## HINTS \& SOLUTIONS

## EXERCISE - 1

## Single Choice

4. $\mathrm{C}(\mathrm{s}) \longrightarrow \mathrm{C}(\mathrm{g}) \quad$ can be obtained as,
$\Delta \mathrm{H}=\Delta \mathrm{H}_{1}-\Delta \mathrm{H}_{2}-\frac{1}{2} \Delta \mathrm{H}_{3}+\Delta \mathrm{H}_{4}$
5. $2 \mathrm{C}+\mathrm{O}_{2} \rightarrow 2 \mathrm{CO} ; \Delta \mathrm{H}=-220 \mathrm{KJ}$

This reaction does not represent complete combustion of carbon, hence heat of combustion of carbon will not be equal to 110 kJ . The negative sign of $\Delta \mathrm{H}$ indicates that this reaction is exothermic. Also, despite being spontaneous reaction, it requires initiation.
6. $\mathrm{H}_{2}(\mathrm{~g})+\mathrm{Br}_{2}(\mathrm{~g}) \longrightarrow 2 \mathrm{HBr}(\mathrm{g}) \quad \Delta \mathrm{H}=\Delta \mathrm{H}^{\circ}{ }_{1}$

$$
\begin{equation*}
\mathrm{Br}_{2}(\mathrm{~g}) \longrightarrow \mathrm{Br}_{2}(\ell) \quad \Delta \mathrm{H}=\Delta \mathrm{H}_{2}^{\circ} \tag{i}
\end{equation*}
$$

$\left[\mathrm{eq}_{1}-\mathrm{eq}_{2}\right.$ ]
$\mathrm{H}_{2}(\mathrm{~g})+\mathrm{Br}_{2}(\mathrm{l}) \longrightarrow 2 \mathrm{HBr}(\mathrm{g}) \quad \Delta \mathrm{H}=\Delta \mathrm{H}^{\circ}{ }_{1}-\Delta \mathrm{H}^{\circ}{ }_{2}$
Required equation, $\frac{1}{2} \mathrm{H}_{2}(\mathrm{~g})+\frac{1}{2} \mathrm{Br}_{2}(\mathrm{l}) \longrightarrow \mathrm{HBr}(\mathrm{g})$
$\Delta \mathrm{H}=\left[\frac{\Delta \mathrm{H}_{1}^{\mathrm{o}}-\Delta \mathrm{H}_{2}^{\mathrm{o}}}{2}\right]$
7. C (diamond) $+\mathrm{O}_{2} \longrightarrow \mathrm{CO}_{2}(\mathrm{~g}) ; \Delta \mathrm{H}=-94.3 \mathrm{kcal}$

C (graphite) $+\mathrm{O}_{2} \longrightarrow \mathrm{CO}_{2}(\mathrm{~g}) ; \Delta \mathrm{H}=-97.6 \mathrm{kcal}$ C (diamond) $\longrightarrow \mathrm{C}$ (Graphite) $\Delta \mathrm{H}=3.3 \mathrm{kcal}$

Heat required to convert 12 gram diamond to graphite $=3.3$
$\therefore$ Heat required to convert 1 gm diamond to graphite
$=\frac{3.3}{12}=0.275$
10. Combustion reaction of solid boron
$\mathrm{B}(\mathrm{s})+\frac{3}{4} \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow \frac{1}{2} \mathrm{~B}_{2} \mathrm{O}_{3}(\mathrm{~s})$
$\Delta \mathrm{H}_{\mathrm{r}}^{\circ}=\Delta \mathrm{H}_{\mathrm{c}}^{\circ}=\frac{1}{2} \Delta \mathrm{H}_{\mathrm{f}}^{\circ}\left(\mathrm{B}_{2} \mathrm{O}_{3}, \mathrm{~s}\right)-\Delta \mathrm{H}_{\mathrm{f}}^{\circ}(\mathrm{B}, \mathrm{s})-\frac{3}{4} \Delta \mathrm{H}_{\mathrm{f}}^{\circ}\left(\mathrm{O}_{2}, \mathrm{~g}\right)$
$\Delta \mathrm{H}_{\mathrm{f}}^{\circ}$ of element in stable state of aggregation is assumed to be zero.
$\Delta H^{\circ}{ }_{C}=\frac{1}{2} \Delta H^{\circ}{ }_{f}\left(\mathbf{B}_{2} \mathbf{O}_{3}, \mathbf{s}\right)$
12. $\mathrm{CS}_{2}(\ell)+3 \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow \mathrm{CO}_{2}(\mathrm{~g})+2 \mathrm{SO}_{2}(\mathrm{~g})$
$\Delta \mathrm{H}=-256 \mathrm{Kcal}$
Let $\Delta \mathrm{H}_{\mathrm{f}}\left(\mathrm{CO}_{2}, \mathrm{~g}\right)=-4 \mathrm{x} \quad$ and $\quad \Delta \mathrm{H}_{\mathrm{f}}\left(\mathrm{SO}_{2}, \mathrm{~g}\right)=-3 \mathrm{x}$
$\Delta \mathrm{H}_{\text {reaction }}=\Delta \mathrm{H}_{\mathrm{f}}\left(\mathrm{CO}_{2}, \mathrm{~g}\right)+2 \Delta \mathrm{H}_{\mathrm{f}}\left(\mathrm{SO}_{2} . \mathrm{g}\right)-\Delta \mathrm{H}_{\mathrm{f}}\left(\mathrm{CS}_{2}, \ell\right)$
$-265=-4 x-6 x-26$
$\mathrm{x}=+23.9$
$\therefore \Delta \mathrm{H}_{\mathrm{f}}\left(\mathrm{SO}_{2}, \mathrm{~g}\right)=3 \mathrm{x}=-71.7 \mathrm{Kcal} / \mathrm{mol}$.
13. $\mathrm{S}+\mathrm{O}_{2} \longrightarrow \mathrm{SO}_{2} \quad \Delta \mathrm{H}=-298.2 \mathrm{KJ} / \mathrm{mole}$
$\mathrm{SO}_{2}+\frac{1}{2} \mathrm{O}_{2} \longrightarrow \mathrm{SO}_{3} \quad \Delta \mathrm{H}=-98.7 \mathrm{KJ} / \mathrm{mole}$
$\mathrm{SO}_{3}+\mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{H}_{2} \mathrm{SO}_{4} \quad \Delta \mathrm{H}=-130.2 \mathrm{KJ} / \mathrm{mole}$
$\mathrm{H}_{2}+\frac{1}{2} \mathrm{O}_{2} \longrightarrow \mathrm{H}_{2} \mathrm{O} \quad \Delta \mathrm{H}=-287.3 \mathrm{KJ} / \mathrm{mole}$
Adding (1),(2),(3) and (4) we get desired equation.
15. $\mathrm{MgCl}_{2} \cdot \mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{MgCl}_{2}(\mathrm{aq}) \Delta \mathrm{H}_{1}=$ ?
$\mathrm{MgCl}_{2}(\mathrm{aq}) \longrightarrow \mathrm{Mg}^{2+}(\mathrm{aq})+2 \mathrm{Cl}^{-}(\mathrm{aq}) \Delta \mathrm{H}_{2}=-30 \mathrm{cal} / \mathrm{mol}$
$\mathrm{MgCl}_{2}(\mathrm{~s}) \longrightarrow \mathrm{Mg}^{2+}(\mathrm{aq})+2 \mathrm{Cl}^{-}(\mathrm{aq}) \Delta \mathrm{H}_{3}=-25 \mathrm{cal} / \mathrm{mol}$
$\Delta \mathrm{H}_{1}+\Delta \mathrm{H}_{2}=\Delta \mathrm{H}_{3}$
$\Delta \mathrm{H}_{1}=\Delta \mathrm{H}_{3}-\Delta \mathrm{H}_{2}=-25+30=+5 \mathrm{cal} / \mathrm{mol}$.
16. $\mathrm{H}^{+}+\mathrm{OH}^{-} \longrightarrow \mathrm{H}_{2} \mathrm{O}(\ell) \quad \Delta \mathrm{H}=-13.7 \mathrm{kcal}$
$\mathrm{CHCl}_{2} \mathrm{COOH} \longrightarrow \mathrm{CHCl}_{2} \mathrm{COO}^{-}+\mathrm{H}^{+}$
$\Delta \mathrm{H}=0.7 \mathrm{kcal}$...(ii)
$\mathrm{CHCl}_{2} \mathrm{COOH}+\mathrm{OH}^{-} \longrightarrow \mathrm{CHCl}_{2} \mathrm{COO}^{-}+\mathrm{H}_{2} \mathrm{O}(\ell) \Delta \mathrm{H}=$ ?
Adding equation (i) and (ii) $\Delta \mathrm{H}=\mathbf{- 1 3} \mathbf{~ k c a l}$.
17. $\mathrm{H}_{3} \mathrm{PO}_{3} \longrightarrow 2 \mathrm{H}^{+}+\mathrm{HPO}_{3}^{2-} ; \Delta_{\mathrm{r}} \mathrm{H}=$ ?
$2 \mathrm{H}^{+}+2 \mathrm{OH}^{-} \longrightarrow 2 \mathrm{H}_{2} \mathrm{O}$;
$\Delta_{\mathrm{r}} \mathrm{H}=-55.84 \times 2=-111.68$
$-106.68=\Delta_{\text {ion }} H-55.84 \times 2$
$\Delta_{\text {ion }} \mathrm{H}=5 \mathrm{~kJ} / \mathrm{mol}$.
20. $\frac{1}{2} \mathrm{~A}-\mathrm{A}+\frac{1}{2} \mathrm{~B}-\mathrm{B} \rightarrow \mathrm{AB} \Delta \mathrm{H}=-100 \mathrm{KJ} /$ mole
$\frac{1}{2} x+\frac{1}{2}(0.5 x)-x=-100 \Rightarrow \frac{x}{2}+0.25 x-x=-100$
$\Rightarrow-0.25 x=-100 \Rightarrow x=400 \mathrm{KJ} /$ mole
Bond enthalpy $=\mathbf{4 0 0} \mathbf{k J} / \mathbf{m o l}$.
21. Given $\quad \mathrm{H}_{2}(\mathrm{~g}) \longrightarrow 2 \mathrm{H}(\mathrm{g}) ; \quad \Delta \mathrm{H}=104 \mathrm{kcal}$

$$
\begin{array}{ll}
\mathrm{Cl}_{2}(\mathrm{~g}) \longrightarrow 2 \mathrm{Cl}(\mathrm{~g}) ; & \Delta \mathrm{H}=58 \mathrm{kcal} \ldots(2)  \tag{2}\\
\mathrm{HCl}(\mathrm{~g}) \longrightarrow \mathrm{H}(\mathrm{~g})+\mathrm{Cl}(\mathrm{~g}) ; & \Delta \mathrm{H}=103 \mathrm{kcal} . . .(31)
\end{array}
$$

Heat of formation for HCl

$$
\frac{1}{2} \mathrm{H}_{2}(\mathrm{~g})+\frac{1}{2} \mathrm{Cl}_{2}(\mathrm{~g}) \longrightarrow \mathrm{HCl}(\mathrm{~g}) ; \quad \Delta \mathrm{H}=?
$$

Divide equation (1) and (2) by 2, and then add

$$
\begin{array}{r}
\frac{1}{2} \mathrm{H}_{2}(\mathrm{~g})+\frac{1}{2} \mathrm{Cl}_{2}(\mathrm{~g}) \longrightarrow \mathrm{H}(\mathrm{~g})+\mathrm{Cl}(\mathrm{~g}) \\
\Delta \mathrm{H}=81 \mathrm{kcal} \tag{4}
\end{array}
$$

Subtracting equation (3) from equation (4)

$$
\mathrm{HCl}(\mathrm{~g}) \longrightarrow \mathrm{H}(\mathrm{~g})+\mathrm{Cl}(\mathrm{~g}) ; \quad \Delta \mathrm{H}=103 \mathrm{kcal} \ldots(3)
$$

$\frac{1}{2} \mathrm{H}_{2}(\mathrm{~g})+\frac{1}{2} \mathrm{Cl}_{2}(\mathrm{~g}) \longrightarrow \mathrm{HCl}(\mathrm{g}) ; \Delta \mathrm{H}=-22.0 \mathrm{kcal}$
$\therefore$ Enthalpy of formation of HCl gas $=\mathbf{- 2 2 . 0} \mathbf{~ k c a l}$
22. $\Delta \mathrm{H}^{\circ}=-92.2$
$\Delta \mathrm{C}_{\mathrm{P}}=2 \mathrm{C}_{\mathrm{P}}\left(\mathrm{NH}_{3}, \mathrm{~g}\right)-\mathrm{C}_{\mathrm{P}}\left(\mathrm{N}_{2}, \mathrm{~g}\right)-3 \mathrm{C}_{\mathrm{P}}\left(\mathrm{H}_{2}\right)$
$=2 \times 35.1-29.1-3 \times 28.8$

$$
=70.2-29.1-86.4=-45.3 \mathrm{~J} / \mathrm{K}
$$

$\Delta \mathrm{H}^{\circ}{ }_{100^{\circ} \mathrm{C}}=\Delta \mathrm{H}^{\circ}{ }_{25^{\circ} \mathrm{C}}+\Delta \mathrm{C}_{\mathrm{P}}(\Delta \mathrm{T})=-92.2-\frac{45.3 \times 75}{1000}$
$\Delta \mathrm{H}^{\circ}{ }_{100^{\circ} \mathrm{C}}=-92.2-1.3975=-95.6 \mathrm{~kJ} / \mathrm{mole}$
Then, reaction at $100^{\circ} \mathrm{C}$ as compared to that at $25^{\circ} \mathrm{C}$ will be more exothermic.
23. Let mixture contain $x$ mole of steam $\& y$ mole oxygen then,
Here, temperature is constant. So, amount of heat released $=$ amount of heat gain
$\mathrm{x} \times 132=\mathrm{y}(220) \quad \Rightarrow \quad \frac{\mathrm{x}}{\mathrm{y}}=\frac{220}{132}=\frac{1.66}{1}$
$\Rightarrow \mathrm{y}: \mathrm{x}=1: \mathbf{0 . 6}$
25. $\mathrm{FeO}+\mathrm{Fe}_{2} \mathrm{O}_{3}$
$2 \mathrm{x} \quad \mathrm{x}$
$\mathrm{Fe}+\frac{1}{2} \mathrm{O}_{2} \longrightarrow \mathrm{FeO} \quad \Delta \mathrm{H}_{\mathrm{f}}^{\mathrm{O}}=-65 \mathrm{Kcal} / \mathrm{mole}$
$2 \mathrm{Fe}+\frac{3}{2} \mathrm{O}_{2} \longrightarrow \mathrm{Fe}_{2} \mathrm{O}_{3} \quad \Delta \mathrm{H}_{\mathrm{f}}^{\mathrm{O}}=-197 \mathrm{Kcal} / \mathrm{mole}$
$2 \mathrm{FeO}+\frac{1}{2} \mathrm{O}_{2} \longrightarrow \mathrm{Fe}_{2} \mathrm{O}_{3}$
$\Delta \mathrm{H}=-197+65 \times 2 \Rightarrow \Delta \mathrm{H}=-67 \mathrm{Kcal} / \mathrm{mole}$
$2 \mathrm{FeO}+\frac{1}{2} \mathrm{O}_{2} \longrightarrow \mathrm{Fe}_{2} \mathrm{O}_{3}$

$$
\begin{array}{lc}
\frac{2}{3} & \frac{1}{3} \\
\frac{2}{3}-2 x & \frac{1}{3}+x \\
\frac{2}{3}-2 x \\
\frac{1}{3}+x & =\frac{1}{2}
\end{array} \quad \Rightarrow x=\frac{1}{5}
$$

So, energy released $=\frac{1}{5} \times 67=13.4 \mathbf{k c a l} /$ mole
28. $\mathrm{C}_{8} \mathrm{H}_{18}(\ell)+\frac{25}{2} \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow 8 \mathrm{CO}_{2}(\mathrm{~g})+9 \mathrm{H}_{2} \mathrm{O}(\ell)$

$$
\begin{aligned}
& \Delta \mathrm{n}_{\mathrm{g}}=8-\frac{25}{2}=\frac{16-25}{2}=-\frac{9}{2}=-4.5 \\
& \Delta \mathrm{H}-\Delta \mathrm{E}=\Delta \mathrm{n}_{\mathrm{g}} \mathrm{RT}=-\frac{4.5 \times 8.314 \times 298}{1000}=-\mathbf{1 1 . 1 5} \mathbf{~ k J}
\end{aligned}
$$

32. $\mathrm{Q}=\mathrm{mS} \Delta \mathrm{T}_{1} \Rightarrow \frac{\mathrm{Q}_{\mathrm{R}}}{2}=\frac{\mathrm{m}}{2} \mathrm{~S} \Delta \mathrm{~T}_{1} \Rightarrow$ So, $\Delta \mathrm{T}_{1}=\Delta \mathrm{T}_{2}$
33. Assuming density of solution is $1 \mathrm{~g} / \mathrm{cc}$ and specipic heat is $4.2 \mathrm{~J} / \mathrm{gc}$

$$
\mathrm{q}=\mathrm{ms} \Delta \mathrm{~T}=100 \times 4.2 \times 3
$$

millimoles of acid nuetralized $=5$
$\Delta \mathrm{H}=-100 \times 4.2 \times 3 \times \frac{1000}{5}=-2.52 \times 10^{2} \mathrm{~kJ} / \mathrm{mole}$.
34. $(1) \mathrm{H}_{2} \mathrm{O}(\ell) \longrightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{g}) \quad \Delta \mathrm{H}=40.6 \mathrm{KJ} / \mathrm{mole}$
(2) $2 \mathrm{H}(\mathrm{g}) \longrightarrow \mathrm{H}_{2}(\mathrm{~g}) \quad \Delta \mathrm{H}=-435.0 \mathrm{KJ} / \mathrm{mole}$
(3) $2 \mathrm{O}(\mathrm{g}) \longrightarrow \mathrm{O}_{2}(\mathrm{~g}) \quad \Delta \mathrm{H}=-489.6 \mathrm{KJ} / \mathrm{mole}$
(4) $2 \mathrm{H}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \longrightarrow \mathrm{H}_{2} \mathrm{O}(\ell) \Delta \mathrm{H}=-571.6 \mathrm{KJ} / \mathrm{mole}$

(1) Calculation of $\Delta \mathrm{H}_{\mathrm{f}}{ }_{\mathbf{f}}\left(\mathrm{H}_{2} \mathrm{O}, \ell\right)$
$2 \mathrm{H}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{H}_{2} \mathrm{O}(\ell) \Delta \mathrm{H}=-571.6 \mathrm{KJ} / \mathrm{mole}$ $\Delta \mathrm{H}_{\mathrm{r}}^{\circ}=2 \Delta \mathrm{H}_{\mathrm{F}}^{\circ}\left(\mathrm{H}_{2} \mathrm{O}, \ell\right)-\underset{\mathrm{r}}{2 \Delta \mathrm{H}^{\circ}\left\{\mathrm{H}_{2},(\mathrm{~g})\right\}-\Delta \mathrm{H}_{\mathrm{F}}^{\circ}\left(\mathrm{O}_{2}, \mathrm{~g}\right)} \underset{\downarrow}{\downarrow}{ }^{\downarrow} \mathrm{Zero} \quad$ Zero
$-571.6=2 \Delta \mathrm{H}_{\mathrm{F}}^{\circ}\left(\mathrm{H}_{2} \mathrm{O}, \ell\right)$ so $\quad \Delta \mathrm{H}_{\mathrm{F}}^{\circ}\left(\mathrm{H}_{2} \mathrm{O}, \ell\right)=-285.8$

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(2) Calculation of $\Delta \mathrm{H}_{\mathrm{F}}^{\circ}\left(\mathrm{H}_{2} \mathrm{O}, \mathrm{g}\right)$
$\mathrm{H}_{2} \mathrm{O}(\ell) \longrightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{g}) \quad \Delta \mathrm{H}=40.6$
$\Delta \mathrm{H}_{\mathrm{r}}=\Delta \mathrm{H}_{\mathrm{F}}^{\circ}\left(\mathrm{H}_{2} \mathrm{O}, \mathrm{g}\right)-\Delta \mathrm{H}^{\circ}\left(\mathrm{H}_{2} \mathrm{O}, \ell\right)$
$\Delta \mathrm{H}_{\mathrm{F}}^{\circ}\left(\mathrm{H}_{2} \mathrm{O}, \mathrm{g}\right)=\Delta \mathrm{H}_{\mathrm{F}}^{\circ}\left(\mathrm{H}_{2} \mathrm{O}, \ell\right)+\Delta \mathrm{H}_{\mathrm{r}}$
$=-285.8+40=-245.8$
(3)

$\Delta \mathrm{Hr}=\epsilon_{\mathrm{H}-\mathrm{H}}+\frac{1}{2} \epsilon_{\mathrm{O}-\mathrm{O}}-2 \epsilon_{\mathrm{O}-\mathrm{H}}$
$\Rightarrow-245.8=+435+\frac{1}{2}(489.6)-2 \times \epsilon_{\mathrm{O}-\mathrm{H}}$
$2 \epsilon_{\mathrm{O}-\mathrm{H}}=435+244.8+245.8$
$\Rightarrow 2 \epsilon_{\mathrm{O}-\mathrm{H}}=925.6$
$\in \mathrm{O}-\mathrm{H}=462.8$
35. $\mathrm{Au}(\mathrm{OH})_{3}+4 \mathrm{HCl} \longrightarrow \mathrm{HAuCl}_{4}+3 \mathrm{H}_{2} \mathrm{O}, \quad \Delta \mathrm{H}=-28 \mathrm{kcal}$ $\mathrm{HAuBr}_{4}+3 \mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{Au}(\mathrm{OH})_{3}+4 \mathrm{HBr}, \Delta \mathrm{H}=+36.8 \mathrm{kcal}$
$\mathrm{HAuBr}_{4}+4 \mathrm{HCl} \longrightarrow \mathrm{HAuCl}_{4}+3 \mathrm{H}_{2} \mathrm{O}, \Delta \mathrm{H}=+8.8 \mathrm{kcal}$ When $100 \%$ conversion, heat absorbed $=8.8 \mathrm{Kcal}$
$\%$ conversion $=\frac{0.44}{8.8} \times 100=5 \%$
36. $\Delta \mathrm{H}_{\mathrm{F}}{ }^{\circ} \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}(\ell)=-66 \mathrm{Kcal} / \mathrm{mole}$
$2 \mathrm{C}+3 \mathrm{H}_{2}+\frac{1}{2} \mathrm{O}_{2} \longrightarrow \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}$
$\Delta \mathrm{H}=-66 \mathrm{kcal} / \mathrm{mole}$
$\mathrm{CH}_{3}-\mathrm{O}-\mathrm{CH}_{3}+3 \mathrm{O}_{2} \longrightarrow 2 \mathrm{CO}_{2}+3 \mathrm{H}_{2} \mathrm{O}$
$\Delta \mathrm{H}=-348 \mathrm{kcal} / \mathrm{mole}$
$\left[\mathrm{H}_{2}(\mathrm{~g})+\frac{1}{2} \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow \mathrm{H}_{2} \mathrm{O}\right.$
$\Delta \mathrm{H}_{3}-68 \mathrm{kcal} / \mathrm{mole}$
$\left[\mathrm{C}+\mathrm{O}_{2} \longrightarrow \mathrm{CO}_{2} \quad \Delta \mathrm{H}_{4}=-94 \mathrm{kcal} / \mathrm{mole}\right.$
Target equation $=-$ eq $1-$ eq $2+3$ eq $3+2$ eq 2
$\Delta \mathrm{H}=+66+348-3 \times 68-2 \times 94=+66+348-204-188$
$\Rightarrow \Delta \mathrm{H}=22 \mathrm{Kcal} / \mathrm{mole}$
$\Delta \mathrm{H}=\Delta \mathrm{E}+\Delta \mathrm{ngRT} \quad \Rightarrow \quad 22=\Delta \mathrm{E}+1 \times 2 \times 298 \times 10^{-3}$
$\Rightarrow \Delta \mathrm{E}=21.4 \mathrm{Kcal} / \mathrm{mole}$
37.

$\Delta \mathrm{H}=4 \mathrm{E}_{\mathrm{Xe}-\mathrm{F}}+\Delta \mathrm{H}_{\text {loni }}\left[\mathrm{Xe} \rightarrow \mathrm{Xe}^{+}\right]-\Delta \mathrm{E}_{\mathrm{F}-\mathrm{F}}-\Delta \mathrm{H}_{\text {eg }}\left[\mathrm{F} \rightarrow \mathrm{F}^{-}\right]$
$=4 \times 34+279-85-38=136+279-123=415-213$
$=292 \mathrm{kcal} / \mathrm{mole}$.
39. $-12250 x-13000(1-x)=-12500$
$750 x=500 \Rightarrow x=2 / 3$
So, required ratio is $=\frac{2}{1}$
40. $1 \mathrm{M} \mathrm{H}_{2} \mathrm{SO}_{4}=2 \mathrm{~g}$ eq. of $\mathrm{H}_{2} \mathrm{SO}_{4}$
hence, $y=2 x$ or $x=\frac{1}{2} y$.
42. $\mathrm{P}_{4}(\mathrm{~s}) \rightarrow 4 \mathrm{P}(\mathrm{g}) \quad \Delta \mathrm{H}=53.2 \times 6$
$\mathrm{H}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{H}(\mathrm{g}) \quad \Delta \mathrm{H}=104.2$
$\frac{1}{4} \mathrm{P}_{4}(\mathrm{~s})+\frac{3}{2} \mathrm{H}_{2}(\mathrm{~g}) \rightarrow \mathrm{PH}_{3}(\mathrm{~g}) \Delta \mathrm{H}=5.5$
$\frac{1}{4} \times 6 \times 53.2+\frac{3}{2} \times 104.2-3 \epsilon_{\mathrm{P}-\mathrm{H}}=5.5$
$\Rightarrow \quad \epsilon_{\mathrm{P}-\mathrm{H}}=76.866$ i.e. $76.9 \mathrm{kcal} \mathrm{mol}^{-1}$

## EXERCISE - 2

## Part \# I : Multiple Choice

3. $\Delta \mathrm{H}_{\mathrm{r}}=\left[2\left(\Delta \mathrm{H}_{\mathrm{f}}\right)_{\mathrm{N}_{2} \mathrm{O}_{5}}+4\left(\Delta \mathrm{H}_{\mathrm{f}}\right)_{\mathrm{HPO}_{3}}-4\left(\Delta \mathrm{H}_{5}\right)_{\mathrm{HNO}_{3}}\right.$

$$
\left.-\left(\Delta \mathrm{H}_{\mathrm{f}}\right)_{\mathrm{P}_{4} \mathrm{O}_{10}}\right]
$$

$\Delta \mathrm{H}_{\mathrm{r}}=[2(-43.1)+4(-948.5)-4(-174.1)-(-2984.0)]$
$=-199.8$
5. $\Delta \mathrm{H}_{\mathrm{r}}^{\circ}=\left[4 \Delta \mathrm{H}_{\mathrm{C}-\mathrm{H}}+4 \Delta \mathrm{H}_{\mathrm{Cl}-\mathrm{Cl}}-4 \Delta \mathrm{H}_{\mathrm{C}-\mathrm{Cl}}-4 \Delta \mathrm{H}_{\mathrm{C}-\mathrm{Cl}}\right]$
$=[4 \times 414+4 \times 243-4 \times 331-4 \times 4313]$
$\Delta \mathrm{H}_{\mathrm{r}}^{\circ}=420$
6. For $\Delta \mathrm{H}_{\mathrm{g}}=0, \Delta \mathrm{H}=\Delta \mathrm{E}$

$$
\Delta \mathrm{H}_{\mathrm{g}} \neq 0, \Delta \mathrm{H} \neq \Delta \mathrm{E}
$$

9. Heat evolve $=\mathrm{mC}_{\mathrm{v}} \Delta \mathrm{t}=100 \times 4.2 \times 10=4.2 \mathrm{~kJ}$
for 0.1 mole the enthalpy change $=4.2 \mathrm{~kJ}$
for 1 mole the enthalpy change $=42 \mathrm{~kJ}$
10. $\mathrm{HCl}+\mathrm{NaOH} \longrightarrow \mathrm{NaCl}+\mathrm{H}_{2} \mathrm{O}$
enthalpy change $=\mathrm{mC}_{\mathrm{v}} \mathrm{dT}=100 \times 4.2 \times 3$

$$
=1.26 \mathrm{~kJ}
$$

enthalpy change for 5 millimole $=1.26 \mathrm{~kJ}$
enthalpy change for 1 mole $\Rightarrow \frac{1.26}{5 \times 10^{-3}}$
$\Rightarrow 2.52 \times 10^{2} \mathrm{~kJ}$
13. $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH} \longrightarrow \mathrm{C}_{2} \mathrm{H}_{4}+\mathrm{H}_{2} \mathrm{O} \ldots$ (i) $\Delta \mathrm{H}=45.54$
$8 \mathrm{a} \quad 8 \mathrm{a}$
$\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH} \longrightarrow \mathrm{CH}_{3} \mathrm{CHO}+\mathrm{H}_{2} \ldots$ (ii) $\quad \Delta \mathrm{H}=68.91$
a
a
$8 a+a=1$
$a=\frac{1}{9}$
energy involve in (i) reaction $=45.54 \times \frac{8}{9}$
energy involve in (iii) reaction $=68.91 \times \frac{1}{9}$
total involve in (i) + (iii) are $\Rightarrow 48.137 \mathrm{Kg}$
14. $\mathrm{HAuBr}_{4}+4 \mathrm{HCl} \longrightarrow \mathrm{HAuCl}_{4}+4 \mathrm{HBr} \quad \Delta \mathrm{H}=8.8$ $\%$ conversion $=\frac{0.44}{8.8} \times 100=5 \%$

## Part \# II : Assertion \& Reason

1. Heat of neutralisation for strong acid and strong base combination is constant is equal to -13.7 Kcal or -57.1 KJ.
2. For reaction $\mathrm{C}(\mathrm{s})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g}) ; \Delta \mathrm{H}=\Delta \mathrm{U}$

## EXERCISE - 3

Part \# I : Matrix Match Type

1. (A) This is combustion reaction as well as formation reaction of $\mathrm{CO}_{2}$.
(B) This is sublimation, atomization as well as formation reaction of $\mathrm{C}(\mathrm{g})$.
(C) This is combustion reaction of $\mathrm{CO}(\mathrm{g})$.
(D) This is atomization of $\mathrm{CH}_{4}(\mathrm{~g})$.

## Part \# II : Comprehension

Comprehension \#1:
2. $\mathrm{C}(\mathrm{s})+\mathrm{H}_{2} \mathrm{O}(\mathrm{g}) \longrightarrow \mathrm{H}_{2}(\mathrm{~g})+\mathrm{CO}(\mathrm{g})$;

$$
\Delta \mathrm{H}=-110.53+241.81=131.28 \mathrm{~kJ}
$$

For 100 moles of air heat liberated $=21 \times 314 \mathrm{~kJ}$.
No. of moles of $\mathrm{H}_{2} \mathrm{O}$ converted to product
$=\frac{21 \times 314}{131.28}=50.23$
No. of moles of $\mathrm{H}_{2} \mathrm{O}$ taken $=\frac{50.23}{0.75}=66.97$.

| Gas | $\mathrm{H}_{2}$ | CO | $\mathrm{N}_{2}$ | $\mathrm{H}_{2} \mathrm{O}$ | $\mathrm{CO}_{2}$ |
| :---: | :--- | :--- | :--- | :--- | :--- |
| No. of moles | 50.23 | 50.23 | 79 | 16.74 | 21 |
| $\%(\mathrm{v} / \mathrm{v})$ | 23.1 | 23.1 | 36.4 | 7.7 | 9.7 |

Comprehension \#2:

1. $\Delta \mathrm{H}_{\text {ionisation }}=\Delta \mathrm{H}^{\circ}{ }_{\text {neutralisation }}-\Delta \mathrm{H}^{\circ}\left(\mathrm{H}+\mathrm{OH}^{-} \longrightarrow \mathrm{H}_{2} \mathrm{O}\right)$
$=-49.86-(-55.84) \mathrm{kJ} / \mathrm{mole}$
$=5.98 \mathrm{~kJ} / \mathrm{mole}$
2. For max. rise in temp.; max. neutralization of $\mathrm{H}^{+}$and $\mathrm{OH}^{-}$ required.
If we take equal volume, all $\mathrm{H}^{+}(5 \mathrm{~m}$-mole $)$ will react with all $\mathrm{OH}^{-}(5 \mathrm{~m}$-mole $)$.

Comprehension \# 4 :

1. $\Delta \mathrm{H}_{\mathrm{r}}=\left[\left(\Delta \mathrm{H}_{\mathrm{f}}\right)_{\mathrm{C}_{2} \mathrm{~F}_{4}}+2\left(\Delta \mathrm{H}_{\mathrm{f}}\right)_{\mathrm{HCl}}-2\left(\Delta \mathrm{H}_{\mathrm{f}}\right)_{\mathrm{CHClF}_{2}}\right]$
$=[-658.3+2(-92.3)+2(485.2)]$
$=127.5 \mathrm{~kJ} / \mathrm{mole}$
2. Add eq. (i), (ii) and (iii)
$\mathrm{CX}_{4}(\mathrm{~g}) \longrightarrow \mathrm{C}(\mathrm{g})+4 \mathrm{X}$
$\Delta \mathrm{H}=-\Delta \mathrm{H}_{1}+718+2 \mathrm{D}(\mathrm{X}-\mathrm{X})$
$\mathrm{X}=\mathrm{F}$
$\Delta \mathrm{H}=+679.6+718+2 \times 154.7$
$\Delta \mathrm{H}=1707$
Average bond energy of $\mathrm{C}-\mathrm{F}$ bond $=\frac{1707}{4}=426.75$

$$
\mathrm{X}=\mathrm{Cl}
$$

$\Delta \mathrm{H}=106.6+718+2(246.7)=1318$
Average bond energy of $\mathrm{C}-\mathrm{Cl}$ bond $=329.5 \mathrm{Kg}$
3. $\mathrm{C}-\mathrm{Cl}$ bond energy $=329.5$
$\mathrm{C}-\mathrm{H}$ bond energy $=416.1$
$\mathrm{C}-\mathrm{F}$ bond energy $=426.75$
Order of reactivity $\mathrm{C}-\mathrm{Cl}>\mathrm{C}-\mathrm{H}>\mathrm{C}-\mathrm{F}$

## Comprehension \# 5 :

1. (i) $\Delta H=(v+w+x+y+z)$
(ii) $\left(\Delta \mathrm{H}_{\mathrm{f}}\right)_{\mathrm{K}^{+}}=\frac{\mathrm{w}}{2}$
(iii) $(\Delta H)_{E A}$ for $H=\frac{y}{2}$
(iv) $(\Delta \mathrm{H})_{\text {lattice }}$ for $\mathrm{KH}=\frac{\mathrm{z}}{2}$
2. (i) electron affinity is exothermic
(ii) ionization is endothermic
3. $(\Delta \mathrm{H})_{\mathrm{r}}=2 \times 90+2 \times 418+436-2 \times 78-2 \times 710$
$(\Delta \mathrm{H})_{\mathrm{r}}=-124 \mathrm{~kJ} / \mathrm{mole}$
4. $\left(\Delta \mathrm{H}_{\mathrm{f}}\right)_{\mathrm{KH}}=-\frac{124}{2} \Rightarrow-62 \mathrm{~kJ} / \mathrm{mole}$
5. Meq. of $\mathrm{KH}=$ Meq. of HCl
$\frac{0.1}{\mathrm{E}_{\mathrm{KH}}} \times 1000=25 \times 0.1$
Valency factor of K is 1 hence

| $\mathrm{E}_{\mathrm{K}}=\mathrm{M}_{\mathrm{K}}$ | $\mathrm{M}_{\mathrm{K}}=39$ |
| :--- | :--- |
| $\mathrm{E}_{\mathrm{KH}}=40$ | $\mathrm{E}_{\mathrm{KH}}=\mathrm{E}_{\mathrm{K}}=\mathrm{E}_{\mathrm{H}}$ |
| $40=\mathrm{E}_{\mathrm{K}}+1$ | $\mathrm{E}_{\mathrm{K}} \Rightarrow 39$ |

## EXERCISE - 4

## Subjective Type

3. $\Delta \mathrm{H}_{2}-24=-0.024 \times(523-473) \mathrm{cal} / \mathrm{g}$.
$\therefore \quad \Delta \mathrm{H}_{2}=22.8 \mathrm{cal} / \mathrm{g}$.
4. When the heat capacities of all substances participating in a chemical reaction are assumed to be constant over the range of temperatures involved kirchoff's law integrates to
$\Delta \mathrm{H}^{\circ}\left(\mathrm{T}_{2}\right)=\Delta \mathrm{H}^{\circ}\left(\mathrm{T}_{1}\right)+\Delta \mathrm{C}_{\mathrm{p}}\left(\mathrm{T}_{2}-\mathrm{T}_{1}\right)$

$$
\begin{aligned}
& \Delta \mathrm{C}_{\mathrm{P}}=\sum_{\text {Products }} v \mathrm{C}_{\mathrm{p}, \mathrm{~m}}^{0}-\sum_{\text {Reactants }} \mathrm{vC}_{\mathrm{p}, \mathrm{~m}}^{0}- \\
& \Delta \mathrm{C}_{\mathrm{P}}=\mathrm{C}_{\mathrm{p}}\left(\mathrm{~N}_{2} \mathrm{O}_{4}, \mathrm{~g}\right)-2 \mathrm{C}_{\mathrm{p}}\left(\mathrm{NO}_{2}, \mathrm{~g}\right) \\
&=(77.28)-(2) \times\left(37.20 \mathrm{j} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}\right) \\
&=+2.88 \mathrm{JK}^{-1} \mathrm{~mol}^{-1} \\
& \Delta \mathrm{H}^{\circ}(373 \mathrm{~K})=\Delta \mathrm{H}^{\circ}(298 \mathrm{~K})+\Delta \mathrm{C}_{\mathrm{p}} \Delta \mathrm{~T} \\
&=\left(-57.20 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)+\left(2.88 \mathrm{~J} \mathrm{~K}^{-1}\right) \times(75 \mathrm{~K}) \\
&=\{(-57.20)+(0.22)\} \mathrm{kJ} \mathrm{~mol}^{-1} \\
&=-56.98 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{aligned}
$$

6. Given reaction can be obtained as follows :

$$
\begin{array}{ll}
\mathrm{B}_{2} \mathrm{H}_{6}(\mathrm{~g}) \longrightarrow 2 \mathrm{~B}(\mathrm{~s})+3 \mathrm{H}_{2}(\mathrm{~g}) & \Delta \mathrm{H}=-36 \mathrm{~kJ} \mathrm{~mol}^{-1} \\
2 \mathrm{~B}(\mathrm{~s})+(3 / 2) \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow \mathrm{B}_{2} \mathrm{O}_{3}(\mathrm{~s}) & \Delta \mathrm{H}=-1273 \mathrm{~kJ} \mathrm{~mol}^{-1} \\
3\left[\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \longrightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{~g})\right] \quad & \Delta \mathrm{H}=3 \times 44 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{array} \begin{array}{r}
3\left[\mathrm{H}_{\mathrm{g}}(\mathrm{~s})+(1 / 2) \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow \mathrm{H}_{2}(1)\right. \\
\Delta \mathrm{H}=-3 \times 286 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{array}
$$

Add
7. Equal volume of $\mathrm{H}_{2}(\mathrm{~g}) \& \mathrm{CO}(\mathrm{g})$

Total volume $=112 \mathrm{~L}$
So, volume of $\mathrm{CO}=$ volume of $\mathrm{H}_{2}=56 \mathrm{~L}$
Mole of $\mathrm{CO}=$ Mole of $\mathrm{H}_{2}=2.5$ mole
$\mathrm{H}_{2}(\mathrm{~g})+\frac{1}{2} \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{g}) \quad \Delta \mathrm{H}=-241.8 \mathrm{~kJ}$
For $\quad 1$ mole $\quad \Delta \mathrm{H}=-241.8 \mathrm{~kJ}$
For $\quad 2.5$ mole $\quad \Delta \mathrm{H}=-241.8 \times 2.5$
Similarly, $\mathrm{CO}(\mathrm{g})+\frac{1}{2} \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow \mathrm{CO}_{2}(\mathrm{~g})$

$$
\begin{aligned}
& \Delta \mathrm{H}=-283 \mathrm{~kJ} \\
& \Delta \mathrm{H}=-283 \times 2.5 \mathrm{~kJ}
\end{aligned}
$$

Total Heat evolved $=[-241.8+(-283] 2.5=-1312 \mathrm{~kJ}$
8. $\mathrm{K}(\mathrm{s})+\frac{1}{2} \mathrm{O}_{2}(\mathrm{~g})+\frac{1}{2} \mathrm{H}_{2}(\mathrm{~g}) \longrightarrow \mathrm{KOH} \quad \Delta \mathrm{H}=$ ?
$\mathrm{H}_{2}+\frac{1}{2} \mathrm{O}_{2} \longrightarrow \mathrm{H}_{2} \mathrm{O} \quad \Delta \mathrm{H}=-68 \mathrm{kcal}$
...(i)
$\mathrm{K}+\mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{KOH}($ aq. $)+\frac{1}{2} \mathrm{H}_{2}(\mathrm{~g})$
$\Delta \mathrm{H}=-48 \mathrm{kcal}$
$\mathrm{KOH}+$ water $\longrightarrow \mathrm{KOH}$ (aq.) $\Delta \mathrm{H}=-14 \mathrm{kcal} \quad$..(iii)
$\Delta \mathrm{H}_{\mathrm{f}, \mathrm{KOH}}=(\mathrm{i})+($ iii) - (iiii)
$\Delta \mathrm{H}_{\mathrm{f}, \mathrm{KOH}}=-48-68-(-14)=-102$ kcal.
9. Heat generated $=\mathrm{C}_{\mathrm{T}} \Delta \mathrm{T}=1260 \times 0.667 \mathrm{cal}$.

$$
\begin{aligned}
& \therefore \quad \mathrm{n}_{\mathrm{CH}_{4}} \\
&=\frac{1260 \times 0.667}{210.8 \times 10^{3}} \\
& \mathrm{n}_{\text {total }} \\
&=\frac{\mathrm{PV}}{\mathrm{RT}}=3.98 \times 10^{-2}
\end{aligned}
$$

$\therefore \quad \mathrm{mol} \%=\frac{1260 \times 0.667}{210.8 \times 10^{3} \times 3.98 \times 10^{-2}} \times 100 \%=10 \%$ Ans.
12. We have

Amount of carbon $=\frac{12.0 \mathrm{~g}}{12.0 \mathrm{~g} \mathrm{~mol}^{-1}}=1 \mathrm{~mol}$
The equations to be considered are
C (graphite) $+1 / 2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}(\mathrm{g}) \Delta \mathrm{H}^{0}=-110.5 \mathrm{~kJ} \mathrm{~mol}^{-1}$
C (graphite) $+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g}) \Delta \mathrm{H}^{0}=-393.5 \mathrm{~kJ} \mathrm{~mol}^{-1}$
Let the amount x of carbon be converted into CO and the remaining (i.e. $1.0 \mathrm{~mol}-\mathrm{x}$ ) into $\mathrm{CO}_{2}$. we will have $[\mathrm{x}(-110.5)+(1.0 \mathrm{~mol}-\mathrm{x})(-393.5)] \mathrm{kJ} \mathrm{mol}^{-1}=-313.8 \mathrm{~kJ}$

Which gives $\mathrm{x}=\frac{313.8+393.5}{393.5-110.5} \mathrm{~mol}=0.282 \mathrm{~mol}$
Amount of oxygen needed $=\left[\frac{0.282}{2}+(1.0-0.282)\right]$ $\mathrm{mol}=0.859 \mathrm{~mol}$
Mass of oxygen needed $=(0.859 \mathrm{~mol})\left(32 \mathrm{~g} \mathrm{~mol}^{-1}\right)=27.48 \mathrm{~g}$
15. Equation (vi) can be generated by the following manipulations.
Eq. (i) - Eq. (iii) - Eq. (iii) - Eq. (iv) - $1 / 2$ Eq. (v)
Carrying out the corresponding manipulations on $\Delta \mathrm{H}_{\mathrm{L}}{ }^{\circ}$, we get

$$
\begin{aligned}
& \Delta \mathrm{H}_{\mathrm{L}}^{0}=(-563-419-88+322-79) \mathrm{kJ} \mathrm{~mol}^{-1} \\
& \quad=-829 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{aligned}
$$

16. (i) $\mathrm{CHCl}_{2} \mathrm{COOH}+\mathrm{NaOH} \longrightarrow \mathrm{CHCl}_{2} \mathrm{COONa}+\mathrm{H}_{2} \mathrm{O}$ $\Delta \mathrm{H}=-12830 \mathrm{Cal}$
(ii) $\mathrm{HCl}+\mathrm{NaOH} \longrightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{NaCl}$
$\Delta \mathrm{H}=-13680 \mathrm{Cal}$
(iii) $\mathrm{NH}_{4} \mathrm{OH}+\mathrm{HCl} \longrightarrow \mathrm{NH}_{4} \mathrm{Cl}+\mathrm{H}_{2} \mathrm{O}$ $\Delta \mathrm{H}=-12270 \mathrm{Cal}$
(iv) $\mathrm{CHCl}_{2} \mathrm{COOH}+\mathrm{NH}_{4} \mathrm{OH} \longrightarrow \mathrm{CHCl}_{2} \mathrm{COONH}_{4}+\mathrm{H}_{2} \mathrm{O}$ $\Delta \mathrm{H}=$ ?
(iv) $=$ (i) + (iii) - (ii) $=-12830-12270+13680=-11420$ Cal
Heats of ionization of $\mathrm{CHCl}_{2} \mathrm{COOH}=-13680+12830$ $=-850 \mathrm{cal}$
Heats of ionization of $\mathrm{NH}_{4} \mathrm{OH}=-13680+12270=-1410 \mathrm{cal}$
17. Given total solution $=200+400=600 \mathrm{~mL}$.

200 mL of 1 MHCl neutralize 400 mL of 0.5 M NaOH
$\therefore$ Meq. $=\mathrm{N} \times \mathrm{V}$
$\therefore \mathrm{mM}$ or Meq. of acid and base $=200$ (For mono valent
nature)
i.e., 200 Meq . of HCl react with 200 Meq . of NaOH to produce heat $=\Delta \mathrm{H}$
1000 Meq. of $\mathrm{HCl}+1000$ Meq. of NaOH will give heat $=5 \times \Delta \mathrm{H}$.
i.e, heat of neutralization. Now,
$\Delta H$, i.e., Heat produced during neutralization of 200 Meq . of acid and base

$$
\begin{aligned}
= & \text { Heat taken up by calorimeter }+ \text { solution }=\mathrm{m}_{1} \mathrm{~s}_{1} \Delta \mathrm{~T} \\
& +\mathrm{m}_{2} \mathrm{~s}_{2} \Delta \mathrm{~T} \\
= & 12 \times 4.4+600 \times 1 \times 4.4=2692.8 \mathrm{cal}
\end{aligned}
$$

$\therefore$ Heat of neutralization $=-5 \times 2692.8 \mathrm{cal}=-13.464 \mathrm{kcal}$
18.

$\Delta \mathrm{Hr}=2 \epsilon_{\mathrm{C}-\mathrm{H}}+2 \epsilon_{\mathrm{C}-\mathrm{Cl}}=2 \times 414+2 \times 330=828+660$ $=1488 \mathrm{~kJ} / \mathrm{mol}$.
20. To calculate the average $S-F$ bond enthalpy, we determine the enthalpy change for the following reaction.
$\mathrm{S}(\mathrm{g})+6 \mathrm{~F}(\mathrm{~g}) \rightarrow \mathrm{SF}_{6}(\mathrm{~g})$
$\Delta \mathrm{H}_{\mathrm{f}}^{0} 275 \mathrm{~kJ} \mathrm{~mol}^{-1} \quad 80 \mathrm{~kJ} \mathrm{~mol}^{-1} 1100 \mathrm{~kJ} \mathrm{~mol}^{-1}$
$\Delta \mathrm{H}_{\mathrm{f}}^{0}=\Delta \mathrm{H}_{\mathrm{f}}^{0}\left(\mathrm{~F}_{6}, \mathrm{~g}\right)-\left[\Delta \mathrm{H}_{\mathrm{f}}^{0}(\mathrm{~S}, \mathrm{~g})+6 \Delta \mathrm{H}_{\mathrm{f}}^{0}(\mathrm{~F}, \mathrm{~g})\right]$
$=[-1100-(275+6 \times 80)] \mathrm{kJ} \mathrm{mol}^{-1}$
Hence $\varepsilon(\mathrm{S}-\mathrm{F})=\frac{-\Delta \mathrm{H}_{\mathrm{f}}^{0}\left(\mathrm{SF}_{6}, \mathrm{~g}\right)}{6}=\frac{1855 \mathrm{~kJ} \mathrm{~mol}^{-1}}{6}$
$=309.2 \mathrm{~kJ} \mathrm{~mol}^{-1}$
22. $\mathrm{H}_{2}(\mathrm{~g})+\mathrm{Cl}_{2}(\mathrm{~g}) \longrightarrow 2 \mathrm{H}-\mathrm{Cl}$

$\Delta \mathrm{H}_{\mathrm{r}}=\epsilon_{\mathrm{H}-\mathrm{H}}+\epsilon_{\mathrm{Cl}-\mathrm{Cl}}-2 \epsilon_{\mathrm{H}-\mathrm{Cl}}=435+240-2 \times 430$
$\Delta \mathrm{H}_{\mathrm{r}}=-185 \mathrm{~kJ}$
$\Delta \mathrm{S}=2 \mathrm{~S}^{\circ}{ }_{\mathrm{m}} \mathrm{HCl}-\mathrm{S}_{\mathrm{m}}^{\circ} \mathrm{H}_{2}(\mathrm{~g})-\mathrm{S}_{\mathrm{m}}^{\circ} \mathrm{Cl}_{2}(\mathrm{~g})=2 \times 187-131-223$
$\Delta \mathrm{S}=20 \mathrm{~J} / \mathrm{mole} \mathrm{K}$
$\Delta \mathrm{G}=\Delta \mathrm{H}-\mathrm{T} \Delta \mathrm{S}=-185-\frac{300 \times 20}{1000}=-186-6=-191 \mathrm{KJ}$.
23. Target equation: $\mathrm{N}_{2} \mathrm{H}_{4}(\ell)+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{N}_{2}(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{O}(\ell)$ which can be obtained by the given manipulation.

$$
\frac{1}{4} \times(i)-\frac{3}{4}(i i)+\frac{9}{4}(i v)-\frac{1}{8}(\text { iiii })
$$

Hence, $\Delta \mathrm{H}$ for targeted equation is

$$
\begin{aligned}
& \frac{1}{4}(-1011)-\frac{3}{4}(-317)+\frac{9}{4}(-286)-\frac{1}{8}(-286) \\
& =\frac{1}{4}[-1011+3 \times 317-9 \times 286+0.5 \times 286] \\
& =-622.75 \mathrm{~kJ} / \text { mole hydrazine }
\end{aligned}
$$

Now, $\quad-622.75=2 \times(-286)-\Delta \mathrm{H}_{\mathrm{f}}\left(\mathrm{N}_{2} \mathrm{H}_{4}\right)$
$\Rightarrow \quad \Delta \mathrm{H}_{\mathrm{f}}\left(\mathrm{N}_{2} \mathrm{H}_{4}\right)=+50.75 \mathrm{~kJ} / \mathrm{mol}$
Yes it is an endothermic compound.
25. (i) C (s) $+\mathrm{O}_{2}$ (g) $\longrightarrow \mathrm{CO}_{2}$ (g); $\Delta \mathrm{H}_{\mathrm{f}}^{\circ}=-393.33 \mathrm{KJ} / \mathrm{mol}$;

$$
\Delta \mathrm{H}_{\mathrm{f}}^{\circ}=\frac{590}{18} \times 12
$$

(ii) $\mathrm{H}_{2}(\mathrm{~g})+\frac{1}{2} \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow \mathrm{H}_{2} \mathrm{O}(\ell) ; \Delta \mathrm{H}_{\mathrm{f}}^{\circ}=-286 \mathrm{KJ} / \mathrm{mol}$;

$$
\Delta \mathrm{H}_{\mathrm{f}}^{\circ}=\frac{15889}{55.5}
$$

(iii) $\mathrm{C}_{6} \mathrm{H}_{6}(\ell)+\frac{15}{2} \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow 6 \mathrm{CO}_{2}(\mathrm{~g})+3 \mathrm{H}_{2} \mathrm{O}(\ell)$
$\therefore \quad \Delta \mathrm{H}^{\mathrm{o}}=[6(-393.33)+3(-286)]-50=-3268 \mathrm{KJ} / \mathrm{mol}$ Mass of benzene is $=0.87 \times 100=87 \mathrm{~g}$
$\therefore \quad$ Heat evolved from 87 gm benzene $=3645 \mathrm{KJ}$ Ans.
27. $\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}(\mathrm{~s})+6 \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow 6 \mathrm{CO}_{2}+6 \mathrm{H}_{2} \mathrm{O}(\ell)$

No. of Mole of $\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}=\frac{0.36}{180}=2 \times 10^{-3} \mathrm{~mole}$
$\mathrm{C}=\frac{\mathrm{q}}{\Delta \mathrm{T}} \quad \therefore \quad \mathrm{q}=\mathrm{C} \times \Delta \mathrm{T}=640 \times 10 \mathrm{~J}=6.4 \mathrm{~kJ}$

Heat released per mole $=\frac{6.4}{2 \times 10^{-3}}=3.2 \times 10^{3} \mathrm{~kJ}=\mathbf{3 . 2} \mathbf{M J}$
$\Delta \mathrm{U}=-3.2 \mathrm{MJ}$
$\Delta \mathrm{H}=\Delta \mathrm{U}+\Delta \mathrm{n}_{\mathrm{g}}$ RT here $\quad \Delta \mathrm{n}_{\mathrm{g}}=0$
$\Delta \mathrm{H}=\Delta \mathrm{U}=-3.2 \mathrm{MJ} \mathrm{mole}^{-1}$
28. By the equations $C_{p}=f(T)$, we find
$\Delta \mathrm{C}_{\mathrm{p}}=\left(\mathrm{C}_{\mathrm{p}}\right)_{\mathrm{CO}}-\left(\mathrm{C}_{\mathrm{p}}\right)_{\mathrm{c}}-1 / 2\left(\mathrm{C}_{\mathrm{P}}\right)_{\mathrm{O}_{2}}$
$=2.37-4.973 \times 10^{-3} \mathrm{~T}+1.585 \times 10^{-6} \mathrm{~T}^{2}$
The condition where $\Delta \mathrm{H}^{\circ}$ does not depend on the temperature is the equation $\Delta \mathrm{C}_{\mathrm{p}}=0$,
i.e. $2.37 \times 4.973 \times 10^{-3} \mathrm{~T}+1.585 \times 10^{-6} \mathrm{~T}^{2}=0$,
where $\mathrm{T} \approx 586$.
Since the terms of the equation $\Delta \mathrm{C}_{\mathrm{p}}=\mathrm{f}(\mathrm{T})$ containing $T$ are negative, then at $\mathrm{T}>586$ we have $\Delta \mathrm{C}_{\mathrm{p}}<0$. i.e. at this temperature $\Delta \mathrm{H}^{\circ}$ passes through a minimum.
30. On mixing $\mathrm{CaCl}_{2}(\mathrm{aq})$ and $\mathrm{Na}_{2} \mathrm{CO}_{3}$
$\mathrm{CaCl}_{2}+\mathrm{Na}_{2} \mathrm{CO}_{3} \rightarrow \mathrm{CaCO}_{3}+2 \mathrm{NaCl}$
Solutions are very dilute and thus. $100 \%$ dissociation occurs.
$\mathrm{Ca}^{+2}(\mathrm{aq})+2 \mathrm{Cl}^{-}(\mathrm{aq})+2 \mathrm{Na}^{+}(\mathrm{aq})+\mathrm{CO}_{3}^{-2}(\mathrm{aq})$

$$
\rightarrow \mathrm{CaCO}_{3} \downarrow+2 \mathrm{Na}^{+}(\mathrm{aq})+2 \mathrm{Cl}^{-}(\mathrm{aq})
$$

or $\quad \mathrm{Ca}^{+2}(\mathrm{aq})+\mathrm{CO}_{3}^{-2}(\mathrm{aq}) \rightarrow \mathrm{CaCO}_{3}(\mathrm{~s})$
$\therefore \quad \Delta \mathrm{H}=\Sigma \mathrm{H}_{\text {Products }}^{0}-\Sigma \mathrm{H}_{\text {reactants }}^{0}$
or $\quad \Delta \mathrm{H}=\Delta \mathrm{H}_{\mathrm{fCaCO}_{3}}^{0}-\left[\begin{array}{ll}\Delta \mathrm{H}_{\mathrm{fCa}^{+2}}^{0} & \Delta \mathrm{H}_{\mathrm{fCO}_{3}^{-2}}^{0}\end{array}\right]$
$\therefore \quad \Delta \mathrm{H}^{0}$ of a compound $=\Delta \mathrm{H}_{\text {formation }}^{0}$
$=-288.5-(-129.80-161.65)=2.95 \mathrm{kcal}$
31. trans - 2 - butene $\longrightarrow$ cis - 2 - butene

$$
\Delta \mathrm{H}=+0.95 \mathrm{kcal}
$$

cis - 2 - butene $\longrightarrow 1$ - butene
$\Delta \mathrm{H}=+1.8 \mathrm{kcal}$
1 - butene $+6 \mathrm{O}_{2} \longrightarrow 4 \mathrm{CO}_{2}+4 \mathrm{H}_{2} \mathrm{O}$ $\Delta \mathrm{H}=-650 \mathrm{kcal}$
Adding above three eqution gives :
trans -2 -butene $+6 \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow 4 \mathrm{CO}_{2}(\mathrm{~g})+4 \mathrm{H}_{2} \mathrm{O}$ $\Delta \mathrm{H}=-647.25 \mathrm{kcal}$



$\Delta \mathrm{H}=-603.25 \mathrm{kcal}$
$-603.25=8 \times 98+2 \times 80+$ B.E. $(\mathrm{C}=\mathrm{C})+$ $6 \times 118-8 \times 196-8 \times 110$

$$
\text { B.E. }(\mathrm{C}=\mathrm{C})=192.75 \mathrm{kcal} .
$$

32. In polymerisation of ethylene, double bond of ethylene is broken and two single bonds are formed.
$\mathrm{CH}_{2}=\mathrm{CH}_{2} \longrightarrow\left(-\mathrm{CH}_{2}-\mathrm{CH}_{2}-\right)$
$\Delta \mathrm{H}_{\text {poly }}=\mathrm{E}_{\mathrm{C}=\mathrm{C}}-2 \mathrm{E}_{\mathrm{C}-\mathrm{C}}=-72$
$\Rightarrow \mathrm{E}_{\mathrm{C}=\mathrm{C}}-2 \mathrm{E}_{\mathrm{C}-\mathrm{C}}=-72$
$6 \mathrm{C}(\mathrm{s})+3 \mathrm{H}_{2}(\mathrm{~g}) \longrightarrow \mathrm{C}_{6} \mathrm{H}_{6}(\ell) \quad \Delta \mathrm{H}=49 \mathrm{~kJ} / \mathrm{mole}$
$\Delta \mathrm{H}_{\text {resonance }}=\Delta \mathrm{H}_{\text {exp }}-\Delta \mathrm{H}_{\text {cal }}$
$\Delta \mathrm{H}_{\text {cal }}=49-\left(-\Delta \mathrm{H}_{\text {resonance }}\right)=49-(-152)=201$
(1) $6 \mathrm{C}(\mathrm{s})+3 \mathrm{H}_{2}(\mathrm{~g}) \longrightarrow \mathrm{C}_{6} \mathrm{H}_{6}(\ell) \quad \Delta \mathrm{H}_{\text {cal }}=201$
(2) $\mathrm{C}_{6} \mathrm{H}_{6}(\ell) \longrightarrow \mathrm{C}_{6} \mathrm{H}_{6}(\mathrm{~g}) \quad \Delta \mathrm{H}=144$

Adding 1 \& 2

$$
\begin{aligned}
& 6 \mathrm{C}(\mathrm{~s})+3 \mathrm{H}_{2}(\mathrm{~g}) \longrightarrow \mathrm{C}_{6} \mathrm{H}_{6}(\mathrm{~g}) \quad \Delta \mathrm{H}=345 \\
& \downarrow \quad \downarrow \\
& 6 \mathrm{C}(\mathrm{~g})+6 \mathrm{H}(\mathrm{~g})
\end{aligned}
$$

$\Delta \mathrm{H}=6 \times 715+3 \times 436-6 \mathrm{E}_{\mathrm{C}-\mathrm{H}}-3 \mathrm{E}_{\mathrm{C}=\mathrm{C}}-3 \mathrm{E}_{\mathrm{C}-\mathrm{C}}$
$345=4290+1308-6 \times 415-3 \mathrm{E}_{\mathrm{C}=\mathrm{C}}-\mathrm{E}_{\mathrm{C}-\mathrm{C}}$
$3 \mathrm{E}_{\mathrm{C}=\mathrm{C}}+3 \mathrm{E}_{\mathrm{C}-\mathrm{C}}=2763 \mathrm{So} \mathrm{E}_{\mathrm{C}=\mathrm{C}}+\mathrm{E}_{\mathrm{C}-\mathrm{C}}=921$
$\mathrm{E}_{\mathrm{C}=\mathrm{C}}+\mathrm{E}_{\mathrm{C}-\mathrm{C}}=921$
$\mathrm{E}_{\mathrm{C}=\mathrm{C}}-2 \mathrm{E}_{\mathrm{C}-\mathrm{C}}=-72$
On solving (i) and (ii) equation, $3 \mathrm{E}_{\mathrm{c}-\mathrm{C}}=993$
$\mathrm{E}_{\mathrm{C}-\mathrm{C}}=331 \mathrm{~kJ} / \mathrm{mole}$, So, $\mathrm{E}_{\mathrm{C}=\mathrm{C}}=590 \mathrm{~kJ} / \mathrm{mole}$

## EXERCISE - 5

## Part \# I : AIEEE/JEE-MAIN

1. $\mathrm{C}(\mathrm{s})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g}) ; \Delta \mathrm{H}=-393.5 \mathrm{~kJ} \mathrm{~mol}^{-1}$
$\mathrm{CO}(\mathrm{g})+\frac{1}{2} \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g}) ; \Delta \mathrm{H}=-283 \mathrm{~kJ} \mathrm{~mol}^{-1}$

On subraction equation (2) from equation (1), we get $\mathrm{C}(\mathrm{s})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}(\mathrm{g}) ; \Delta \mathrm{H}=-110.5 \mathrm{~kJ} \mathrm{~mol}^{-1}$.
The enthalpy of formation of carbon monoxide per mole $=-110.5 \mathrm{~kJ} \mathrm{~mol}^{-1}$.
2. Let the bond dissociation energy of $X Y, X_{2}$ and $Y_{2}$ be $x, x$ and $\mathrm{x}, \frac{\mathrm{x}}{2} \mathrm{KJ} /$ mol respectively,
$\frac{1}{2} \mathrm{X}_{2}+\frac{1}{2} \mathrm{Y}_{2} \rightarrow \mathrm{XY} ; \Delta \mathrm{H} f=-200 \mathrm{KJ} \mathrm{mol}^{-1}$.
$\Delta \mathrm{H}$ reaction $=$ [(sum of bond dissociation energy of all reactants) - (sum of bond dissociation energy of all product)]

$$
\begin{aligned}
& =\left[\frac{1}{2} \Delta \mathrm{H}_{\mathrm{X} 2}+\frac{1}{2} \Delta \mathrm{H}_{\mathrm{Y} 2}-\Delta \mathrm{H}_{\mathrm{XY}}\right] \\
& =\frac{\mathrm{x}}{2}+\frac{0.5 \mathrm{x}}{2}-\mathrm{x}=-200
\end{aligned}
$$

$$
\therefore \quad \mathrm{x}=\frac{200}{0.25}=800 \mathrm{KJ} \mathrm{~mol}^{-1}
$$

3. $\frac{1}{2} \mathrm{I}_{2}(\mathrm{~s})+\frac{1}{2} \mathrm{CI}_{2}(\mathrm{~g}) \rightarrow \mathrm{ICI}(\mathrm{g})$
$\Delta \mathrm{H}_{\mathrm{f}, \mathrm{ICI}}(\mathrm{g})=\left[\frac{1}{2} \Delta \mathrm{H}_{\mathrm{I}_{2}(\mathrm{~s}) \rightarrow \mathrm{I}_{2}(\mathrm{~g})}+\frac{1}{2} \Delta \mathrm{H}_{\mathrm{I}-\mathrm{I}}+\frac{1}{2} \Delta \mathrm{H}_{\mathrm{CI}-\mathrm{CI}}\right]-$
$\left[\Delta \mathrm{H}_{\mathrm{I}-\mathrm{CI}}\right]$
$=\left[\frac{1}{2} \times 62.76+\frac{1}{2} 151.0+\frac{1}{2} \times 242.3\right]-[211.3]$
$=16.73 \mathrm{~kJ} / \mathrm{mol}$.
4. $\Delta \mathrm{H}-\Delta \mathrm{U}=\Delta \mathrm{n}_{\mathrm{g}} \mathrm{RT}$
$\mathrm{C}(\mathrm{s})+1 / 2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}(\mathrm{g})$
$\Delta \mathrm{n}_{\mathrm{g}}=1-\frac{1}{2}=+\frac{1}{2} \quad \Delta \mathrm{H}-\Delta \mathrm{U}=\frac{1}{2} \times 8.314 \times 298$
$=1238.78 \mathrm{~J} \mathrm{~mol}^{-1}$

## CHEMISTRY FOR JEE MAIN \& ADVANCED

5. $\mathrm{C}+2 \mathrm{H}_{2} \rightarrow \mathrm{CH}_{4} ; \Delta \mathrm{H}^{\mathrm{o}}=-74.8 \mathrm{~kJ} \mathrm{~mol}^{-1}$

In order to calculate average energy for $\mathrm{C}-\mathrm{H}$ bond formation we should know the followng data.
C (graphite) $\rightarrow \mathrm{C}(\mathrm{g}) ; \Delta \mathrm{H}_{f}{ }^{\circ}=$ enthalpy of sublimation of carbon
$\mathrm{H}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{H}(\mathrm{g}) ; \Delta \mathrm{H}^{\circ}$ bond dissociation energy of $\mathrm{H}_{2}$.
6. $\mathrm{H}_{2}(\mathrm{~g})+\frac{1}{2} \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow \mathrm{H}_{2} \mathrm{O}(\ell) \quad \Delta \mathrm{H}=-286.20 \mathrm{~kJ}$
$\Delta \mathrm{H}_{\mathrm{r}}=\Delta \mathrm{H}_{\mathrm{f}}\left(\mathrm{H}_{2} \mathrm{O}, \ell\right)-\Delta \mathrm{H}_{\mathrm{f}}\left(\mathrm{H}_{2}, \mathrm{~g}\right)-\frac{1}{2} \Delta \mathrm{H}_{\mathrm{f}}\left(\mathrm{O}_{2}, \mathrm{~g}\right)$
$-286.20=\Delta \mathrm{H}_{\mathrm{f}}\left(\mathrm{H}_{2} \mathrm{O}(\ell)\right)$
So $\Delta \mathrm{H}_{\mathrm{f}}\left(\mathrm{H}_{2} \mathrm{O}, \ell\right)=-286.20 \mathrm{KJ} / \mathrm{mole}$
$\mathrm{H}_{2} \mathrm{O}(\ell) \longrightarrow \mathrm{H}^{+}(\mathrm{aq})+\mathrm{OH}^{-}(\mathrm{aq}) \quad \Delta \mathrm{H}=57.32 \mathrm{~kJ}$
$\Delta \mathrm{H}_{\mathrm{r}}=\Delta \mathrm{H}_{\mathrm{f}}^{\mathrm{o}}\left(\mathrm{H}^{+}, \mathrm{aq}\right)+\Delta \mathrm{H}_{\mathrm{f}}^{\mathrm{o}}\left(\mathrm{OH}^{-}, \mathrm{aq}\right)-\Delta \mathrm{H}_{\mathrm{f}}^{\mathrm{o}}\left(\mathrm{H}_{2} \mathrm{O}, \ell\right)$
$57.32=0+\Delta \mathrm{H}_{\mathrm{f}}{ }_{\mathrm{f}}\left(\mathrm{OH}^{-}, \mathrm{aq}\right)-(-286.20)$
$\Delta \mathrm{H}_{\mathrm{f}}{ }_{\mathrm{f}}\left(\mathrm{OH}^{-}, \mathrm{aq}\right)=57.32-286.20=-228.88 \mathrm{~kJ}$.
7. $\mathrm{N}_{2}(\mathrm{~g})+\frac{3}{2} \mathrm{H}_{2}(\mathrm{~g}) \longrightarrow \mathrm{NH}_{3}(\mathrm{~g}) ; \quad \Delta \mathrm{H}_{\mathrm{f}}^{\mathrm{o}}=-46.0 \mathrm{~kJ} \mathrm{~mol}^{-1}$
$2 \mathrm{H}(\mathrm{g}) \longrightarrow \mathrm{H}_{2}(\mathrm{~g}) \quad ; \quad \Delta \mathrm{H}_{\mathrm{f}}^{\mathrm{o}}=-436 \mathrm{~kJ} \mathrm{~mol}^{-1}$
$2 \mathrm{~N}(\mathrm{~g}) \longrightarrow \mathrm{N}_{2}(\mathrm{~g}) \quad ; \quad \Delta \mathrm{H}_{\mathrm{f}}^{\mathrm{o}}=-712 \mathrm{~kJ} \mathrm{~mol}^{-1}$
$\mathrm{NH}_{3}(\mathrm{~g}) \longrightarrow \frac{1}{2} \mathrm{~N}_{2}(\mathrm{~g})+\frac{3}{2} \mathrm{H}_{2}(\mathrm{~g}) \quad ; \quad \Delta \mathrm{H}=+46$
$\frac{3}{2} \mathrm{H}_{2} \longrightarrow 3 \mathrm{H} \quad ; \quad \Delta \mathrm{H}=+436 \times \frac{3}{2}$
$\frac{1}{2} \mathrm{~N}_{2} \longrightarrow \mathrm{~N} \quad ; \quad \Delta \mathrm{H}=+712 \times \frac{1}{2}$
$\mathrm{NH}_{3}(\mathrm{~g}) \longrightarrow \mathrm{N}(\mathrm{g})+3 \mathrm{H}(\mathrm{g}) \quad ; \quad \Delta \mathrm{H}=+1056 \mathrm{~kJ} \mathrm{~mol}^{-1}$
Average bond enthalpy of $\mathrm{N}-\mathrm{H}$ bond $=\frac{1056}{3}$

$$
=+352 \mathrm{~kJ} \mathrm{~mol}^{-1}
$$

8. $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}(\ell)+3 \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow 2 \mathrm{CO}_{2}(\mathrm{~g})+3 \mathrm{H}_{2} \mathrm{O}(\ell)$
$\Delta \mathrm{n}_{\mathrm{g}}=2-3=-1$
$\Delta \mathrm{U}=\Delta \mathrm{H}-\Delta \mathrm{n}_{\mathrm{g}} \mathrm{RT}$
$=-1366.5-(-1) \times \frac{8.314}{10^{3}} \times 300$
$=-1366.5+0.8314 \times 3=-1364 \mathrm{KJ}$
9. $4 \mathrm{NO}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \longrightarrow 2 \mathrm{~N}_{2} \mathrm{O}_{5}(\mathrm{~g}), \Delta \mathrm{H}=-111 \mathrm{~kg}$

$-111-54=\Delta \mathrm{H}^{\prime}$
$\Delta \mathrm{H}^{\prime}=-165 \mathrm{KJ}$
10. $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}(\ell)+3 \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow 2 \mathrm{CO}_{2}(\mathrm{~g})+3 \mathrm{H}_{2} \mathrm{O}(\ell)$
$\Delta \mathrm{E}=-1364.47 \mathrm{~kJ} / \mathrm{mole}$
$\Delta \mathrm{H}=$ ?
$\Delta \mathrm{n}_{\mathrm{g}}=-1$
$\because \Delta \mathrm{H}=-1366.95 \mathrm{~kJ} /$ mole
11. $-\frac{\mathrm{R} \times 298 \ln 1.6 \times 10^{12}}{2}$
$=\Delta \mathrm{G}_{\mathrm{r}}^{\mathrm{o}}=2 \Delta \mathrm{G}_{\mathrm{NO}_{2}}^{0}-2 \Delta \mathrm{G}_{\mathrm{NO}}^{0}$
$\Delta \mathrm{G}_{\mathrm{NO}_{2}}^{0}=86.6 \times 10^{3}-\frac{298 \mathrm{~K} \ell \mathrm{n} 1.6 \times 10^{12}}{2}$
12. $\Delta H_{c}^{0}(c)=-393.5$
$\Delta H_{c}^{0}(\mathrm{w}, \mathrm{g})=-283.5$
$\mathrm{C}_{\text {grophitro }}+\frac{1}{2} \mathrm{O}_{2}(\mathrm{q}) \longrightarrow \mathrm{CO}(\mathrm{q})$
$\Delta \mathrm{H}_{\mathrm{F}}^{0}(\mathrm{w}, \mathrm{g})=\Delta \mathrm{H}_{\mathrm{O}}^{0}(\mathrm{c})-\Delta \mathrm{H}_{\mathrm{c}}^{0}(\mathrm{co}, \mathrm{g})$

$$
=-393.5+283.5
$$

$$
=-110.0 \mathrm{Kg} .
$$

## Part \# II : IIT-JEE ADVANCED

1. $\mathrm{n}=\frac{3.5}{28}$
$\Delta \mathrm{T}=\mathrm{T}_{2}-\mathrm{T}_{1}=298.45-298=0.45$
$\mathrm{C}_{\mathrm{V}}=2.5 \mathrm{~kJ} \mathrm{k}^{-1}=2500 \mathrm{JK}^{-1}$
$\mathrm{C}_{\mathrm{P}}=\mathrm{C}_{\mathrm{V}}+\mathrm{R}=2500+8.314=2508.314 \mathrm{JK}^{-1}$
$\mathrm{Q}_{\mathrm{P}}=\mathrm{C}_{\mathrm{P}} \Delta \mathrm{T}=1128.74 \mathrm{~J}$
$\Delta \mathrm{H}=\frac{\mathrm{Q}_{\mathrm{p}}}{\mathrm{n}}=\frac{1128.74}{3.5 / 28}=9030 \mathrm{~J} \mathrm{~mol}^{-1}=9.030 \mathrm{KJ} \mathrm{mol}^{-1}=$
$9 \mathrm{KJ} \mathrm{mol}^{-1}$.
2. $\Delta \mathrm{H}_{\mathrm{f}}^{\circ}\left(\mathrm{Cl}_{2}, \mathrm{~g}\right)=0, \quad$ As $\Delta \mathrm{H}_{\mathrm{f}}^{\circ}$ of elements in their standard state is taken to be zero.
3. $\mathrm{E}_{\mathrm{C}-\mathrm{C}} \cong 100 \mathrm{KCal} / \mathrm{mole}$.
4. 


$\therefore \quad \Delta \mathrm{H}=+1410+330-(350 \times 2)-\varepsilon_{\mathrm{C}=\mathrm{C}}=+225$
$\therefore \quad \varepsilon_{\mathrm{C}=\mathrm{C}}=1740-700-225=+815 \mathrm{KJ} / \mathrm{mol}$.
5. $\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}(\mathrm{~s})+6 \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow 6 \mathrm{CO}_{2}(\mathrm{~g})+6 \mathrm{H}_{2} \mathrm{O}(\ell)$
$\Delta_{\mathrm{C}} \mathrm{H}=6 \times \Delta_{\mathrm{f}} \mathrm{H}\left(\mathrm{CO}_{2}\right)+6 \Delta_{\mathrm{f}} \mathrm{H}\left(\mathrm{H}_{2} \mathrm{O}\right)-\Delta_{\mathrm{f}} \mathrm{H}\left(\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}\right)-$ $6 \Delta_{\mathrm{f}}\left(\mathrm{O}_{2}, \mathrm{~g}\right)$
$=6 \times(-400-300)-(-1300)-0$
$=-4200+1300$
$=-2900 \mathrm{KJ} / \mathrm{mol}$
For one gram of glucose, enthalpy of combustion
$=-\frac{2900}{180}=-16.11 \mathrm{KJ} / \mathrm{g}$.

## MOCK TEST

3. $\mathrm{C}(\mathrm{s}) \longrightarrow \mathrm{C}(\mathrm{g})$ can be obtained as, $\Delta \mathrm{H}=\Delta \mathrm{H}_{1}-\Delta \mathrm{H}_{2}-\frac{1}{2} \Delta \mathrm{H}_{3}+\Delta \mathrm{H}_{4}$
4. Combustion reaction of solid boron
$\mathrm{B}(\mathrm{s})+\frac{3}{4} \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow \frac{1}{2} \mathrm{~B}_{2} \mathrm{O}_{3}(\mathrm{~s})$
$\Delta \mathrm{H}_{\mathrm{r}}^{\circ}=\Delta \mathrm{H}_{\mathrm{c}}^{\circ}=\frac{1}{2} \Delta \mathrm{H}_{\mathrm{f}}^{\circ}\left(\mathrm{B}_{2} \mathrm{O}_{3}, \mathrm{~s}\right)-\Delta \mathrm{H}_{\mathrm{f}}^{\circ}(\mathrm{B}, \mathrm{s})-\frac{3}{4} \Delta \mathrm{H}_{\mathrm{f}}^{\circ}\left(\mathrm{O}_{2}, \mathrm{~g}\right)$
$\Delta H_{f}{ }^{\circ}$ of element in stable state of aggregation is assumed to be zero.
$\Delta H^{\circ} \mathbf{C}=\frac{1}{2} \Delta H^{\circ} \mathbf{f}\left(\mathbf{B}_{2} \mathbf{O}_{3}, s\right)$
5. $\mathrm{MgCl}_{2} \cdot \mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{MgCl}_{2}(\mathrm{aq}) \Delta \mathrm{H}_{1}=$ ?
$\mathrm{MgCl}_{2}(\mathrm{aq}) \longrightarrow \mathrm{Mg}^{2+}(\mathrm{aq})+2 \mathrm{Cl}^{-}(\mathrm{aq}) \Delta \mathrm{H}_{2}=-30 \mathrm{cal} / \mathrm{mol}$
$\mathrm{MgCl}_{2}(\mathrm{~s}) \longrightarrow \mathrm{Mg}^{2+}(\mathrm{aq})+2 \mathrm{Cl}^{-}(\mathrm{aq}) \Delta \mathrm{H}_{3}=-25 \mathrm{cal} / \mathrm{mol}$
$\Delta \mathrm{H}_{1}+\Delta \mathrm{H}_{2}=\Delta \mathrm{H}_{3}$
$\Delta \mathrm{H}_{1}=\Delta \mathrm{H}_{3}-\Delta \mathrm{H}_{2}=-25+30=+5 \mathrm{cal} / \mathrm{mol}$.
6. $\mathrm{H}_{3} \mathrm{PO}_{3} \longrightarrow 2 \mathrm{H}^{+}+\mathrm{HPO}_{3}^{2-} ; \Delta_{\mathrm{r}} \mathrm{H}=$ ?
$2 \mathrm{H}^{+}+2 \mathrm{OH}^{-} \longrightarrow 2 \mathrm{H}_{2} \mathrm{O}$;
$\Delta_{\mathrm{r}} \mathrm{H}=-55.84 \times 2=-111.68$
$-106.68=\Delta_{\text {ion }} \mathrm{H}-55.84 \times 2$
$\Delta_{\text {ion }} \mathrm{H}=5 \mathrm{~kJ} / \mathrm{mol}$.
7. Given $\mathrm{H}_{2}(\mathrm{~g}) \longrightarrow 2 \mathrm{H}(\mathrm{g}) ; \quad \Delta \mathrm{H}=104 \mathrm{kcal} \ldots(1)$

$$
\begin{array}{ll}
\mathrm{Cl}_{2}(\mathrm{~g}) \longrightarrow 2 \mathrm{Cl}(\mathrm{~g}) ; & \Delta \mathrm{H}=58 \mathrm{kcal} . . \\
\mathrm{HCl}(\mathrm{~g}) \longrightarrow \mathrm{H}(\mathrm{~g})+\mathrm{Cl}(\mathrm{~g}) ; & \Delta \mathrm{H}=103 \mathrm{kcal} . \tag{3}
\end{array}
$$

Heat of formation for HCl
$\frac{1}{2} \mathrm{H}_{2}(\mathrm{~g})+\frac{1}{2} \mathrm{Cl}_{2}(\mathrm{~g}) \longrightarrow \mathrm{HCl}(\mathrm{g}) ; \quad \Delta \mathrm{H}=$ ?
Divide equation (1) and (2) by 2 , and then add
$\frac{1}{2} \mathrm{H}_{2}(\mathrm{~g})+\frac{1}{2} \mathrm{Cl}_{2}(\mathrm{~g}) \longrightarrow \mathrm{H}(\mathrm{g})+\mathrm{Cl}(\mathrm{g})$;

$$
\begin{equation*}
\Delta \mathrm{H}=81 \mathrm{kcal} \tag{4}
\end{equation*}
$$

Subtracting equation (3) from equation (4)
$\mathrm{HCl}(\mathrm{g}) \longrightarrow \mathrm{H}(\mathrm{g})+\mathrm{Cl}(\mathrm{g}) ; \quad \Delta \mathrm{H}=103 \mathrm{kcal} \ldots$ (3)
$\frac{1}{2} \mathrm{H}_{2}(\mathrm{~g})+\frac{1}{2} \mathrm{Cl}_{2}(\mathrm{~g}) \longrightarrow \mathrm{HCl}(\mathrm{g})$;

$$
\Delta \mathrm{H}=-22.0 \mathrm{kcal}
$$

$\therefore$ Enthalpy of formation of HCl gas $=\mathbf{- 2 2 . 0} \mathbf{~ k c a l}$
10. $\frac{1}{2} \mathrm{~A}-\mathrm{A}+\frac{1}{2} \mathrm{~B}-\mathrm{B} \rightarrow \mathrm{AB} \Delta \mathrm{H}=-100 \mathrm{KJ} / \mathrm{mole}$
$\frac{1}{2} x+\frac{1}{2}(0.5 x)-x=-100 \Rightarrow \frac{x}{2}+0.25 x-x=-100$
$\Rightarrow-0.25 \mathrm{x}=-100 \quad \Rightarrow \mathrm{x}=400 \mathrm{KJ} / \mathrm{mole}$
Bond enthalpy $=\mathbf{4 0 0} \mathbf{~ k J} / \mathbf{m o l}$.
13. Heat of neutralisation for strong acid and strong base combination is constant is equal to -13.7 Kcal or -57.1 KJ.
14. For reaction $\mathrm{C}(\mathrm{s})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g}) ; \Delta \mathrm{H}=\Delta \mathrm{U}$
15. $\Delta \mathrm{H}_{\text {ionisation }}=\Delta \mathrm{H}^{\circ}{ }_{\text {neutralisation }}-\Delta \mathrm{H}^{\circ}\left(\mathrm{H}+\mathrm{OH}^{-} \longrightarrow \mathrm{H}_{2} \mathrm{O}\right)$ $=-49.86-(-55.84) \mathrm{kJ} /$ mole
$=5.98 \mathrm{~kJ} /$ mole
17. For max. rise in temp.; max. neutralization of $\mathrm{H}^{+}$and $\mathrm{OH}^{-}$ required.
If we take equal volume, all $\mathrm{H}^{+}(5 \mathrm{~m}$-mole $)$ will react with all $\mathrm{OH}^{-}(5 \mathrm{~m}-\mathrm{mole})$.

## CHEMISTRY FOR JEE MAIN \& ADVANCED

18. (A) This is combustion reaction as well as formation reaction of $\mathrm{CO}_{2}$.
(B) This is sublimation, atomization as well as formation reaction of $\mathrm{C}(\mathrm{g})$.
(C) This is combustion reaction of $\mathrm{CO}(\mathrm{g})$.
(D) This is atomization of $\mathrm{CH}_{4}(\mathrm{~g})$.
19. (i) C (s) $+\mathrm{O}_{2}$ (g) $\longrightarrow \mathrm{CO}_{2}(\mathrm{~g}) ; \Delta \mathrm{H}_{\mathrm{f}}^{\circ}=-393.33 \mathrm{KJ} / \mathrm{mol}$;
$\Delta \mathrm{H}_{\mathrm{f}}^{\circ}=\frac{590}{18} \times 12$
(ii) $\mathrm{H}_{2}(\mathrm{~g})+\frac{1}{2} \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow \mathrm{H}_{2} \mathrm{O}(\ell)$;

$$
\Delta H_{f}^{\circ}=-286 \mathrm{KJ} / \mathrm{mol} ; \Delta \mathrm{H}_{\mathrm{f}}^{\circ}=\frac{15889}{55.5}
$$

(iii) $\mathrm{C}_{6} \mathrm{H}_{6}(\ell)+\frac{15}{2} \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow 6 \mathrm{CO}_{2}(\mathrm{~g})+3 \mathrm{H}_{2} \mathrm{O}(\ell)$
$\therefore \quad \Delta \mathrm{H}^{\mathrm{o}}=[6(-393.33)+3(-286)]-50=-3268 \mathrm{KJ} / \mathrm{mol}$ Mass of benzene is $=0.87 \times 100=87 \mathrm{~g}$
$\therefore \quad$ Heat evolved from 87 gm benzene $=3645$ KJ Ans.
21. $\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}(\mathrm{~s})+6 \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow 6 \mathrm{CO}_{2}+6 \mathrm{H}_{2} \mathrm{O}(\ell)$

No. of Mole of $\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}=\frac{0.36}{180}=2 \times 10^{-3} \mathrm{~mole}$
$C=\frac{q}{\Delta T} \quad \therefore \quad q=C \times \Delta T=640 \times 10 J=6.4 k J$
Heat released per mole $=\frac{6.4}{2 \times 10^{-3}}=3.2 \times 10^{3} \mathrm{~kJ}=\mathbf{3 . 2} \mathbf{~ M J}$
$\Delta \mathrm{U}=-3.2 \mathrm{MJ}$
$\Delta \mathrm{H}=\Delta \mathrm{U}+\Delta \mathrm{n}_{\mathrm{g}} \mathrm{RT}$ here $\Delta \mathrm{n}_{\mathrm{g}}=0$
$\Delta \mathrm{H}=\Delta \mathrm{U}=-\mathbf{3 . 2} \mathrm{MJ} \mathrm{mole}^{-1}$

