$$\Delta H_{(\text{Per mole})} = \text{B.E. of Reactants} - \text{B.E. of products}$$

$$(\text{B.E. of } C=C + 4 \times \text{B.E. of } C-H) - (2 \times \text{B.E. of } C-C + 4 \times \text{B.E. of } C-H)$$

Same logic can also be used in following reactions as well.

$$nN_{2(g)} + nH_{2(g)} \longrightarrow \left(NH-NH \right)_{n(g)}$$

$$n(H_3C-C\equiv C-CH_3)_{(g)} \longrightarrow \left(CH_2-CH=CH-CH_2 \right)_{n(g)}$$

CALCULATING RESONANCE ENERGY

Section - 7

Resonance energy, as we know, is the difference in energy between resonance hybrid and the canonical form of the compound. It can be easily calculated using the following key points :

(i) If the resonance hybrid is more stable than the canonical forms, resonance energy is negative otherwise positive.

(ii) Simply figure out, which of the resonance hybrid and the canonical form is more stable based on the $\Delta_r H$ values as explained :

- **(a)** **$\Delta_f H^\ominus$:** More negative is $\Delta_f H^\ominus$, more is the stability as this means when compound is formed, energy is getting lost to attain lower energy than the reactants.
- **(b)** **$\Delta_c H^\ominus$ or $\Delta_{\text{Hydrogenation}} H^\ominus$:** More negative value in this case means less stability as more heat released means this compound is more reactive.

Note **:** In **(a)**, the compound under analysis is the product whereas in **(b)**, that compound is the reactant.

(iii) Now, calculate ΔH for the theoretical (canonical) and actual (resonance hybrid) compound and calculate the difference between the two to get resonance energy.

Illustration - 18 *The standard molar enthalpies of formation of cyclohexane(ℓ) and benzene(ℓ) at 25°C are −156 and +49 kJ/mole respectively. The standard enthalpy of hydrogenation of cyclohexene(ℓ) at 25°C is –119 kJ/mole. Use this data to estimate the magnitude of the resonance energy of benzene.*

SOLUTION :

Given : $C_6H_{10}(\ell) + H_2(g) \longrightarrow C_6H_{12}(\ell)$; $\Delta_{\text{Hydrogenation}} H^\ominus = -119$ kJ/mole

Find the actual heat of hydrogenation of benzene from Hess's law as follows :

1. $6C(s) + 6H_2(g) \longrightarrow C_6H_{12}(\ell)$; $\Delta_f H^\ominus = -156$ kJ/mole
2. $6C(s) + 3H_2(g) \longrightarrow C_6H_6(\ell)$; $\Delta_f H^\ominus = +49$ kJ/mole

$C_6H_6(\ell) + 3H_2(g) \longrightarrow C_6H_{12}(\ell)$; $\Delta_{\text{Hydrogenation}} H^\ominus$

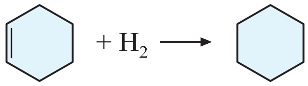
$\Rightarrow$ $(\Delta_{\text{Hydrogenation}} H^\ominus)_{\text{Actual}} = -156 - 49 = -205$ kJ/mole [***Note*** **:** $\Delta_{\text{Hydrogenation}} H^\ominus$ is always negative]

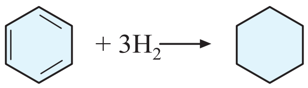
Now, $$\begin{pmatrix}\text{hypothetical heat of}\\ \text{hydrogenation of benzene}\end{pmatrix} \equiv \begin{pmatrix}\text{heat of hydrogenation of}\\ \text{cyclohexatriene}\end{pmatrix}$$

$$\equiv 3 \times \begin{pmatrix}\text{heat of hydrogenation}\\ \text{of cyclohexane}\end{pmatrix}$$

$$= 3 \times (-119) = -357 \text{ kJ/mole}$$

Here, we have assumed that there are only 3 double bonds in benzene (kekule's structure) and in hydrogenating it, the energy obtained will be roughly 3 times of hydrogenating cyclohexene.

⇒  $(\Delta_{\text{Hydrogenation}} H^{\ominus})_{\text{Cyclohexene}}$

and  $(\Delta_{\text{Hydrogenation}} H^{\ominus})_{\text{Theoretical Benzene}} = 3 \times (\Delta_{\text{Hydrogenation}} H^{\ominus})_{\text{Cyclohexene}}$

Clearly, heat of hydrogenation for theoretical benzene is more negative and thus, it is less stable. So, Resonance energy should be negative (since actual benzene is more stable).

⇒ Resonance energy $= -357 - (-205) = -152$ kJ/mole of benzene

Illustration - 19 *Calculate the resonance energy of isoprene (C_5H_8) from the data given.*

Standard Heats of combustion of isoprene, carbon and hydrogen are –3186, –393.5 and –285.83 kJ/mole respectively. Bond energies of C = C, C – C, C – H and H – H bonds are 615, 348, 413, 435.8 kJ/mole respectively. Standard Heat of sublimation of graphite is 718.3 kJ/mole.

SOLUTION :

Calculate $\Delta_f H^{\ominus}$ of isoprene from its heat of combustion (This will give the value for the actual isoprene existing in nature).

$$5C\,(s) + 4H_2\,(g) \longrightarrow C_5H_8\,(g) \quad ; \quad \Delta_f H^{\ominus} = ?$$

1. $C_5H_8\,(g) + 7\,O_2\,(g) \longrightarrow 5\,CO_2\,(g) + 4\,H_2O\,(\ell)$; $\Delta_r H_1^{\ominus} = -3186$ kJ/mole

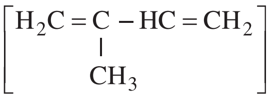
2. $C(s) + O_2\,(g) \longrightarrow CO_2\,(g)$; $\Delta_r H_2^{\ominus} = -393.5$ kJ/mole

3. $H_2\,(g) + 1/2\,O_2\,(g) \longrightarrow H_2O\,(\ell)$; $\Delta_r H_3^{\ominus} = -285.83$ kJ/mole

Now operating 5(2) + 4(3) – 1 to get the equation of heat of formation.

From Hess's Law we have : $\Delta_f H^{\ominus} = 5\Delta_r H_2^{\ominus} + 4\Delta_r H_3^{\ominus} - \Delta_r H_1^{\ominus}$

⇒ $\Delta_f H^{\ominus} = 5(-393.5) + 4(-285.83) - (-3186)$ ⇒ $(\Delta_f H^{\ominus})_{\text{actual}} = 75.18$ kJ / mole

Now calculate heat of formation using the bond energies and structure of isoprene. 

$$\left[\begin{array}{l} H_2C = \underset{\displaystyle |\atop\displaystyle CH_3}{C} - HC = CH_2 \end{array}\right]$$

Note : Data calculations from the bond energy concept is always theoretical.

1. Bond Breaking : (ΔH_1)

$5\,[\,C(s) \longrightarrow C(g)\ ;\ +718.3\,]$

$4\,[\,H_2(g) \longrightarrow 2H\ ;\ +435.8\,]$ $\Rightarrow$ $\Delta H_1 = 5 \times 718.3 + 4 \times 435.8 = +5334.7\ \text{kJ}$

2. Bond Formation : (ΔH_2)

$8[\,C + H \longrightarrow C - H\ ;\ -413\,]$

$2[\,C + C \longrightarrow C - C\ ;\ 348\,]$

$2[\,C + C \longrightarrow C = C\ ;\ -615\,]$ $\Rightarrow$ $\Delta H_2 = -(8 \times 413 + 2 \times 348 + 2 \times 615) = -5230\ \text{kJ}$

From Hess's Law : $(\Delta_f H^{\ominus})_{\text{Theoretical}} = \Delta H_1 + \Delta H_2$

$(\Delta_f H^{\ominus})_{\text{Theoretical}} = 5334.7 + (-5230) = 104.7\ \text{kJ}$

$\Rightarrow$ Resonance Energy $= 75.18 - 104.7 = -29.52\ \text{kJ}$

IN-CHAPTER EXERCISE

1. *Find* $\Delta_f H^{\ominus}$ *of* Fe_2O_3 *if the standard heat of reaction :* $Fe_2O_3(s) + 3\,CO(g) \longrightarrow 2\,Fe(s) + 3\,CO_2(g)$ *is* -6.6 *kcal.*

Given, $\Delta_f H^{\ominus}\ CO(g) = -26.4$ *kcal,* $\Delta_f H^{\ominus}\ CO_2(g) = -94.1$ *kcal.*

2. *Enthalpies of formation of* $FeO(s)$ *and* $Fe_2O_3(s)$ *are* -267.9, -822.2 *kJ/mol respectively. Calculate the enthalpy of the reaction:* $2\,FeO(s) + \frac{1}{2}O_2(g) \longrightarrow Fe_2O_3(s)$

3. *The enthalpy change involved in the oxidation of glucose is* -2880 *kJ/mol. 25% of this energy is available for muscular work. If 100 kJ of the muscular work is needed to walk one kilometre, what is the maximum distance that a person will be able to walk after eating 120 gm glucose ?*

4. *An athlete is given 90 gm of glucose* $(C_6H_{12}O_6)$ *to generate 1760 kJ of energy. He utilizes 80% of this gained energy in the event. In order to avoid storage of energy in the body, calculate the mass of water he would need to perspire. The enthalpy of evaporation of water is 44 kJ/mol.*

5. *The standard heat of formation at 298 K for* $CCl_4(\ell)$, $H_2O(\ell)$, $CO_2(g)$ *and* $HCl(g)$ *are* -106.7, -241.8, -393.7*and* -92.5 *kJ/mol. Calculate the standard heat of reaction :* $CCl_4(\ell) + 2H_2O(\ell) \longrightarrow CO_2(g) + 4\,HCl(g)$

6. *The standard enthalpy of combustion at 25°C of hydrogen, cyclohexene* (C_6H_{10}) *and cyclohexane* (C_6H_{12}) *are* -241, -3800 *and* -3920 *kJ/mol respectively. Calculate the enthalpy of hydrogenation of cyclohexene.*

7. *The standard enthalpies of formation of* $H(g)$, $Br(g)$ *and* $HBr(g)$ *are 218.0, 111.8 and* -36.4 *kJ/mol respectively. Calculate the enthalpy changes of the following reactions:*

(i) $H(g) + Br(g) \longrightarrow HBr(g)$ **(ii)** $H(g) + Br_2(\ell) \longrightarrow HBr(g) + Br(g)$

8. *Calculate the* $\Delta_r H^{\ominus}$ *for the reduction of* $Fe_2O_3(s)$ *by* $Al(s)$ *at 25°C. The enthalpies of formation of* Fe_2O_3 *and* Al_2O_3 *are* -825.5 *and* -1675.7 *kJ/mol respectively.*

9. *Calculate the enthalpy of formation of* $KOH(s)$ *from the following data :*

(I) $K(s) + H_2O + aq \longrightarrow KOH(aq) + \frac{1}{2}H_2(g)$ $\Delta_r H = -200.8$ *kJ/mol*

(II) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell)$ $\Delta_r H = -286.3$ *kJ/mol*

(III) $KOH(s) + aq \longrightarrow KOH(aq)$ $\Delta_r H = -58.6$ *kJ/mol*

10. *The bond dissociation energies of gaseous* $H_2(g)$, $Cl_2(g)$ *and* $HCl(g)$ *are* 435, 242 *and* 430 *kJ/mol respectively. Calculate the enthalpy of formation of* $HCl(g)$.

11. 0.16 *gm of methane was subjected to combustion at* 27°*C in a bomb calorimeter. The temperature of calorimeter system (including water) was found to rise by* 0.5°*C, calculate the heat of combustion of methane* at (I) *constant volume* (II) *constant pressure. Thermal capacity of the calorimeter-system is* 18.0 *kJ/K.*

12. *Determine the heat of hydrogenation of ethylene from the following data. The bond energies of* $H–H$: 104 ; $C–C$: 80 ; $C–H$: 99 ; $C = C$: 145. *All energies are in kcal/mol.*

13. *The polymerisation of ethylene to linear polyethylene is represented by the reaction* :

$$nCH_2{=}CH_2 \longrightarrow (CH_2{-}CH_2)_n$$

where n has large integral value. Given that average enthalpies of bond dissociation for C=C and C–C at 298 *K are* +590 *and* +331 *kJ/mol respectively. Calculate the enthalpy of polymerisation of ethylene at* 298 *K*

14. *How much heat is liberated when one mole of gaseous* Na^+ *combines with one mole of* Cl^- *ion to form solid NaCl? Use the data given below* :

$Na(s) + \frac{1}{2}Cl_2(g) \longrightarrow NaCl(s)$; $\Delta_r H = -98.2$ *kcal*

$Na(s) \longrightarrow Na(g)$; $\Delta_r H = +26.0$ *kcal*

$Na(g) \longrightarrow Na^+(g) + 1e^-$; $\Delta_r H = +120.0$ *kcal*

$Cl_2(g) \longrightarrow 2Cl(g)$; $\Delta_r H = +58.0$ *kcal*

$Cl^-(g) \longrightarrow Cl(g) + 1e^-$; $\Delta_r H = +87.3$ *kcal*

15. *In a constant volume calorimeter*, 3.5 *g of a gas with molecular weight* 28 *was burnt in excess oxygen at* 298.0 *K. The temperature of the calorimeter was found to increase from* 298.0 *K to* 298.35 *K due to the combustion process. Given that the heat capacity of the calorimeter is* 2.5 *kJ* K^{-1}, *find the enthalpy of combustion of the gas in kJ* mol^{-1}.

16. *Reaction of gaseous fluorine*(F_2) *with compound X yields a single product Y, whose mass percent composition is* 61.7% *F and* 38.3% *Cl. Calculate* $\Delta_r H^\ominus$ *(in kJ/mol) for the synthesis of Y using following information :*

$2ClF(g) + O_2(g) \longrightarrow Cl_2O(g) + OF_2(g)$ $\quad \Delta_r H^\ominus = 205$ *kJ/mol*

$2ClF_3(g) + 2O_2(g) \longrightarrow Cl_2O(g) + 3OF_2(g)$ $\quad \Delta_r H^\ominus = 533$ *kJ/mol*

$\Delta_f H^\ominus (OF_2) = 24.7$ *kJ/mol*

17. *The heat of combustion of ethene gas is* 330 *kcal* mol^{-1}. *Calculate* $C = C$ *bond energy (in kcal/mol).*

Bond energy of $C – H$ *bond is* 93.6 *kcal/mol.* $\Delta_f H^\ominus$ *for* $CO_2(g)$ *and* $H_2O(\ell)$ *are* –94.2 *kcal/mol* and –61 *kcal/mol respectively.*

Heat of atomisation of carbon and hydrogen are 150 *and* 104 *kcal/mol respectively.*

18. *Calculate the enthalpy of formation of sulphuric acid* (ℓ) *from the following data* :

(i) $S(s) + O_2(g) \longrightarrow SO_2(g)$; $\Delta_r H = -71.0\,kcal/mol$

(ii) $SO_2(g) + \frac{1}{2}O_2(g) \longrightarrow SO_3(g)$; $\Delta_r H = -23.5\,kcal/mol$

(iii) $SO_3(g) + H_2O(\ell) \longrightarrow H_2SO_4(\ell)$; $\Delta_r H = -31.2\,kcal/mol$

(iv) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell)$; $\Delta_r H = -68.5\,kcal/mol$

Choose the correct alternative. Only one choice is correct. However, question marks '*' may have more than one correct option.

***19.** *Which of the following is/are state function(s)?*

(A) *Enthalpy* **(B)** *Heat* **(C)** *Entropy* **(D)** *Gibb's energy*

***20.** *Which of the following is (are) intensive thermodynamic properties?*

(A) *Volume* **(B)** *Kinetic energy* **(C)** *Standard Emf* **(D)** *Specific conductance*

21. *For the reaction* $A \longrightarrow B$; $\Delta H = +25$ *kJ/mole. For the reaction* $B \longrightarrow C$; $\Delta H = -18$*kJ/mole. The decreasing order of enthalpy of A, B, C following the order :*

(A) *A, B, C* **(B)** *B, C, A* **(C)** *C, B, A* **(D)** *C, A, B*

22. $\Delta_f H^{\ominus}$ *of atomic B is 134 kcal/mol and* $\Delta_f H^{\ominus}$ *of atomic F is 118.9 kcal/mol.* $\Delta_f H^{\ominus}$ *of* $BF_3(g)$ *is – 271.8 kcal/mol.*

Average B–F bond energy would be :

(A) 97.7 *kcal/mol* **(B)** 116.6 *kcal/mol* **(C)** 135.4 *kcal/mol* **(D)** 254.3 *kcal/mole*

23. *If* $\Delta_f H^{\ominus}$ *of* $CO_2(g) = -393.5$ *kJ/mol,* $\Delta_f H^{\ominus}$ *of* $H_2O(\ell) = -285.8$ *kJ/mol,* $\Delta_c H^{\ominus} C_2H_6 = -1560$ *kJ/mol, the enthalpy of formation of* $C_2H_6(g)$ *is :*

(A) –640 *kJ/mol* **(B)** –168 *kJ/mol* **(C)** –83.8 *kJ/mol* **(D)** 244 *kJ/mol*

24. *Given the equations:*

$$\frac{1}{4}P_4(g) \longrightarrow P(g)\ ; \qquad \Delta_r H^{\ominus} = +74.2\ kcal$$

$$\frac{1}{2}H_2(g) \longrightarrow H(g)\ ; \qquad \Delta_r H^{\ominus} = +52.1\ kcal$$

$$P(g) + 3H(g) \longrightarrow PH_3(g)\ ; \qquad \Delta_r H^{\ominus} = -229.3\ kcal$$

Determine the overall change in enthalpy, $\Delta_r H$, *for* $4PH_3(g) \longrightarrow P_4(g) + 6H_2(g)$

(A) –4.8 *kcal* **(B)** –2.2 *kcal* **(C)** + 2.2 *kcal* **(D)** + 12.7 *kcal*

25. *Given that :*

$$2SO_3(g) \longrightarrow 2SO_2(g) + O_2(g)\ ;\ \Delta_r H^{\ominus} = +197.8\ kJ/mol$$

$$S(s) + \left(\frac{3}{2}\right)O_2(g) \longrightarrow SO_3(g)\ ;\ \Delta_r H^{\ominus} = -395.7\ kJ/mol$$

Determine the heat of formation for SO_2.

(A) + 98.9 *kJ/mol* **(B)** + 197.8 *kJ/mol* **(C)** + 691.8 *kJ/mol* **(D)** – 296.8 *kJ/mol*

26. *Given that:*

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(\ell)\ ; \qquad \Delta_r H^{\ominus} = -571\ kJ/mol$$

$$C_3H_4(g) + 4O_2(g) \longrightarrow 3CO_2(g) + 2H_2O(\ell)\ ; \qquad \Delta_r H^{\ominus} = -1941\ kJ/mol$$

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(\ell)\ ; \qquad \Delta_r H^{\ominus} = -2220\ kJ/mol$$

Calculate the $\Delta_r H^{\ominus}$ *value for the reaction :* $C_3H_4(g) + 2H_2(g) \longrightarrow C_3H_8(g)$

(A) – 292 *kJ/mol* **(B)** + 292 *kJ/mol* **(C)** + 850 *kJ/mol* **(D)** – 850 *kJ/mol*

27. *Use the following reactions :*

(i) $S(s) + O_2(g) \longrightarrow SO_2(g)\ ; \qquad \Delta_r H = -297\ kJ/mole$

(ii) $S(s) + \frac{3}{2}O_2(g) \longrightarrow SO_3(g)\ ;\ \Delta_r H = -396\ kJ/mole$ **(iii)** $O_2(g) \longrightarrow 2O(g)\ ;\ \Delta_r H = 495\ kJ/mole$

How would you add up the reaction energies above to get the reaction giving the S–O bond energy in SO_3?

$$SO_3(g) \longrightarrow SO_2(g) + O(g)$$

(A) (i) – (ii) + 1/2 (iii) **(B)** (i) + (ii) + 1/2(iii) **(C)** (i) – (ii) – (iii) **(D)** (i) – (ii) + 3/2(iii)

28. *Using the following energy values, determine the lattice energy of $KF(s)$:*

Property	**Energy ($kJ\ mol^{-1}$)**	**Property**	**Energy ($kJ\ mol^{-1}$)**
$\Delta_a H^{\ominus}$ of $K(s)$	90	$\Delta_{IE} H^{\ominus}$ of $K(g)$	419
$\Delta_a H^{\ominus}$ of $F_2(g)$	158	$\Delta_{EA} H^{\ominus}$ of $F(g)$	– 328
$\Delta_f H^{\ominus}$ of $KF(s)$	– 567		

(A) 51 *kJ* **(B)** 827 *kJ* **(C)** 1145 *kJ* **(D)** 1483 *kJ*

29. *Given the information below, what is the standard enthalpy of formation for $Al_2O_3(s)$?*

$$2Al_2O_3(s) \longrightarrow 4Al(s) + 3O_2(g)\ ;\ \Delta_r H^{\ominus} = 3352\ kJ$$

(A) – 6704 **(B)** –3352 **(C)** –1676 **(D)** 1676

30. *The enthalpy of combustion for octane (a major component of gasoline) is –47.8 kJ/g. How much energy is released by burning 1.0 L of octane (density 0.740 g/mL)?*

(A) – 35400 *kJ* **(B)** –64600 *kJ* **(C)** –47800 *kJ* **(D)** –57200 *kJ*

31. *The standard heat of combustion of propane is –2220.1 kJ mol^{-1}. The standard heat of vaporisation of liquid water is 44.0 kJ mol^{-1}. What is $\Delta_r H^{\ominus}$ of :* $C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(g)$?

(A) –2220.1 *kJ* **(B)** –2044.1 *kJ* **(C)** –2396.1 *kJ* **(D)** –2176.1 *kJ*

32. *The dissociation energy of CH_4 and C_2H_6 to convert them into gaseous atoms are 360 and 620 kcal/mol respectively. The bond energy of C – C bond is :*

(A) 260 *kcal mol^{-1}* **(B)** 180 *kcal mol^{-1}* **(C)** 130 *kcal mol^{-1}* **(D)** 80 *kcal mol^{-1}*

33. *The enthalpy change for the following reaction is 368 kJ. Calculate the average O — F bond energy.*

$$OF_2(g) \longrightarrow O(g) + 2F(g)$$

(A) 184 *kJ/mol* **(B)** 368 *kJ/mol* **(C)** 536 *kJ/mol* **(D)** 786 *kJ/mol*

34. *Based on the values of Bond energies given, $\Delta_f H^{\ominus}$ of $N_2H_4(g)$ is :*

Given : $N - N = 159\ kJ\ mol^{-1}\ ;\ H - H = 436\ kJ\ mol^{-1}$

$N \equiv N = 941 kJ\ mol^{-1}\ ;\ N - H = 398\ kJ\ mol^{-1}$

(A) 711 *kJ/mol* **(B)** 62 *kJ/mol* **(C)** – 98 *kJ/mol* **(D)** –711 *kJ/mol*

35. *Consider the reaction at 300 K*

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g),\ \Delta_r H^{\ominus} = -185\ kJ$$

If 3 mole of H_2 completely react with 3 mol of Cl_2 to form HCl, $\Delta_r U^{\ominus}$ of the reaction will be

(A) *zero* **(B)** 185 *kJ* **(C)** 555 *kJ* **(D)** *None of these*