AL-Mustaqbal University College Department of Medical Physics The Second Stage
Thermodynamics and Heat
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## Lecture . 6

## Special cases of the equation $\Delta H=\Delta E+P \Delta V$

1) Reactions involving gaseous substances

Where $\left(\mathbf{n}_{\mathbf{R}} \neq \mathbf{n}_{\mathbf{P}}\right)$ and in which the volume changes are large and cannot be neglected, and by imposing the behavior of gases ideally,

$$
\begin{aligned}
& \mathbf{P V} V_{R}=n_{R} R T \\
& P V_{P}=n_{p} R T
\end{aligned}
$$

Where :
$\mathbf{n}_{\mathrm{R}}$ : Number of gas moles produced.
$\mathbf{n}_{\mathbf{R}}$ : Number of gas moles interacting (At constant pressure and temperature).
T: Temperature in kelvin (K).
$\mathbf{R}$ : The general Fixed of gases (8.314 J / K. Mole) .

From the equation:

$$
\Delta \mathbf{H}=\Delta \mathbf{E}+\mathbf{P} \Delta \mathbf{V}
$$

We will modify $\mathrm{P} \Delta \mathrm{V}$ as follows:

$$
\begin{aligned}
& \mathbf{P} \Delta \mathbf{V}=\mathbf{P}\left(\mathbf{V}_{\mathbf{P}}-\mathbf{V}_{\mathbf{R}}\right) \\
& \mathbf{P} \Delta \mathbf{V}=\mathbf{P} \mathbf{V}_{\mathbf{P}}-\mathbf{P} \mathbf{V}_{\mathbf{R}} \\
& \mathbf{P} \Delta \mathbf{V}=\mathbf{n}_{\mathbf{P}} \mathbf{R T}-\mathbf{n}_{\mathbf{R}} \mathbf{R T} \\
& \mathbf{P} \Delta \mathbf{V}=\mathbf{R T}\left(\mathbf{n}_{\mathbf{P}}-\mathbf{n}_{\mathbf{R}}\right) \\
& \mathbf{P} \Delta \mathbf{V}=\Delta \mathbf{n}_{(\mathrm{g})} \mathbf{R T}
\end{aligned}
$$

Compensate the last equation in equation $\Delta \mathrm{H}=\Delta \mathrm{E}+\mathrm{P} \Delta \mathrm{V}$,therefore we get on :

$$
\Delta \mathbf{H}=\Delta \mathbf{E}+\Delta \mathbf{n}_{(\mathrm{g})} \mathbf{R T}
$$

## 2) Reactions in which interacting and resulting gases are involved)

Where $\left(\mathbf{n}_{\mathbf{P}}=\mathbf{n}_{\mathbf{R}}\right)$ and therefore the value of $\Delta \mathbf{n}=0$

Then the equation:

$$
\Delta \mathbf{H}=\Delta \mathbf{E}+\mathbf{P} \Delta \mathbf{V}
$$

From the equation:
Since
$\Delta H=\Delta E+\Delta n$ RT

$$
\Delta \mathbf{n}=0
$$

$$
\therefore \Delta \mathbf{H}=\Delta \mathbf{E}
$$

## 3) Reactions involving solid or liquid substances only (not involving gas

 substances):In which the volume changes are small $\Delta \mathrm{V}=0$ and therefore can be neglected, then
the equation:

$$
\Delta \mathbf{H}=\Delta \mathbf{E}+\mathbf{P} \Delta \mathbf{V}
$$

$$
\Delta \mathbf{n}=0
$$

$$
\therefore \Delta \mathbf{H}=\Delta \mathbf{E}
$$

## Example :

Calculating the change in the internal energy of the reaction:
$\mathrm{Zn}_{(\mathrm{s})}+\mathrm{H}_{2} \mathrm{SO}_{4(\mathrm{~L})} \mathrm{ZnSO}_{4(\mathrm{aq})}+\mathrm{H}_{2(\mathrm{~g})}$
If the released heat is 34200 Cal of zinc at $\left(17^{\circ} \mathrm{C}\right)$
Note that ( $\mathrm{R}=2 \mathrm{Cal} /$ mole K )

## Solution :

$\Delta \mathrm{n}=1-0=1$
Applying the relationship $\Delta \mathrm{H}=\Delta \mathrm{E}+\Delta \mathrm{n}$ RT
$\Delta \mathrm{E}=\Delta \mathrm{H}-\mathrm{n} \mathrm{RT}$
$\Delta \mathrm{E}=[(-34200 \mathrm{Cal})-(1 \mathrm{x} 2 \times(17+273)]$
$\Delta \mathrm{E}=-34780 \mathrm{Cal}$

## Example :

If the change in internal energy is equal to -333 kJ for the following interaction:
$\mathrm{NH}_{4} \mathrm{Cl}_{\text {(aq) }}+\mathrm{NaNO}_{2 \text { (aq) }} \rightarrow \mathrm{N}_{2(\mathrm{~g})}+2 \mathrm{H}_{2} \mathrm{O}_{\text {(L) }}+\mathrm{NaCl}_{\text {(aq) }}$
When one mole of $\mathrm{N}_{2}$ is produced, if the production of one mole of nitrogen makes the system increase by 22.4 L , at one air pressure. Calculate the change in the Enthalpy interaction?

Solution :
$\Delta \mathrm{E}=-333 \mathrm{X} 10^{3} \mathrm{~J}, \quad \mathrm{P}=1$ atom $\quad, \Delta \mathrm{V}=22.4 \mathrm{~L}$
$\mathrm{P} \Delta \mathrm{V}=1$ atom $\mathrm{X} 22.4 \mathrm{~L}=22.4 \mathrm{~L}$. atom
22.4 L. atom X 101.325 J / L. atom $=2269.68 \mathrm{~J}$

Applying the relationship: $\Delta \mathrm{H}=\Delta \mathrm{E}+\mathrm{P} \Delta \mathrm{V}$
$\Delta \mathrm{H}=\left[\left(-333 \times 10^{3}\right)+(1 \times 22.4) 101.325\right]$
$\Delta \mathrm{H}=-330730.88 \mathrm{~J}$
$\Delta \mathrm{H}=-330.73 \mathrm{~kJ}$

## Example :

If the heat associated with combustion of one molten gasoline is equal to( -3264.3) kJ at a fixed volume and temperature ( 298 K ) , Calculate the change in the enthalpy of the reaction $(\Delta \mathrm{H})$, if you know that gasoline burns with oxygen equation: $\mathrm{C}_{6} \mathrm{H}_{6(\mathrm{~L})}+7.5 \mathrm{O}_{2(\mathrm{~g})} \rightarrow 6 \mathrm{CO}_{2}(\mathrm{~g})+3 \mathrm{H}_{2} \mathrm{O}(\mathrm{L})$

Note that the value of $(\mathrm{R}=8.314 \mathrm{~J} / \mathrm{mole} . \mathrm{K})$.

## Solution :

The amount of heat at a fixed volume reflects the internal energy:
$\mathrm{q}_{\mathrm{v}}=\Delta \mathrm{E}$
$\Delta \mathrm{E}=-3264.3 \times 10^{3} \mathrm{~J}$
$\Delta \mathrm{n}=\mathrm{n}_{\mathrm{p}}-\mathrm{n}_{\mathrm{R}}=6-7.5=-1.5$
$\Delta \mathrm{H}=\Delta \mathrm{E}+\Delta \mathrm{n}$ RT
$\Delta \mathrm{H}=\left(-3264.3 \times 10^{3} \mathrm{~J}\right)+(-1.5$ mole $\times 8.314 \mathrm{~J} / \mathrm{K}$. mole $\times 298 \mathrm{~K})$
$\Delta \mathrm{H}=-3268016.358 \mathrm{~J}$
$\Delta \mathrm{H}=-3268.02 \mathrm{~kJ}$

