

THERMOCHEMISTRY

Thermochemistry is the study of the energy and heat associated with chemical reactions and/or physical transformations. Thermochemistry coalesces the concepts of thermodynamics with the concept of energy in the form of chemical bonds. The subject commonly includes calculations of such quantities as heat capacity, heat of combustion, heat of formation, enthalpy.

A reaction may release or absorb energy, and a phase change may do the same, such as in melting and boiling. Thermochemistry focuses on these energy changes, particularly on the system's energy exchange with its surroundings.

ENTHALPY

Chemical reactions are generally carried out at constant pressure (atmospheric pressure) so it has been found useful to define a new state function **Enthalpy** (H) (earlier defined in thermodynamics):

$$H = U + PV$$

and hence, $\Delta H = \Delta U + \Delta(PV)$

At constant pressure

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

Combining with first law,

$$\Delta H = q_p$$

Hence, transfer of heat at constant pressure brings about a change in the enthalpy of the system.

Enthalpy change, $\Delta_r H$ of a reaction-Reaction enthalpy-Heat of reaction

The enthalpy change accompanying a reaction is called the reaction enthalpy. It may also be defined as the amount of heat lost or gained in the chemical reaction, when all the reactants and products are maintained at the same temperature and pressure. The enthalpy change of a chemical reaction may be given as

$$\begin{aligned}\Delta_r H &= (\text{sum of enthalpies of products}) - (\text{sum of enthalpy of reactants}) \\ &= \sum (\nu_p H)_{\text{products}} - \sum (\nu_p H)_{\text{reactants}}\end{aligned}$$

where ν is the stoichiometric coefficients of reactants and products, respectively.

Types of Reactions :

- (i) **Exothermic Reactions** : Heat is evolved during the reaction. For such reactions $\Delta_r H$ is negative, which implies that

$$\sum \nu_p H (\text{products}) < \sum \nu_R H (\text{reactants})$$

- (ii) **Endothermic Reactions** : Heat is absorbed during the reaction. For such reactions $\Delta_r H$ is positive, which implies that

$$\sum \nu_p H (\text{products}) > \sum \nu_R H (\text{reactants})$$

Note :

1. For a reaction whose $\Delta H = +ve$ and $\Delta E = -ve$, what will be the classification as exothermic and endothermic.
2. In general, reactions have ΔH and ΔE of same sign unless the values of ΔH and ΔE are exceptionally small

Factors affecting ΔH of the reactions are :

- (i) Physical states of reactants & products
 - (ii) Allotropic forms of elements
 - (iii) Reaction conditions (constant pressure or constant volume)
- (i) Condition of constant P or V : Heat changes at constant volume are expressed as ΔE
Heat changes at constant pressure are expressed as ΔH
Also for a change $\Delta H = \Delta E + P\Delta V$ (1)
where P is the pressure and ΔV is change in volume.
Also ΔH and ΔE are related together as

$$\Delta H = \Delta E + \Delta n_g RT \quad \text{.....(2)}$$

Where ΔH and ΔE are change in enthalpy and change in internal energy for a given change respectively.

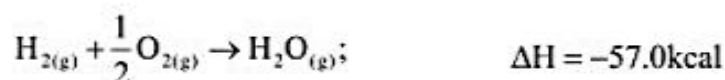
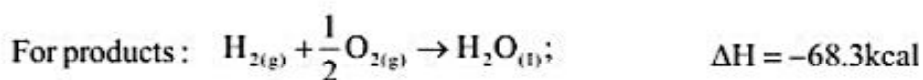
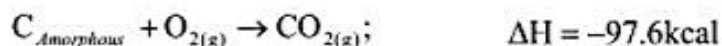
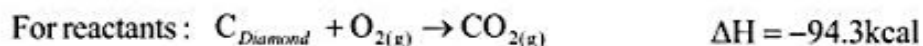
Δn_g = Moles of gaseous products - Moles of gaseous reactants.

R = Molar gas constant

T = Temperature in Kelvin

NOTE : While using eq. (2) for numerical one should keep in mind that for

- a. For calculation of Δn_g only gaseous moles of reactants and products are considered
 - b. If $\Delta n_g = 0$; $\Delta H = \Delta E$
 - c. Δn_g may be +ve or -ve integer or fraction.
 - d. Put R in the same units in which ΔH and ΔE are given.
 - e. Normally reactions are carried out at constant pressure and therefore, heat changes are to be taken as ΔH unless stated otherwise.
- (ii) Physical nature of reactants and products :



Therefore, it is necessary to write physical state of reactants and products while writing thermochemical equation.

- (iii) Temperature : The variation of ΔH or ΔE with temperature is expressed in terms of Kirchhoff's equation as, $\Delta H_2 - \Delta H_1 = \Delta C_p(T_2 - T_1)$ or $\Delta E_2 - \Delta E_1 = \Delta C_v(T_2 - T_1)$

Where ΔH and ΔE are heats of reaction at temperature T_1

ΔH_1 and ΔE_1 are heats of reaction at temperature T_2

$$\Delta C_p = \sum \nu_p C_{p(\text{Product})} - \sum \nu_p C_{p(\text{Reactant})}$$

$$\Delta C_v = \sum \nu_p C_{v(\text{Product})} - \sum \nu_p C_{v(\text{Reactant})}$$

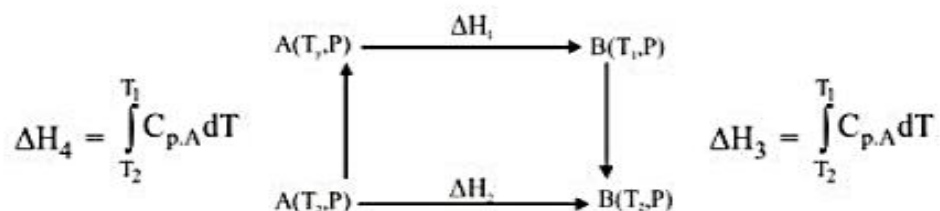
C_p and C_v are molar specific heats at constant P and V respectively.

Note :

1. The above expression should be used only when all the gases involved are ideal and reaction occurs at constant temperature.
2. It is advisable to start with $\Delta H = \Delta E + \Delta(PV)$ which is a general expression and then depending upon data appropriate expressions should be used.

Variation of enthalpy with temperature (Kirchoff's Equation) :- The enthalpy of chemical reactions and phase transition do vary with temperature. Although the variation in ΔH with temperature is usually small compared to the value of ΔH itself.

consider a reaction $A \rightarrow B$ at temperature T_1 and pressure P



Since H is state function :- Change in enthalpy in cyclic process is equal to zero. To calculate enthalpy change (ΔH_2) at temperature T_2 at constant pressure consider cyclic process shown in figure. It is clear ΔH_3 = change in enthalpy of A when temperature is raised from T_1 to T_2 at constant

pressure. $\Delta H_3 = \int_{T_1}^{T_2} C_{p,A} dT$

ΔH_4 = Change in enthalpy taking 1 mole of B at constant pressure from T_1 to T_2

$$\Delta H_4 = \int_{T_1}^{T_2} C_{p,B} dT \quad \text{now :}$$

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

$$\Rightarrow \Delta H_2 - \Delta H_1 = \Delta H_3 + \Delta H_4 \quad \Rightarrow \Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} (C_{p,B} - C_{p,A}) dT$$

$$\Rightarrow \Delta H_2 - \Delta H_1 = \Delta_r C_p (T_2 - T_1)$$

If $\Delta_r C_p$ is independent of 'temperature'

Standard enthalpy of Reaction, $\Delta_r H^\circ$:

As enthalpy of a reaction depends on the conditions under which a reaction is carried out, it is necessary to specify some standard conditions. The standard enthalpy of reaction is the enthalpy change for a reaction, when all the participating substance (reactants and products) are in their standard condition.

Note :1. **The standard condition are :**

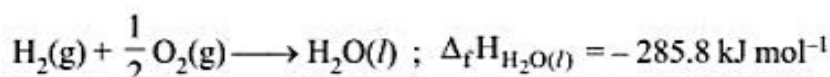
* Solid / liquid / gas should be at 1 bar

* For substance dissolved in solution concentration should be 1M.

2. Standard conditions in Thermodynamics does not specify any temperature. However in Electrochemistry it is taken as 298K.

Enthalpy changes in chemical reactions :**(1) Enthalpy of Formation, $\Delta_f H$:**

It is the enthalpy change when one mole of a substance is formed from its elements in their most abundant naturally occurring form (also called reference states).

**Note :**1. By convention, enthalpy of formation $\Delta_f H$, of an element in reference state is taken as zero.

2. The enthalpy of formation can be used to determine the enthalpy change of any reaction as

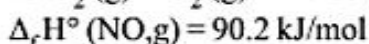
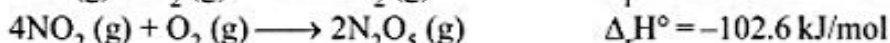
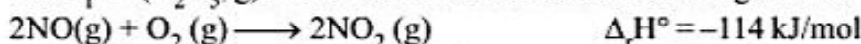
$$\Delta_r H = \sum_i a_i \Delta_f H_{(\text{Products})} - \sum_i b_i \Delta_f H_{(\text{reactants})}$$

where a_i and b_i represent the coefficients of the products and reactants in the balanced chemical equation.

3. $\Delta_f H$ data can be used to compare stability of isomer and allotropes

4. The reference state of commonly used elements are :

Elements	Reference state
C	C _(graphite)
S	S _{8(Rhombic)}
P	P _{4(white)}
O	O _{2(g)}
H	H _{2(g)}
Br	Br _{2(l)}
Metal	M _(s) [except Hg _(l)]
P	P _{4(white)}

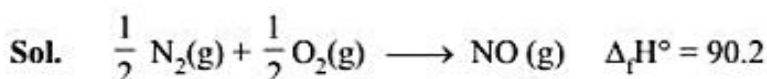
Illustration1. The $\Delta_f H^\circ$ (N₂O₅, g) in kJ/mol on the basic of the following data is :

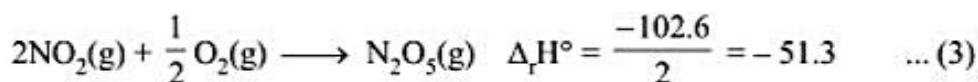
(A) 15.1

(B) 30.2

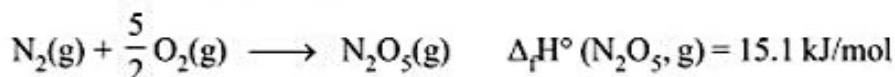
(C) -36.2

(D) None of these

Ans. (A)



Addition of (1), (2) and (3) equation



Exercise

1. How much heat will be required at constant pressure to form 1.28 kg of CaC_2 from CaO(s) & C(s) ?

Given: $\Delta_f H^\circ (\text{CaO, s}) = -152 \text{ kcal/mol}$.

$\Delta_f H^\circ (\text{CaC}_2, \text{s}) = -14 \text{ kcal/mol}$

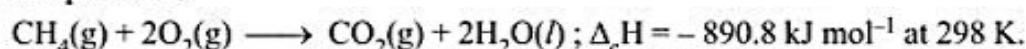
$\Delta_f H^\circ (\text{CO, g}) = -26 \text{ kcal/mol}$

(A) +112 kcal (B) 224 kcal (C) 3840 kcal (D) 2240 kcal

Ans. (D)

(2) Enthalpy of Combustion, $\Delta_c H$:

It is the enthalpy change when one mole of the substance undergo complete combustion to give combustion products.



The combustion products of the substances are

Elements	Combustion products
C	$\text{CO}_{2(\text{graphite})}$
H	$\text{H}_2\text{O}_{(l)}$ or $\text{H}_2\text{O}_{(g)}$ [depends on condition]
S	$\text{SO}_{2(g)}$

Illustration

1. The heat of combustion of sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}\text{(s)}$ at constant volume is $-1348.9 \text{ kcal mol}^{-1}$ at 25°C , then the heat of reaction at constant pressure, when stem is produced, is

Sol. The combustion equation of sucrose is



Here,

$\Delta n_g = \text{sum of gaseous product moles} - \text{sum of gaseous reactant moles}$

$$\Delta n_g = 11$$

$$\Delta H = \Delta E + \Delta n_g RT,$$

$$\text{Here, } \Delta E = -1348.9 \text{ kcal}$$

$$R = 2.0 \text{ cal, } T = 25 + 273 = 298 \text{ K}$$

$$\therefore \Delta H = (-1348.9 \times 1000) + 11 \times 2 \times 298$$

$$= -1348900 + 6556 = -1342344 \text{ cal}$$

$$= -1342.344 \text{ kcal}$$

Exercise

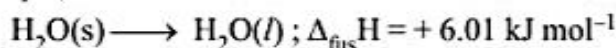
1. For the given heat of reaction,
 (i) $\text{C(s)} + \text{O}_2(\text{g}) = \text{CO}_2(\text{g}) + 97 \text{ kcal}$ (ii) $\text{CO}_2(\text{g}) + \text{C(s)} = 2\text{CO(g)} - 39 \text{ kcal}$
 the heat of combustion of CO(g) is :

Ans. 69 kcal

(3) Enthalpy changes during phase transformations :

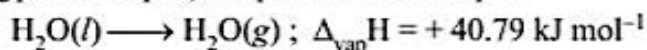
- (i) **Enthalpy of Fusion, $\Delta_{\text{fus}} H$:** It is the enthalpy change that accompanies melting of one mole of a solid substance at constant temperature (melting point of solid) and pressure.

for example,



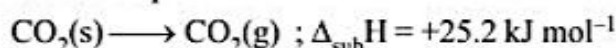
- (ii) **Enthalpy of Vaporisation, $\Delta_{\text{vap}} H$:**

It is the enthalpy change required to vapourise one mole of a liquid substance at constant temperature (boiling point of liquid) and pressure for example :



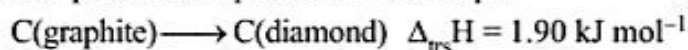
- (iii) **Enthalpy of Sublimation, $\Delta_{\text{sub}} H$:**

It is the enthalpy change required to sublime one mole of a solid substance at constant temperature and pressure. For example



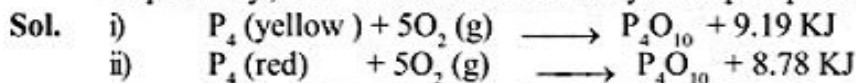
- (iv) **Enthalpy of Transition :**

It is the enthalpy change when one mole of one allotropic form changes to another under conditions of constant temperature and pressure. For example



Illustration

1. The heats of combustion of yellow phosphorus and red phosphorous are - 9.19 KJ and - 8.78 KJ respectively, then heat of transition of yellow phosphorus to red phosphorous is



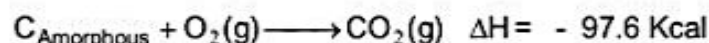
Subtracting, $\text{P}_4(\text{yellow}) - \text{P}_4(\text{red}) = 1.13 \text{ KJ}$

$\Rightarrow \text{P}_4(\text{yellow}) = \text{P}_4(\text{red}) + 1.13 \text{ KJ}$

So, heat of transition of yellow to red phosphorus is - 1.13 KJ

Exercise

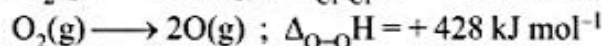
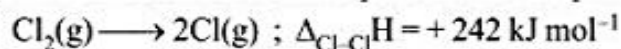
1. The heat of transition for carbon from the following



Ans. 3.3 KJ/mol

(4) Bond Enthalpies (Bond energies), $\Delta_{\text{bond}} H$:

The bond enthalpy of diatomic molecules like H_2 , Cl_2 , O_2 etc. may be defined as the enthalpy change when one mole of covalent bonds of a gaseous covalent substance is broken to form products in the gas phase, under conditions of constant pressure and temperature. For example



In case of polyatomic molecules, bond dissociation enthalpy is different for different bonds within the same molecule. In such cases, mean bond enthalpy is used. Mean bond enthalpy may be defined as the average enthalpy change to dissociate a particular type of bond in the compounds.

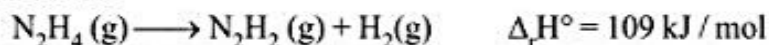
In gas phase reactions, the standard enthalpy of reaction, $\Delta_r H^\circ$, is related with the bond enthalpies of reactants and products as

$$\Delta_r H^\circ = \Sigma \text{ bond enthalpies (reactants)} - \Sigma \text{ bond enthalpies (products)}$$

$$= \Sigma \epsilon \text{ of reactants} - \Sigma \epsilon \text{ of products}$$

Illustration

1. For the reaction



Calculate the bond enthalpy of $N=N$.

Given : B.E. ($N-N$) = 163 kJ/mol, B.E. ($N-H$) = 391 kJ/mol, B.E. ($H-H$) = 436 kJ/mol

Sol. The equation :

$$\Delta H = 109 = \epsilon_{N-N} + 4\epsilon_{N-H} - \epsilon_{H-H} - 2\epsilon_{N-H} - \epsilon_{N=N}$$

$$\epsilon_{N=N} = 163 + 2 \times 391 - 436 - 109 = 400 \text{ kJ/mole}$$

Exercise

1. What is the Bond energy (In kJ/mol) of $C-H$ in Methane from the following data?

$$\Delta H_f [CO_2(g)] = - 394 \text{ kJ / mol}$$

$$\Delta H_f [H_2O(l)] = - 285 \text{ kJ / mol}$$

$$\Delta H_{\text{sublimation}} \{\text{Carbon (graphite)}\} = + 716 \text{ kJ/mol}$$

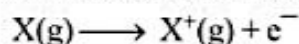
$$\Delta H_{\text{combustion}} [CH_4(g)] = - 890 \text{ kJ / mol}$$

$$\text{Bond energy (H-H)} = 435 \text{ kJ/mol}$$

Ans. 415 kJ/mol

(5) Ionisation Enthalpy ($\Delta_i H$)

It is the enthalpy change when an electron is removed from an isolated gaseous atom or in its ground state under conditions of constant temperature and pressure.

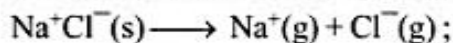
**(6) Electron Gain Enthalpy ($\Delta_{eg} H$)**

It is the enthalpy change when an electron is added to a neutral gaseous atom to convert it into a negative ion under conditions of constant temperature and pressure.



(7) Lattice Enthalpy ($\Delta_{\text{lattice}} H$)

The lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state under conditions of constant temperature and pressure.

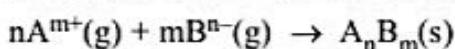


$$\Delta_{\text{lattice}} H = + 788 \text{ kJ mol}^{-1}$$

Lattice enthalpy can also be defined for the reverse process. In that case the value of ΔH_{LE} will be negative.

Born–Haber Cycle For NaCl :

This cycle is based on thermochemical changes taking place in the formation of a lattice. This cycle can be used to determine lattice energy which cannot be directly measured. It is defined as that energy released when one mole of the ionic compound (lattice) is formed its isolated ions in the gaseous state under standard condition.



$$\Delta H = - U \text{ (lattice energy)}$$

Formation of NaCl(s) lattice involves thus.

$$S + I + \frac{\epsilon_{\text{Cl-Cl}}}{2} - E - U = q$$

hence, U can be calculated.

here, S = enthalpy of sublimation of Na(s) = $\Delta H_{\text{sublimation}}$

I = ionisation of energy of Na(g) = $\Delta H_{\text{ionization}}$

ϵ = bond energy of Cl_2

U = lattice energy

q = enthalpy of formation of NaCl(s) = $\Delta H_{\text{formation}}$

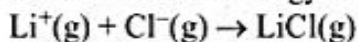
If lattice is $\text{MgX}_2(\text{s})$ then

$$S + (I_1 + I_2) + \epsilon - 2E - U = q$$

where, $(I_1 + I_2)$ = total ionisation energy to form $\text{Mg}^{2+}(\text{g})$.

Illustration

1. Calculate lattice energy for the change,



Given that

$\Delta H_{\text{sublimation}}$ of Li = $160.67 \text{ kJ mol}^{-1}$,

$\Delta H_{\text{ionisation}}$ of Li(g) = $520.07 \text{ kJ mol}^{-1}$,

ΔH_f of LiCl(s) = $- 401.66 \text{ kJ mol}^{-1}$.

$\Delta H_{\text{Dissociation}}$ of Cl_2 = $244.34 \text{ kJ mol}^{-1}$,

$\Delta H_{\text{E.A}}$ of Cl(g) = $- 365.26 \text{ kJ mol}^{-1}$,

- Sol. Considering the different changes that occur in the formation of solid lithium chloride based on the data given the lattice energy of the above can be constituted as :

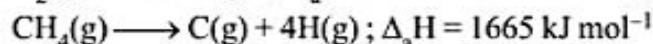
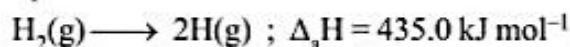
$$\Delta H_f^\circ = \Delta H_{\text{subl.}} + \Delta H_{\text{I.E.}} + \frac{1}{2} \Delta H_{\text{Diss.}} + \Delta H_{\text{E.A}} + \Delta H_{\text{lattice}}$$

$$\begin{aligned} \text{or } \Delta H_{\text{lattice}} &= \Delta H_f^\circ - \Delta H_{\text{subl.}} - \Delta H_{\text{I.E.}} - \frac{1}{2} \Delta H_{\text{Diss.}} - \Delta H_{\text{E.A}} \\ &= - 839.31 \text{ kJ mol}^{-1} \end{aligned}$$

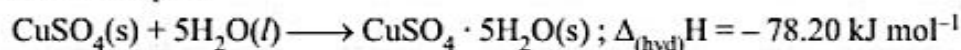
(8) Enthalpy of Atomisation, $\Delta_a H$:

It is the enthalpy change when one mole of a substance is completely dissociated into atoms in the gaseous state, under constant pressure and temperature condition.

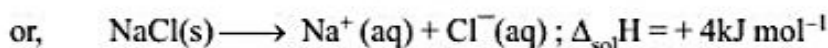
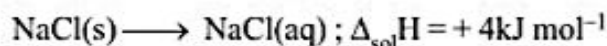
For example

**(9) Enthalpy of Hydration, $\Delta_{hyd} H$:**

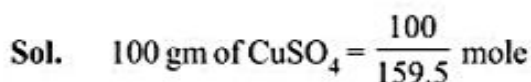
It is the enthalpy change when one mole of an anhydrous (or partly hydrated) compound combines with the required number of moles of water to form a specific hydrate at the specified temperature and pressure. For example :

**(10) Enthalpy of Solution, $\Delta_{sol} H$:**

It is the enthalpy change when one mole of a substance is dissolved in a specified amount of solvent under conditions of constant temperature and pressure. When large volume of solvent is taken, the enthalpy change is called enthalpy of solution at infinite dilution. For example

**Illustration**

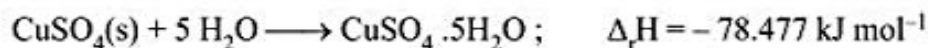
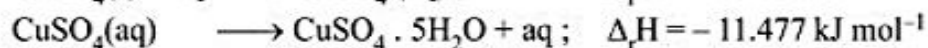
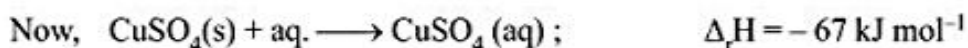
1. 100 gm of anhydrous $CuSO_4$, when dissolved in excess of water produces 42 kJ of heat. The same amount of $CuSO_4 \cdot 5H_2O$ on dissolving in large excess of water absorbed 4.60 kJ. What is the heat of hydration $CuSO_4$?



$$\text{Heat of solution of } CuSO_4 \text{ per mole} = -\frac{42 \times 159.5}{100} = -66.99 \text{ kJ} \Rightarrow -67 \text{ kJ}$$

$$100 \text{ gm of } CuSO_4 \cdot 5H_2O = \frac{100}{249.5} \text{ mole}$$

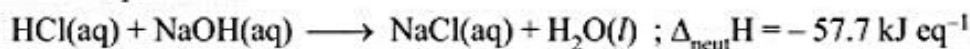
$$\text{Heat of solution per mole } (CuSO_4 \cdot 5H_2O) = 4.6 \times \frac{249.5}{100} = 11.477 \text{ kJ}$$



\therefore Enthalpy of hydration of $CuSO_4(s) ; \Delta H = -78.477 \text{ kJ mol}^{-1}$ **Ans.**

(11) Enthalpy of Neutralisation $\Delta_{\text{neut}}H$:

It is the enthalpy change when one g-equivalent of an acid and one g-equivalent of a base undergo complete neutralisation in aqueous solution and all the reactants & products are at the same specified temperature and pressure.

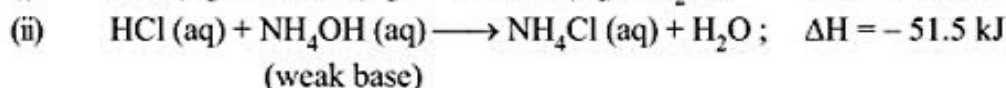
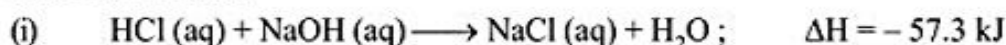


The enthalpy of neutralisation of strong acid and strong base is always constant (-57.7 kJ eq^{-1}), independent from the acid and base taken. However, the magnitude of enthalpy change of neutralisation decreases when any one of the acid or base taken is weak.

The value (-57.7 kJ eq^{-1}) is the value when acids and bases are taken in their infinitely diluted state. If acids and bases are having some other concentration, then value will differ.

Illustration

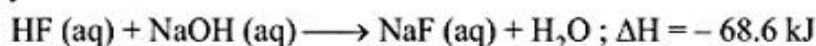
1. Heat of neutralization (ΔH) of NH_4OH and HF are -51.5 and -68.6 kJ respectively. Calculate their heat of dissociation?



Sol. \therefore The heat of dissociation of NH_4OH ,

$$\Delta H = -51.5 - (-57.3) = 5.8 \text{ kJ}$$

Similarly we have



\therefore The heat of dissociation of HF ,

$$\Delta H = -68.6 - (-57.3) = -11.3 \text{ kJ}$$

Exercise

1. Calculate $\Delta_{\text{neut}}H$ of HA . If bond dissociation energy of H-A is 5 KJ/mol

Ans. -52.7 KJ/mol

(12) Resonance energy :

When two or more double bond are in conjugation, there is possibility of delocalization of electron through conjugation. The Phenomenon is called resonance. Due to resonance, the molecule gain stability. The actual structure of molecule is average of many possible canonical structure possible for molecule. When ever there is possibility of Resonance energy is difference in energy of most stable canonical structure and energy of actual molecule.

When ever there is possibility of resonance in molecule, the molecule become more stable and bond breaking become difficult.

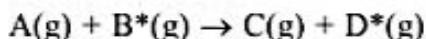
Calculation of resonance energy using bond energy :

Resonance energy can be calculated using the formula

$$\Delta H (\text{Actual}) - \Delta H (\text{theoretical}) = \text{resonance energy of products} - \text{Resonance energy of reactants}$$

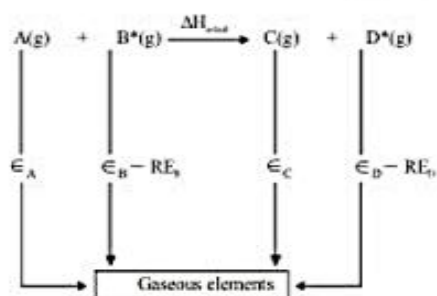
The proof of above formula is given by following diagram.

Consider a reaction



where (*) showing that molecules exhibit phenomena of resonance. Remember where ever resonance take place, bond breaking become difficult.

Actual energy required to break a bond is equal to $\epsilon_{\text{actual}} = \epsilon_{\text{theoretical}} - \text{resonance energy}$



$$\Delta H_{\text{actual}} = \epsilon_A + \epsilon_B - R.E_B - \{\epsilon_C + \epsilon_D - R.E_D\}$$

$$\Delta H_{\text{actual}} = (\epsilon_A + \epsilon_B - \epsilon_C - \epsilon_D) + R.E_B - R.E_D$$

$$[\Delta H_{\text{actual}} - \Delta H_{\text{Theoretical}} = R.E_{\text{Products}} - R.E_{\text{reactants}}]$$

Note : The value of resonance energy may be positive or negative, but assign it's sign on the basis that resonance always increases the stability and decreases the energy of molecule. Due to resonance in a molecule, bond breaking become difficult hence actual energy required to break a bond = theoretical bond energy – resonance energy.

Illustration

1. Calculate resonance energy of $C_6H_6(g)$.

Given: $\Delta H_f [C_6H_6(g)] = -360 \text{ kJ mol}^{-1}$

$$\Delta H_{\text{Sub}} [C(\text{graphite})] = 716 \text{ kJ mol}^{-1}$$

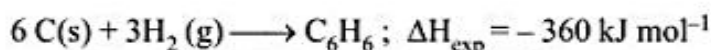
$$B.E_{H-H} = 437 \text{ kJ mol}^{-1}$$

$$B.E_{C-C} = 620 \text{ kJ mol}^{-1}$$

$$B.E_{C-C} = 340 \text{ kJ mol}^{-1}$$

$$B.E_{C-H} = 490 \text{ kJ mol}^{-1}$$

Sol. For C_6H_6



$$\begin{aligned} \therefore \Delta H_{\text{cal}} &= -[3(C-C) + 3(C=C) + 6(C-H)] + [6C_{s \rightarrow g} + 3(H-H)] \\ &= -[3 \times 340 + 3 \times 620 + 6 \times 490] + [6 \times 716 + 3 \times 437] \\ &= -5820 + 5607 = -213 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \therefore \text{Resonance energy} &= \text{Exp. } \Delta H_f - \text{Calculated } \Delta H_f \\ &= -360 - (-213) = -360 + 213 = -147 \text{ kJ mol}^{-1} \end{aligned}$$

Exercise

1. The standard molar enthalpies of formation of cyclohexane (*l*) and benzene (*l*) at 25°C are –156 and +49 kJ mol⁻¹ respectively. The standard enthalpy of hydrogenation of cyclohexene (*l*) at 25°C is –119 kJ mol⁻¹. Use these data to estimate the magnitude of the resonance energy of benzene.

Ans. 152 KJ

Different types of standard enthalpy changes (Based on IUPAC recommendations) :

	Transition Enthalpy	Example	Definition	Symbol
1.	Enthalpy of formation	$\text{K(s)} + \frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{KCl(s)}$	One mole of the compound formed from its elements	$\Delta_f H^\circ$ or ΔH°_f
2.	Enthalpy of combustion	$\text{C}_2\text{H}_6(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\ell)$	One mole of the compound (fuel) is burnt completely in oxygen	$\Delta_c H^\circ$ or ΔH°_c
3.	Enthalpy of fusion	$\text{H}_2\text{O(s)} \rightarrow \text{H}_2\text{O(g)}$	One mole of the liquid is formed from the solid without a change in temperature	$\Delta_{\text{fus}} H^\circ$ or $\Delta H^\circ_{\text{fus}}$
4.	Enthalpy of vaporisation	$\text{H}_2\text{O}(\ell) \rightarrow \text{H}_2\text{O(g)}$	One mole of the vapour formed from the liquid without a change in temperature	$\Delta_{\text{vap}} H^\circ$ or $\Delta H^\circ_{\text{vap}}$
5.	Enthalpy of sublimation	$\text{I}_2(\text{g}) \rightarrow \text{I}_2(\text{g})$	One mole of the vapour formed from the solid	$\Delta_{\text{sub}} H^\circ$ or $\Delta H^\circ_{\text{sub}}$
6.	Enthalpy of atomisation	$\text{H}_2(\text{g}) \rightarrow 2\text{H(g)}$	One mole of the substance broken into isolated atoms in the gas phases	$\Delta_{\text{at}} H^\circ$ or $\Delta H^\circ_{\text{at}}$
7.	Enthalpy of reaction	$\text{A} \rightarrow \text{B}$	Enthalpy change taking place in a reaction	$\Delta_r H^\circ$ or ΔH°_r

8.	Enthalpy of neutralisation	$\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{H}_2\text{O} + \text{NaCl(aq)}$	One mole of water formed by the neutralisation of an acid by a base	$\Delta_{\text{n}}\text{H}^\circ$ or $\Delta\text{H}_{\text{n}}^\circ$
9.	Enthalpy of ionisation	$\text{Na(g)} \rightarrow \text{Na}^+(\text{g}) + \text{e}^-$	One mole atoms ionised—all species in gaseous phase	$\Delta_{\text{ion}}\text{H}^\circ$ or $\Delta\text{H}_{\text{ion}}^\circ$
10.	Electron-gain enthalpy	$\text{X(g)} \rightarrow \text{e}^- \rightarrow \text{X}^-(\text{g})$	One mole of anions being formed all species in the gaseous phase	$\Delta_{\text{eg}}\text{H}^\circ$ or $\Delta\text{H}_{\text{eg}}^\circ$
11.	Lattice enthalpy	$\text{NaCl(s)} \rightarrow \text{Na}^+(\text{g}) + \text{Cl}^-(\text{g})$	One mole of a crystal completely separated into isolated particles in the gaseous phase	$\Delta_{\text{L}}\text{H}^\circ$ or $\Delta\text{H}_{\text{L}}^\circ$ or U
12.	Bond dissociation enthalpy (bond A – B)	$\text{HCl(g)} \rightarrow \text{H(g)} + \text{Cl(g)}$	One mole of bonds broken – all produce in the gaseous phase	$\Delta\text{H}_{\text{A-B}}^\circ = \epsilon_{\text{A-B}}$
13.	Enthalpy of solution	$\text{NaCl(s)} + \text{H}_2\text{O(excess)} \rightarrow \text{NaCl(aq)}$	One mole of the solute dissolved in excess of solvent so that further dilution produces no enthalpy change	$\Delta_{\text{sol}}\text{H}^\circ$ or $\Delta\text{H}_{\text{sol}}^\circ$
14.	Enthalpy of hydration	$\text{X}^+(\text{g}) \rightarrow \text{X}^+(\text{aq})$	One mole of the ion in gaseous phase is hydrated	$\Delta_{\text{hyd}}\text{H}^\circ$ or $\Delta\text{H}_{\text{hyd}}^\circ$
15.	Enthalpy of mixing	pure substance \rightarrow mixture	One mole each of the two or more substances is mixed	$\Delta_{\text{mix}}\text{H}^\circ$ or $\Delta\text{H}_{\text{mix}}^\circ$

CALORIMETRY - MEASURING HEATS OF REACTIONS

All calorimetric techniques are based on the measurement of heat that may be generated (exothermic process), consumed (endothermic process) or simply dissipated by a sample. There are numerous methods to measure such heat. Any process that results in heat being generated and exchanged with the environment is a candidate for a calorimetric study.

A calorimeter is a device used to measure heat of reaction. In order to measure heats of reactions, we often enclose reactants in a calorimeter, initiate the reaction, and measure the temperature difference before and after the reaction. The temperature difference enables us to evaluate the heat released in the reaction.

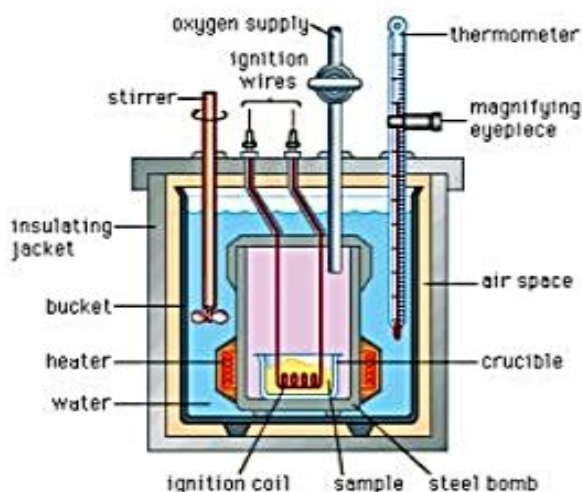
Two basic types of calorimetry are discussed :

- (a) measurement based on constant volume.
- (b) measurements based on constant pressure.

A calorimeter may be operated under constant volume which measures internal energy change ΔU by bomb calorimeter or constant (atmosphere) pressure, which measures enthalpy change ΔH by calorimeter. Whichever kind to use, heat capacity of the calorimeter is required.

The heat capacity is the amount of heat required to raise the temperature of the entire calorimeter by 1 K, and it is usually determined experimentally before or after the actual measurements of heat of reaction. The heat capacity of the calorimeter is determined by transferring a known amount of heat into it and measuring its temperature increase.

- (i) **Bomb calorimeter (ΔU measurement) :** For chemical reactions, heat absorbed at constant volume, is measured in a bomb Calorimeter. In this Calorimeter, a steel vessel (the bomb) is immersed in a water bath. A combustible substance is burnt in pure oxygen supplied in the bomb. Heat evolved during the reaction is transferred to the water around the bomb and its temperature is monitored. Since the bomb Calorimeter is sealed, its volume does not change, i.e., the energy changes associated with reactions are measured at constant volume.



Since volume does not change, a bomb calorimeter measures the heat evolved under constant volume,

$$q_v,$$

$$q_v = C \Delta T,$$

where ΔT is the temperature increase. The q_v so measured is also called the change in internal energy, ΔE .

$$\Delta E = q_v = C \times \Delta T$$

Illustration

1. A calorimeter with heat capacity equivalent to having 13.3 moles of water is used to measure the heat of combustion from 0.303 g of sugar ($C_{12}H_{22}O_{11}$). The temperature increase was found to be 5.0 K. Calculate the heat released, the amount of heat released by 1.0 g, and 1.0 mole of sugar.

Sol. Heat released, q_v ,

$$q_v = 13.3 \times 75.2 \times 5.0 \text{ K} \\ = 5000 \text{ J}$$

The amount of heat released by 1.0 g would be,

$$5000 \text{ J} / 0.303 \text{ g} = 16.5 \text{ kJ / g}$$

Since the molecular weight of sugar is 342 g/mol, the amount of heat released by 1.0 mole would be $16.5 \times 342 = 5643 \text{ kJ/mol}$.

2. The temperature of a calorimeter increases 0.10 K when 7.52 J of electric energy is used to heat it. What is the heat capacity of the calorimeter?

Sol. Dividing the amount of energy by the temperature increase yields the heat capacity, C ,
 $C = 7.52 / 0.10 = 75.2 \text{ J/K}$.

Exercise

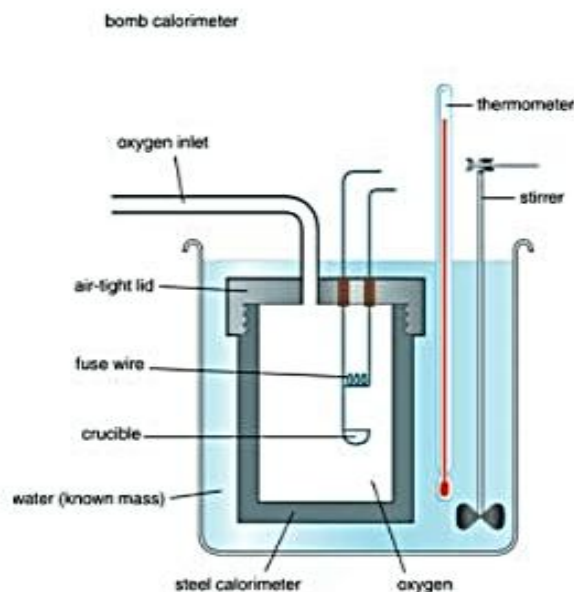
1. The heat released by one mole of sugar from a bomb calorimeter experiment is 5648 kJ/mol. Calculate the enthalpy of combustion per mole of sugar.

Ans. 5648 kJ/mol

Note:

More heat is given off if the reaction is carried out at constant pressure, since the P-V work ($1.5 RT$) due to the compression of 1.5 moles of gases in the reactants would contribute to dH . If 1.0 mole water is decomposed by electrolysis at constant pressure, we must supply an amount of energy equivalent to enthalpy change, dH , a little more than internal energy, dE . More energy must be supplied to perform the P-V work to be done by the products (H_2 and O_2).

- (ii) **ΔH measurement**: Measurement of heat change at constant pressure (generally at atmospheric pressure) can be done in a Calorimeter shown in the figure. In this case, the Calorimeter is left open to atmosphere. As the reaction occurs in the Calorimeter, the temperature change is noticed and then heat of reaction is measured with the knowledge of heat capacity of Calorimeter system.

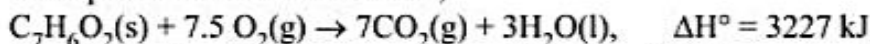


The heat capacity of the calorimeter can also be determined by burning an exactly known amount of a standard substance, whose enthalpy of combustion has been determined. Benzoic acid, $C_7H_6O_2$, is one such standard. The problem below illustrates the calculations.

Illustration

- When 0.1025 g of benzoic acid was burnt in a bomb calorimeter the temperature of the calorimeter increased by 2.165°C . For benzoic acid $\Delta H^\circ_{\text{comb}} = -3227\text{ kJ mol}^{-1}$. Calculate the heat capacity of the calorimeter.

Sol. The equation for the combustion is,



Since 7.5 moles of O_2 gas is needed, and 7 moles of CO_2 is produced, some pressure-volume work is done, to the calorimeter:

$$P V = \Delta n_g R T, \text{ where } \Delta n = (7 - 7.5) = -0.5\text{ mol}$$

$$\Delta E = \Delta H - \Delta n_g R T$$

$$= -3227 - (-0.5 \times 8.314298 \times 298)$$

$$= -3226\text{ kJ/mol (a small correction)}$$

The amount of heat produced by 0.1025 g benzoic acid is

$$q = 0.1025/122.13 \times 3226 = 2.680\text{ kJ}$$

Thus, the heat capacity is

$$C = q_v / \Delta T = 2.680 / 2.165 = 1.238\text{ kJ / K.}$$

After the heat capacity is determined, the calorimeter is ready to be used to measure the enthalpy of combustion of other substances.

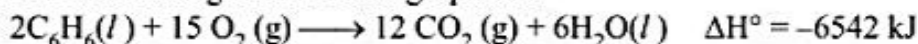
Exercise

- When 0.7022 g of oxalic acid ($C_2O_4H_2$) is burnt in the calorimeter. The temperature increased by 1.602°C . The heat capacity of the calorimeter is 1.238 kJ/K . Calculate $\Delta H^\circ_{\text{comb}}$.

Ans. -250.6 kJ/mol

SOLVED EXAMPLE

Q.1 Benzene burns according to the following equation



What is the ΔE° for the combustion of 1.5 mol of benzene

- (A) -3271 kJ (B) -9813 kJ (C) -4906.5 kJ (D) None of these

Ans. (D)

Sol. $\Delta n = -3$

$$\Delta H^\circ = \Delta E^\circ + (\Delta n_g)RT$$

$$\Rightarrow -6542 = \Delta E^\circ + (-3)(8.31)(298) \times 10^{-3} \quad \Rightarrow \quad \Delta E^\circ = -6534 \text{ kJ}$$

Q.2 What is the value of change in internal energy at 1 atm in the process

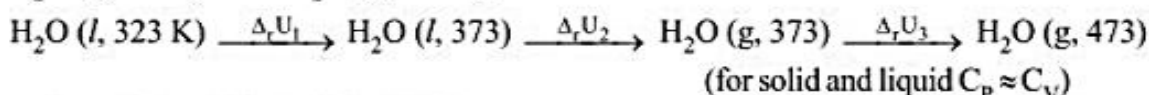


Given: $C_{p(\text{H}_2\text{O}, l)} = 75.3 \text{ JK}^{-1} \text{ mol}^{-1}$; $C_{p(\text{H}_2\text{O}, g)} = 33.314 \text{ JK}^{-1} \text{ mol}^{-1}$; ΔH_{vap} at 373 K = 40.7 kJ/mol

- (A) 109.1 kJ/mol (B) 37.6 kJ/mol (C) 43.86 kJ/mol (D) 48.36 kJ/mol

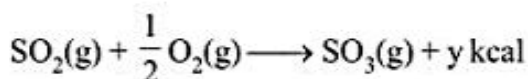
Ans. (C)

Sol. $\text{H}_2\text{O}(l, 323 \text{ K}) \longrightarrow \text{H}_2\text{O}(g, 473 \text{ K})$



$$\begin{aligned} \text{and } \Delta_r U &= \Delta_r U_1 + \Delta_r U_2 + \Delta_r U_3 \\ &= C_{v,m} \Delta T + (\Delta_r H_2 - \Delta n_g RT) + C_{v,m} \Delta T \\ &= \frac{75.3 \times 50}{1000} + \left(40.7 - \frac{1 \times 8.314 \times 398}{1000} \right) + \frac{(33.314 - 8.314) \times 100}{1000} \\ \Delta_r U &\approx 43.86 \text{ kJ/mol} \end{aligned}$$

Q.3 $\text{S}(s) + \frac{3}{2} \text{O}_2(g) \longrightarrow \text{SO}_3(g) + 2x \text{ kcal}$



Find out the heat of formation of $\text{SO}_2(g)$

- (A) $(y - 2x)$ (B) $(2x + y)$ (C) $(x + y)$ (D) $2x/y$

Ans. (A)

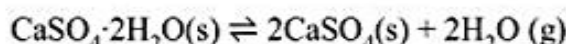
Q.4 The molar heat capacities at constant pressure (assumed constant with respect to temperature) of A, B and C are in ratio of 1.5 : 3.0 : 2.5. If enthalpy change for the exothermic reaction $\text{A} + 2\text{B} \longrightarrow 3\text{C}$ at 300 K and 310 K is ΔH_1 and ΔH_2 respectively then

- (A) $\Delta H_1 > \Delta H_2$
 (B) $\Delta H_1 < \Delta H_2$
 (C) $\Delta H_1 = \Delta H_2$
 (D) If $T_2 > T_1$ then $\Delta H_2 > \Delta H_1$ & if $T_2 < T_1$ then $\Delta H_2 < \Delta H_1$

Ans. (C)

Sol. $\Delta_r C_p = 3 \times 2.5 - 1 \times 1.5 - 2 \times 3 \Rightarrow 0$; $\therefore \Delta H_1 = \Delta H_2$

- Q.5** Solid $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is taken in a container fitted with a frictionless piston initially containing no other gases. The external pressure is maintained at 1 atm and the container is heated till the equilibrium is achieved.



If $\Delta H^\circ = +30 \text{ Kcal/mol}$ and $\Delta S^\circ = +40 \text{ cal/K}$, at what temperature equilibrium will be established in the container. (Ignore variation of ΔH° and ΔS° with temperature.)

- (A) 600 K (B) 750 K (C) 700 K (D) 300 K

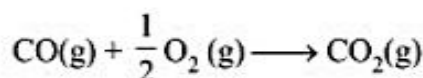
Ans. (B)

Sol. At Eq. $\Delta G^\circ = 0$

$$\Delta H^\circ = T\Delta S^\circ$$

$$\Rightarrow T = \frac{\Delta H^\circ}{\Delta S^\circ} = 750 \text{ K}$$

- Q.6** For the reaction



using data given in table find out incorrect statement(s) among the following.

	$\Delta H_f^\circ (\text{kJ/mole})$	$S^\circ (\text{J/Kmole})$
$\text{CO}(\text{g})$	-110	+197
$\text{O}_2(\text{g})$	0	+205
$\text{CO}_2(\text{g})$	-395	+213

Assume vibration modes of motion do not contribute to heat capacity at low temperature.

(A) $\Delta H^\circ > \Delta U^\circ$ for the reaction at 298K.

(B) In standard state condition, the reaction $\text{CO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$ attain equilibrium at very high temperature.

(C) At low temperature $\frac{d(\Delta H)^\circ}{dT} = -\text{ive}$

(D) In a CO , O_2 fuel cell electrical energy obtained by cell $> |\Delta H_{\text{combustion}}^\circ [\text{CO}(\text{g})]|$

Ans. (A)

Sol. $\Delta H^\circ - \Delta U^\circ = \Delta n_g RT$

since $\Delta n_g = -\text{ve}$

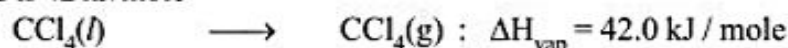
$$\Rightarrow \Delta H^\circ - \Delta U^\circ \leq 0$$

$$\Delta H^\circ = -\text{ve}$$

$$\Delta S^\circ = -\text{ve} \quad ; \quad C_p = \frac{3}{2}R + R \quad ; \quad = \frac{5}{2}R$$

$$\Delta_r C_p = -\text{ve}$$

- Q.7** The heat of vaporisation : ΔH_{vap} , of CCl_4 at 27°C is 42 kJ/mole



If 1 mole of liquid CCl_4 at 27°C has entropy of 214 J/K mole, what is the entropy (in J/K-mol) of 1 mole of vapour in equilibrium with liquid at this temperature.

- (A) 74 (B) 454 (C) 354 (D) 254

Ans. (C)

Sol. If liquid CCl_4 is in equilibrium with its vapour then

$$\frac{\Delta H_{\text{vap } 27^\circ\text{C}}}{300} = \Delta S_{\text{vap}} = S_{\text{CCl}_4(\text{g})} - S_{\text{CCl}_4(\text{l})}$$

$$\Rightarrow \frac{42,000}{300} = S_{\text{CCl}_4(\text{g})} - 214 \text{ J/K mole}$$

$$140 + 214 = 354 \text{ J/K mole}$$

Q.8 If $\Delta H_{\text{vaporisation}}$ of substance X (l) (molar mass : 30 g/mol) is 300 J/g at its boiling point 300 K, then molar entropy change for reversible condensation process is

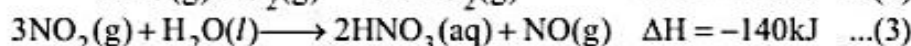
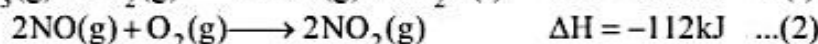
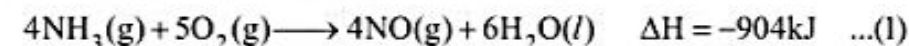
(A) 30 J/mol.K (B) -300 J/mol.K (C) -30 J/mol.K (D) None of these

Ans. (C)

Sol. $\Delta H_{\text{vaporisation}} = 300 \times 30 \text{ J/mol}$

$$\Delta S_{\text{condensation}} = \frac{-\Delta H_{\text{vaporisation}}}{T_{\text{boiling point}}} \Rightarrow \frac{-300 \times 30}{300} \text{ J/mol.K} \Rightarrow -30 \text{ J/mol.K} \quad \text{Ans.}$$

Q.9 The following sequence of reaction occurs in commercial production of aqueous nitric acid.



Determine the total heat liberated (in kJ/mol) at constant pressure for the production of exactly 1 mole of aqueous nitric acid from NH_3 by this process.

(A) 986 (B) 493 (C) 246.5 (D) None of these

Ans. (B)

Sol. 1 mole of $\text{HNO}_3 = \frac{3}{2}$ moles of $\text{NO}_2 \longrightarrow \frac{3}{2}$ mole of $\text{NO} \longrightarrow \frac{3}{2}$ mole of NH_3

$$-\left(\frac{3}{2} \times \frac{1}{4}\right)(904) - \left(\frac{3}{2} \times \frac{1}{2}\right)(112) - \left(\frac{3}{2} \times \frac{1}{3}\right)(140) = 493 \text{ kJ/mol}$$

Heat liberated = 493 kJ/mol

Q.10 If $\Delta H_{\text{vaporisation}}$ of $(\text{C}_2\text{H}_5)_2\text{O}$ (l) is 350 J/g at its boiling point 300 K, then molar entropy change for condensation process is

(A) 86.33 J/mol.K (B) -86.33 J/mol.K (C) -1.16 J/mol.K (D) 1.16

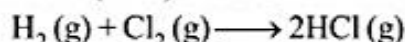
Ans. (B)

Sol. $\Delta H_{\text{vaporisation}} = 350 \times 74 \text{ J/mol}$

$$\Delta S_{\text{condensation}} = \frac{-\Delta H_{\text{vaporisation}}}{T_{\text{boiling point}}}$$

$$= \frac{-350 \times 74}{300} \text{ J/mol.K} = -86.33 \text{ J/mol.K} \quad \text{Ans.}$$

Q.11 Calculate ΔG (in kJ) for the reaction at 300 K,



Given at 300 K : $\text{BE}_{\text{H-H}} = 435 \text{ kJ mol}^{-1}$, $\text{BE}_{\text{Cl-Cl}} = 240 \text{ kJ mol}^{-1}$, $\text{BE}_{\text{HCl}} = 430 \text{ kJ mol}^{-1}$

Entropies of H_2 , Cl_2 and HCl are 131, 223 and $187 \text{ JK}^{-1} \text{ mol}^{-1}$ respectively.

- (A) 191 (B) 291 (C) -191 (D) None of these

Ans. (C)

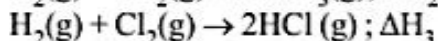
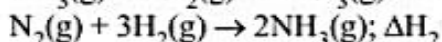
Sol. $\Delta H = (435 + 240 - 2 \times 430) = -185 \text{ kJ mol}^{-1}$

$$\Delta S = \frac{2 \times 187 - (131 + 223)}{1000} = \frac{20}{1000} \text{ kJ mol}^{-1}$$

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

$$= -185 - \frac{300 \times 20}{1000} = -185 - 6 = -191 \text{ kJ mol}^{-1}$$

Q.12 $\text{NH}_3(\text{g}) + 3\text{Cl}_2(\text{g}) \rightarrow \text{NCl}_3(\text{g}) + 3\text{HCl}(\text{g})$; $-\Delta H_1$



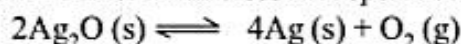
The heat of formation of $\text{NCl}_3(\text{g})$ in the terms of ΔH_1 , ΔH_2 and ΔH_3 is

(A) $\Delta H_f = -\Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$ (B) $\Delta H_f = \Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$

(C) $\Delta H_f = \Delta H_1 - \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$ (D) None

Ans. (A)

Q.13 If $\text{Ag}_2\text{O}(\text{s})$ is exposed to atmosphere having pressure 1 atm and temperature 27°C . Under these conditions comment whether it will dissociate spontaneously or not.



Given:	$\Delta H_f^\circ (\text{kJ/mol})$	$\Delta S^\circ (\text{J/Kmol})$ at 27°C
$\text{Ag}(\text{s})$	0	42.0
$\text{Ag}_2\text{O}(\text{s})$	-30	121.0
$\text{O}_2(\text{g})$	0	204.0

(Air consist of 20% O_2 by volume)

Take : $R = 8.3 \text{ JK}^{-1} \text{ mol}^{-1}$

Sol. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$\Delta H^\circ = \Delta H_f^\circ (\text{product}) - \Delta H_f^\circ (\text{reactants})$$

$$= 2 \times 30 = 60 \text{ kJ}$$

$$\Delta S^\circ = 204 + 4(42) - 2(121) = +130$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 60000 - 300 \times 130$$

$$\Delta G^\circ = 21000 \text{ J} = -RT \ln K$$

$$\log K = -\left(\frac{21000}{300 \times 8.3 \times 2.3}\right)$$

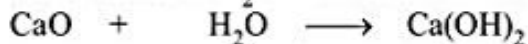
$$K_p = 2.15 \times 10^{-4} \text{ atm}$$

The dissociation of Ag_2O is nonspontaneous at 27°C

- Q.14** A 500 gm sample of water is reacted with an equimolar amount of CaO (both at an initial temp of 25°C). What is the final temperature of the product? [Assume that the product absorbs all of the heat released in the reaction] Heat produced per mol of Ca(OH)₂ is 65.2 kJ and specific heat Ca(OH)₂ is 1.2 J/g°C.
 (A) $\approx 735^\circ\text{C}$ (B) $\approx 760^\circ\text{C}$ (C) $\approx 746^\circ\text{C}$ (D) $\approx 789^\circ\text{C}$

Ans. (B)

Sol. No. of moles of H₂O = No. of moles of CaO = No. of moles Ca(OH)₂ produced = 500/18



$$\text{Total heat released} = \frac{500}{18} \times 65.2 \times 1000 \text{ J}$$

$$\text{Mass of Ca(OH)}_2 \text{ produced} = \frac{500}{18} \times 74 \text{ gm}$$

$$\therefore \frac{500}{18} \times 74 \times 1.2 \times (T - 25) = \frac{500}{18} \times 65.2 \times 1000$$

$$88.8(T - 25) = 65200 \quad ; \quad T = 734.23 + 25 \Rightarrow 759.23^\circ\text{C}$$

- Q.15** The enthalpy of formation of ethane and benzene from the gaseous atoms are -2839.2 and -5506 KJ/mol respectively. Bond enthalpy of C=C bond is

Given: Resonance energy of benzene = -23.68 KJ/mol

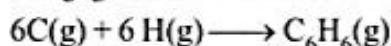
Bond enthalpy of C-H bond = 411.0 KJ/mol

- (A) 373.98 KJ/mol (B) 632.24 KJ/mol (C) 647.5 KJ/mol (D) 1896.72 KJ/mol

Ans. (B)

Sol. $-2839.2 = 0 - [6 \times 411 + \Delta H_{\text{C-C}}]$

$$\Delta H_{\text{C-C}} = 373.2 \text{ KJ/mol}$$



$$\Delta H_{\text{theoretical}} = 0 - [6 \times 411 + 3 \times 373.2 + 3x]$$

R.E. = Actual - Theoretical

$$-23.68 = -5506 + [6 \times 411 + 3 \times 373.2 + 3x]$$

$$3x = 5506 - 23.68 - 2466 - 1119.6$$

$$x = 632.24 \text{ KJ/mol} \quad \text{or} \quad \Delta H_{\text{C=C}} = 632.24 \text{ KJ/mol}$$

- Q.16** The reaction $\text{CH}_4\text{(g)} + \text{Cl}_2\text{(g)} \longrightarrow \text{CH}_3\text{Cl(g)} + \text{HCl(g)}$ has $\Delta H = -25 \text{ kCal}$.

Bond	Bond Energy kCal
$\epsilon_{\text{C-Cl}}$	84
$\epsilon_{\text{H-Cl}}$	103
$\epsilon_{\text{C-H}}$	x
$\epsilon_{\text{Cl-Cl}}$	y
x : y = 9 : 5	

From the given data, what is the bond energy of Cl-Cl bond

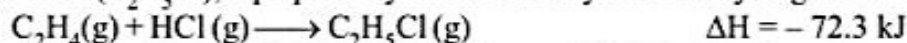
- (A) 70 kCal (B) 80 kCal (C) 67.75 kCal (D) 57.75 kCal

Ans. (D)

Sol. $-25 \times 10^3 \text{ cal} = +E_{\text{C-H}} + E_{\text{Cl-Cl}} - (E_{\text{C-Cl}} + E_{\text{H-Cl}}) = x + y - (84 \times 10^3 + 103 \times 10^3) \text{ cal}$
 $x + y = 162 \times 10^3 \text{ cal}$

$$\frac{9}{5}y + y \quad ; \quad y = \frac{162 \times 10^3}{\left(1 + \frac{9}{5}\right)} \text{ cal} = 57.75 \text{ Kcal}$$

Q.17 Ethyl chloride ($\text{C}_2\text{H}_5\text{Cl}$), is prepared by reaction of ethylene with hydrogen chloride:



What is the value of ΔE (in kJ), if 98 g of ethylene and 109.5 g of HCl are allowed to react at 300 K.

(A) -64.81 (B) -190.71 (C) -209.41 (D) -224.38

Ans. (C)

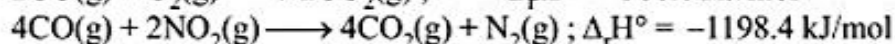
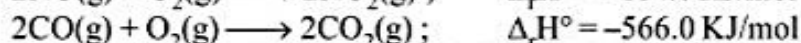
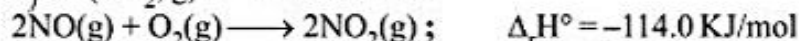
Sol. No. of mole of $\text{C}_2\text{H}_4 = \frac{98}{28} = 3.5$, No. of mole of HCl (Limiting Reagent) = $\frac{109.5}{36.5} = 3$

$$\Delta H = \Delta E + \Delta n_g RT \quad ; \quad -72.3 = \Delta E + (-1 \times 8.314 \times 300)/1000$$

$$\Delta E = -69.80 \text{ ; for three mole } \Delta E = -69.80 \times 3 \Rightarrow -209.41 \text{ kJ/mol} \quad \text{Ans.}$$

Q.18 (i) Determine $\Delta_f H^\circ$ (NO , g) at 25°C . Using the following information

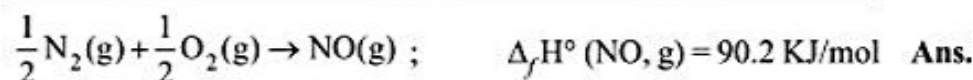
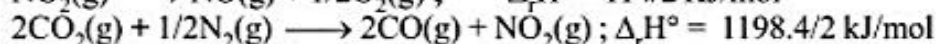
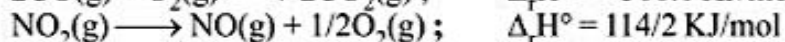
$$\Delta_f H^\circ (\text{CO}_2, \text{g}) = -393.5 \text{ KJ/mol}$$



(ii) Calculate the equilibrium pressure (in Pascal) for the conversion of graphite to diamond at 25°C . The densities of graphite and diamond may be taken to be 2.20 and 3.40 g/cc respectively independent of pressure.

$$\text{Given : } \Delta G^\circ (\text{C (graphite)} \rightarrow \text{C (diamond)}) = 2900 \text{ J/mol.}$$

Sol. (i) $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{CO}_2(\text{g}) \quad ; \quad \Delta_r H^\circ = -566.0 \text{ KJ/mol}$



(ii) $\Delta G_2 - \Delta G_1 = \Delta V[P_2 - P_1]$

$$\Delta V = 12 \times \left[\frac{1}{3.4} - \frac{1}{2.2} \right] \times 10^{-6} \text{ m}^3 \text{mol}^{-1}$$

$$\Delta V = -\frac{14.4}{3.4 \times 2.2} \times 10^{-6} \Rightarrow -1.925 \times 10^{-6} \text{ m}^3 \text{mol}^{-1}$$

Let P_2 is equilibrium pressure; $\Delta G_2 = 0$; $P_2 = 1 \text{ bar} = 10^5 \text{ Pa}$

$$0 - \Delta G_1 = -1.925 \times 10^{-6} [P_2 - 1]$$

$$2900 = 1.925 \times 10^{-6} [P_2 - P_1]$$

$$P_2 = \frac{2900}{1.925 \times 10^{-6}} + P_1$$

$$\Rightarrow 1506.5 \times 10^6 + 10^5$$

$$P_2 = 1.50 \times 10^9 \text{ Pa} \quad \text{Ans.}$$

Q.19 Which of the following do(es) not represent ΔH formation of the product.

- (I) $\frac{1}{2} \text{H}_2(\text{g}) + (\text{aq}) \longrightarrow \text{H}^+(\text{aq})$ (II) $\frac{2}{3} \text{O}_3(\text{g}) \longrightarrow \text{O}_2(\text{g})$
 (III) $\text{NH}_4^+(\text{g}) + \text{Cl}^-(\text{g}) \longrightarrow \text{NH}_4\text{Cl}(\text{s})$ (IV) $\text{P}_4(\text{black}) + 5\text{O}_2(\text{g}) \longrightarrow \text{P}_4\text{O}_{10}(\text{s})$
 (V) Reaction representing $\Delta H_{\text{combustion}}$ of C (graphite).
 (A) I, IV, V (B) II, IV (C) II, III, IV (D) II, III, IV, V

Ans.

(C)

Sol.

(I) ΔH_f of H^+

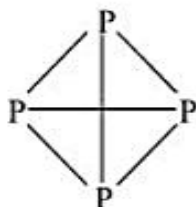
(V) ΔH_f of $\text{CO}_2(\text{g})$

$\therefore \text{II} \rightarrow \text{O}_2(\text{g}) \longrightarrow \text{O}_2(\text{g}) \quad \Delta H_f \text{ O}_2$

$\text{III} \rightarrow \frac{1}{2} \text{N}_2 + 2\text{H}_2 + \frac{1}{2} \text{Cl}_2 \quad \Delta H_f \text{ NH}_4\text{Cl}$

$\text{IV} \rightarrow \text{P}_4(\text{white}) + \dots \quad \Delta H_f \text{ P}_4\text{O}_{10} \quad ; \text{option (C)}$

Q.20 White phosphorus is a tetra-atomic solid $\text{P}_4(\text{s})$ at room temperature.



Find average (P-P) bond enthalpy in kJ/mol.

Given: $\Delta H_{\text{sublimation}}$ of $\text{P}_4(\text{s}) = 59 \text{ kJ/mol}$

$\Delta H_{\text{atomisation}}$ of $\text{P}_4(\text{s}) = 1265 \text{ kJ/mol}$

Sol. $(\text{P-P}) = \frac{1265 - 59}{6} = 201$

Q.21 Calculate the strength of H-bond between $\text{F}^-(\text{g})$ and $\text{CH}_3\text{COOH}(\text{g})$ from the given data.

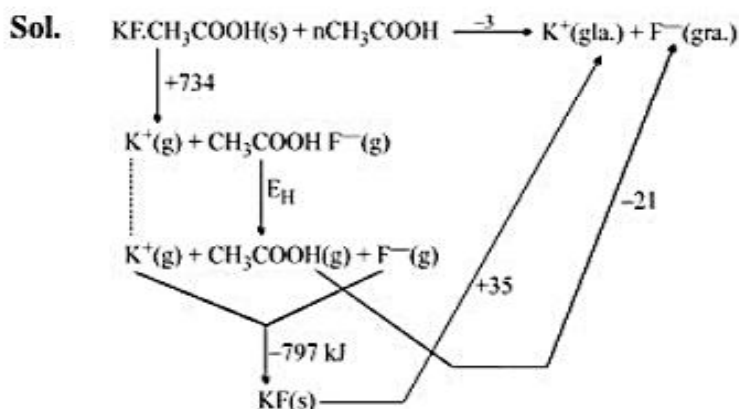
$\Delta H_{\text{solution}} [\text{KF} \cdot \text{CH}_3\text{COOH}(\text{s})]$ in glacial acetic acid = -3 kJ/mole

$\Delta H_{\text{solution}} [\text{KF}(\text{s})]$ in glacial acetic acid = $+35 \text{ kJ/mole}$

Lattice Enthalpy $\text{KF}(\text{s})$ = $+797 \text{ kJ/mole}$

Lattice enthalpy of $\text{KF} \cdot \text{CH}_3\text{COOH}(\text{s})$ = $+734 \text{ kJ/mole}$

$\Delta H_{\text{vaporization}} [\text{CH}_3\text{COOH}(\text{l})]$ = $+21 \text{ kJ/mole}$



$$-3 = +734 + E_H - 797 + 35 - 21$$

$$E_H = -3 - 734 - 35 + 797 + 21 = +46 \text{ kJ/mole}$$

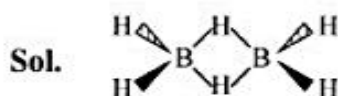
Q.22 Find the Bond enthalpy (in kJ/mol) of one "three centre two electron bond" in B_2H_6 {B-H-B \rightarrow 2B(g) + H(g)} from the given data.

$$\Delta H_f^\circ [BH_3(g)] = 100 \text{ kJ/mole}$$

$$\Delta H_f^\circ [B_2H_6(g)] = 36 \text{ kJ/mole}$$

$$\Delta H_{\text{atm}} [B(s)] = 565 \text{ kJ/mole}$$

$$\Delta H_{\text{atm}} [H_2(g)] = 218 \text{ kJ/mole}$$



B. E. of B-H:

$$3E_{B-H} = 565 + 654 - 100$$

$$E_{B-H} = 373$$

$$B(s) + \frac{3}{2} H_2 \xrightarrow{100} BH_3(g)$$

$$\begin{array}{ccc} \downarrow +565 & \downarrow 3 \times 218 & \downarrow 3E_{B-H} \\ B(g) + 3H(g) & & \end{array}$$

$$2B(s) + 3H_2(g) \xrightarrow{+36} B_2H_6$$

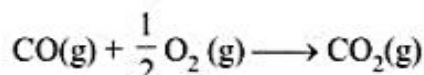
$$\begin{array}{ccc} \downarrow & & \downarrow \\ 2B(g) + 6H(g) & & \end{array}$$

$$\begin{array}{ccc} & & \downarrow 4E_{B-H} \\ & & 2E_{B-H-B} \end{array}$$

$$2E_{B-H-B} = 2 \times 565 + 6 \times 218 - 36 - 4 \times 373$$

$$E_{B-H-B} = 455 \text{ kJ/mol} = 4.55 \times 10^2 \text{ kJ/mole}$$

Q.23 For the reaction



using data given in table find out incorrect statement(s) among the following.

	ΔH_f° (kJ / mole)	S° (J / K mole)
CO(g)	-110	+197
O ₂ (g)	0	+205
CO ₂ (g)	-395	+213

Assume vibration modes of motion do not contribute to heat capacity at low temperature.

(A) $\Delta H^\circ > \Delta U^\circ$ for the reaction at 298K.

(B) In standard state condition, the reaction $CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)$ attain equilibrium at very high temperature.

(C) At low temperature $\frac{d(\Delta H)^\circ}{dT} = -ve$

(D) In a CO, O₂ fuel cell electrical energy obtained by cell $> |\Delta H_{\text{combustion}}^\circ [CO(g)]|$

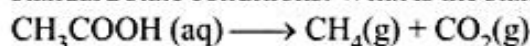
Ans. (A)

Sol. $\Delta H^\circ - \Delta U^\circ = \Delta n_g RT$
 since $\Delta n_g = -ve$
 $\Rightarrow \Delta H^\circ - \Delta U^\circ \leq 0$

$$\Delta H^\circ = -ve$$

$$\Delta S^\circ = -ve \quad ; \quad C_p = \frac{3}{2}R + R \quad ; \quad = \frac{5}{2}R \quad ; \quad \Delta_r C_p = -ve$$

Q.24 At temperatures above 85 K, decarboxylation of acetic acid becomes a spontaneous process under standard state conditions. What is the standard entropy change (in J/K-mol) of the reaction.



$$\text{Given: } \Delta_f H^\circ [\text{CH}_3\text{COOH (aq)}] = -484 \text{ kJ/mole}$$

$$\Delta_f H^\circ [\text{CO}_2\text{(g)}] = -392 \text{ kJ/mole}$$

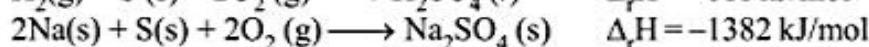
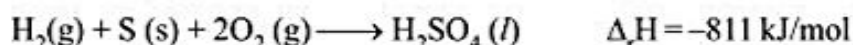
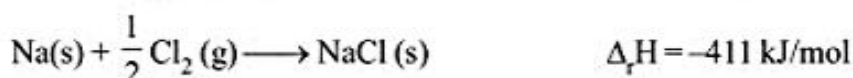
$$\Delta_f H^\circ [\text{CH}_4\text{(g)}] = -75 \text{ kJ/mole}$$

Sol. At 85 K the process must be at equilibrium under standard state condition:

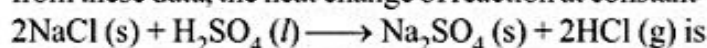
$$\Delta G^\circ = 0$$

$$\Delta H^\circ = T\Delta S^\circ \Rightarrow \Delta S^\circ = \frac{\Delta H^\circ}{T} = \frac{[-392 - 75 - (-484)] \times 10^3}{85} = 2.00 \times 10^2 \text{ J/K-mol}$$

Q.25 The enthalpy changes of the following reactions at 27°C are

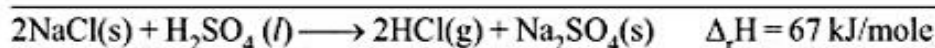
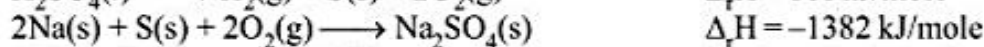
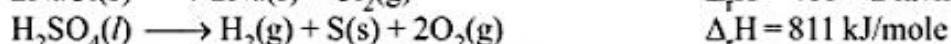


from these data, the heat change of reaction at constant volume (in kJ/mol) at 27°C for the process



(A) 67 (B) 62.02 (C) 71.98 (D) None

Ans. (B)



$$67 = \Delta_r U + \frac{2 \times 8.3 \times 300}{1000}; \quad \Delta_r U = 62.02 \text{ kJ/mole}$$

Q.26 Calculate $|\Delta_f G^\circ|$ for $(\text{NH}_4\text{Cl, s})$ at 350 K.

$$\text{Given: } \Delta_f H^\circ (\text{NH}_4\text{Cl, s}) = -314.5 \text{ kJ/mol}$$

$$S_{\text{N}_2\text{(g)}}^\circ = 192 \text{ JK}^{-1}\text{mol}^{-1}; \quad S_{\text{H}_2\text{(g)}}^\circ = 130.5 \text{ JK}^{-1}\text{mol}^{-1}$$

$$S_{\text{Cl}_2\text{(g)}}^\circ = 223 \text{ JK}^{-1}\text{mol}^{-1}; \quad S_{\text{NH}_4\text{Cl(s)}}^\circ = 94.5 \text{ JK}^{-1}\text{mol}^{-1}; \quad \text{All given data at 300K.}$$

$$\Delta_r C_p = -20 \text{ J/mol-K}; \quad \ln\left(\frac{350}{300}\right) = 0.15$$

Sol. $\Delta_f S^\circ (\text{NH}_4\text{Cl}, s) \text{ at } 300 \text{ K} = S^\circ_{\text{NH}_4\text{Cl}(s)} - \left[\frac{1}{2} S^\circ_{\text{N}_2} + 2S^\circ_{\text{H}_2} + \frac{1}{2} S^\circ_{\text{Cl}_2} \right]$

$$= 94.5 - \left(\frac{1}{2} \times 192 + 2 \times 130.5 + \frac{1}{2} \times 223 \right)$$

$$= 94.5 - (96 + 261 + 111.5)$$

$$\Delta_f S^\circ_{300} = -374 \text{ JK}^{-1}\text{mol}^{-1}$$

$$\Delta_f S^\circ_{310} = \Delta_f S^\circ_{300} + \Delta_r C_p \ln \left(\frac{350}{300} \right)$$

$$= -374 - 20 \times (0.15) = -377 \text{ JK}^{-1}\text{mol}^{-1}$$

$$\Delta_f H^\circ_{310} = \Delta_f H^\circ_{300} + \Delta_r C_p [350 - 300]$$

$$= -314.5 - \frac{20 \times 50}{1000} = -315.5$$

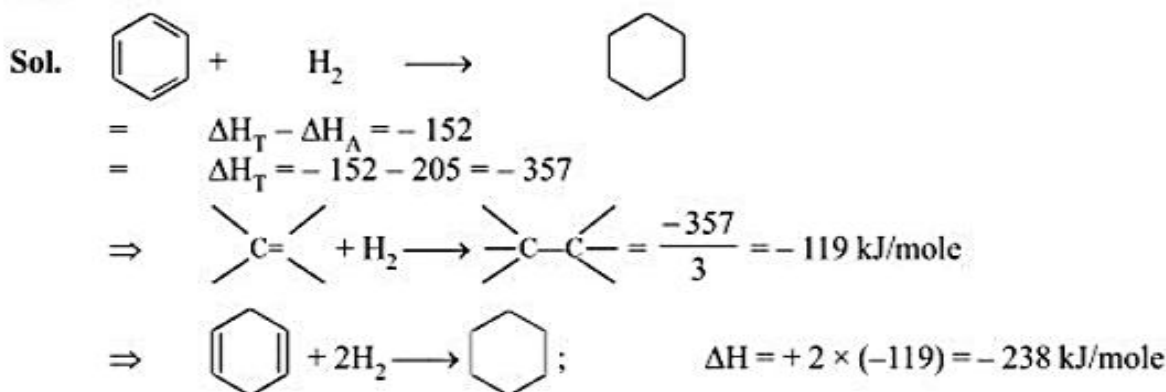
$$\Delta_f G^\circ_{350} = \Delta_f H^\circ - T \Delta_f S^\circ$$

$$= -315.5 - \frac{350 \times (-377)}{1000} \Rightarrow -183.55 \text{ kJ/mol}$$

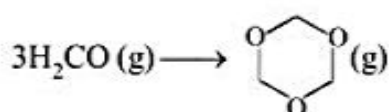
$$|\Delta_f G^\circ_{350}| = 183.55 \text{ kJ/mol} \Rightarrow 183 \text{ kJ/mol}$$

- Q.27** If enthalpy of hydrogenation of $\text{C}_6\text{H}_6(l)$ into $\text{C}_6\text{H}_{12}(l)$ is -205 kJ & resonance energy of $\text{C}_6\text{H}_6(l)$ -152 kJ/mol then enthalpy of hydrogenation of 1,4-cyclohexadiene (l) is
 Assume ΔH_{vap} of $\text{C}_6\text{H}_6(l)$, $\text{C}_6\text{H}_8(l)$, $\text{C}_6\text{H}_{12}(l)$ all are equal
 (A) -535.5 kJ/mol (B) -238 kJ/mol (C) -357 kJ/mol (D) None

Ans. (B)



- Q.28** The enthalpy of gas phase trimerization of one mole of gaseous formaldehyde in (kJ/mole)
 Bond energies (kJ/mole)



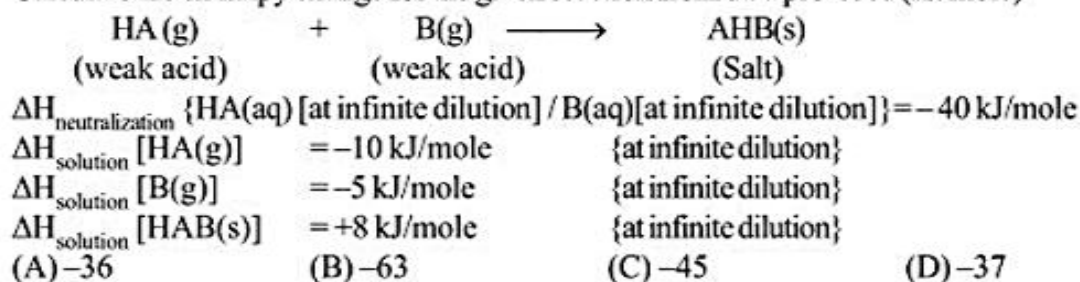
$\epsilon_{\text{C=O}}$	$\epsilon_{\text{C-O}}$	$\epsilon_{\text{C-H}}$
700	360	410

- (A) -20 (B) -60 (C) -10 (D) -50

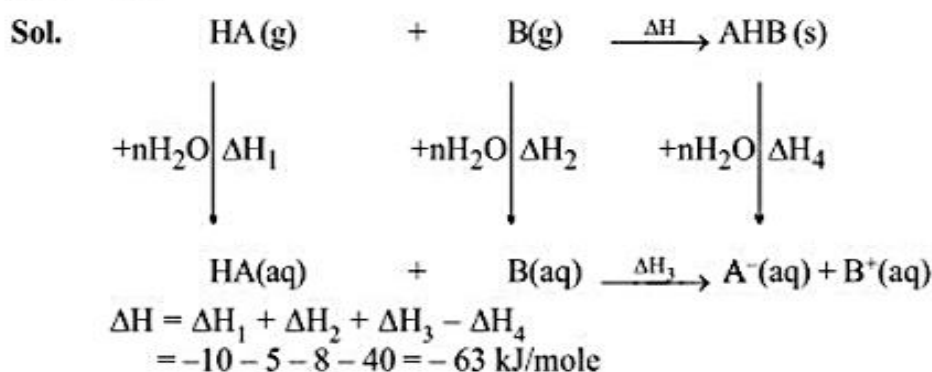
Ans. (A)

Sol. $\Delta H = \epsilon_{C=O} - 2 \epsilon_{C-O} \Rightarrow 700 - 720 = -20 \text{ kJ/mole}$




Q.29 Calculate the enthalpy change for the given reaction from data provided (kJ/mole)

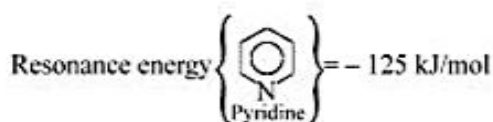


Ans. (B)




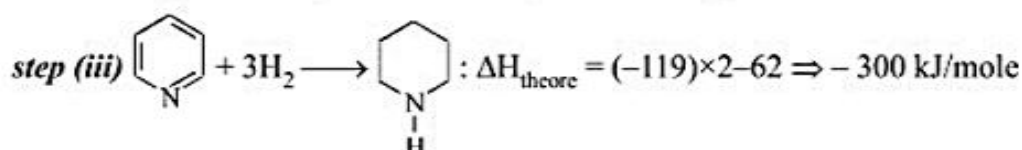
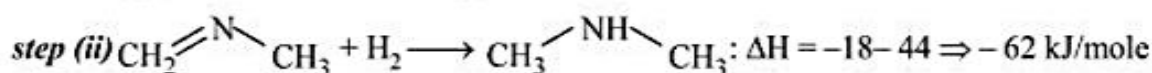
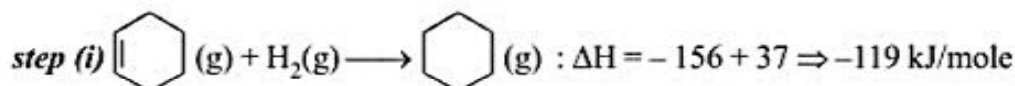
Q.30 Estimate ΔH_f° {pyridine (l)} from the given data.

Compound	$\Delta H_{f,298 \text{ K}}^\circ$ in kJ/mole
$\text{CH}_2=\text{N}-\text{CH}_3(\text{g})$	+ 44
$\text{CH}_3-\text{NH}-\text{CH}_3(\text{g})$	- 18
 (g)	- 37
 (g)	- 156
 N-H(g)	- 50



Sol.

ΔH of Hydrogenation of 



$\Delta H_{\text{actual}} \text{ for (iii)} = -300 + \frac{125}{\text{R.E.}} = \boxed{-175 \text{ kJ/mole}}$ Ans.

$$\Delta H_f \left\{ \text{C}_6\text{H}_5\text{NH}_2(\text{g}) \right\} - \Delta H_f \left\{ \text{C}_6\text{H}_5\text{N}(\text{g}) \right\} \Rightarrow -175$$

$$\Delta H_f^\circ \left\{ \text{C}_6\text{H}_5\text{N}(\text{g}) \right\} = -50 + 175 \Rightarrow +125$$

$$\text{final step } \Delta H_f^\circ \left\{ \text{C}_6\text{H}_5\text{N}(\text{l}) \right\} = +125 - 40 \Rightarrow \boxed{+85 \text{ kJ / mole}} \quad \text{Ans.}$$

- Q.31** The standard enthalpy of atomisation of $\text{PCl}_3(\text{g})$ is 195 Kcal/mol. What will be the standard enthalpy of atomisation of $\text{PCl}_5(\text{g})$, if the bond dissociation energies of axial P–Cl bonds in $\text{PCl}_5(\text{g})$ are 10% lesser and the bond dissociation energies of equatorial P–Cl bonds in $\text{PCl}_5(\text{g})$ are 10% higher than the bond dissociation energies of P–Cl bonds in $\text{PCl}_3(\text{g})$.

(A) 195 Kcal / mol (B) 325 Kcal / mol (C) 331.5 Kcal / mol (D) 318.5 Kcal / mol

Ans. (C)



$$3\text{BE}_{\text{P-Cl}} = 195 \text{ kcal/mol}$$

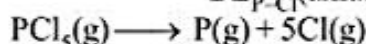
$$\text{BE}_{\text{P-Cl}} = 65 \text{ kcal/mole}$$

equatorial

in PCl_5 3P–Cl bonds are equatorial

$$\text{BE}_{\text{P-Cl}}(\text{eq}) = 65 \times 1.1 = 71.5 \text{ kcal}$$

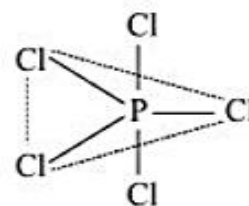
$$\text{BE}_{\text{P-Cl}}(\text{axial}) = 65 \times 0.9 = 58.5 \text{ kcal}$$



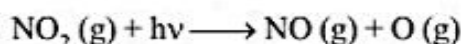
$$3\text{BE}_{\text{P-Cl}} + 3\text{BE}_{\text{P-Cl}}(\text{axial}) = 3 \times 71.5 + 2 \times 58.5 = 331.5 \text{ kcal}$$

(equatorial)

$$\Delta H = 331.5 \text{ kcal.}$$



- Q.32** An important reaction in production of smog is



If light of wavelength $4.4 \times 10^{-7} \text{ m}$ is used to cause above reaction. Calculate N–N bond enthalpy.

$$\text{Given: } \Delta H_f[\text{NO}(\text{g})] = 91 \text{ kJ mol}^{-1} ;$$

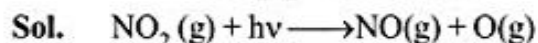
$$h = 6.6 \times 10^{-34} \text{ J s}$$

$$\Delta H_f[\text{N}_2\text{O}_4(\text{g})] = 9 \text{ kJ mol}^{-1} ;$$

$$c = 3 \times 10^8 \text{ ms}^{-1}$$

$$\Delta H_{\text{O=O}} = 498 \text{ kJ mol}^{-1} ;$$

$$N_A = 6 \times 10^{23}$$



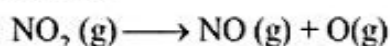
ΔH for the reaction

$$\Delta H = N_A \times \frac{hc}{\lambda}$$

$$= 6 \times 10^{23} \times \frac{6.6 \times 10^{-34} \times 3 \times 10^8}{4.4 \times 10^{-7}}$$

$$= +270 \text{ kJ mol}^{-1}$$

for the reaction,



$$\Delta_r H = \sum \Delta H_f \text{ Product} - \sum \Delta H_f \text{ Reactant}$$

$$+ 270 \text{ kJ mol}^{-1} = 91 + \frac{498}{2} - \Delta H_f \text{ NO}_2(\text{g})$$

$$\Delta H_f(\text{NO}_2)(\text{g}) = + 70 \text{ kJ mol}^{-1}$$

Now for the reaction,



$$\Delta_r H = \sum \Delta H_f \text{ Product} - \sum \Delta H_f \text{ Reactant}$$

$$= + 9 - (2 \times 70) = - 131 \text{ kJ mol}^{-1}$$

Thus bond energy for N–N bond = + 131 kJ mol⁻¹