of Solution at a dilution point in which No further change in heat occur.

* Condition ⟶ ions → aq
ions ⟶ 1M

e.g

$NH_4Cl \xrightarrow{H_2O} NH_4^+_{(aq)} + Cl^-_{(aq)}$

$KCl \xrightarrow{H_2O} K^+_{(aq)} + Cl^-_{(aq)}$

* endothermic Solute: → which absorb the heat
↓
solvent → cooling

NaOH put in H_2O → so solution (H_2O) cool.
absorb heat from H_2O

* Exothermic solute:
↓
solvent → heating

Enthalpy of Atomization:

* Molecule ⟶ (convert) ⟶ atom

* Atoms ⟶ 1M
(in standard state)

✗ $H_{2(g)} \longrightarrow 2H$ ΔH_r

✓ $\frac{1}{2} H_{2(g)} \longrightarrow H$ ΔH_{ato}

* ΔH = +ve & -ve:

* enthalpy of formation
* enthalpy of Reaction
* " " Solution
* " " lattice

* ΔH = +ve:

* atomization
* ionization enthalpy
* 2nd E.A enthalpy
* 1st E.A of (Be, Mg, Al)
* Bond dissociation enthalpy
* Bond breaking

* ΔH = -ve:

* Hydration
* Combustion
* Neutralization
* 1st E.A
* Bond formation.

Measurement of Enthalpy

Calorimetry:

Study of measuring of heat of energy or enthalpy.

* Measure by Temperature change

Direct	indirect
* For single step rxn	* Multi step rxn.
* No side rxn	* Side rxn.
* Rxn Complete	* Rxn incomplete

Direct

* All reactants convert to product
* No protective Coating
* Rate → intermediate
*
* Glass Calorimetry
  ↓
  Simple Calo
  * Constant pressure Calo
  *
  ($CH_4 + O_2 \rightarrow CO_2 + H_2O$)
  ↓
  direct (bomb)

Indirect

* All reactants not Convert to product.
* protective coating present
* Rate → very fast / very slow.
* Hess's Law used
* Bomb calorimetry
  ↓
  * Constant Volume Calor
  * used for organic compound in food
  * ($Al + O_2 \rightarrow Al_2O_3$) indirect

Heat Capacity

Amount of heat required to rise temperature of 1°C of a substance.

* extensive property
* Nature of Substance dependant.

$C \propto$ attractive forces

$C = \frac{q}{\Delta T}$ unit JC^{-1}, JK^{-1}

Q# Max heat Capacity

5 Kg H_2O < 10 Kg H_2O | 5 Kg H_2O < 5 Kg Cu

5 Kg H_2O > 5 Kg $Br_{2(l)}$

Specific heat Capacity

Heat require to raise Temperature of unit mass by 1°c.

unit mass → 1Kg, 1g

$C_s = \frac{C}{mass}$ $C_s = \frac{q}{\Delta T m}$

unit → $\frac{J}{K\,Kg}$

* intensive property
* depend on Nature of Substance.

$C_s \propto$ attractive forces

Max Cs: 5 Kg H_2O = 10 Kg H_2O

Max Cs: 5 kg H_2O < 5 Kg Cu

Molar heat Capacity

heat Capacity for one mole.

$C_m = C_s \times M.mass$

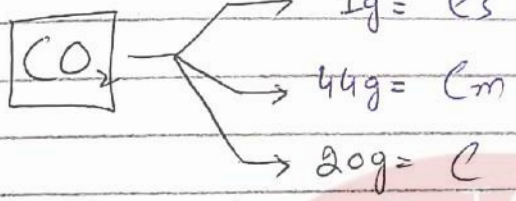
H_2O

1g (Cs) × 18 = 18g (C_m)

$C_m > C_s$ by M.M times

Q# The C_m of ${}^{12}_{6}C$ is how much greater than its C_s.

(a) 12 times



$C_m = C_s \times M.M$

$C_m = \frac{q}{\Delta T \times m} \times M.M \Rightarrow C_m = \frac{q}{\Delta T \times n}$

($C_m \rightarrow J K^{-1} \cdot mol^{-1}$)

* intensive property
* depend on Nature.
* C_m ∝ attractive forces imp

$\Rightarrow C_m = \frac{q_v}{\Delta T n} \Rightarrow C_m = \frac{\Delta U}{\Delta T \cdot n}$ $\quad \Delta U = C_m \times \Delta T \cdot n$ imp

$\Rightarrow C_m = \frac{q_p}{\Delta T n} \Rightarrow C_m = \frac{\Delta H}{\Delta T \cdot n}$ $\quad \Delta H = C_m \times \Delta T \cdot n$

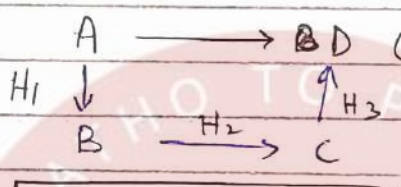
$\Rightarrow C_s = \frac{q}{\Delta T \cdot m}$ $\quad q = C_s \times \Delta T \cdot m$ imp

$q_v = C_s \times \Delta T \cdot m \Rightarrow \Delta U = C_s \times \Delta T \cdot m$ imp

$q_p = C_s \times \Delta T \cdot m \Rightarrow \Delta H = C_s \times \Delta T \cdot m$

Hess's Law

* ΔH ~~Rxn~~ is independant of path
* enthalpy same either Rxn occurs in one or more step
* Analogue to Law of conservation of energy.
* defined ΔH



$$\Delta H = H_1 + H_2 + H_3$$

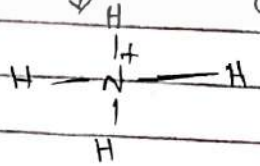
Application:

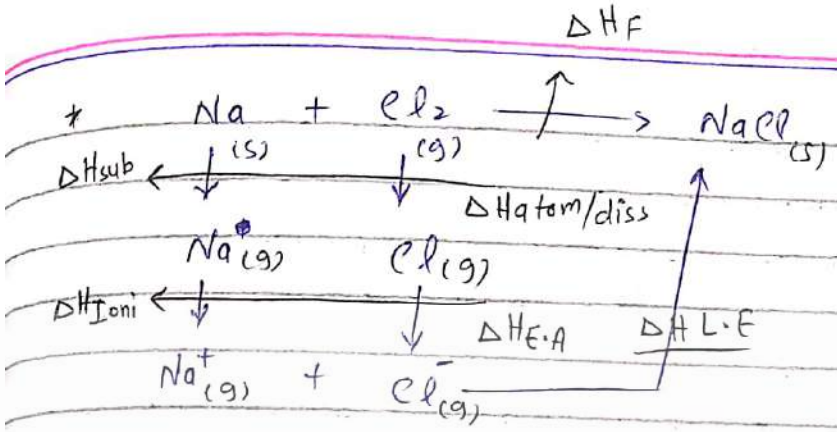
1) Born Haber's process:

* used to Find Lattice energy
* valid for Binary Compound
  ↓
  (one type of Cation & one type of anion)

For
* Fully Ionic Compound.

e.g.
* NaCl ✓
* $MgCl_2$ ✓
* $Ca(OH)_2$ X
  of H
  ↓
  C-Bond
* Na_2SO_4 X
  ↓
  C·B
* $NaHClO_4$ X
* NH_4Cl → X (co-ord)





$$\Delta H_f = \Delta H_{sub} + \Delta H_{Ion} + \frac{\Delta H_D}{2} + \Delta H_{E.A} + \Delta H_{L.E}$$

$$\Delta H_{L.E} = \Delta H_f - \left(\Delta H_{sub} + \Delta H_{ion} + \frac{\Delta H_D}{2} + \Delta H_{E.A}\right)$$

Q# what is the ΔH_{sub} in formation of NaCl if $\Delta H_{L.E} = -20J$, $\Delta H_f = 40J$ & $\Delta H_{E.A} = -15J$

(2) ΔH from Bond energy:

Co-effi

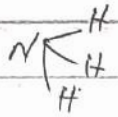
$$\Delta H = \sum n B.E_{(R)} - \sum n B.E_{(P)}$$

Q# $3H_2 + N_2 \longrightarrow 2NH_3$

H—H B.E = −10J

N≡N B.E = +15J

N—H B.E = 20J



$$\Delta H = (3H_2 + N_2) - (2NH_3)$$

$$= [3(H-H) + (N\equiv N)] - [6(N-H)]$$

$$= [3(-10) + (15)] - [6(20)]$$

$$= (-30 + 15) - 120 = -135J$$

$$= -15 - 120$$

Q#

$CH_4 + 2O_2 \longrightarrow CO_2 + H_2O \quad (\Delta H = -120\,J)$

$C-H \quad B.E = -15\,J$

$O=O \quad B.E = 20\,J \qquad C=O \quad B.E = -40\,J$

$(H-O \quad B.E = ?)$

$\Delta H = [(CH_4) + 2(O_2)] - [(CO_2) + 2(H_2O)]$

$= [4(C-H) + 2(O=O)] - [2(C=O) + 4(H-O)]$

$-120 = [4(-15) + 2(20\,J)] - [2(-40\,J) + 4(H-O)]$

$120\,J = (-20\,J) - (-80 + 4(H-O)]$

~~$120\,J = -20\,J +$~~ $4(H-O) = 180$

$(H-O) = \frac{180}{4}$ $\quad \boxed{H-O = 45\,J}$

④ From enthalpy of Formation

$$\boxed{\Delta H = \sum \Delta H_f^{\circ}_{(P)} - \sum \Delta H_f^{\circ}_{(R)}}$$

element standard state $\Delta H_f^{\circ} = 0$

Q#

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

CH_4 (g) $\quad O_2$ (g) $\quad CO_2$ (g) $\quad H_2O$ (l)

$CH_4 = \Delta H_f^{\circ} = -15\,J \qquad O_2\ (l)\ \Delta H_f^{\circ} = +15\,J$

$CO_2 = \Delta H_f = 40\,J \qquad H_2O\ \Delta H_f = -30\,J$

$\Delta H = [(CO_2) + 2(H_2O)] - [(CH_4) + 2(O_2)]$

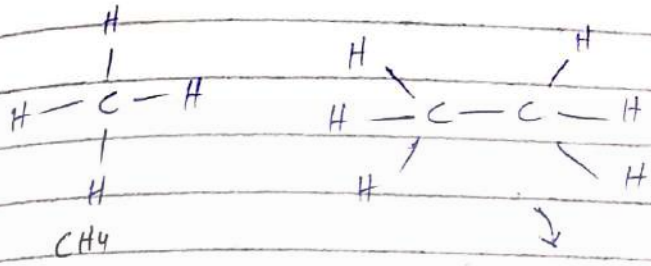
$= [(40\,J + 2(-30)] - [(-15\,J) + 2(0)]$

$= -20 + 25$

$\boxed{\Delta H = 5\,J}$

New Lec

Q# if ΔH for CH_4 is 360J & C_2H_6 is 620J then B.E of C-C.



CH_4

$4(C-H) = 320J$

$\frac{360}{4} = 90J$

$= 6(C-H)$

$= 6(90)$

$= 540$

$C-C = 620 - 540$

$\boxed{C-C = 80J}$

(#) ΔH from enthalpy of other Rxn:

$C + \frac{1}{2}O_2 \longrightarrow CO \quad \Delta H = ?$

if

$C + O_2 \longrightarrow CO_2 \quad \Delta H = 10J$

$CO + \frac{1}{2}O_2 \longrightarrow CO_2 \quad \Delta H = 20J$

Sol:

$C + O_2 \longrightarrow CO_2 \quad \Delta H = 10J$

$CO_2 \longrightarrow CO + \frac{1}{2}O_2 \quad \Delta H = -20J$

$(\Delta H = H_1 + H_2)$

$C + \frac{1}{2}O_2 \longrightarrow CO \quad \boxed{\Delta H = -10J}$

(#) $C + 2H_2 \longrightarrow CH_4 \quad \Delta H = ?$

if

✓ $C + O_2 \longrightarrow CO_2 \quad \Delta H = 20J$

$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O \quad \Delta H = -10J$

✓ $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O \quad \Delta H = -45J$

$C + O_2 \longrightarrow \Delta H = 20J$

$2H_2 + O_2 \longrightarrow 2H_2O = -20J$ (Xing by 2)

$CO_2 + 2H_2O \longrightarrow CH_4 + 2O_2 \quad \Delta H = +15J$

$C + 2H_2 \longrightarrow CH_4 \quad \boxed{\Delta H = +15J}$