# Chapter 5 "Thermochemistry"

Section 17.1 The Flow of Energy – Heat and Work • OBJECTIVES:

 Explain how energy, heat, and work are related.



Section 17.1 The Flow of Energy – Heat and Work • OBJECTIVES:

 <u>Classify</u> processes as either exothermic or endothermic. Section 17.1 The Flow of Energy – Heat and Work • OBJECTIVES:

Identify the units used to measure heat transfer.



Section 17.1 The Flow of Energy – Heat and Work • OBJECTIVES: • Distinguish between heat

capacity and specific heat.

**Energy Transformations**  Thermochemistry - concerned with heat changes that occur during chemical reactions Energy - capacity for doing work or supplying heat weightless, odorless, tasteless if within the chemical substancescalled chemical potential energy

**Energy Transformations**  Gasoline contains a significant amount of chemical potential energy Heat - represented by "q", is energy that transfers from one object to another, because of a temperature difference between them.

- only changes can be detected!
- flows from warmer  $\rightarrow$  cooler object

Essentially all chemical reactions, and changes in physical state, involve either:

a) <u>release</u> of heat, or
b) <u>absorption</u> of heat

 In studying heat changes, think of defining these two parts:

- the <u>system</u> the part of the universe on which you focus your attention
- the <u>surroundings</u> includes everything else in the universe

 Together, the system and it's surroundings constitute the universe

 Thermochemistry is concerned with the flow of heat from the system to it's surroundings, and vice-versa.

 The Law of Conservation of Energy states that in any chemical or physical process, energy is neither created nor destroyed.

 All the energy is accounted for as work, stored energy, or heat.

Heat flowing into a system from it's surroundings:

- defined as positive
- q has a positive value
- called <u>endothermic</u>

-system gains heat as the surroundings cool down

 Heat flowing <u>out of</u> a system into it's surroundings:

- defined as negative
- q has a negative value
- called <u>exothermic</u>

-system *loses heat* as the surroundings heat up

Exothermic and Endothermic
 Fig. 17.2, page 506 - on the left, the system (the people) gain heat from it's surroundings (the fire)

this is endothermic

 On the right, the system (the body) cools as perspiration evaporates, and heat flows to the surroundings

• this is exothermic

**Exothermic and Endothermic**  Every reaction has an energy change associated with it \*\* Gummy Bear Sacrifice \*\* Exothermic reactions release energy, usually in the form of heat. Endothermic reactions absorb energy Energy is stored in bonds between atoms

## Units for Measuring Heat Flow

- A <u>calorie</u> is defined as the quantity of heat needed to raise the temperature of 1 g of pure water 1 °C.
  - Used except when referring to food
  - a <u>Calorie</u>, (written with a capital C), always refers to the energy in food
  - 1 Calorie = 1 kilocalorie = 1000 cal.

Units for Measuring Heat Flow
2) The calorie is also related to the <u>Joule</u>, the SI unit of heat and energy

- named after James Prescott Joule
- 4.184 J = 1 cal
- Heat Capacity the amount of heat needed to increase the temperature of an object exactly 1 °C
- Depends on both the object's mass and its chemical composition

Heat Capacity and Specific Heat **Specific Heat Capacity - the** amount of heat it takes to raise the temperature of 1 gram of the substance by 1 °C (abbreviated "C") often called simply "Specific Heat" Note Table 17.1, page 508 Water has a HUGE value, when it is compared to other chemicals

TABLE 17-1         Specific Heats of Some Common           Substances at 298.15 K	
Substance	Specific heat J/(g•K)
Water ( <i>l</i> )	(4.18) ←
Water (s)	2.06
Water (g)	1.87
Ammonia (g)	2.09
Benzene (l)	1.74
Ethanol ( <i>l</i> )	2.44
Ethanol (g)	1.42
Aluminum (s)	0.897
Calcium (s)	0.647
Carbon, graphite (s)	0.709
Copper (s)	0.385
Gold (s)	0.129
Iron (s)	0.449
Mercury ( <i>l</i> )	0.140
Lead (s)	0.129.

Heat Capacity and Specific Heat • For water, C = 4.18 J/(g °C), and also C = 1.00 cal/(g °C)Thus, for water: it takes a long time to heat up, and • it takes a long time to cool off! Water is used as a coolant! Note Figure 17.4, page 509

Heat Capacity and Specific Heat To calculate, use the formula:  $q = mass (g) \times \Delta T \times C$ heat is abbreviated as "q"  $\wedge \Delta T = change in temperature$ C = Specific Heat Units are either J/(g °C) or cal/(g °C)



Section 11.2 Measuring and Expressing Enthalpy Changes • OBJECTIVES:

 <u>Describe</u> how calorimeters are used to measure heat flow. Section 11.2 Measuring and Expressing Enthalpy Changes

<u>Construct</u>
 thermochemical
 equations.

Section 11.2 Measuring and Expressing Enthalpy Changes OBJECTIVES:

 <u>Solve</u> for enthalpy changes in chemical reactions by using heats of reaction.

## Calorimetry

 <u>Calorimetry</u> - the precise measurement of the heat into or out of a system for chemical and physical processes.

 The device used to measure the absorption or release of heat in chemical or physical processes is called a <u>Calorimeter</u>

## Calorimetry

 Foam cups are excellent heat insulators, and are commonly used as simple calorimeters

• Fig. 17.5, page 511

 For systems at constant pressure, the heat content is the same as a property called <u>Enthalpy (H)</u> of the system



A foam cup calorimeter – here, two cups are nestled together for better insulation

Calorimetry • Changes in enthalpy =  $\Delta H$  $\diamond q = \Delta H$  These terms will be used interchangeably in this textbook • Thus,  $q = \Delta H = m \times C \times \Delta T$  $\wedge \Delta H$  is negative for an exothermic reaction ♦ AH is positive for an endothermic reaction

## Calorimetry

 Calorimetry experiments can be performed at a constant volume using a device called a "bomb calorimeter" - a closed system Used by nutritionists to measure energy content of food



## SAMPLE PROBLEM 17.2 - Page 513

### Enthalpy Change in a Calorimetry Experiment

When 25.0 mL of water containing 0.025 mol HCl at 25.0°C is added to 25.0 mL of water containing 0.025 mol NaOH at 25.0°C in a foam cup calorimeter, a reaction occurs. Calculate the enthalpy change in kJ) during this reaction if the highest temperature observed is 32.0°C. Assume the densities of the solutions are 1.00 g/mL

#### Analyze List the knowns and the unknown.

#### Knowns

- $C_{water} = 4.18 \text{ J/}(\text{g}^{\circ}\text{C})$   $T_{i} = 25.0^{\circ}\text{C}$
- V<sub>final</sub> V<sub>HCl</sub> + V<sub>NaOH</sub>
- T<sub>f</sub> = 32.0°C
- 25.0 mL + 25.0 mL 50.0 mL Density<sub>solution</sub> 1.00 g/mL

### Unknown

• ΔH = ? kJ

Use dimensional analysis to determine the mass of the water. You must also calculate  $\Delta T$ . Use  $\Delta H = -q_{surr} = -m \times C \times \Delta T$  to solve for  $\Delta H$ .

### Calculate Solve for the unknown.

First, calculate the total mass of the water.

$$m = (50.0 \text{ part}) \times \left(\frac{1.00 \text{ g}}{\text{part}}\right) = 50.0 \text{ g}$$
Now calculate  $\Delta T$   

$$\Delta T = T_{\text{f}} = T_{\text{i}} = 32.0^{\circ}\text{C} = 25.0^{\circ}\text{C} = 7.0^{\circ}\text{C}$$
Use the values for  $m$ .  $G_{\text{partor}}$  and  $\Delta T$  to calculate  $\Delta H$ .  

$$\Delta H = -m \times C \times \Delta T = -(50.0 \text{ g})(4.18 \text{ J}/(\text{g} \times {}^{\circ}\text{E}))(7.0^{\circ}\text{E})$$

$$= -1463 \text{ J} = -1.5 \times 10^{2} \text{ J} = -1.5 \text{ kJ}$$



Exothermic The products are lower in energy than the reactants Thus, energy is released.  $\Delta H = -395 \text{ kJ}$  The negative sign does not mean negative energy, but instead that energy is lost.



Endothermic The products are higher in energy than the reactants Thus, energy is absorbed.  $\Delta H = +176 \text{ kJ}$  The positive sign means energy is absorbed

# Chemistry Happens in MOLES

 An equation that includes energy is called a <u>thermochemical equation</u>

◆  $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + 802.2 \text{ kJ}$ 

 1 mole of CH<sub>4</sub> releases 802.2 kJ of energy.

 When you make 802.2 kJ you also make 2 moles of water  A heat of reaction is the heat change for the equation, exactly as written

 The physical state of reactants and products <u>must</u> also be given.

 Standard conditions for the reaction is 101.3 kPa (1 atm.) and 25 °C (different from STP)

 $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + 802.2 \text{ kJ}$  If 10. 3 grams of CH₄ are burned completely, how much heat will be produced? 10.3 g CH<sub>4</sub>  $\begin{pmatrix} 1 \text{ mol CH}_4 \\ 16.05 \text{ g CH}_4 \end{pmatrix} \begin{pmatrix} 802.2 \text{ kJ} \\ 1 \text{ mol CH}_4 \end{pmatrix}$ = 514 kJ Thus,  $\Delta H = -514$  kJ for this reaction

## SAMPLE PROBLEM 17.3 - Page 516

### Using the Heat of Reaction to Calculate Enthalpy Change

Using the thermochemical equation in Figure 17.7b on page 515, calculate the amount of heat (in kJ) required to decompose 2.24 mol NaHCO<sub>3</sub>(s).

### Analyze List the knowns and the unknown.

•2.24 mol NaHCO<sub>2</sub>(s) decomposes

Unknown • ΔH = ? kJ

ΔH = 129 kJ (for 2 mol NaHCO<sub>3</sub>)

Use the thermochemical equation,

 $2\mathrm{NaHCO}_3(s) + 129 \text{ kJ} \longrightarrow \mathrm{Na}_2\mathrm{CO}_3(s) + \mathrm{H}_2\mathrm{O}(g) + \mathrm{CO}_2(g),$ 

to write a conversion factor relating kilojoules of heat and moles of NaHCO<sub>3</sub>. Then use the conversion factor to determine  $\Delta H$  for 2.24 mol NaHCO<sub>3</sub>.

### Calculate Solve for the unknown.

The thermochemical equation indicates that 129 kJ are needed to decompose 2 mol NaHCO<sub>3</sub>(s). Use this relationship to write the follow-ing conversion factor.





# Summary, so far...

Enthalpy The heat content a substance has at a given temperature and pressure Can't be measured directly because there is no set starting point The reactants start with a heat content The products end up with a heat content So we can measure how much enthalpy changes

Enthalpy Symbol is H • Change in enthalpy is  $\Delta H$  (delta H) If heat is *released*, the heat content of the products is *lower*  $\Delta H$  is negative (exothermic) If heat is absorbed, the heat content of the products is *higher*  $\Delta H$  is positive (endothermic)



## Reactants →

Energy



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Heat of Reaction The heat that is released or absorbed in a chemical reaction ◆ Equivalent to ∆H ◆ C + O<sub>2</sub>(g) → CO<sub>2</sub>(g) + 393.5 kJ ◆ C + O<sub>2</sub>(g) → CO<sub>2</sub>(g)  $\Delta H = -393.5 \text{ kJ}$  In thermochemical equation, it is important to indicate the physical state ◆  $H_2(g) + 1/2O_2(g) \rightarrow H_2O(g) \Delta H = -241.8 \text{ kJ}$ •  $H_2(g) + 1/2O_2(g) \rightarrow H_2O(I) \Delta H = -285.8 \text{ kJ}$ 

Heat of Combustion The heat from the reaction that completely burns 1 mole of a substance: ◆ C +  $O_2(g) \rightarrow CO_2(g) + 393.5 \text{ kJ}$ ◆ C + O<sub>2</sub>(g) → CO<sub>2</sub>(g)  $\Delta$ H = -393.5 kJ

# Note Table 17.2, page 517

# Section 17.3 Heat in Changes of State

## OBJECTIVES:

 <u>Classify</u> the enthalpy change that occurs when a substance melts, freezes, boils, condenses, or dissolves.

# Section 17.3 Heat in Changes of State

## OBJECTIVES:

 <u>Solve</u> for the enthalpy change that occurs when a substance melts, freezes, boils, condenses, or dissolves.

## Heat in Changes of State • Molar Heat of Fusion ( $\Delta H_{fus}$ ) – the heat absorbed by one mole of a substance in *melting* from a solid to a liquid $\mathbf{Q} = \mathbf{MASS} \times \Delta \mathbf{H}_{fus}$ (there is no temperature change) • Molar Heat of Solidification ( $\Delta H_{solid}$ ) = heat lost when one mole of liquid solidifies (or freezes) to a solid $\diamond$ q = mass x $\Delta H_{solid}$ (no temperature change)

Heat in Changes of State Heat absorbed by a melting solid is equal to heat lost when a liquid solidifies • Thus,  $\Delta H_{fus} = -\Delta H_{solid}$ Note Table 17.3, page 522

## SAMPLE PROBLEM 17.4 - Page 521

## Using the Heat of Fusion in Phase-Change Calculations

How many grams of ice at 0°C will melt if 2.25 kJ of heat are added?



$$H_2O(s) + 6.01 \text{ kJ} \longrightarrow H_2O(l)$$

to find the number of moles of ice that can be melted by the addition of 2.25 kJ of heat. Convert moles of ice to grams of ice.

### Calculate Solve for the unknown.

Express  $\Delta H_{fus}$  and the molar mass of ice as conversion factors.

 $\frac{1 \text{ mol ice}}{6.01 \text{ kJ}} \text{ and } \frac{18.0 \text{ g ice}}{1 \text{ mol ice}}$ Multiply the known enthalpy change (2.25 kJ) by the conversion factors  $m_{\text{ice}} = 2.25 \text{ kJ} \times \frac{1 \text{ mol ice}}{6.01 \text{ kJ}} \times \frac{18.0 \text{ g ice}}{1 \text{ mol ice}}$  = 6.74 g ice

# Heats of Vaporization and Condensation

When liquids absorb heat at their boiling points, they become vapors.
 Molar Heat of Vaporization (ΔH<sub>vap</sub>) = the amount of heat necessary to vaporize one mole of a given liquid.
 q = mass x ΔH<sub>vap</sub> (no temperature change)
 Table 17.3, page 522

# Heats of Vaporization and Condensation

- Condensation is the opposite of vaporization.
- Molar Heat of Condensation (ΔH<sub>cond</sub>)
   = amount of heat released when one mole of vapor condenses to a liquid

$$\Delta H_{vap} = - \Delta H_{cond}$$

Heats of Vaporization and Condensation Note Figure 17.10, page 523 The large values for water  $\Delta H_{vap}$  and  $\Delta H_{cond}$  are the reason hot vapors such as steam is very dangerous

 You can receive a scalding burn from steam when the heat of condensation is released!

 $H_2O_{(g)} \rightarrow H_2O_{(I)} \quad \Delta H_{cond} = -40.7 \text{kJ/mol}$ 

## SAMPLE PROBLEM 17.5 -Page 524

#### Using the Heat of Vaporization in Phase-Change Calculations

How much heat (in kJ) is absorbed when 24.8 g  $H_2O(l)$  at 100°C and 101.3 kPa is converted to steam at 100°C?

### Analyze List the knowns and the unknown.

• Initial and final conditions are  $100^{\circ}$ C •  $\Delta H = ? kJ$ and 101.3 kPa

mass of water converted to steam = 24.8 g

ΔH<sub>vap</sub> = 40.7 kJ/mol

Refer to the following thermochemical equation.

 $H_2O(l) + 40.7 \text{ kJ/mol} \longrightarrow H_2O(g)$ 

 $\Delta H_{vap}$  is given in kJ/mol, but the quantity of water is given in grams. You must first convert grams of water to moles of water. Then multiply by  $\Delta H_{vap}$ .

#### Calculate Solve for the unknown.

 $= 56.1 \, \text{kJ}$ 

The required conversion factors come from  $\Delta H_{vap}$  and the molar mass of water.

 $\frac{1 \mod H_2O(l)}{18.0 \ g \ H_2O(l)}$  and  $\frac{40.7 \ kJ}{1 \mod H_2O(l)}$ 

 $\Delta H = 24.8 \text{ g.H}_2\Theta(t) \times \frac{1 \text{ mol H}_2\Theta(t)}{18.0 \text{ g.H}_2\Theta(t)} \times \frac{40.7 \text{ kJ}}{1 \text{ mol H}_2\Theta(t)}$ 

Multiply the mass of water in grams by the conversion factors.

## Heat of Solution Heat changes can also occur when a solute dissolves in a solvent. • Molar Heat of Solution ( $\Delta H_{soln}$ ) = heat change caused by dissolution of one mole of substance Sodium hydroxide provides a good example of an exothermic molar heat of solution:

Heat of Solution NaOH<sub>(s)</sub>  $\xrightarrow{H_2O_{(l)}}$  Na<sup>1+</sup><sub>(aq)</sub> + OH<sup>1-</sup><sub>(aq)</sub>  $\Delta H_{soln} = -445.1 \text{ kJ/mol}$ The heat is released as the ions separate (by dissolving) and interact with water, releasing 445.1 kJ of heat as  $\Delta H_{soln}$  -thus becoming so hot it steams!

## SAMPLE PROBLEM 17.6 - Page 526

## **Calculating the Heat Change in Solution Formation**

How much heat (in kJ) is released when 2.500 mol NaOH(s) is dissolved in water?

Unknown

 $\bullet \Delta H = ? kI$ 

= -1113 kJ

Analyze List the knowns and the unknown.

## Knowns

- $\bullet \Delta H_{soln} = -445.1 \text{ kJ/mol}$
- amount of NaOH(s) dissolved = 2.500 mol

Use the heat of solution from the following chemical equation to solve for the amount of heat released ( $\Delta H$ ).

 $NaOH(s) \xrightarrow{H_2O(2)} Na^+(aq) + OH^-(aq) + 445.1 \text{ kJ/mol}$ 

## Calculate Solve for the unknown.

Multiply the number of moles of NaOH by  $\Delta H_{sol}$ 

$$\Delta H = 2.500 \text{ mol NaOH(3)} \times \frac{-445.1}{1 \text{ mol NaO}}$$

Section 17.4 Calculating Heats of Reaction
OBJECTIVES:

 <u>State</u> Hess's law of heat summation and <u>describe</u> how it is used in chemistry. Section 17.4 Calculating Heats of Reaction
OBJECTIVES:

 <u>Solve</u> for enthalpy changes by using Hess's law or standard heats of formation.

## Hess's Law



 If you <u>add two or more</u> thermochemical equations to give a final equation, then you can also add the heats of reaction to give the final heat of reaction. Called <u>Hess's law of heat</u> summation Example shown on page 528 for graphite and diamonds

## How Does It Work? If you turn an equation around, you change 1) the sign: If $H_2(g) + 1/2 O_2(g) \rightarrow H_2O(g) \Delta H = -285.5 \text{ kJ}$ then, $H_2O(g) \rightarrow H_2(g) + 1/2 O_2(g) \Delta H = +285.5 \text{ kJ}$ also, 2) If you multiply the equation by a number, you multiply the heat by that number: $2 H_2O(g) \rightarrow 2 H_2(g) + O_2(g) \Delta H = +571.0 \text{ kJ}$ 3) Or, you can just leave the equation "as is"

Hess's Law - Procedure Options: 1. Use the equation as written 2. Reverse the equation (and change heat sign + to -, etc.) 3. Increase the coefficients in the equation (and increase heat by same amount) Note sample from page 529

## **Standard Heats of Formation** $\bullet$ The $\Delta H$ for a reaction that produces 1 mol of a compound from its elements at standard conditions Standard conditions: 25°C and 1 atm. • Symbol is $\Delta H$ The standard heat of formation of an element in it's standard state is arbitrarily set at "0" This includes the diatomics

**Standard Heats of Formation**  Table 17.4, page 530 has standard heats of formation The heat of a reaction can be calculated by: subtracting the heats of formation of the reactants from the products  $\Delta H^{o} = (\Delta H_{f}^{0} \text{ Products}) - (\Delta H_{f}^{0} \text{ Reactants})$ 

## SAMPLE PROBLEM 17.7 - Page 531

#### Calculating the Standard Heat of Reaction

What is the standard heat of reaction  $(\Delta H^0)$  for the reaction of CO(g) with O<sub>2</sub>(g) to form CO<sub>2</sub>(g)?

#### Analyze List the knowns and the unknown.

#### Knowns

(from Table 17.4)



- $\Delta H_f^0 O_2(g) = 0$  kJ/mol (free element)
- ΔH<sub>f</sub><sup>0</sup>CO(g) = -110.5 kJ/mol
- ΔH<sub>f</sub><sup>0</sup>CO<sub>2</sub>(g) = -393.5 kJ/mol

Balance the equation of the reaction of CO(g) with  $O_2(g)$  to form  $CO_2(g)$ . Then determine  $\Delta H^0$  using the standard heats of formation of the reactants and products.

#### Calculate Solve for the unknown.

First, write the balanced equation.

$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$$

Next, find and add the  $\Delta H_{f}^{0}$  of all of the reactants, taking into account the number of moles of each.

$$\Delta H_{f}^{0}(\text{reactants}) = 2 \mod \Theta(g) = \frac{-110.5 \text{ kJ}}{1 \mod \Theta(g)} + 0 \text{ kJ}$$

Then, find the  $\Delta H_f^0$  of the product in a similar way.



**Another Example**  $\bullet \operatorname{CH}_4(g) + 2\operatorname{O}_2(g) \to \operatorname{CO}_2(g) + 2\operatorname{H}_2\operatorname{O}(g)$  $\Delta H_{f}^{0} CH_{4}(g) = -74.86 \text{ kJ/mol}$  $\Delta H_{f}^{0} O_{2}(g) = 0 \text{ kJ/mol}$  $\Delta H_{f}^{0}$  CO<sub>2</sub>(g) = - 393.5 kJ/mol  $\Delta H_{f}^{0}$  H<sub>2</sub>O(g) = - 241.8 kJ/mol ΔH= - 802.4 kJ

# **End of Chapter 17**