

**Chemistry 30**  
**Thermochemistry Notes**

**A. Energy Changes**

- **Energy** is the capacity to do work, generate heat and/or generate electricity
- Energy can be converted to other forms, but the total energy of the system remains the same
  - (1<sup>st</sup> Law of Thermodynamics)
- With every energy conversion (change), energy is always lost as heat
  - (2<sup>nd</sup> Law of Thermodynamics)
- the primary sources of energy are:
  1. chemical: fossil fuels, plants
  2. nuclear: uranium, hydrogen
  3. solar: radiant energy, wind, hydroelectric
  4. geothermal: geysers, hot springs
- there are 4 types of energy changes:
  1. temperature change: 10's kJ
    - a. molecules gain/lose energy and move faster/slower
  2. phase change (change in state): 10's kJ
    - a. \_\_\_\_\_ bonds (between molecules) are broken/formed
    - b. Ex. Water melting or freezing
  3. chemical change (one substance converted to another): 100-1000's kJ
    - a. \_\_\_\_\_ bonds (within a molecule) are formed/broken
    - b. Ex. Water being made from hydrogen and oxygen
  4. nuclear change (one element converted to another): millions kJ
    - a. \_\_\_\_\_ bonds (within the nucleus) of an atom are broken

## B. Temperature Changes

- **Temperature** or **kinetic energy ( $E_K$ )** is the energy of motion of particles...increase in temperature means an increase in  $E_K$
- \_\_\_\_\_ is the transfer of thermal energy
- $\Delta E_K$  is the change in kinetic energy (results in a change in temperature)
- $E_K$  of a particle can be classified as:
  1. **vibrational motion**: rapid back and forth movement of bundled atoms with no change of location -- solid, liquid, gas
  2. **rotational motion**: molecular rotation, no change in position -- liquid, gas
  3. **translational motion**: motion from one point to another --liquid, gas
- **Specific Heat capacity** is heat required to change the temperature of a "unit mass" of a substance by  $1^\circ\text{C}$

$$\Delta E_K = q = mc\Delta t$$

where:  $\Delta E_K$  = change in kinetic energy in J  
 $q$  = heat energy in J  
 $m$  = mass in g  
 $\Delta t$  = change in temperature in  $^\circ\text{C}$   
 $c$  = specific heat capacity in  $\text{J/g}^\circ\text{C}$

### Example

Find the heat required to change 2.50 g of water from  $10.0^\circ\text{C}$  to  $27.0^\circ\text{C}$ .

$$c_{\text{H}_2\text{O}} = 4.19 \text{ J/g}^\circ\text{C}.$$

$$\begin{aligned} c &= 4.19 \text{ J/g}^\circ\text{C} & q &= mc\Delta t \\ m &= 2.50 \text{ g} & &= (2.50 \text{ g})(4.19 \text{ J/g}^\circ\text{C})(17.0^\circ\text{C}) \\ \Delta t &= 17.0^\circ\text{C} & &= 178.075 \text{ J} \\ & & &= \mathbf{178 \text{ J}} \end{aligned}$$

## C. Phase Changes

### 1. The Basics

- **Phase change** is a change of state (s, l, or g)
- phase changes always involve energy changes but do not involve a change in temperature
  - ex. Ice melts at 0°C, and only 0°C
  - ∴ are associated with **potential energy** and not kinetic energy

### Types of Phase Changes

**Endothermic** = melting, vaporization (boiling), sublimation

- energy from the surroundings separates the bonded molecules thereby increasing their potential energy, or  $E_p$
- phase changes that absorb heat

**Exothermic** = freezing, condensation, deposition

- Energy is released to the surroundings when molecules bond together, thereby decreasing their potential energy
- Phase changes that release heat

### **System vs. Surroundings:**

- System refers to what is undergoing the change
- Surroundings refers to what is around the system (where heat is coming from or going to)

### 3. Enthalpy

- \_\_\_\_\_ is the total kinetic and potential energy of a chemical system under constant pressure and temperature
- Enthalpy is symbolized by **H**
- Unfortunately, the enthalpy of individual substances cannot be measured directly
  - $E_K$  can with a thermometer but how do you measure  $E_P$ ?
- Changes in enthalpy occur whenever heat is released or absorbed in a physical or chemical change...fortunately, this can be measured
- Change in enthalpy is symbolized by  **$\Delta H$**
- During a phase change  $E_K$  remains constant
  - $\therefore$  the change in  $E_P$  is the enthalpy change ( **$\Delta H$** )
- Endothermic enthalpy changes are *positive* values
  - this means energy is absorbed (gained)
- Exothermic enthalpy changes are *negative* values
  - this means energy is released (lost)

#### 4. Molar Enthalpy

- Molar enthalpy is the enthalpy change per mole of a substance
- Molar enthalpy is symbolized by **H**
- subscripts are added to indicate the phase change being described

eg)  $H_{2O_{\text{melting}}} = H_{\text{fus}} = 6.01 \text{ kJ/mol}$   
 $H_{2O_{\text{boiling}}} = H_{\text{vap}} = 40.65 \text{ kJ/mol}$   
 $Na_{\text{melting}} = H_{\text{fus}} = 2.6 \text{ kJ/mol}$   
 $Na_{\text{boiling}} = H_{\text{vap}} = 101 \text{ kJ/mol}$   
\*\*\*see Table 10.3 pg 293 in Nelson  
\*\*\*you may have to change these values from kJ/mol to J/mol

- molar enthalpy can be used to calculate the enthalpy change of a phase change:

$$\Delta H = nH$$

where:  $\Delta H$  = enthalpy change in J or kJ  
 $n$  = number of moles in mol  
 $H$  = molar enthalpy in J/mol or kJ/mol

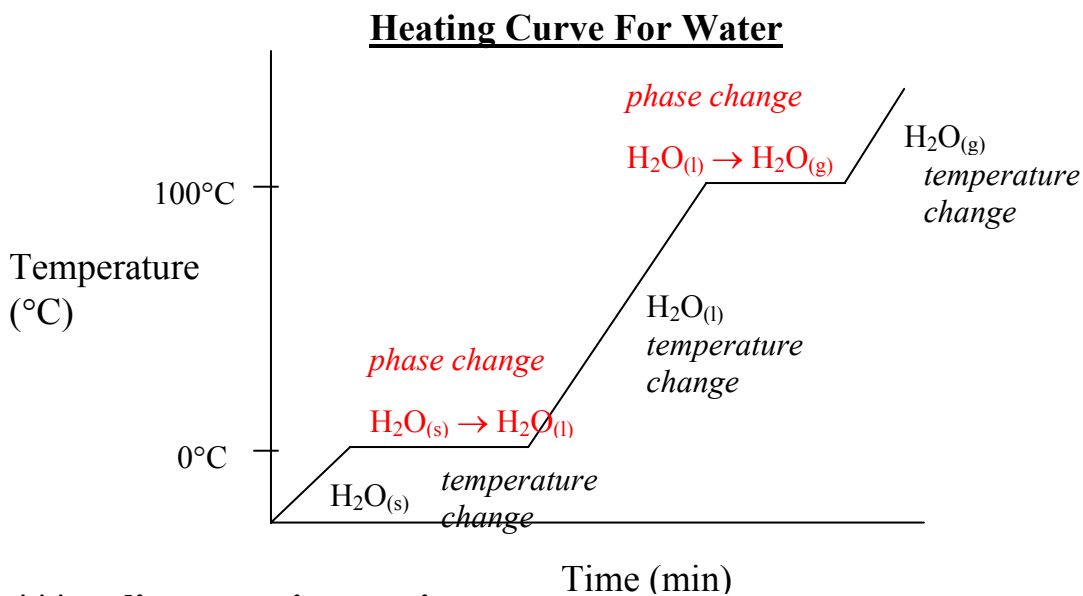
\*\*\*remember that the H's could have a subscript depending on the phase change eg)  $\Delta H_{\text{fus}}$  and  $H_{\text{fus}}$ , or  $\Delta H_{\text{vap}}$  and  $H_{\text{vap}}$

#### Example

Find the energy required to melt 2.50 g of ice at 0°C.

## 2. Heating Curves

- a heating curve is a graph illustrating melting and boiling
- phase changes and changes in temperature are both represented on the diagram
- during temperature changes the  $E_K$  of the molecules change
- during phase changes there is no change in temperature therefore  $E_K$  remains constant...only the  $E_P$  (potential energy) changes as energy from the surroundings separates the bonded molecules (intermolecular forces)



**\*\*\*cooling curve is opposite**

#### D. Total Energy Changes

- the total energy change that a substance goes through can be determined using a heating curve and the formulas  $q=mc\Delta t$  and  $\Delta H=nH$

##### Steps:

1. Always draw the heating curve first!!!!
2. On the curve, put a point where you begin and a point where you end (temperatures). Connect the dots with a line that stands out.
3. Determine which formulas are needed and which part of the curve they apply to.
  - each time you meet a new line, you have a new formula
  - diagonal lines represent a change in temperature
    - i.  $\therefore q=mc\Delta t$
  - horizontal lines represent a phase change
    - i.  $\Delta H=nH$  (vap or fus)
4. Perform the calculation.

Example

Find the total energy required to change 1.0 g of ice at  $-20^{\circ}\text{C}$  to steam at  $110^{\circ}\text{C}$ .

- if the energy value is positive = endothermic reaction
- if the energy value is negative = exothermic reaction

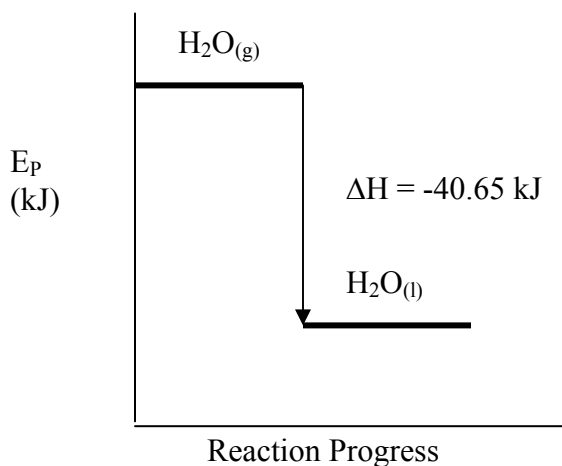
***Your Assignment: pg 297-299 #21a-d, 22a-b***

## Quiz

### F. Potential Energy Diagrams

- a *potential energy diagram* is a theoretical description of an enthalpy change
- it shows the energy transfer resulting from changes in chemical potential energy due to the breakage or formation of intermolecular bonds
- an increase in  $E_p$  describes an endothermic process (positive)
- a decrease in  $E_p$  describes an exothermic process (negative)

#### The Condensation of One Mole of Steam



- Make sure you include:

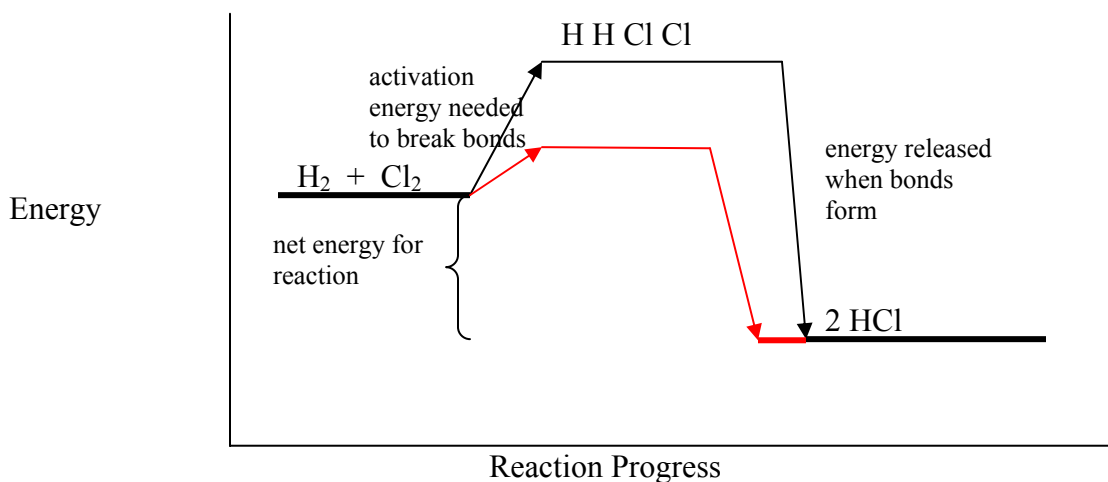
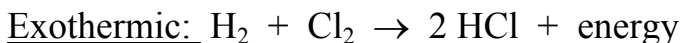
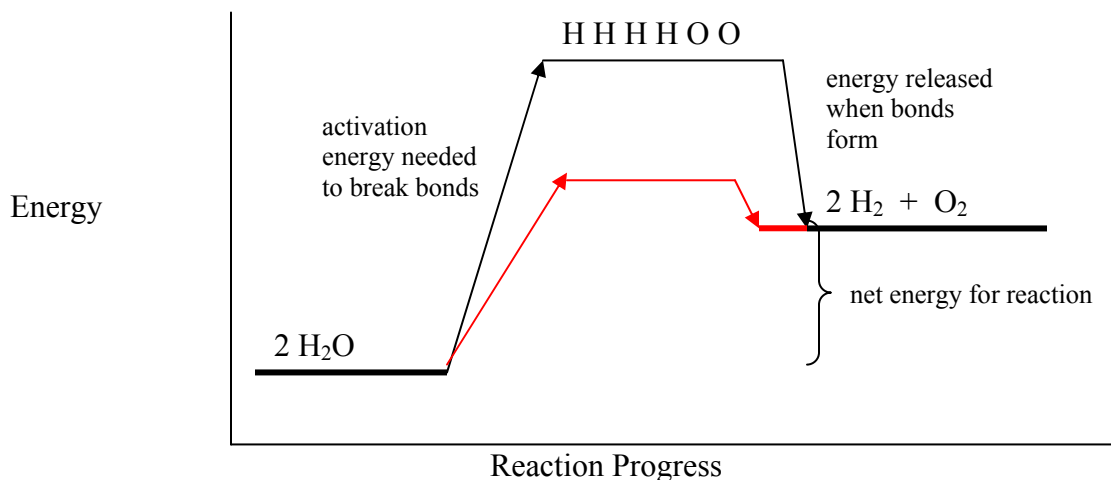
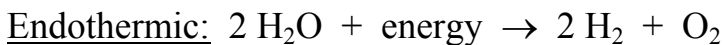
***Your Assignment:***

***Read pg. 300***

***pg 300 #23-26***

## J. Bond Energy

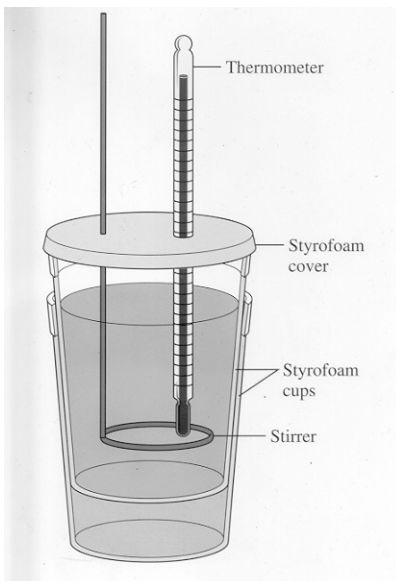
- *bond energy* is the energy required to break a chemical bond or the energy released when a bond is formed
- in both endothermic and exothermic reactions, the energy required to “pull apart” the atoms in the reactants is called the *activation energy*
- the activation energy is always higher than the energy contained in the reactants and the products



- if a *catalyst* is used, it acts to lower the activation energy for the reaction (\*\*typical diploma question)...see red line on above diagrams

## Calorimetry

- **Calorimetry** is a technological process of measuring energy changes using an isolated system (matter and energy cannot move in and out)
- the isolated system used to determine the heat involved in a phase change or in a chemical reaction is called a *calorimeter*
- Compare isolated, closed and open systems in terms of movement of matter and energy.
- Calorimeters differ in design depending on what type of reaction is being measured.
  - For phase changes (melting, solidification) a simple calorimeter can be used.



- it is assumed that no energy is gained or lost by the system except for the energy required or released by the reaction or phase change
- calorimeters can be used to calculate the specific heat capacity of a substance, the enthalpy (heat) of dissolving, the enthalpy (heat) of reaction etc

## Calorimetry of Phase Changes

Melting, solidifying, dissolving (solution)

### Example

**1.** 15.0g of ice is added to a calorimeter that contains 250mL of water at 21.0°C. If the final temperature of the water was 18.5°C calculate the experimental molar enthalpy value for ice melting. How does the value compare with the value in the data booklet?

$$\text{Heat lost (water)} = \text{heat gained (ice melting)}$$

**2.** When 80.0 g of NaOH is added to 850 mL of water at 23.0°C, the temperature of the water rose to 28.5°C after the NaOH had dissolved. Calculate the molar enthalpy of dissolving.

$$\text{heat lost (dissolving)} = \text{heat gained (water)}$$

**3.** When 52.5 g of LiNO<sub>3</sub> is added to 150 mL of water in a calorimeter the initial temperature of the water was 18.0°C and after the LiNO<sub>3</sub> the temperature was 16.5°C. Calculate the molar enthalpy of dissolving.

$$\text{heat lost (water)} = \text{heat gained (dissolving)}$$

## Using Calorimetry to calculate specific heat capacity of metals

### Example

150 g of unknown metal X is at 100°C. It is placed in a calorimeter with 200 mL of water at 23.0°C. If the final temperature of the water reached is 25.0°C, what is the specific heat capacity of metal X?

$$\begin{array}{rcl} \text{heat lost (metal)} & = & \text{heat gained (water)} \\ q & = & q \end{array}$$

## **LAB: Calorimetry – Dissolving Ammonium Nitrate**

## Chemical Change

- a *chemical change* is a transformation involving an energy change in which one substance is converted into another substance
- uses of chemical energy (exothermic):
  1. steam generators from burning fossil fuels
  2. motor vehicles where fuel is burned
  3. natural gas, propane, coal, wood burned for heating
  4. batteries
  5. living organisms, cellular respiration
- A calorimeter can be used to quantify the amount of heat lost or gained by a chemical reaction (still sticking to the heat lost = heat gained principle!!!!)

$$\text{heat lost/gained (rxn)} = \text{heat gained/lost (water)}$$

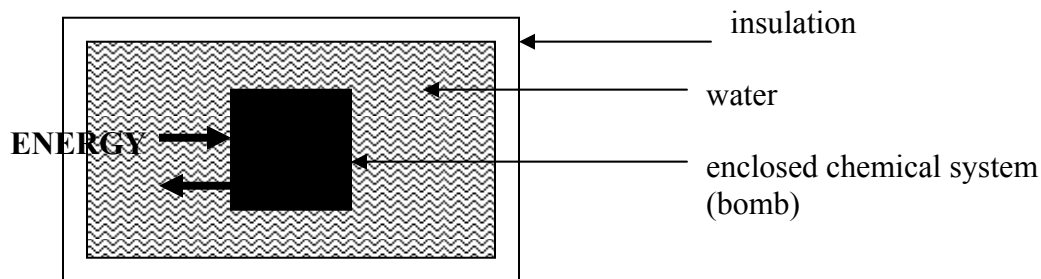
$$\Delta H_{\text{rxn}} = q$$

$$nH_{\text{rxn}} = mc\Delta t$$

\*\*\*rxn = any type of reaction eg) combustion, neutralization, formation etc.

- For chemical reactions like combustion a more complicated design must be used to handle the large amounts of heat produced from the reaction.
  - A typical calorimeter for combustion reactions is shown below.

### Bomb Calorimeter



- here's how it works:
  - reacting substances are placed in the bomb
  - bomb is placed in the calorimeter
  - initial temp of water is recorded
  - reaction is initiated
  - final (maximum) temp of water is recorded

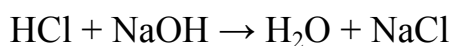
## Using Calorimetry to determine Enthalpy of Chemical Reactions

Common coffee cup calorimeters can be used to measure enthalpy for reactions that take place in aqueous solutions. We assume that the solution has the same density as water.

### 1. Neutralization reactions between acids and bases

#### Example:

150.0mL of 0.200mol/L HCl(aq) was added to 150.0mL of 0.200mol/L NaOH(aq) in a coffee cup calorimeter. Initial temperature of both solutions was 25.0°C. The final temperature was 27.1°C. Write a balanced chemical equation for the reaction and determine  $\Delta H$  (heat released) for the reaction.



150 mL of HCl + 150mL of NaOH = 300mL

(These are dilute situations so we assume same density as water)

Mass of H<sub>2</sub>O = 300g

$\Delta t = 27.1 - 25.0 = 2.1\text{oC}$

$$\begin{aligned} \text{Heat released (rxn)} &= \text{Heat absorbed (H}_2\text{O)} \\ \Delta H &= q = mc\Delta t \\ \Delta H &= (300.0\text{g})(4.19)(2.1) \\ \Delta H &= 2.6\text{kJ} \end{aligned}$$

### LAB: Calorimetry: Neutralization Reactions

**Combustion reactions produce too much heat to be done in a regular coffee cup calorimeter so they are done in a calorimeter that can handle the heat produced by the reaction.**

Example 1

A 2.65 g sample of methanol ( $\text{CH}_3\text{OH}$ ) was burned in a calorimeter which contained 500 mL of water at  $25.0^\circ\text{C}$ . If the final temperature of the water is  $50.0^\circ\text{C}$ , what is the molar heat of combustion for methanol?

$$\text{heat lost (combustion)} = \text{heat gained (water)}$$

Example 2

An 8.40 g sample of  $\text{N}_{2(\text{g})}$  is reacted with pure oxygen in a bomb calorimeter containing 1.00 kg of water to produce  $\text{N}_2\text{O}$ . The temperature of the water dropped by  $5.82^\circ\text{C}$ . What is the molar heat of formation of  $\text{N}_2\text{O}$ ?

(Hint: The combustion of  $\text{N}_2$  to form  $\text{N}_2\text{O}$  is also a formation reaction)

## Industrial Bomb Calorimeters

- industrial calorimeters are used in research to measure the heat of combustion of food, fuel, oil, crops, and explosives
- modern calorimeters have fixed components eg) volume of water used, container (bomb) material, stirrer and thermometer
- in calculating the energy of combustion, you take all components of the calorimeter into account:

$$E_{\text{total}} = \underline{mc}\Delta t (\text{H}_2\text{O}) + \underline{mc}\Delta t (\text{stirrer}) + \underline{mc}\Delta t (\text{thermometer}) + \underline{mc}\Delta t (\text{bomb})$$

- all of the “mc” parts are constant so they are replaced by one constant C, the heat capacity of the entire system in kJ/°C

### Example 1

A 1.50 g sample of methane is completely burned in a calorimeter with a heat capacity of 11.3 kJ/°C. The temperature increased from 20.15°C to 27.45°C. Calculate the molar enthalpy of combustion for methane.

$$\text{heat lost (combustion)} = \text{heat gained (calorimeter)}$$

### Example 2

When 3.00 g of butter is burned in a bomb calorimeter with a heat capacity of 9.22 kJ/°C the temperature changes from 19.62°C to 31.89°C. Calculate the specific enthalpy of combustion in **kJ/g**.

\*\*\*note that in this question we are asked for enthalpy of combustion in kJ/g not kJ/mol. We substitute mass in for moles in the formula  $\Delta H_{\text{comb}} = nH_{\text{comb}}$

$$\text{heat lost (combustion)} = \text{heat gained (calorimeter)}$$

## Metal Can Calorimeters

- Some calorimetry problems involve metal containers that absorb energy.
- In these cases you need to calculate the energy absorbed by the metal container as well.

Example:

In an aluminum calorimeter, 20.0g of nitrogen,  $N_{2(g)}$ , was burned in oxygen,  $O_{2(g)}$ , to produce nitrogen monoxide,  $NO_{(g)}$ . From the following data, find the enthalpy of reaction.

Data:

Mass of $N_2$ burned	- 20.0g
Mass of aluminum container	- 70.37g
Specific heat of Al	- 0.900 J/g °C
Volume of $H_2O$	- 500.0mL
Initial Temp.	- 72.60 oC
Final Temp.	- 12.80oC

$$\Delta H = \text{heat released}_{H_2O} + \text{heat released}_{Al}$$

## Reaction Enthalpies

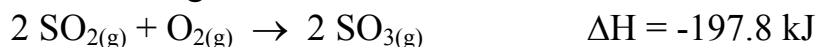
- The enthalpy change of a reaction refers to changes in  $E_p$  and is called the \_\_\_\_\_.
- This is the amount of heat released/absorbed by a chemical reaction
- the heat (enthalpy) of reaction,  $\Delta H$ , can be expressed in 4 ways:

### 1. Outside Equation

- the heat of reaction can be given as a  $\Delta H$  value outside of the equation  
eg)  $2 \text{SO}_{2(g)} + \text{O}_{2(g)} \rightarrow 2 \text{SO}_{3(g)} \quad \Delta H = -197.8 \text{ kJ}$

#### Example

Calculate the molar enthalpy of reaction (H) for sulphur dioxide ( $\text{SO}_{2(g)}$ ) using the following information:

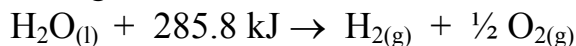


### 2. Inside Equation

- the heat of reaction can be written in the equation
- endothermic reaction...heat is on reactant side
- exothermic reaction...heat is on product side

#### Example

Calculate the molar enthalpy (H) for oxygen in the decomposition of water using the following information:



### 3. Molar Enthalpy, H

- use the formula  $\Delta H = nH$  to calculate H

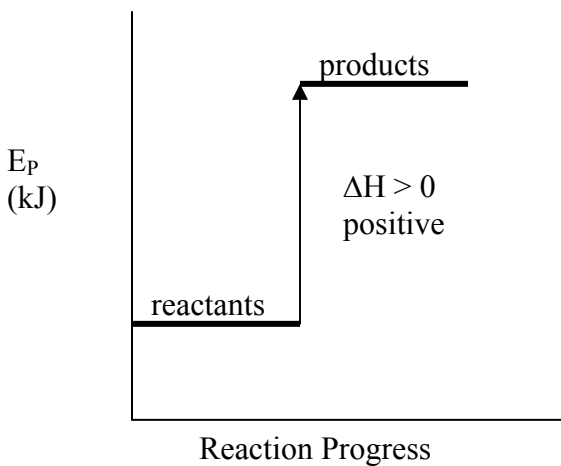
Example:

Find the molar enthalpy when 5.0 g of butane produces 850 kJ of energy.

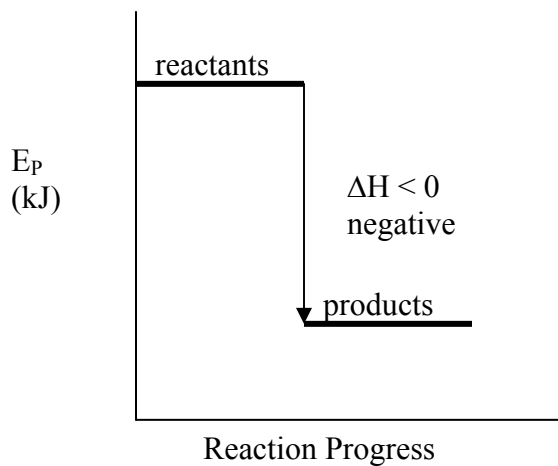
### 4. Potential Energy Diagram

- very similar to the  $E_p$  diagrams for phase changes...reactants are separated from the products
  - Endothermic – products have more energy than reactants
  - Exothermic – reactants have more energy than products

#### Endothermic



#### Exothermic



***Your Assignment: pg 319-320 #1-6***

## K. Predicting Enthalpy ( $\Delta H_r$ ) Changes for Reactions

### 1. Using Hess's Law

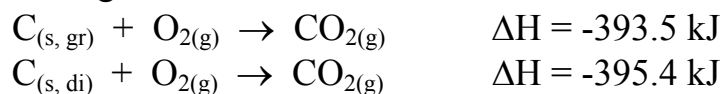
- because of the law of conservation of energy, the heat of reaction is the same whether the reactants are converted to the products in a single reaction or in a series of reactions
- G.H. Hess (1840) suggested that *if two or more thermochemical equations are added to give a final equation then the enthalpies can be added to give the enthalpy for the final equation*
- sometimes the heat of reaction for a chemical change is not easily measured due to time of reaction, cost, rarity of reactants etc. so we use Hess's Law to calculate  $\Delta H_r$

#### Steps:

1. Write the net reaction equation, if it is not given.
2. Manipulate the given equations so they will add to yield the net equation.
  - 
  -
3. Cancel the reactants and products where possible to simplify (you should end up with your net equation!)
4. Add the component enthalpy changes to get the net enthalpy change.
5. Determine molar enthalpy, if required.

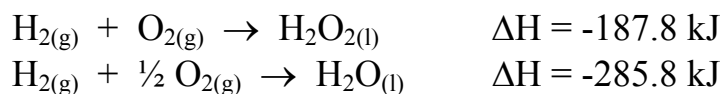
### Example 1

Find the heat of reaction and draw the  $E_P$  diagram for  $C_{(s, di)} \rightarrow C_{(s, gr)}$  using the following reactions:



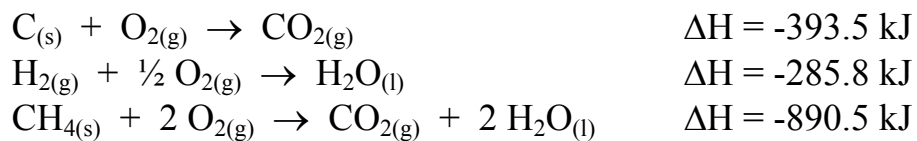
### Example 2

Find the heat of reaction for  $H_2O_{2(l)} \rightarrow H_2O_{(l)} + \frac{1}{2} O_{2(g)}$  using the following reactions:



### Example 3

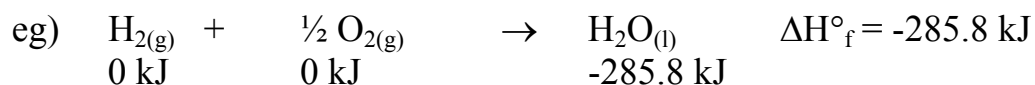
Find the heat of reaction for  $C_{(s)} + 2 H_{2(g)} \rightarrow CH_{4(g)}$  using the following reactions:



***Your Assignment: pg 323-324 #7-10***

## 2. Using Standard Heats of Formation $\Delta H_f^\circ$

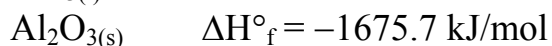
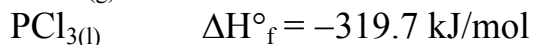
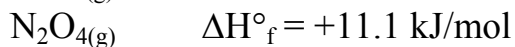
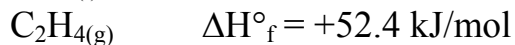
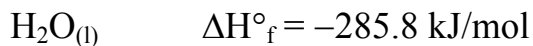
- sometimes it is not easy to measure the heat change for a reaction (too slow/expensive)
- in this case,  $\Delta H$  can be determined using heats of formation
- *heats of formation* ( $\Delta H_f$ ) are the changes in  $E_p$  that occur when compounds are formed from their elements
- $\Delta H_f$  for elements cannot be directly measured therefore they are designated as zero...all other  $\Delta H_f$  values are in reference to this
- Standard Molar Enthalpy –
  - A molar enthalpy determined when the initial and final conditions of the chemical system are SATP
  - Takes into account all the energy required to change the reaction system from SATP to initiate the reaction and all the energy released following reaction as it cools to SATP
  - Reported as  $H_r^\circ$  to indicate the standard molar enthalpy
  - Ex.  $H_r^\circ_{\text{CH}_3\text{OH}} = -239.1\text{kJ/mol}$
- $\Delta H_f^\circ$  for common compounds are listed on pages 6-7 in data booklet



### Compound Stability:

- the  $\Delta H^\circ_f$  is an indirect measure of the stability of a compound
- the more exothermic the formation, the more stable the compound (this means you have to add that energy to decompose it)

eg) List the following compounds in order from most stable to least stable.



### Formula:

- Hess's Law formula states that the  $\Delta H_r$  is the difference between the standard heats of formation of the reactants and the products

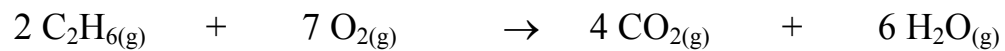
- This method is identical to Hess's Law except we are using only formation reactions for our reactions we are rearranging.

Example 1:

Calculate the standard heat of combustion for  $2 \text{CO}_{(g)} + \text{O}_{2(g)} \rightarrow 2 \text{CO}_{2(g)}$  and draw the  $E_p$  diagram for this reaction.

Example 2:

Find the molar heat of combustion of ethane.



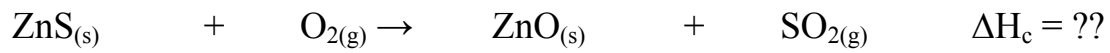
**Assignment** pg. 329 – 330 # 11-13

## Multi-step Energy Calculations:

- Energy calculations rarely involve only a single step calculation
- In practical situations, several energy calculations may be required
- These calculations may involve a combination of energy change definitions such as:
  - Heat flow –
    - $q = mc\Delta t$
  - Enthalpy changes -
    - $\Delta H = nH$
  - Hess's Law –
    - $\Delta H_{\text{net}} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \dots$
  - Using formation reactions
    - $\Delta H_r = \sum nH_{f(\text{prod})} - \sum nH_{f(\text{react.})}$

Example:

What quantity of energy can be obtained from the roasting (combustion) of 50.0kg of zinc sulfide ore?



**Step 1:** Determine  $\Delta H_c^\circ$  HOW??

$$\Delta H_c^\circ = \sum n H_{f(\text{products})}^\circ - \sum n H_{f(\text{reactants})}^\circ$$

**Step 2:** Determine  $H_c^\circ$  zinc sulfide

$$H_c^\circ = \Delta H_c^\circ / n$$

**Step 3:** Determine  $\Delta H_c^\circ$  for 50.0kg of zinc sulfide

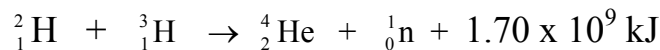
$$\underline{\Delta H_c^\circ = (m/M) H_c^\circ}$$

## M. Nuclear Change

- enthalpy changes in nuclear reactions are the result of  $E_p$  changes as rearrangements among the subatomic particles (protons and neutrons) occur ie) intranuclear forces
- there are two types of nuclear reactions:

### 1. Fusion (Joining)

- fusion of hydrogen to helium occurs on the sun and other stars
- these types of reaction produce the greatest amount of energy and are necessary for life on Earth
- require a great deal of heat and pressure

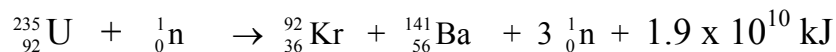


Top number = mass number (protons + neutrons)

Bottom number = number of protons

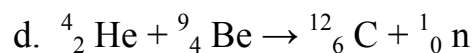
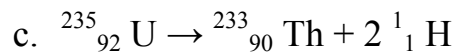
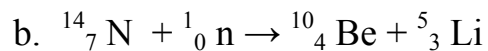
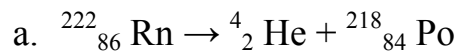
### 2. Fission (Splitting)

- basis for nuclear power plants
- uranium atoms can be split into two smaller nuclei which produces large quantities of energy
- was discovered in the late 1930's when uranium was bombarded by neutrons causing it to split



- the neutrons produced by fission allow a chain reaction to occur to keep the reaction self sustaining

1. Fission is a reaction in which a large nucleus breaks into smaller nuclei. Fusion is a reaction in which smaller nuclei combine to produce a larger nucleus. Identify fusion and fission reactions in the following four equations



## **L. Energy Systems in Biological Processes**

Photosynthesis:

Cellular Respiration:

\*\*Water vapor condenses into liquid

## **N. Society and Technological Connections**

- we must assess the risks and benefits of relying on fossil fuels and nuclear energy as energy sources
- we are limited by our scientific knowledge and by the technology that has been developed to date
- fossil fuels are the most common source of energy
- many aspects of our society are based on the price of fuels like gasoline (eg. impending war on Iraq)

### **Advantages vs. Disadvantages of Fossil Fuels**

<b><u>Advantages</u></b>	<b><u>Disadvantages</u></b>

### **Advantages vs. Disadvantages of Nuclear Power**

<b><u>Advantages</u></b>	<b><u>Disadvantages</u></b>