## Thermodynamics - Energy Relationships in Chemical Reactions: <br> energy - The capacity to do work.



## potential-Energy due to an objects position.


chemical-Energy stored in the structural bonds of substances.


Types of Energy cont... thermal-Energy associated from the random motion of atoms and molecules.
heat- The transfer of thermal energy between two bodies at different temperatures.

## Law of Conservation of Energy - Energy is niether created nor destroyed but simply converted from one form to another.

Most energy changes involve the exchange of heat(q) or work(w).

## System:

system- Part of universe of interest or under study.

## surroundings- The universe outside of the

 system.SURROUNDINGS


Types of systems: open system- System that exchanges mass and energy(usually heat).
closed system- System that allows the exchange of energy(heat) but not mass.
isolated system- System that does not allow the transfer of energy or mass.

## Exothermic/Endothermic Processes:

exothermic- Any process that gives off heat to the surroundings.
Ex: Combustion of natural gas.
$\mathrm{CH}_{4}(\mathrm{~g})+2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \quad \mathrm{CO}_{2}(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})+$ energy


## endothermic- Any process in which heat must be supplied. Ex: Melting of Ice. $\mathrm{H}_{2} \mathrm{O}(\mathrm{s})+$ energy $\rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{l})$



## Enthalpy:

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

H: heat content
E: Internal energy Can not measure $H$. Can measure the change in enthalpy $(\Delta \mathbf{H})$
$\Delta \mathbf{H}=\mathbf{H}$ (products) - $\mathbf{H}$ (reactants)
$\Delta H$ is a measure of the heat absorbed or given off.
$\begin{array}{ll}\Delta \mathbf{H}=+\# & \\ \Delta \mathbf{H}=-\# & \text { endothermic } \\ \Delta & \text { exothermic }\end{array}$

## Ex:

When $1 \mathrm{~mol}_{\mathrm{H}_{2}}(\mathrm{~g})$ reacts with $1 / 2 \mathrm{~mol} \mathrm{O}_{2}(\mathrm{~g})$ to produce $1 \mathbf{~ m o l ~} \mathrm{H}_{2} \mathrm{O}(\mathrm{l})$ and 286 kJ of heat is evolved.
$\mathrm{H}_{2}(\mathrm{~g})+\mathbf{1 / 2 \mathrm { O } _ { 2 }}(\mathrm{g}) \rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \quad \Delta \mathrm{H}=-286 \mathrm{~kJ}$

When the equation is reversed, the sign of $\Delta H$ is changed.
Ex:
$\mathrm{H}_{2} \mathrm{O}(\mathrm{s}) \rightarrow \quad \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \Delta \mathrm{H}=+6.0 \mathrm{~kJ}$
$\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightarrow \quad \mathrm{H}_{2} \mathrm{O}(\mathrm{s}) \Delta \mathrm{H}=-6.0 \mathrm{~kJ}$

## If the coefficients in the quation are

 multiplied by a factor, the $\Delta H$ value must be also multiplied by the factor.$\mathrm{H}_{2} \mathrm{O}(\mathrm{s}) \rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \Delta \mathrm{H}=+6.0 \mathrm{~kJ}$
$2 \mathrm{H}_{2} \mathrm{O}(\mathrm{s}) \rightarrow 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \Delta \mathrm{H}=\Delta \mathrm{H}=2 \times+6.0 \mathrm{~kJ}$

$$
\Delta H=+12 \mathrm{~kJ}
$$

## Ex:

If 36.0 g of $\mathrm{HI}(\mathrm{g})$ is reacted to produce $\mathrm{H}_{\mathbf{2}}(\mathrm{g})$ and $\mathrm{I}_{2}(\mathrm{~s})$, how much heat is liberated?
$2 \mathrm{HI}(\mathrm{g}) \rightarrow \mathrm{H}_{2}(\mathrm{~g})+\mathrm{I}_{2}(\mathrm{~s}) \quad \Delta \mathrm{H}=-51.8 \mathrm{~kJ}$

## Hess's Law:

Hess's law states that the change in enthalpy for any chemical reaction is the same whether the reaction occurs in one step or in several steps.

$$
\mathrm{A} \rightarrow \mathrm{D} \quad \Delta \mathrm{H}=3 \mathrm{~kJ} \quad \text { One step }
$$

$\mathrm{A} \rightarrow \mathrm{C} \Delta \mathrm{H}=1 \mathrm{~kJ}$
$\mathrm{C} \rightarrow \mathrm{D} \Delta \mathrm{H}=2 \mathrm{~kJ}$
$\mathrm{A} \rightarrow \mathrm{D} \quad \Delta \mathrm{H}=3 \mathrm{~kJ} \quad$ Two steps

# Can be used to find $\Delta H$ for reactions that 

 can not be measured directly. Ex:$\mathrm{C}(\mathrm{graph})+2 \mathrm{H}_{2}(\mathrm{~g}) \rightarrow \mathrm{CH}_{4}(\mathrm{~g}) \quad \Delta \mathrm{H}=?$

## Given data:

1. C (graph) $+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g}) \Delta \mathrm{H}=-393.5 \mathrm{~kJ}$
2. $\mathrm{H}_{2}(\mathrm{~g})+1 / 2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \Delta \mathrm{H}=-285.9 \mathrm{~kJ}$
3. $\mathrm{CH}_{4}(\mathrm{~g})+2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})$

$$
\Delta H=-890.4 \mathrm{~kJ}
$$

## Calorimetry:

Method of measuring heat changes $(\mathbf{q})$.
q: heat given off or absorbed by a system.
C: Heat Capacity
$\Delta t$ : final temperature - initial temperature
Heat capacity- The amount of heat required to raise the temperature of a given mass of a substance by $1^{\circ} \mathrm{C}$.

Specific heat- The amount of heat required to raise the temperature $1^{\circ} \mathrm{C}$ for 1 g of substance.
C = mass $\times$ sp_heat
$q=\mathbf{C} \Delta t \quad$ or $\quad q=\left(\operatorname{mass} \times s p \_h e a t\right) \Delta t$
For water: sp_heat $=4.184 \mathrm{~J} / \mathrm{g}^{\circ} \mathrm{C}$
Ex:
How much heat is absorbed by a 125 g sample of water when it is heated from $20.00^{\circ} \mathrm{C}$ to $25.00^{\circ} \mathrm{C}$.

## Bomb Calorimetry(constant volume):



## Constant Volume Calorimetry

 Used to measure the heat evolved by combustion.$$
\mathbf{q}_{\mathrm{sys}}=\mathbf{q}_{\mathrm{cal}} \quad+\mathbf{q}_{\mathrm{rxn}}=\mathbf{0}
$$

$$
\text { thus }-q_{\mathrm{rxn}}=\mathrm{q}_{\mathrm{cal}}
$$

Since $q=C \Delta t$, thus to find $q_{r x n}$
$-q_{\text {rxn }}=q_{\text {cal }} \quad$ where $\quad q_{c a l}=C_{c a l} \Delta t$

Ex: Combustion of glucose.
$\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}(\mathrm{~s})+6 \mathrm{O}_{2}(\mathrm{~g}) \quad \rightarrow \quad 6 \mathrm{CO}_{2}(\mathrm{~g})+6 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})$
A 3.00 g sample of glucose, $\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}$, is placed in the bomb calorimeter. The combustion causes the temperature to increase by
$6.50{ }^{\circ} \mathrm{C}$. The heat capacity of the calorimeter is $7.23 \mathrm{~kJ} /{ }^{\circ} \mathrm{C}$. Calculate the molar heat of combustion of glucose in units of $\mathrm{kJ} /$ mole.

Ex2: A 1.567 g sample of $\mathrm{C}_{10} \mathrm{H}_{8}(\mathrm{~s})$ is burned in a calorimeter and a temperature increase of $8.37^{\circ} \mathrm{C}$ is noted. The heat of combustion of $\mathrm{C}_{10} \mathrm{H}_{8}$ is $5153.9 \mathrm{~kJ} / \mathrm{mole}$. Determine the heat capacity of the calorimeter.

When 1.227 g of $\mathrm{C}_{10} \mathrm{H}_{14} \mathrm{O}(\mathrm{s})$ is burned in the same calorimeter, a temperature increase of $6.12^{\circ} \mathrm{C}$ is observed. What is the heat of combustion in $\mathrm{kJ} / \mathrm{mole}$ of $\mathrm{C}_{10} \mathrm{H}_{14} \mathrm{O}$ ?

## Coffee Cup Calorimetry(constant pressure):



## Standard Enthalpy of Formation $\left(\Delta \mathbf{H}^{\circ}{ }^{\circ}\right)$ : "O" Indicates standard conditions ( $1 \mathbf{~ a t m}$ and reference temperature, usually $\mathbf{2 5}^{\circ} \mathrm{C}$ )

$\Delta H_{f}{ }^{\circ}$ : The value of $\Delta H$ that corresponds to a reaction in which 1 mole of a substance is formed from its elements in their most stable form.

For all elements in their most stable form,
$\Delta \mathbf{H}_{\mathrm{f}}{ }^{\circ}=\mathbf{0}$

## If the enthalpy of formation $\left(\Delta \mathbf{H}_{f}{ }^{\circ}\right)$ of

 ethene $\left(\mathrm{C}_{2} \mathrm{H}_{4}\right)$ is $52.30 \mathrm{~kJ} / \mathrm{mole}$, write the reaction equation this enthalpy change would correspond.
## Can use $\Delta \mathbf{H}_{f}{ }^{\circ}$ values to determine $\Delta \mathbf{H}^{\circ}$ of any

 reaction.$\Delta \mathbf{H}^{\circ}=\Sigma \Delta \mathbf{H}_{\mathrm{f}}{ }^{\circ}($ products $)-\Sigma \Delta \mathbf{H}_{\mathrm{f}}{ }^{\circ}($ reactants $)$ Ex:
$2 \mathrm{NH}_{3}(\mathrm{~g})+3 \mathrm{Cl}_{2}(\mathrm{~g}) \rightarrow \mathrm{N}_{2}(\mathrm{~g})+6 \mathrm{HCl}(\mathrm{g}) \Delta \mathrm{H}^{\circ}=?$

## Given:

$$
\begin{array}{cc}
\text { Compound } & \Delta \mathrm{H}_{\mathrm{f}}{ }^{\circ}(\mathrm{kJ} / \text { mole }) \\
\hline \mathrm{HCl}^{(\mathrm{g})} \mathrm{g} & -92.3 \\
\mathrm{~N}_{2}(\mathrm{~g}) & 0 \\
\mathrm{NH}_{3}(\mathrm{~g}) & -46.19 \\
\mathrm{Cl}_{2}(\mathrm{~g}) & 0
\end{array}
$$

