## Chapter 6: Thermochemistry (Chemical Energy) (Ch6 in Chang, Ch6 in Jespersen)

Energy is defined as the capacity to do work, or transfer heat.

Work (w)-force (F) applied through a distance.
Force - any kind of push or pull on an object.

$$
\begin{array}{ll}
\mathrm{F}=\mathrm{ma} & \left(\mathrm{~kg} \cdot \frac{\mathrm{~m}}{\mathrm{~s}^{2}}\right) \\
\mathrm{W}=\mathrm{F} \times \mathrm{d} & \left(\mathrm{~kg} \cdot \frac{\mathrm{~m}}{\mathrm{~s}^{2}} \times m\right)
\end{array}
$$

Chemists define work as directed energy change resulting from a process.

The SI unit of work is the Joule $\quad 1 \mathrm{~J}=1 \mathrm{~kg} \mathrm{~m} / \mathrm{s}^{2}$
(Also the calorie $\quad 1 \mathrm{cal}=4.184 \mathrm{~J}$ (exactly); and the Nutritional calorie $1 \mathrm{Cal}=1000 \mathrm{cal}=1 \mathrm{kcal}$.
A calorie is the energy needed to increase the temperature of 1 g of water by $1^{\circ} \mathrm{C}$ at standard atmospheric pressure. But since this depends on the atmospheric pressure and the starting temperature, there are several different definitions of the "calorie").

There are many different types of Energy:
Radiant Energy is energy that comes from the sun (heating the Earth's surface and the atmosphere).
Thermal Energy is the energy associated with the random motion of atoms and molecules.
Chemical Energy is stored within the structural units of chemical substances. It is determined by the type and arrangement of the atoms of the substance.

Nuclear Energy is the energy stored within the collection of protons and neutrons of an atom.
Kinetic Energy is the energy of motion. Chemists usually relate this to molecular and electronic motion and movement. It depends on the mass ( m ), and speed (v) of an object.

$$
\mathrm{ke}=\frac{1}{2} \mathrm{~m} \mathrm{v}^{2}
$$

Potential Energy is due to the position relative to other objects.
It is "stored energy" that results from attraction or repulsion (e.g. gravity or electrostatic attraction/repulsion).

$$
\mathbf{P E}=\mathbf{m g h} \quad \text { (due to gravity) }
$$

The force of electrostatic attraction (or repulsion) between charged particles (Coulombs Law):

$$
\mathrm{F}=\mathrm{k} \frac{\mathrm{Q}_{1} \mathrm{Q}_{2}}{\mathrm{~d}^{2}}
$$

When one form of energy disappears, some other form of energy (of equal magnitude) must appear.
$\Rightarrow$ Law of Conservation of energy: the total quantity of energy in the universe is assumed constant.

## Transferring Energy: Work and Heat

Heat is the transfer of thermal energy between two bodies that are at different temperatures.
(Remember that temperature is related to the average kinetic energy of an object's particles).

Thermochemistry is the study of heat change in chemical reactions.

## Systems and Surroundings

To discuss the energy changes associated with chemical reactions we must first define the specific part of the universe that is of interest to us, which we call the "system".

System - what we study (e.g. a beaker or flask).
Surroundings - the rest of the universe outside of our system (e.g. the room where the experiment is performed).

We will study/use three types of systems (open, closed and isolated)...

Open system - can exchange mass (matter) and energy with surroundings (most common).

Closed system - can exchange energy but not matter with surroundings.

Isolated system - does not allow the transfer of either mass or energy.
(E.g. sealed, vacuum coated thermos flask)

(a)

(b)

(c)

Adiabatic Process is defined as a process that occurs in an isolated system, meaning where neither energy nor matter crosses the system/surroundings boundary.
(When permitted) Energy can be exchanged with the surroundings as heat and/or work.

## Energy Changes and Energy Conservation

Thermochemistry is a subset of Thermodynamics, which is the scientific study of the interconversion of heat and other kinds of energy.

The First Law of Thermodynamics: Energy is neither created nor destroyed.
Energy is conserved. Any energy lost by the system is gained by the surroundings.

Internal Energy (E) - is the sum of all kinetic and potential energy of all components of the system (translational, rotational, vibrational, electronic, nuclear, etc).

It is very difficult to determine or measure the absolute total energy of entities, but it is more convenient to measure the change in Internal Energy $(\Delta \mathrm{E})$ for a given process:

$$
\Delta \mathbf{E}=\mathbf{E}_{\text {final }}-\mathbf{E}_{\text {initial }}
$$

Thermodynamic quantities have three parts: number, unit and sign ( + or - ).

$$
+\Delta \mathrm{E} \text { means } \quad \mathrm{E}_{\mathrm{f}}>\mathrm{E}_{\mathrm{i}}
$$

system gained E from surroundings (energy coming in)
$-\Delta E$ means $\quad E_{f}<E_{i}$
system lost E to surroundings

(energy going out)

Heat (q) added to the system, and/or (w) work done on the system, increases the internal energy.


## Endothermic and Exothermic Processes

Endothermic - the system absorbs heat. Heat flows into system from surroundings. ( $+\Delta \mathrm{E}$ )
Exothermic - the system evolves heat. Heat flows out of system and into surroundings. ( $-\Delta \mathrm{E}$ )

## Relating $\Delta E$ to Heat (q) and Work (w)

Energy is defined as the capacity to do work, or transfer heat.

Energy can be exchanged with the surroundings as heat (q) and/ or work (w).

So we can write this as:

$$
\Delta \mathbf{E}=\mathbf{q}+\mathbf{w}
$$



The battery can be drained either by heating the wrench, or by work and heat by powering the fan.

## Internal Energy is a State Function

The state of a system is defined by the values of all relevant macroscopic properties that specify an object's current condition. E.g. composition, energy, temperature, pressure and volume, etc.

A state function is a property of a system that is determined by specifying its condition (in terms of temperature, pressure, internal energy, etc.).

The value of a state function does not depend on the particular history of the sample, only its present condition.
The change in the state function depends only on the initial and final states of the system, not how the change occurs.


State functions do not depend on the path by which the system arrived at its present state.
A state function describes the equilibrium state of a system.

The climbers gain the same gravitational potential energy whether they take the red or blue path.
(Note that work is not a state function, since the red path is longer and would take more energy.
Work is a process function).

## Work by Expansion

Previously we have seen that (one form of) work can be defined as force times distance (mechanical work).
Mechanical work can also be expressed by expansion or compression of a gas.
Pressure-volume work (or PV work) occurs when the volume (V) of a system changes:

$$
\begin{aligned}
P \times V= & \frac{F}{d^{2}} \times d^{3}=F d=w \quad 1 \mathrm{~L} \cdot \mathrm{~atm}=101.3 \mathrm{~J} \\
& \text { pressure }
\end{aligned}
$$

So at constant pressure (such as atmospheric):

$$
\text { Work, w = } \mathbf{P} \Delta \mathbf{V}
$$

Where $\quad \mathrm{P}=$ opposing pressure against which the system (e.g. a piston) pushes.

$$
\Delta \mathbf{V}=\text { change in volume of gas during expansion }=\mathbf{V}_{\text {final }}-\mathbf{V}_{\text {initial. }}
$$

For expansion, since $\mathbf{V}_{\text {final }}>\mathbf{V}_{\text {initial }}$,
then $\Delta \mathrm{V}$ must be positive.
So expansion work is negative (meaning work is done by system. The system is pushing the piston back).


Problem: If a gas expands in volume from 1.0 to 4.0 L at constant temperature against a constant pressure of 2.4 atm, how much work is done by the gas?

```
Work = - P\DeltaV
    = -2.4 atm }\times(4.0-1.0) 
    = -7.2 L atm
```


## Enthalpy

The change in Internal Energy ( $\mathbf{\Delta E}$ ) has two components, work (w) and heat (q).

If we operate under a constant volume, then $\mathbf{\Delta V}=\mathbf{0}$ (and so no $P V$ work is done):

$$
\begin{aligned}
\Delta \mathrm{E} & =q+w \\
& =q-P \Delta V \\
\Delta \mathrm{E} & =q_{v} \quad \text { at constant } V \text { (as indicated by the subscript). }
\end{aligned}
$$

Practically it is inconvenient to operate under constant volume, it is much easier to operate under constant pressure (e.g. at atmospheric pressure)...

Heat ( $\mathbf{q}$ ) transferred under constant-pressure conditions is called enthalpy, $\mathbf{H}$.
Enthalpy is a state function.

$$
\begin{aligned}
\mathrm{E}=\mathrm{q}+\mathrm{w} \quad \text { so } \quad \mathrm{q} & =\mathrm{E}-\mathrm{W} \quad \text { but } \quad \mathrm{W}=-\mathrm{PV} \\
\mathrm{H} & =\mathrm{E}+\mathrm{PV}
\end{aligned}
$$

$\mathrm{E}=$ internal energy; $\mathrm{P}=$ pressure $; \mathrm{V}=$ volume of the system
The change in enthalpy, $\Delta \mathrm{H}$, equals the heat, $\mathrm{q}_{\mathrm{p}}$ gained or lost by the system when the process occurs under constant pressure (indicated by the subscript p).

$$
\begin{aligned}
\Delta H & =\mathbf{H}_{\text {final }}-\mathbf{H}_{\text {initial }} \\
& =\mathbf{q}_{\mathrm{p}}
\end{aligned}
$$

| We know | $\Delta \mathrm{E}$ | $=\mathrm{q}+\mathrm{w}=\mathrm{q}-\mathrm{P} \Delta \mathrm{V}$ |
| :--- | :--- | :--- |
| At constant P | $\Delta \mathrm{E}$ | $=\mathrm{q}_{\mathrm{p}}-\mathrm{P} \Delta \mathrm{V}$ |
| Rearrange to give | $\mathrm{q}_{\mathrm{p}}$ | $=\Delta \mathrm{E}+\mathrm{P} \Delta \mathrm{V}$ |
| But also | $\mathrm{q}_{\mathrm{p}}$ | $=\Delta H$ |
| so | $\Delta H$ | $=\Delta \mathrm{E}+\mathrm{P} \Delta \mathrm{V}$ |

- If $\Delta \mathrm{H}$ is positive the system has gained heat from the surroundings, and is an endothermic process.
- If $\Delta \mathrm{H}$ is negative, the system has released heat to the surroundings, and is an exothermic process.

To recap - for a reaction:
At constant volume, the heat change, $\mathrm{q}_{\mathrm{v}}=\Delta \mathrm{E}$.
At constant pressure, the heat change, $\mathrm{q}_{\mathrm{p}}=\Delta \mathrm{H}$ (this is the more common scenario).

## The Thermodynamic Standard State

We generally deal with changes in (not absolute values of) energy, so we need some type of reference point.
The standard state of a material (pure substance, mixture or solution) is the reference point used to calculate its properties under different conditions.

It is that of a pure substance in a specified state (its most stable form and physical state), at 1 atm pressure and at $25^{\circ} \mathrm{C}$; and 1 M concentration for all substances in solution.

It is indicated by the superscript ${ }^{\circ}$ :
E.g. $\quad \Delta \mathrm{H}^{\circ}$ (means the standard change in Enthalpy) $\quad \Delta \mathrm{S}^{\circ} \quad \Delta \mathrm{G}^{\circ} \quad \mathrm{E}^{\circ}$

Now we are ready to talk about reactions...

## Enthalpies of Physical and Chemical Change -Thermochemical Equations

For a chemical reaction, the Enthalpy of Reaction is the change in enthalpy going from reactants to products.

$$
\Delta \mathbf{H}=\mathbf{H}_{\text {products }}-\mathbf{H}_{\text {reactants }}
$$

The heat of reaction is $\Delta \mathbf{H}_{\mathrm{rxn}}$.

$$
\mathbf{2} \mathbf{H}_{\mathbf{2}}(\mathbf{g}) \quad+\mathbf{O}_{2}(\mathbf{g}) \quad \rightarrow \quad \mathbf{2} \mathbf{H}_{\mathbf{2}} \mathbf{O}(\mathbf{l}) \quad \Delta \mathrm{H}_{\mathrm{rxn}}=-483.6 \mathrm{~kJ} / \mathrm{mol}
$$

Enthalpy can be viewed as a measure of how much heat is stored as potential energy in the system, or as "heat content".

## Three helpful guidelines

1. Enthalpy is an extensive property. The magnitude of $\Delta \mathrm{H}$ is directly proportional to amount of reactant consumed in the process.

$$
\mathbf{C H}_{4}(\mathrm{~g})+\mathbf{2} \mathbf{O}_{2}(\mathrm{~g}) \rightarrow \mathbf{C O}_{\mathbf{2}}(\mathrm{g})+\mathbf{2} \mathbf{H}_{\mathbf{2}} \mathbf{O}(\mathbf{l}) \quad \Delta \mathrm{H}=-890 \mathrm{~kJ} / \mathrm{mol}
$$

The combustion of two moles of $\mathrm{CH}_{4}$ would release double the energy, meaning $-1780 \mathrm{~kJ} / \mathrm{mol}$.
2. The enthalpy change for a reaction is equal in magnitude but opposite in sign to $\Delta \mathrm{H}$ for the reverse reaction.

| $\mathrm{CH}_{4}(\mathrm{~g})$ | + | $2 \mathrm{O}_{2}(\mathrm{~g})$ | $\rightarrow$ | $\mathrm{CO}_{2}(\mathrm{~g})$ | + | $2 \mathrm{H}_{2} \mathrm{O}$ (l) | $\Delta \mathrm{H}=-890 \mathrm{~kJ} / \mathrm{mol}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{CO}_{2}(\mathrm{~g})$ | + | $2 \mathrm{H}_{2} \mathrm{O}$ (l) | $\rightarrow$ | $\mathrm{CH}_{4}(\mathrm{~g})$ | + | $2 \mathrm{O}_{2}(\mathrm{~g})$ | $\Delta \mathrm{H}=+890 \mathrm{~kJ} / \mathrm{mol}$ |

3. The enthalpy change for a reaction depends on the physical state of the reactants and products.

$$
\begin{aligned}
& \mathbf{H}_{2} \mathbf{O}(\mathrm{l}) \quad \rightarrow \quad \mathrm{H}_{2} \mathbf{O}(\mathrm{~g}) \quad \Delta \mathrm{H}=+44 \mathrm{~kJ} / \mathrm{mol} \\
& \mathbf{C H}_{\mathbf{4}}(\mathbf{g})+\mathbf{2} \mathbf{O}_{\mathbf{2}}(\mathrm{g}) \rightarrow \mathbf{C O}_{\mathbf{2}}(\mathrm{g}) \quad+\quad \mathbf{2} \mathbf{H}_{\mathbf{2}} \mathbf{O}(\mathrm{l}) \quad \Delta \mathrm{H}=-890 \mathrm{~kJ} / \mathrm{mol} \\
& \mathbf{2} \mathbf{H}_{2} \mathbf{O}(\mathrm{l}) \quad \rightarrow \quad \mathbf{2} \mathbf{H}_{2} \mathbf{O}(\mathrm{~g}) \quad \Delta \mathrm{H}=+88 \mathrm{~kJ} / \mathrm{mol}
\end{aligned}
$$

Sum and cancel to give ...
$\mathbf{C H}_{4}(\mathrm{~g})+\mathbf{2} \mathbf{O}_{\mathbf{2}}(\mathrm{g}) \rightarrow \mathbf{C O}_{\mathbf{2}}(\mathrm{g})+\mathbf{2} \mathbf{H}_{\mathbf{2}} \mathbf{O}(\mathrm{g}) \quad \Delta \mathrm{H}=-802 \mathrm{~kJ} / \mathrm{mol}$

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Problem: The combustion of butane produces heat according to the equation:

$$
2 \mathrm{C}_{4} \mathrm{H}_{10}(\mathrm{~g})+\mathbf{1 3} \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathbf{8} \mathbf{C O}_{2}(\mathrm{~g})+\mathbf{1 0} \mathbf{H}_{2} \mathbf{O}(\mathbf{I}) \quad \Delta \mathrm{H}^{\circ}{ }_{\mathrm{rxn}}=-5314 \mathrm{~kJ} / \mathrm{mol}
$$

What is the heat of combustion per gram of butane?

2 moles of $\mathrm{C}_{4} \mathrm{H}_{10}$ generate $-5314 \mathrm{~kJ} / \mathrm{mol}$
Molar mass $\mathrm{C}_{4} \mathrm{H}_{10}=4(12.01)+10(1.008)=58.12 \mathrm{~g} / \mathrm{mol}$

So $2 \times 58.12 \mathrm{~g} / \mathrm{mol}$ generates $-5314 \mathrm{~kJ} / \mathrm{mol}$
Therefore heat of combustion per $\mathrm{g}=\underline{-5314 \mathrm{~kJ} / \mathrm{mol}}$
$116.24 \mathrm{~g} / \mathrm{mol}$
$=-45.72 \mathrm{~kJ} / \mathrm{g}$

## Calorimetry and Heat Capacity

Calorimetry is the measurement of heat changes. (Apparatus used is a calorimeter).
Understanding calorimetry depends on the concepts of specific heat, and heat capacity.

## Heat Capacity and Specific Heat

Heat capacity (C) is the amount of heat required to raise the temperature of a given quantity of substance by 1 K (or $1^{\circ} \mathrm{C}$ ).

Specific heat (s) or specific heat capacity is the heat capacity of one gram of substance.
Molar heat capacity is the heat capacity of 1 mol of substance.

There is a practical issue - we cannot measure heat directly, but heat gained or lost $(\mathrm{q})$ is directly proportional to the temperature change $(\Delta t)$.

$$
\begin{array}{ll}
\mathrm{q}=\mathbf{C} \Delta \mathrm{t} & \text { where } \mathbf{C} \text { is the heat capacity, with units of } \mathrm{J} /{ }^{\circ} \mathrm{C} \text {, or } \mathrm{J} / \mathrm{K} . \\
\mathbf{C}=\mathrm{s} \mathrm{~m} & \text { where } \mathrm{m}=\text { mass in grams, } \mathrm{s} \text { has units of } \mathrm{J} / \mathrm{g}^{\circ} \mathrm{C} .
\end{array}
$$

So combining these: $\quad \mathbf{q}=\mathbf{s} \mathbf{m} \Delta \mathbf{t} \quad$ (Heat exchanged $=$ Specific Heat $\times$ mass $\times$ temperature change)

Table of Specific Heats for some Substances

| Substance | Specific Heat $\left(\mathrm{J} \mathrm{g}^{-1}{ }^{\circ} \mathrm{C}^{-1}\right)$ |
| :--- | :--- |
| Carbon (graphite) | 0.711 |
| Copper | 0.387 |
| Ethyl alcohol | 2.45 |
| Gold | 0.129 |
| Granite | 0.803 |
| Iron | 0.4498 |
| Lead | 0.128 |
| Olive oil | 2.0 |
| Silver | 0.235 |
| Water (liquid) | 4.184 |

Larger specific heats mean it takes more energy to heat them up; and conversely, they release a larger amount of heat as they cool.

Notice the large value for water - great for a cooling system like your body; or a heating system like radiators; also explains maritime climates.

Problem: The specific heat of ethylene glycol is $2.42 \mathrm{~J} / \mathrm{gK}$. How many Joules of heat are necessary to raise the temperature of 62.0 g of ethylene glycol from $15.2^{\circ} \mathrm{C}$ to $40.8^{\circ} \mathrm{C}$ ?

REMEMBER

$$
\Delta \mathrm{t} \text { in }{ }^{\circ} \mathrm{C}=\Delta \mathrm{t} \text { in } \mathrm{K} . \quad \Delta \mathrm{t}=\mathrm{t}_{\text {final }}-\mathrm{t}_{\text {initial }}
$$

$$
\begin{aligned}
\mathrm{q}=\mathrm{m} \mathrm{~s} \Delta \mathrm{t} & =(62.0 \mathrm{~g})\left(2.42 \frac{\mathrm{~J}}{\mathrm{~g} \mathrm{~K}}\right)\left(40.8-15.2^{\circ} \mathrm{C}\left(\frac{1 \mathrm{~K}}{1^{\circ} \mathrm{C}}\right)\right) \\
& =3841 \mathrm{~J} \\
& =3.84 \mathrm{~kJ}
\end{aligned}
$$

Problem: A piece of a newly synthesized material of mass 12.0 g at $88.0^{\circ} \mathrm{C}$ is placed in a calorimeter containing 100.0 g of water at $20.0^{\circ} \mathrm{C}$. If the final temperature of the system is $24.0^{\circ} \mathrm{C}$, what is the specific heat capacity of this material?

$$
\begin{aligned}
& \mathrm{q}_{\mathrm{H} 2 \mathrm{O}}=-\mathrm{q}_{\text {material }} \quad \mathrm{s}_{\mathrm{H} 2 \mathrm{O}}=4.184 \frac{\mathrm{~J}}{\mathrm{~g}{ }^{\circ} \mathrm{C}} \quad \Delta \mathrm{t}=\mathrm{t}_{\text {final }}-\mathrm{t}_{\text {initial }} \\
& \mathrm{m}_{\mathrm{H} 2 \mathrm{O}} \mathrm{~S}_{\mathrm{H} 2 \mathrm{O}} \Delta \mathrm{t}_{\mathrm{H} 2 \mathrm{O}}=-\left(\mathrm{m}_{\text {mat }} \mathrm{S}_{\mathrm{mat}} \Delta \mathrm{t}_{\mathrm{mat}}\right) \\
& \mathrm{S}_{\mathrm{mat}}=\frac{\mathrm{m}_{\mathrm{H} 2 \mathrm{O}} \mathrm{~S}_{\mathrm{H} 2 \mathrm{O}} \Delta \mathrm{t}_{\mathrm{H} 2 \mathrm{O}}}{-\mathrm{m}_{\text {mat }} \Delta \mathrm{t}_{\text {mat }}} \\
&=\frac{(100.0 \mathrm{~g})\left(4.184 \frac{\mathrm{~J}}{\mathrm{~g}^{\circ} \mathrm{C}}\right)\left(24.0-20.0^{\circ} \mathrm{C}\right)}{-(12.0 \mathrm{~g})\left(24.0-88.0^{\circ} \mathrm{C}\right)} \\
&=2.18 \frac{\mathrm{~J}}{\mathrm{~g}^{\circ} \mathrm{C}}
\end{aligned}
$$

There are two common forms of Calorimeter: constant pressure and constant volume.

Constant Pressure Calorimetry is the simplest.
E.g. a Styrofoam cup calorimeter.

Since it is open to the atmosphere, it is constant Pressure.
But we approximate this as an isolated system.
Heat is exchanged between the reaction and the solution (water).
The thermometer measures the change in temperature.
The heat of the reaction, $\quad-\mathrm{q}_{\mathrm{p}}=\mathrm{q}_{\text {solution }}$

$$
\begin{aligned}
& =\mathrm{C} \Delta \mathrm{t} \\
& =\mathrm{s} \mathrm{~m} \Delta \mathrm{t}
\end{aligned}
$$



Problem: When a 9.55 g sample of solid sodium hydroxide dissolves in 100.0 g of water in a Styrofoam cup calorimeter, the temperature rises from $23.6{ }^{\circ} \mathrm{C}$ to $47.4^{\circ} \mathrm{C}$.

Calculate $\Delta \mathrm{H}$ (in $\mathrm{kJ} / \mathrm{mol} \mathrm{NaOH}$ ) for the solution process:

```
NaOH(s) }->\quad\mp@subsup{\textrm{Na}}{}{+}(\textrm{aq})\quad+\mp@subsup{\textrm{OH}}{}{-}(\textrm{aq}
```

(Assume the specific heat of the solution is the same as that of pure water).

$$
\begin{aligned}
& \mathrm{q}_{\text {soln }}=\mathrm{m} \mathrm{~s} \Delta \mathrm{t}=-\mathrm{q}_{\mathrm{rxx}} \quad \mathrm{~s}_{\mathrm{H} 2 \mathrm{O}}=4.184 \frac{\mathrm{~J}}{\mathrm{~g}^{\mathrm{o}} \mathrm{C}} \quad \Delta \mathrm{t}=\mathrm{t}_{\text {final }}-\mathrm{t}_{\text {initial }} \\
& \mathrm{m}_{\text {soln }}=9.55+100.0 \mathrm{~g}=109.55 \mathrm{~g} \\
& \mathrm{q}_{\text {soln }}=(109.55 \mathrm{~g})\left(4.184 \frac{\mathrm{~J}}{\mathrm{~g}^{\circ} \mathrm{C}}\right)\left(47.4-23.6^{\circ} \mathrm{C}\right)=10908.9 \mathrm{~J} \\
& 9.55 \mathrm{~g} \mathrm{NaOH} \times \frac{1 \mathrm{~mol} \mathrm{NaOH}}{40.00 \mathrm{~g} \mathrm{NaOH}}=0.23875 \mathrm{~mol} \\
& \Delta \mathrm{H}=\quad \frac{-10908.9 \mathrm{~J} \frac{\mathrm{~kJ}}{1000 \mathrm{~J}}}{0.23875 \mathrm{~mol}}=-45.7 \frac{\mathrm{~kJ}}{\mathrm{~mol}}
\end{aligned}
$$

$$
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$$

Constant Volume Calorimetry
A bomb calorimeter is used for constant volume reactions.

A known amount of compound is placed the bomb.
The sturdy bomb does not change its volume.

Gas is added to achieve the desired pressure.
The bomb is immersed in a known amount of water.
Ignition causes the reaction, and the heat released raises the temperature of the water.

The bomb and the water create an isolated system.
$\mathbf{\Delta E}=\mathbf{q}-\mathbf{P} \Delta \mathbf{V}=\mathbf{q}_{\mathbf{v}}$ for constant volume.

where $\mathrm{C}_{\mathrm{cal}}=$ heat capacity of the calorimeter (determined by known samples, calibration).

## Standard Heats of Formation

There are some standard enthalpy changes associated with certain processes:

- Enthalpies of vaporization, $\Delta \mathrm{H}_{\text {vap }}$ (liquid to gas)
- Enthalpies of fusion, $\Delta \mathrm{H}_{\text {fus }}$ (solid to liquid)
- Enthalpies of combustion
- Enthalpy of formation, $\Delta \mathrm{H}_{\mathrm{f}}$, (or heat of formation), the formation of a compound from its constituent elements.

One of the most useful pieces of information for chemists is...
The standard enthalpy of formation of a compound, $\Delta \mathbf{H}_{\mathrm{f}}^{\mathbf{o}}$ is the change in enthalpy for the reaction that forms 1 mol of the compound from its elements, with all substances in their standard states.
(Recall that standard state means the most stable form and physical state of the element at 1 atm and $25^{\circ} \mathrm{C}$ ).
E.g. the formation of $\mathrm{CO}_{2}$ uses solid C , gaseous $\mathrm{O}_{2}$, and makes gaseous $\mathrm{CO}_{2}$; and for oxygen, we use $\mathrm{O}_{2}$ not $\mathrm{O}_{3}$.

$$
\mathrm{C}(\mathrm{~s})+\mathrm{O}_{2}(\mathrm{~g}) \quad \rightarrow \quad \mathrm{CO}_{2}(\mathrm{~g})
$$

The standard enthalpy of formation of the most stable form of any element is zero.
$\underline{\text { Standard Enthalpies of Formation of Some Inorganic Substances at } 25^{\circ} \mathrm{C}}$

| Substance | $\Delta H_{\mathrm{f}}(\mathbf{k J} / \mathrm{mol})$ | Substance | $\Delta H^{\text {i }}$ ( $\left.\mathbf{k J} / \mathrm{mol}\right)$ |
| :---: | :---: | :---: | :---: |
| $\mathrm{Ag}(\mathrm{s})$ | 0 | $\mathrm{H}_{2} \mathrm{O}_{2}(l)$ | -187.6 |
| $\mathrm{AgCl}(s)$ | -127.0 | $\mathrm{Hg}(\mathrm{l})$ | 0 |
| $\mathrm{Al}(\mathrm{s})$ | 0 | $\mathrm{l}_{2}(s)$ | 0 |
| $\mathrm{Al}_{2} \mathrm{O}_{3}(s)$ | -1669.8 | $\mathrm{HI}(\mathrm{g})$ | 25.9 |
| $\mathrm{Br}_{2}(l)$ | 0 | $\mathrm{Mg}(\mathrm{s})$ | 0 |
| $\mathrm{HBr}(\mathrm{g})$ | -36.2 | $\mathrm{MgO}(s)$ | -601.8 |
| C (graphite) | 0 | $\mathrm{MgCO}_{3}(s)$ | -1112.9 |
| C(diamond) | 1.90 | $\mathrm{N}_{2}(\mathrm{~g})$ | 0 |
| $\mathrm{CO}(\mathrm{g})$ | -110.5 | $\mathrm{NH}_{3}(\mathrm{~g})$ | -46.3 |
| $\mathrm{CO}_{2}(\mathrm{~g})$ | -393.5 | $\mathrm{NO}(\mathrm{g})$ | 90.4 |
| $\mathrm{Ca}(\mathrm{s})$ | 0 | $\mathrm{NO}_{2}(\mathrm{~g})$ | 33.85 |
| $\mathrm{CaO}(s)$ | -635.6 | $\mathrm{N}_{2} \mathrm{O}(\mathrm{g})$ | 81.56 |
| $\mathrm{CaCO}_{3}(s)$ | -1206.9 | $\mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g})$ | 9.66 |
| $\mathrm{Cl}_{2}(\mathrm{~g})$ | 0 | $\mathrm{O}(\mathrm{g})$ | 249.4 |
| $\mathrm{HCl}(\mathrm{g})$ | -92.3 | $\mathrm{O}_{2}(\mathrm{~g})$ | 0 |
| $\mathrm{Cu}(\mathrm{s})$ | 0 | $\mathrm{O}_{3}(\mathrm{~g})$ | 142.2 |
| $\mathrm{CuO}(\mathrm{s})$ | -155.2 | S(rhombic) | 0 |
| $\mathrm{F}_{2}(\mathrm{~g})$ | 0 | S (monoclinic) | 0.30 |
| $\mathrm{HF}(\mathrm{g})$ | -271.6 | $\mathrm{SO}_{2}(\mathrm{~g})$ | -296.1 |
| $\mathrm{H}(\mathrm{g})$ | 218.2 | $\mathrm{SO}_{3}(\mathrm{~g})$ | -395.2 |
| $\mathrm{H}_{2}(\mathrm{~g})$ | 0 | $\mathrm{H}_{2} \mathrm{~S}(\mathrm{~g})$ | -20.15 |
| $\mathrm{H}_{2} \mathrm{O}(\mathrm{g})$ | -241.8 | $\mathrm{Zn}(\mathrm{s})$ | 0 |
| $\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$ | -285.8 | $\mathrm{ZnO}(\mathrm{s})$ | -348.0 |

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## Using Enthalpies of Formation to Calculate Enthalpies of Reaction (Direct Method)

We can calculate the standard enthalpy change for any reaction for which we know the $\Delta \mathrm{H}_{\mathrm{f}}{ }_{\mathrm{f}}$ values for all reactants and products.

$$
\begin{aligned}
& \Delta \mathbf{H}^{\circ}{ }_{\mathrm{rxn}} \quad=\quad \mathrm{\Sigma n} \Delta \mathbf{H}^{\circ}{ }_{\mathrm{f}} \text { (products) } \quad-\quad \boldsymbol{\Sigma m \Delta} \mathbf{H}^{\circ}{ }_{\mathrm{f}} \text { (reactants) } \\
& \text { ( } \mathrm{m} \text { and } \mathrm{n} \text { are the equation coefficients) }
\end{aligned}
$$



## Hess's Law (Indirect Method)

Hess's law states that if a reaction is carried out in a series of steps, $\Delta \mathrm{H}$ for the reaction will be equal to the sum of the enthalpy changes for the individual steps.

Hess pointed out that the heat absorbed (or evolved) in a given chemical reaction is the same whether the process takes one step or several steps.

This is useful when a reaction cannot be measured directly.


Trying to calculate: $\mathrm{S}(\mathrm{s})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{SO}_{2}(\mathrm{~g})$
(a) $\mathrm{S}+\frac{3}{2} \mathrm{O}_{2} \quad \rightarrow \mathrm{SO}_{3} \quad \Delta \mathrm{H}=-395.7 \mathrm{~kJ} / \mathrm{mol}$
(b) $\mathrm{SO}_{2}+\frac{1}{2} \mathrm{O}_{2} \rightarrow \mathrm{SO}_{3} \quad \Delta \mathrm{H}=-98.9 \mathrm{~kJ} / \mathrm{mol}$
(c) $\mathrm{SO}_{3} \longrightarrow \mathrm{SO}_{2}+\frac{1}{2} \mathrm{O}_{2} \quad \Delta \mathrm{H}=+98.9 \mathrm{~kJ} / \mathrm{mol}$

Adding (a) and (c) gives:
$\mathbf{S}+\mathbf{O}_{\mathbf{2}} \rightarrow \mathbf{S O}_{\mathbf{2}}$
So $\Delta \mathrm{H}=-395.7+98.9=-296.8 \mathrm{~kJ} / \mathrm{mol}$

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Problem: Calculate the enthalpy change for the reaction:

$$
\mathbf{3} \mathbf{H}_{2}(\mathrm{~g})+\mathrm{O}_{3}(\mathrm{~g}) \quad \rightarrow \quad \mathbf{3} \mathbf{H}_{2} \mathbf{O}(\mathrm{~g})
$$

Given the following enthalpies of reaction:
(a)
$2 \mathrm{H}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g})$
$\rightarrow 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{g})$
$\Delta \mathrm{H}=-483.6 \mathrm{~kJ} / \mathrm{mol}$
(b) $3 \mathrm{O}_{2}(\mathrm{~g})$
$\rightarrow 2 \mathrm{O}_{3}(\mathrm{~g})$
$\Delta \mathrm{H}=+284.6 \mathrm{~kJ} / \mathrm{mol}$
(c) $2 O_{3}(g)$
$\rightarrow 3 \mathrm{O}_{2}(\mathrm{~g})$
$\Delta H=-284.6 \mathrm{~kJ} / \mathrm{mol}$

To generate our desired equation, we must multiply (a) by $\frac{3}{2}$, and (c) by $\frac{1}{2}$.

$$
\begin{array}{rlrl}
3 \mathrm{H}_{2}+\frac{3}{2} \mathrm{O}_{2} & \rightarrow 3 \mathrm{H}_{2} \mathrm{O} & \Delta \mathrm{H}=-725.4 \mathrm{~kJ} / \mathrm{mol} \\
\mathrm{O}_{3} & & \frac{3}{2} \mathrm{O}_{2} & \Delta \mathrm{H}=-142.3 \mathrm{~kJ} / \mathrm{mol}
\end{array}
$$

Adding these gives:

$$
\begin{array}{rlrl}
3 \mathrm{H}_{2}+\frac{3}{2} \mathrm{O}_{2} & \rightarrow 3 \mathrm{H}_{2} \mathrm{O} & \Delta \mathrm{H}=-725.4 \mathrm{~kJ} / \mathrm{mol} \\
& \rightarrow \frac{3}{2} \mathrm{O}_{2} & \Delta \mathrm{H}=-142.3 \mathrm{~kJ} / \mathrm{mol} \\
\mathrm{O}_{3} & & & \\
\Rightarrow \quad \mathbf{3} \mathbf{H}_{\mathbf{2}}(\mathbf{g})+\mathbf{O}_{\mathbf{3}}(\mathbf{g}) & \rightarrow \mathbf{3} \mathbf{H}_{\mathbf{2}} \mathbf{O}(\mathbf{g}) & \Delta \mathrm{H}=-867.7 \mathrm{~kJ} / \mathrm{mol}
\end{array}
$$

Problem: Given the following standard reaction enthalpies:
(a) $\mathrm{O}_{2}(\mathrm{~g})$
$\rightarrow 2 \mathrm{O}(\mathrm{g})$
$\Delta \mathrm{H}^{\circ}=+498.4 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1}$
(b) $\quad \mathrm{NO}(\mathrm{g})+\mathrm{O}_{3}(\mathrm{~g}) \quad \rightarrow \mathrm{NO}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \quad \Delta \mathrm{H}^{\circ}=-200.0 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1}$

If the standard enthalpy of formation of ozone $=+142.7 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1}$, calculate the standard reaction enthalpy for the reaction:

$$
\mathrm{NO}(\mathrm{~g})+\mathrm{O}(\mathrm{~g}) \rightarrow \mathrm{NO}_{2}(\mathrm{~g})
$$

So, (c) The standard enthalpy of formation of ozone: $\frac{3}{2} \mathrm{O}_{2} \rightarrow \mathrm{O}_{3} \quad \Delta \mathrm{H}=142.7 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1}$

So to get our desired equation, we can combine: (c) $-\frac{1}{2}(a)+(b)$.

$$
\begin{array}{rlll}
\frac{3}{2} \mathrm{O}_{2} & \rightarrow \mathrm{O}_{3} & \Delta \mathrm{H}=+142.7 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1} \\
\mathrm{O} & \rightarrow \quad \frac{1}{2} \mathrm{O}_{2} & \Delta \mathrm{H}^{\circ}=-249.2 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1} \\
\mathrm{NO}+\mathrm{O}_{3} & \rightarrow \mathrm{NO}_{2}+\mathrm{O}_{2} & \Delta \mathrm{H}^{\circ}=-200.0 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1} \\
\Rightarrow \quad \mathrm{NO}+\mathrm{O} & \rightarrow \mathrm{NO}_{2} & \Delta \mathrm{H}^{\circ}=142.7-249.2-200.0=-306.5 \mathrm{~kJ} \cdot \mathrm{~mol}^{-1}
\end{array}
$$

Many physical processes also involve the absorption or release of heat.
The heat of solution, $\Delta \mathrm{H}_{\text {soln }}$, is the heat generated or absorbed when a certain amount of solute dissolves in a certain amount of solvent.

The heat of hydration is the enthalpy change associated with the hydration process.
The heat of dilution is the heat change associated with the dilution process.

The heat of solution represents the difference between the enthalpy of the final solution and the enthalpies of its original components (i.e. the solute and the solvent).

The heat of solution can be regarded as the sum of the enthalpy changes of three intermediate steps:

1. The breaking of bonds within the solute, such as the electrostatic attraction between two ions (endothermic)
2. The breaking of intermolecular attractive forces within the solvent, such as hydrogen bonds (endothermic)
3. The formation of new attractive solute-solvent bonds in solution (exothermic).

The value of the overall heat of solution is the sum of these steps.

$$
\Delta \mathrm{H}_{\mathrm{soln}}=\mathrm{U} \quad+\Delta \mathrm{H}_{\mathrm{hydr}}
$$

Where $\mathrm{U}=$ Lattice energy (the energy required to completely separate one mole of a solid ionic compound into gaseous ions).

The gaseous ions then must become hydrated, which is the heat of hydration.

Heats of Solution of Some Ionic Compounds

| Compound | (kJ/mol) |
| :--- | ---: |
| LiCl | -37.1 |
| CaCl | 2 |

Notice this can be overall endo- or exothermic depending on the species.
(If you disolve NaCl in water, it actually takes energy, and cools down the solution).

