These Notes are to SUPPLEMENT the Text, They do NOT Replace reading the Text Material. Additional material that is in the Text will be on your tests! To get the most information, READ THE CHAPTER prior to the Lecture, bring in these lecture notes and make comments on these notes. These notes alone are NOT enough to pass any test! The author is not responsible for typos in these notes.

## Chapter 5. Principals of Chemical Reactivity, Energy \& Chemical Reactions

Thermodynamics is the science of heat and work

- How do we measure and calculate the energy changes in physical and chemical changes
- What is the relationship between heat and work energy changes
- Is a chemical reaction reactant or product favored
- Will a chemical reaction or physical change occur spontaneously

Energy is the capacity to do work

- Kinetic Energy is the energy associated with motion
- Potential Energy is the energy associated with an objects position

Law of Conservation of Energy states energy can neither be created nor destroyed - the total energy of the universe is constant.
System is an object, or collection of objects being studied
Surroundings include everything outside of the system that can exchange energy and/or matter with the system.


Example: Foam coffee cup containing water and a lid and a thermometer and a stirring bar (a calorimeter). The water is the System, the rest is the surroundings.
Transfer of Heat: energy is transferred as heat if 2 objects at different temperatures are brought into contact with each other. Heat flows from higher temperature to lower temperature.
Thermal Equilibrium is when both (or more) objects reach the same temperature
Heating a piece of metal in a flame then plunging it into a beaker of water - energy as heat is transferred from the metal to the water until both temperatures are the same


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- Energy transfer as heat occurs spontaneously from the higher temperature object to the lower temperature object
- The energy transfer of energy as heat continues until both objects are at the same temperature (Thermal Equilibrium).
- After Thermal Equilibrium is reached, the object that had the higher temperature had a temperature decrease and has lost thermal energy. The object that had the lower temperature had a temperature increase and has gained thermal energy.
Exothermic Process is one where energy is transferred as heat from a system to its surroundings. The energy of the system decreases, the energy of the surroundings increases.
Endothermic Process is one where energy is transferred as heat from the surroundings to the system. The energy of the system increases, the energy of the surroundings decreases.
Specific Heat Capacity, ( C ): is the energy transferred as heat that is required to raise the temperature of 1 gram of a substance one Kelvin and has units of joules per gram per Kelvin (J/g K).
$\mathbf{q}=\mathbf{C} * \mathbf{m} * \Delta \mathbf{T} \quad \mathrm{~m}=$ mass of substance in grams, $\Delta \mathrm{T}=\mathrm{T}_{\text {final }}-\mathrm{T}_{\text {initial }}=$ change in temperature $\underline{\mathrm{in} \mathrm{K}}$
Note: $\Delta \mathbf{T}=\mathbf{T}_{\text {final }}-\mathbf{T}_{\text {initial }}$, a positive value indicates the sample increases in temperature, a negative value indicates the sample has lost energy or temperature value.

$\mathrm{C}_{\text {water }}=4.184 \mathrm{~J} / \mathrm{g} * \mathrm{~K}$. YOU NEED TO MEMORIZE THIS VALUE. This is a large value. Waters ability to absorb and carry heat is responsible for smoothing out the climate on earth. A large lake in June, still cold from the winter, will cool off the hot air; it takes a while for all of the water to heat up. The lake, after a summer of warming, will warm the cooler air in Oct. Heat transfer via water vapour blowing from the ocean inland is responsible for cooling the warmer inland areas.
Example 5.1 How much energy does it take to raise the temperature of a cup of coffee ( 250 ml ) from $20.5^{\circ} \mathrm{C}$ to $95.6^{\circ} \mathrm{C}$. Assume the coffee has a density of $1.00 \mathrm{~g} / \mathrm{ml}$ and has a $\mathrm{C}=4.184 \mathrm{j} / \mathrm{g} \mathrm{K}$.
From: Density = Mass (g) / Volume Derive: Mass (g) = Density * Volume
Mass of coffee (wt in g) $=250 . \mathrm{ml}^{*} 1.00 \mathrm{~g} / \mathrm{ml}=250 . \mathrm{g} \quad$ Note: $1 \mathrm{~cm}^{3}=1 \mathrm{ml}$

$$
\begin{aligned}
& \Delta \mathbf{T}=\mathbf{T}_{\text {final }}-\mathbf{T}_{\text {initial }}=\left(95.6^{\circ} \mathrm{C}+273 \mathrm{~K}\right)-\left(20.5^{\circ} \mathrm{C}+273 \mathrm{~K}\right)=+75.1 \mathrm{~K} \\
& \mathbf{q}=\mathbf{C}^{*} \mathbf{m}^{*} \boldsymbol{\Delta} \mathbf{T}=4.184 \mathrm{j} / \mathrm{g} \mathrm{~K}^{*} 250 . \mathrm{g}^{*}+75.1 \mathrm{~K}=7854.6=78600=7.86 \times 10^{4} \mathrm{~J}=78.6 \mathrm{~kJ}
\end{aligned}
$$

Heat Capacity is an intensive property, does not depend on the amount of the substance.

## Energy transferred as heat

What happens when you drop a hot piece of metal into an insulated beaker with water?

Problem: Add a 55.0 g piece of metal heated to $99.8^{\circ} \mathrm{C}$ into a beaker filled with $225 . \mathrm{g}$ of water. The initial water temperature was $21.0^{\circ} \mathrm{C}$, the final temperature was $23.1^{\circ} \mathrm{C}$.

- The metal and water are the System, the beaker et al are the surroundings
- The metal and water will end up at the same temperature
- Assume the only energy transferred is heat within the system
- The values of $q_{\text {water }}$ (heat absorbed) and $q_{\text {metal }}$ (heat released) are numerically equal, but of opposite sign $\mathrm{q}_{\text {water }}+\mathrm{q}_{\text {metal }}=0$

Heat Lost by Metal $=-$ Heat Gained by Water
Heat Lost by Metal + Heat Gained by Water $=0$
$\left(\mathrm{C}_{\text {water }}{ }^{*}\right.$ mass $\left._{\text {water }} * \Delta \mathrm{~T}_{\text {water }}\right)+\left(\mathrm{C}_{\text {metal }} *\right.$ mass metal $\left.^{*} \Delta \mathrm{~T}_{\text {metal }}\right)=0$
$\left[4.184 \mathrm{~J} / \mathrm{g}^{*} \mathrm{~L}^{*} 225 . \mathrm{g} *(296.3 \mathrm{~K}-294.2 \mathrm{~K})\right]+\left[\mathrm{C}_{\text {metal }}{ }^{*} 55.0 \mathrm{~g} *(296.3 \mathrm{~K}-373.0 \mathrm{~K})\right]=0$
$\left[4.184 \mathrm{~J} / \mathrm{g}^{*} \mathrm{~L}^{*} 225 . \mathrm{g}^{*}(296.3 \mathrm{~K}-294.2 \mathrm{~K})\right]=-\left[\mathrm{C}_{\text {metal }}{ }^{*} 55.0 \mathrm{~g}{ }^{*}(296.3 \mathrm{~K}-373.0 \mathrm{~K})\right]$
$\mathbf{C}_{\text {metal }}=\left[4.184 \mathrm{~J} / \mathrm{g}^{*} \mathrm{~L} * 225 . \mathrm{g} * 2.1 \mathrm{~K}\right]=0.46863=\mathbf{0 . 4 6 9} \mathbf{~ J} / \mathbf{g ~ K}$

$$
[55.0 \mathrm{~g} * 76.7 \mathrm{~K}]
$$

OWL 5.288 .5 g iron at a temperature of $78.8^{\circ} \mathrm{C}$ is placed in a beaker of 244 g of water at $18.8{ }^{\circ} \mathrm{C}$. What is the equilibrium temperature? $\mathrm{C}_{\text {iron }}=0.449 \mathrm{~J} / \mathrm{g}^{*} \mathrm{~K} \quad$ STUDENTS FIGURE THIS OUT

### 5.3 Energy and Changes of State

For each of these below, the temperature must remain constant throughout the change of state.
Heat of Fusion is the energy transferred as heat required to convert a substance from a solid at its MP to a liquid

Heat of Vaporization is the energy transferred as heat required to convert a liquid at its BP to a vapor.

## You need to memorize these values:

Heat of Fusion for water at $\mathrm{O}^{\circ} \mathrm{C}$ (solid $\rightarrow$ liquid $\rightarrow$ solid) is $333 \mathrm{~J} / \mathbf{g}$
Heat of Vaporization for water at $100^{\circ} \mathrm{C}$ (liquid $\rightarrow$ vapour $\rightarrow$ liquid) is $2256 \mathrm{~J} / \mathrm{g}$

Example: What energy is required to convert 500.g of water to from a liquid to vapour at $100{ }^{\circ} \mathrm{C}$ ?
$2256 \mathrm{~J} / \mathrm{g}{ }^{*} 500 . \mathrm{g}=1.13 \times 10^{6} \mathrm{~J}=1130 \mathrm{~kJ}=\mathbf{1 . 1 3 \times 1 0 3} \mathbf{~ k J}$ for water liquid to vapour
Note: in books answer of 1130 kJ , you cannot determine the SD of this number!
To melt that much ice to liquid:
$333 \mathrm{~J} / \mathrm{g} * 500 . \mathrm{g}=1.67 \times 10^{5} \mathrm{~J}=167 . \times 10^{3} \mathrm{~J}=\mathbf{1 6 7} \mathbf{~ k J}$ for water ice to liquid

Note on the graph below, it starts with a piece of ice at $-50^{\circ} \mathrm{C}$ changing it to steam at $200{ }^{\circ} \mathrm{C}$

- $2.06 \mathrm{~J} / \mathbf{g ~ K}$ of energy is added to the ice to warm it from $-50^{\circ} \mathrm{C}$ to $0^{\circ} \mathrm{C}$
- $333 \mathrm{~J} / \mathbf{g}$ of energy is added to melt the ice to liquid at $0^{\circ} \mathrm{C}$ - temperature stays constant
- 4.184 J/g K of energy is added to the liquid to warm it from $\mathrm{o}^{\circ} \mathrm{C}$ to $100^{\circ} \mathrm{C}$
- $2256 \mathrm{~J} / \mathrm{g}$ of energy is added to change the liquid to steam at $100^{\circ} \mathrm{C}$ - temp stays constant
- $\mathbf{1 . 8 6 ~ J} / \mathbf{g ~ K}$ of energy is added to the steam to warm it from $100^{\circ} \mathrm{C}$ to $200^{\circ} \mathrm{C}$


Example 5.3
How much energy is required to convert 500 . G of ice at $-50 .{ }^{\circ} \mathrm{C}$ to steam at 200. ${ }^{\circ} \mathrm{C} . \mathrm{C}_{\text {ice }}=2.06 \mathrm{~J} / \mathrm{g}^{*} \mathrm{~K}, \mathrm{C}_{\text {water }}=4.184 \mathrm{~J} / \mathrm{g}^{*} \mathrm{~K}, \mathrm{C}_{\text {vapour }}=1.86 \mathrm{~J} / \mathrm{g}^{*} \mathrm{~K}$.

1. Warm the ice from $-50^{\circ} \mathrm{C}$ to $\mathrm{O}^{\circ} \mathrm{C} . \quad \mathrm{T}_{\mathrm{f}}=\mathrm{O}^{\circ} \mathrm{C}=0 .+273.2=273.2 \mathrm{~K}$

$$
\mathrm{T}_{\mathrm{i}}=-50^{\circ} \mathrm{C} \quad=-50^{\circ} \mathrm{C}+273.2=223.2 \mathrm{~K}
$$

$$
\begin{aligned}
& \mathrm{q}_{1}=\left(\mathrm{C}_{\text {water }}{ }^{*} \text { mass }_{\text {water }}^{*} \Delta \mathrm{~T}_{\text {water }}\right)=\left(\mathrm{C}_{\text {water }}^{*} \text { mass }_{\text {water }}^{*}{ }^{*}\left(\mathrm{~T}_{\text {Final }}-\mathrm{T}_{\text {Initiall }}\right)\right) \\
& \mathrm{q}_{1}=\mathbf{2 . 0 6} \mathbf{~ J} / \mathbf{g ~ K}^{*} 500 \mathrm{~g} *(273.2 \mathrm{~K}-223.2 \mathrm{~K}) \quad=\mathbf{5 . 1 5} \mathbf{x 1 0 4} \mathbf{J}
\end{aligned}
$$

2. To melt ice at $O^{\circ} \mathrm{C}$

$$
\mathrm{q}_{2}=\mathbf{3 3 3} \mathbf{J} / \mathbf{g}^{*} 500 \mathrm{~g} \quad=\mathbf{1 . 6 7} \mathbf{x} \mathbf{1 0} \mathbf{~} \mathbf{J}
$$

3. To raise the temp of the liquid water from $0.0^{\circ} \mathrm{C}$ to $100.0^{\circ} \mathrm{C}$

$$
\mathrm{q}_{3}=\mathbf{4 . 1 8 4} \mathbf{J} / \mathbf{g ~ K}{ }^{*} 500 \mathrm{~g} *(373.2 \mathrm{~K}-273.2 \mathrm{~K}) \quad=\mathbf{2 . 0 9}{ }^{*} \mathbf{1 0}^{5} \mathbf{J}
$$

4. To evaporate water at $100{ }^{\circ} \mathrm{C}$

$$
\mathrm{q}_{4}=\mathbf{2 2 5 6} \mathrm{J} / \mathrm{g}^{*} 500 \mathrm{~g} \quad=\mathbf{1 . 1 3} \times 10^{6} \mathrm{~J}
$$

5. To raise the temp of the water vapour from $100.0^{\circ} \mathrm{C}$ to $200.0^{\circ} \mathrm{C}$

$$
\begin{aligned}
& \mathrm{q}_{5}=\mathbf{1 . 8 6} \mathbf{~ J} / \mathbf{g ~ K}^{*} 500 \mathrm{~g}{ }^{*}(473.2 \mathrm{~K}-373.2 \mathrm{~K}) \quad=\mathbf{9 . 3 0} \mathbf{x} \mathbf{1 0 4} \mathbf{J} \\
& \mathrm{q}_{\text {total }}=\mathrm{q}_{1}+\mathrm{q}_{2}+\mathrm{q}_{3}+\mathrm{q}_{4}+\mathrm{q}_{5} \\
& q_{\text {total }}=\mathbf{5 . 1 5} \times 10^{4} \mathbf{J}+\mathbf{1 . 6 7} \times 105 \mathbf{J}+2.09{ }^{*} \mathbf{1 0 5} \mathbf{J}+\mathbf{1 . 1 3 \times 1 0 ^ { 6 }} \mathbf{J}+9.30 \times 10^{4} \mathbf{J} \\
& \mathbf{q}_{\text {total }}=\mathbf{1 . 6 5 \times 1 0 ^ { 6 }} \mathbf{J} \text { or } 1650 \mathrm{~kJ} \text { (Note incorrect SD) }
\end{aligned}
$$

Example 5.4 How much ice at $\mathrm{o}^{\circ} \mathrm{C}$ will it take to cool the contents of a can of soda (340. ml) from $20.5^{\circ} \mathrm{C}$ to $0.0^{\circ} \mathrm{C}$ ? $\quad \mathrm{C}_{\text {water }}=4.184 \mathrm{~J} / \mathrm{g}^{*} \mathrm{~K}$

STUDENTS DO

### 5.4 The FIRST Law of Thermodynamics

Thermodynamics is the science of heat and work. Energy is transferred as heat between a system and its surroundings; this changes the energy of the system. Work done by a system will also affect the energy of the system.
Sublimation is the change of a substance from a solid directly to a vapour state.
Place a piece of dry ice (solid CO2) in a plastic bag and seal the bag. Place a book on the bag.
As energy is absorbed by the cold dry ice, it will sublime to gaseous CO2. The bag will expand and lift the book.

(a) Pieces of dry ice $\left[\mathrm{CO}_{2}(\mathrm{~s}),-78{ }^{\circ} \mathrm{C}\right]$ are placed in a plastic bag. The dry ice will sublime (change directly from a solid to a gas) upon the input of energy.

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

$\Delta \mathrm{U}=$ Change in energy content
$\mathrm{q}=\quad$ Energy transferred as heat
$\mathrm{w}=$ Energy transferred as work

Internal Energy $\mathbf{U}$ is the sum of the potential and kinetic energy of a system
As the actual Internal Energy of a system is hard to determine, we usually measure the change of Internal Energy - $\Delta \mathbf{U}$
Potential Energy: Energy of the attractive and repulsive nuclear forces and bond energy
Kinetic Energy: Energy of motion
Sign Convention for $q$ and $w$
Energy transferred as
Heat to the system (Endothermic)
Heat from the system (Exothermic)
Work done on a system
Work done by a system

| Sign | Effect on $U_{\text {system }}$ |
| :--- | :--- |
| $q>0(+)$ | U increases |
| $q<0(-)$ | $U$ decreases |
| $w>0(+)$ | U increases |
| $w<o(-)$ | $U$ decreases |

Work (at constant Pressure) $=\mathbf{w}=\mathbf{- P} * \boldsymbol{D V}=$ change in volume at a constant pressure
At a constant volume ( $\Delta \mathrm{V}=0$ ), $\mathbf{w}=\mathbf{- P}$
Most experiments are performed at atmospheric pressure - or at constant pressure.
Looking at the sublimation of CO 2 in a bag and lifting a book, the work done is Pressure - Volume work. The work is the change in volume to lift the book and is done against a constant atmospheric pressure:

Work (at const pressure) $=-\mathrm{P}($ atmospheric Pressure $) * \Delta \mathrm{~V}($ change in volume of the bag $)$
$\Delta \mathrm{U}=\mathrm{q}+\mathrm{w}$
$\Delta \mathrm{U}=\mathrm{q}+-\mathrm{P} \Delta \mathrm{V}$
$\mathrm{q}=\Delta \mathrm{U}+\mathrm{P} \Delta \mathrm{V}$
If the change of volume is zero, then $\mathrm{P} \Delta \mathrm{V}=\mathrm{o}$ and $\Delta \mathrm{U}=\mathrm{q}$, or the energy transferred as heat at constant volume equals the change in internal energy of the system.

## Bicycle Pump:

When the pump handle is pressed down, using external energy, the volume of the pumps internal tube is reduced: $\Delta \mathrm{V}=\mathrm{V}_{\text {final }}-\mathrm{V}_{\text {initial }}=$ Small Value - Bigger Value $=$ Negative Value for $\Delta \mathrm{V}$. The pressure increases. The work done on the system is: $w=P^{*}-\Delta V$


## Define a new term Enthalpy $=\mathbf{H}$

At constant Pressure: $\quad \Delta \mathrm{U}=\mathrm{q}_{\mathrm{p}}+\mathrm{w}_{\mathrm{p}}$ Subscript p is at Constant Pressure.

$$
\Delta \mathrm{U}=\mathrm{q}_{\mathrm{p}}+-\mathrm{P} \Delta \mathrm{~V}
$$

Rearranging $\quad \mathrm{q}_{\mathrm{p}}=\Delta \mathrm{U}+\mathrm{P} \Delta \mathrm{V}$
New Thermodynamic Function called Enthalpy: $\quad \mathbf{H}=\mathbf{U}+\mathbf{P V}$
But, since we usually cannot measure exact values only change in values:
$\boldsymbol{\Delta} \mathbf{H}=\boldsymbol{\Delta} \mathbf{U}+\boldsymbol{\Delta} \mathbf{P} \mathbf{V}=\mathrm{q}_{\mathrm{p}}=$ the energy transferred as heat at constant pressure
$\Delta \mathbf{H}=$ Negative $=$ heat is transferred from the system to the surroundings
$\mathbf{\Delta H}=\mathbf{P o s i t i v e}=$ heat is transferred from the surroundings to the system
State Function define the difference between an initial and a final state, it does not depend on how you get there. Example: If you have a mountain with a direct and an indirect path to get to the top, it does not matter how you get there, just that you get there.
Enthalpy is a State Function. The enthalpy change in heating 1.0 g of water from $20^{\circ} \mathrm{C}$ to $50^{\circ} \mathrm{C}$ does not matter how you do it, it just depends on the difference between the two temperatures.
Functions that are not State Functions would include the distance traveled or elapsed travel time from New York to Denver - it would depend on the route. But the elevation change between New York (Sea Level) and Denver ( 1600 m above sea level) will not depend on how it is measured.
Standard Reaction Enthalpy $=\mathbf{\Delta} \mathbf{H} \quad$ Change in Enthalpy from a chemical reaction

$$
\mathrm{H}_{2} \mathrm{O}_{(\mathrm{g})} \rightarrow \mathrm{H}_{2(\mathrm{~g})}+1 / 2 \mathrm{O}_{2}(\mathrm{~g}) \quad \Delta_{\mathrm{f}} \mathrm{H}^{0}=+241.8 \mathrm{~kJ} / \mathrm{mol}-\mathrm{rxn}
$$

$+\boldsymbol{s i g n}$ for $\Delta H$ indicates an endothermic process, we must put in energy.
Subscript $\mathbf{f}$ is the Standard Enthalpy of Formation
Superscript ${ }^{\circ}$ is the Standard State, the Standard State is 1 bar of pressure and $25^{\circ} \mathrm{C}$
mol-rxn $=$ one mole of reaction $=$ a chemical reaction occurs exactly in the amounts specified by the coefficients of the balanced chemical equation.

Looking at the reverse of the above reaction
$\mathrm{H}_{2}(\mathrm{~g})+1 / 2 \mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{H}_{2} \mathrm{O}_{(\mathrm{g})} \quad \Delta_{\mathrm{f}} \mathrm{H}^{\mathrm{o}}=-241.8 \mathrm{~kJ} / \mathrm{mol}-\mathrm{rxn}$
The enthalpy change is the same value, but of opposite sign. This reaction is exothermic.
These reactions are dependent upon the amount of material used:
$2 \mathrm{H}_{2(\mathrm{~g})}+\mathrm{O}_{2(\mathrm{~g})} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{g})} \quad \Delta_{\mathrm{f}} \mathrm{H}^{\mathrm{o}}=-483.6 \mathrm{~kJ} / \mathrm{mol}-\mathrm{rxn}$
Doubling the amount of starting material, doubles the amount of energy released in this exothermic reaction.

The States of the reaction materials is important, if we replace the gas ${ }_{(\mathrm{g})}$ with gas ${ }_{(1)}$ :
$\mathrm{H}_{2}(\mathrm{~g})+1 / 2 \mathrm{O}_{2(\mathrm{~g})} \rightarrow \mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \quad \Delta_{\mathrm{f}} \mathrm{H}^{\mathrm{o}}=-285.8 \mathrm{~kJ} / \mathrm{mol}-\mathrm{rxn}$

## Enthalpy Summary:

- Enthalpy changes are specific to the reaction and the identities of the reactants and products and their states ( $\mathrm{s}, \mathrm{l}, \mathrm{g}$ ) are important, as are the amount of reactants and products.
- The enthalpy change depends on the number of moles of reaction.
- $\Delta \mathrm{H}$ has a negative value for exothermic reactions and a positive value for endothermic reactions.
- The value for $\Delta \mathrm{H}$ is numerically the same, but of opposite sign, for reactions that are the reverse of each other.
- These are constant pressure reactions

Problem: How much heat energy is generated by burning 454 g of propane, $\mathrm{C}_{3} \mathrm{H}_{8}$ at constant P .
$\mathrm{C}_{3} \mathrm{H}_{8(\mathrm{~g})}+5 \mathrm{O}_{2(\mathrm{~g})} \rightarrow 3 \mathrm{CO}_{2(\mathrm{~g})}+4 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \quad \Delta_{\mathrm{f}} \mathrm{H}^{\mathrm{o}}=-2220 \mathrm{~kJ} / \mathrm{mol}-\mathrm{rxn}$ 454. g

Determine the Mw of $\mathbf{C}_{\mathbf{3}} \mathbf{H s}_{\mathbf{8}}(\mathrm{g}) \quad 3 \mathrm{C} \quad 3^{*} 12.01 \quad 36.03$
$8 \mathrm{H} \quad 8$ * $1.008 \quad 8.064$
454 g * $1 / 47.09 \mathrm{~g} / \mathrm{mole}=\mathbf{1 0 . 3} \mathbf{~ m o l e} \mathbf{C}_{\mathbf{3}} \mathbf{H}_{\mathbf{8}}$
$\mathrm{Mw} \mathrm{C} 3 \mathrm{H}_{8} \quad 47.094=\mathbf{4 7 . 0 9} \mathbf{~ g} / \mathbf{m o l e}$
$\boldsymbol{\Delta}_{\mathbf{f}} \mathbf{H}^{\mathbf{o}}=10.3 \mathrm{~mole}_{3} \mathrm{H}_{8}{ }^{*}\left(1 \mathrm{~mol}-\mathrm{rxn} / 1 \mathrm{~mole}_{3} \mathrm{H}_{8}\right){ }^{*}-2220 \mathrm{~kJ} / \mathrm{mol}-\mathrm{rxn}=-22900=\mathbf{2 . 2 9 \times 1 0 4} \mathbf{~ k J}$

Example 5.5 How much energy is given off by burning 5.00 g of sugar, $\mathrm{C}_{12} \mathrm{H}_{22} \mathrm{O}_{11}$ to $\mathrm{CO}_{2}$ and $\mathrm{H}_{2} \mathrm{O}$.
$\Delta \mathrm{H}=-5645 \mathrm{~kJ} / \mathrm{mol}-\mathrm{rxn}$
STUDENTS WORK THIS ONE OUT
5.6 Calorimetry is the measurement of energy evolved or absorbed as heat in a chemical or physical process. A constant pressure calorimeter used in the lab is also called a "coffee-cup calorimeter"

## "coffee-cup calorimeter"



An example if its use would be to add some magnesium metal to some room temperature HCl . As the reaction proceeds, heat is generated. What is the equilibrium temperature, or determine $\mathrm{q}_{\mathrm{r}}$.
$\mathrm{q}_{\mathrm{r}}+\mathrm{q}_{\text {solution }}=\mathrm{o} \quad \mathrm{q}_{\mathrm{r}}=$ energy absorbed or released by the chemical reaction
$\mathrm{q}_{\text {solution }}=$ the energy gained or lost by the solution.
OWL Example 5.6 o. 0500 g of Mg is placed in the calorimeter along with 100.0 ml of 1.00 M HCl :

$$
\mathrm{Mg}(\mathrm{~s})+2 \mathrm{HCl}_{(\mathrm{aq})} \rightarrow \mathrm{H}_{2(\mathrm{~g})}+\mathrm{MgCl}_{2(\mathrm{aq})}
$$

The temperature increases from $22.21^{\circ} \mathrm{C}$ to $24.46^{\circ} \mathrm{C}$. What is the $\Delta \mathrm{H}$ for this reaction?
$\mathrm{C}_{\text {acid solution }}=4.20 \mathrm{~J} / \mathrm{g}^{*} \mathrm{~K}$, acid solution density is $1.00 \mathrm{~g} / \mathrm{ml}$.

1. Moles of Mg
2. Mass of the solution
3. Determine $\mathrm{q}_{\text {solution }}$
0.050 g Mg * 1 mole $\mathrm{Mg} / 24.31 \mathrm{~g}=0.00206 \mathrm{~mole} \mathrm{Mg}$
( 100.0 g HCl solution * $1.00 \mathrm{~g} / \mathrm{ml}$ ) $+0.0500 \mathrm{~g} \mathrm{Mg}=100.050=100.1 \mathrm{~g}$

$$
\begin{aligned}
& \text { Qsolution }=\mathrm{C} * \mathrm{~m} * \Delta \mathrm{~T}=4.20 \mathrm{j} / \mathrm{g}^{*} \mathrm{~K} * 100.1 \mathrm{~g} *\left(24.46{ }^{\circ} \mathrm{C}-22.21^{\circ} \mathrm{C}\right)= \\
& 945.945=\mathbf{9 4 5} . \mathrm{J}
\end{aligned}
$$

4. Calculate the enthalpy change for the reaction per mole of Mg ?

$$
\mathrm{q}_{\mathrm{r}}+\mathrm{q}_{\text {solution }}=0 \quad \text { then } \mathbf{q}_{\mathbf{r}}=-q_{\text {solution }}=\mathbf{- 9 4 5} . \mathbf{J}
$$

Constant Volume Calorimeter, measure $\Delta U$
These are used to measure the energy content of fuels. A weighed sample is placed inside a "Bomb" which is a fixed volume thick steel container. This container is place in another container with a water jacket separation. The fuel is ignited and the rise in temperature of the bomb and the water jacket measured. $\mathrm{q}_{\mathrm{r}}+\mathrm{q}_{\text {bomb }}+\mathrm{q}_{\text {water }}=\mathrm{o}$
or the heat generated by the reaction, $\mathrm{q}_{\mathrm{r}}$, equals the heat absorbed by the bomb and the water jacket $\mathrm{q}_{\mathrm{bomb}}+\mathrm{q}_{\text {water }}$.


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OWL Example 5.71 .00 g of $\mathrm{C}_{8} \mathrm{H}_{18}$ (Octane) is burned in a constant volume calorimeter. The calorimeter contained 1.20 kg of water whose temperature rose from $25.00{ }^{\circ} \mathrm{C}$ to $33.20{ }^{\circ} \mathrm{C}$. The bombs temperature rise was the same. The bombs $\mathrm{C}_{\mathrm{bomb}}=837 \mathrm{~J} / \mathrm{K}$. (weight of the bomb is included) What is the heat of combustion for octane per mole of octane?
$\mathrm{q}_{\mathrm{r}}+\mathrm{q}_{\text {bomb }}+\mathrm{q}_{\text {water }}=0 \quad$ We need to calculate $\mathrm{q}_{\mathrm{r}}$
$\mathbf{q}_{\text {water }}=\mathrm{C}_{\text {water }}{ }^{*} \mathrm{~m}_{\text {water }} * \Delta \mathrm{~T}=(4.184 \mathrm{~J} / \mathrm{gK}) *\left(1.2{ }^{*} 10^{3} \mathrm{~g}_{\text {water }}\right)^{*}\left(33.20{ }^{\circ} \mathrm{C}-25.00{ }^{\circ} \mathrm{C}\right)=$
$41.2 \times 103 \mathrm{~J}=41.2 \mathrm{~kJ}$
$\mathbf{q}_{\text {bomb }}=\mathrm{C}_{\text {bomb }}{ }^{*} \Delta \mathrm{~T}=(837 \mathrm{~J} / \mathrm{gK})^{*}\left(33.20^{\circ} \mathrm{C}-25.00^{\circ} \mathrm{C}\right)=\mathbf{6 . 8 6} \mathbf{k J}$
$\mathbf{q}_{\mathbf{r}}=-\mathrm{q}_{\text {bomb }}-\mathrm{q}_{\text {water }}=-4.12 \mathrm{~kJ}-6.86 \mathrm{~kJ}=-48.1 \mathrm{~kJ}$ per gram
Mw Octane $8 \mathrm{C} \quad 8^{*} 12.01 \quad 96.08$
$18 \mathrm{H} \quad 18$ * $1.008 \quad \underset{18.144}{ }$
Mw Octane $=114.224=\mathbf{1 1 4 . 2 2} \mathbf{g} /$ mole.$\quad 1$ mole of Octane $=114.22 \mathrm{~g}$
$\mathbf{q r}_{\mathbf{r}}$ per mole $=114.22 *-48.1 \mathrm{~kJ}=-5,49 \mathrm{okJ}$ or $-5.49 \times 1 \mathbf{o n}^{3} \mathbf{k J}$

### 5.7 Enthalpy Calculations

Hess's Law: if a reaction is the sum of two or more reactions, $\Delta_{\mathrm{f}} \mathrm{H}^{0}$ for the overall process is the sum of the $\Delta_{\mathrm{f}} \mathrm{H}^{\mathrm{o}}$ values for those reactions

| Equation 1 | $\mathrm{C}(\mathrm{s})$ | $+1 / 2 \mathrm{O}_{2}(\mathrm{~g})$ | $\rightarrow \mathrm{CO}(\mathrm{g})$ | $\Delta_{\mathrm{f}} \mathrm{Ho}_{1}=?$ |
| :--- | :--- | :--- | :--- | :--- |
| Equation 2 | $\mathrm{CO}(\mathrm{g})$ | $+1 / 2 \mathrm{O}_{2}(\mathrm{~g})$ | $\rightarrow \mathrm{CO}_{2(\mathrm{~g})}$ | $\Delta_{f} \mathrm{H}^{\mathrm{o}}{ }_{2}=-283.0 \mathrm{~kJ} / \mathrm{mol}-\mathrm{rxn}$ |
| Equation 3 | $\mathrm{C}_{(\mathrm{s})}$ | $+\mathrm{O}_{2(\mathrm{~g})}$ | $\rightarrow \mathrm{CO}_{2(\mathrm{~g})}$ | $\Delta_{\mathrm{f}} \mathrm{H}^{\mathrm{o}}{ }_{3}=-393.5 \mathrm{~kJ} / \mathrm{mol}-\mathrm{rxn}$ |

Hess's Law states: $\quad \Delta_{\mathrm{f}} \mathrm{Ho}_{3}=\Delta_{\mathrm{f}} \mathrm{Ho}_{1}+\Delta_{\mathrm{f}} \mathrm{H}^{\mathrm{o}_{2}}$

$$
-393.5 \mathrm{~kJ} / \mathrm{mol}-\mathrm{rxn}=\Delta_{\mathrm{f}} \mathrm{H}^{{ }^{o}}{ }_{1}+-283.0 \mathrm{~kJ} / \text { mol-rxn }
$$

$\Delta_{\mathrm{f}} \mathrm{H}_{1}=-110.5 \mathrm{~kJ} / \mathrm{mol}-\mathrm{rxn}$

## Students go over $\mathbf{H 2}+\mathbf{1} \mathbf{2} \mathbf{O 2} \boldsymbol{\rightarrow} \mathbf{H 2 O}$ example

Standard Enthalpies of Formation $\Delta_{\mathbf{f}} \mathbf{H}^{\mathbf{o}}$ is the enthalpy change for the formation of $\mathbf{1} \mathrm{mol}$ of a compound directly from its component elements in their standard state.
$\Delta_{\mathrm{f}} \mathrm{H}^{\circ}$ for $\mathrm{NaCl}(\mathrm{s})$ at 1 bar is $\quad \mathrm{Na}(\mathrm{s})+1 / 2 \mathrm{Cl}_{2}(\mathrm{~g}) \rightarrow \mathrm{NaCl}_{(\mathrm{s})} \quad \Delta_{\mathrm{f}} \mathrm{H}^{\mathrm{o}}=-411.12 \mathrm{~kJ} / \mathrm{mol}$
Enthalpy Change for a Reaction - to be added yet, but we'll cover it - see your text book

## The Chemistry of Fuels and Energy Resources

## Energy Supply

- Tripled in the past 40 years, will triple in the next 50 years
- Fossil fuels account for $85 \%$ of the total energy used
- US has $5 \%$ of the worlds population, but consumes $23 \%$ of all energy
- In 2007 China passed the US as \#1 emitter of Greenhouse Gases


## Energy Resources \& Usage

Fossil Fuels are cheap raw materials Nonrenewable energy sources
Suns Energy is Renewable Resource
Worlds
Oil reserves will be depleted in 30-8o years
Natural Gas will last 60-200 years
Coal will last 150 - ?
Superconductors are materials that at $30-150 \mathrm{~K}$, offer virtually no resistance to electrical conductivity. They are used in magnetic such as used for MIR's.

Fossil Fuels
originate from Organic Matter
Include Coal, crude oil and Natural Gas
To extract energy from fossil fuels Materials are burned
Combustion process going to completion Fuel $\rightarrow \mathrm{CO} 2 \& \mathrm{H} 2 \mathrm{O}$
Thermal energy Is converted to Mechanical Mechanical Energy is converted to Electrical energy
Hydrocarbons from Fossil Fuels have C and H .

$$
\begin{array}{ll}
\mathrm{C}_{(\mathrm{s})}+\mathrm{O} 2_{(\mathrm{g})} \rightarrow \mathrm{CO}_{2(\mathrm{~g})} & \Delta \mathrm{H}^{\mathrm{o}}=-393.5 \mathrm{~kJ} / \mathrm{Mol}-\mathrm{rxn}=-32.8 \mathrm{~kJ} / \mathrm{g} \mathrm{C} \\
\mathrm{H} 2(\mathrm{~g})+1 / 2 \mathrm{O} 2(\mathrm{~g}) \rightarrow \mathrm{H} 2 \mathrm{O}(\mathrm{~g}) & \Delta \mathrm{H}^{\mathrm{o}}=241.8 \mathrm{~kJ} / \text { Mol-rxn }=-119.8 \mathrm{~kJ} / \mathrm{g} \mathrm{C}
\end{array}
$$

Coal - began to from 290 million years ago, contains $60 \%$ to $95 \%$ Carbon with $\mathrm{H}, \mathrm{O}, \mathrm{S}$ and N
Sulfur from coal forms aid rain $2 \mathrm{SO}_{2(\mathrm{~g})}+\mathrm{O}_{2(\mathrm{~g})} \rightarrow 2 \mathrm{SO}_{3(\mathrm{~g})}$

$$
\mathrm{SO}_{3(\mathrm{~g})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \rightarrow \mathrm{H}_{2} \mathrm{SO}_{4(\mathrm{ag})}
$$

## 3 Categories of Coal <br> Anthracite <br> Bituminous <br> Lignite

Hard Coal Highest Quality, Low S, Uncommon - 2\% of all coal
Soft Coal Highest S, 45\% of all coal, used for power generation
Brown Coal Youngest, small energy per gram
Coke is formed from heating coal in the absence of air. Organics are driven off and captured.
Coal Gasification: convert coal to gaseous fuels. Loose 30-40\% of the energy
Natural Gas is found deep under the earth surface and consists of Methane CH4 and some Ethane $\mathrm{H}_{3} \mathrm{C}-\mathrm{CH}_{3}$ and Propane $\mathrm{H}_{3} \mathrm{C}-\mathrm{CH}_{2}-\mathrm{CH}_{3}$ and Butane $\mathrm{H}_{3} \mathrm{C}-\mathrm{CH} 2-\mathrm{CH} 2-\mathrm{CH} 3$. Also contains $\mathrm{N} 2, \underline{\mathrm{He}, \mathrm{CO}} 2$ and H 2 S .
Petroleum is a mixture of hydrocarbons of 1 to 20 carbon atoms. $85 \%$ of crude petroleum is used for fuel: Gas, Diesel, Heating
Other Fossil Fuels: Methane Hydrate consists of Methane and water, is stable below $\mathrm{O}^{\circ} \mathrm{C}$. Solid to Gas increase 165 x volume. 2x as much Methane Hydrate as all known fossil fuel reserves. This may have been the cause of the Deepwater Horizon explosion.
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Swamp Gas is methane from swamps. Methane from Landfills - used as a fuel
Tar Sands is viscous organic called Bitumen. Alberta, Canada, has $2 x$ the worlds known reserves of petroleum. Extracting is costly - mix with water/steam to extract.

## Environmental Impacts of Fossil Fuel Use

Greenhouse Effect.
For the next two decades, a warming of about $0.2^{\circ} \mathrm{C}$ is projected.
Global Warming is the increase in average global temp and accompanying climate change
Autos form Nitric Acid $\quad \mathrm{N} 2(\mathrm{~g})+\mathrm{O} 2(\mathrm{~g}) \rightarrow 2 \mathrm{NO}(\mathrm{g}) \quad \Delta \mathrm{H}^{0}=180.58 \mathrm{~kJ} / \mathrm{mol}-\mathrm{rxn}$
$2 \mathrm{NO}(\mathrm{g})+\mathrm{O} 2(\mathrm{~g}) \rightarrow 2 \mathrm{NO}(\mathrm{g}) \quad \Delta \mathrm{H}^{\circ}=-114.4 \mathrm{~kJ} / \mathrm{mol}-\mathrm{rxn}$
$3 \mathrm{NO} 2(\mathrm{~g})+\mathrm{H} 2 \mathrm{O}(\mathrm{l}) \rightarrow 2 \mathrm{HNO}_{3}(\mathrm{aq})+\mathrm{NO}(\mathrm{g})$
$\Delta \mathrm{H}^{0}=-71.4 \mathrm{~kJ} /$ mol-rxn

## Fuel Cells Coal fired steam turbines 35-40\% efficient Newer Gas Turbines 50-60\% <br> Fuel Cell 60\%

Fuel Cells are Oxidation and Reduction reactions in two compartments. Electrons flow from Oxidation to Reduction compartment

$$
\mathrm{CH}_{3} \mathrm{OH}_{(\mathrm{l})}+3 / 2 \mathrm{O} 2(\mathrm{~g}) \rightarrow \mathrm{CO} 2(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \Delta \mathrm{H}^{0}=-727 \mathrm{~kJ} / \text { mol-rxn }
$$

Hydrogen Economy: producing, storing and using hydrogen as a fuel (it's a gas at RT)
Oxidation of hydrogen yields 3 times the energy as oxidation of fossil fuels
$\mathrm{H} 2(\mathrm{~g})+1 / 2 \mathrm{O} 2(\mathrm{~g}) \rightarrow \mathrm{H} 2 \mathrm{O}(\mathrm{g}) \quad \Delta \mathrm{H}^{0}=-241 \mathrm{~kJ} / \mathrm{mol}-\mathrm{rxn}=\mathbf{- 1 1 9} \mathbf{k J} / \mathbf{g ~ H 2}$
Propane $\mathrm{H}_{3} \mathrm{C}-\mathrm{CH} 2-\mathrm{CH} 3+5 \mathrm{O} 2(\mathrm{~g}) \rightarrow 3 \mathrm{CO} 2(\mathrm{~g})+4 \mathrm{H} 2 \mathrm{O}(\mathrm{g})$

$$
\Delta \mathrm{H}^{\circ}=-2043 \mathrm{~kJ} / \mathrm{mol}-\mathrm{rxn}=-46 \mathrm{~kJ} / \mathrm{g} \text { Propane }
$$

Problems: Inexpensive method of producing H2
Practical means of storing H2 A distribution system

## Biofuels

## Bioethanol

Solar Energy

