

# Unit 13: Thermochemistry

Chapter 17

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# Section 17.1 – The Flow of Energy

- Thermodynamics is the study of energy and its transformations.
- Energy is the ability to do work or transfer heat.
- Work is the energy used to cause an object with mass to move against a force.
- Heat is the energy used to cause the temperature of an object to increase.



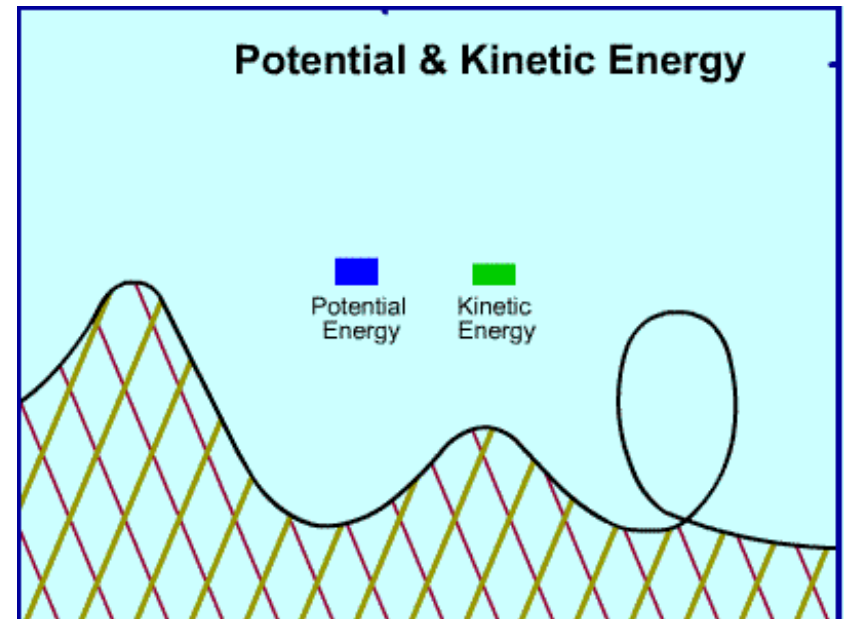
# Kinetic and Potential Energy

● Kinetic energy is the energy of motion.

$$KE = \frac{1}{2}mv^2$$

● Potential energy is the energy that an object possesses due to its position.

$$PE = mgh$$



# Electrostatic Potential Energy

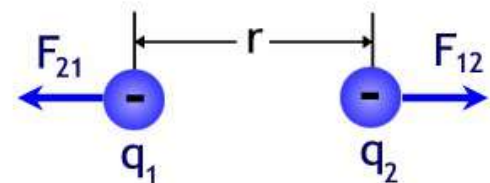
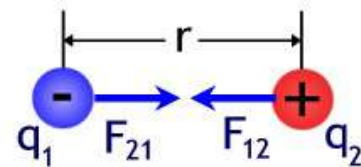
- Electrostatic potential energy arises from the interactions between charged particles.

$$E_{el} = \frac{\kappa Q_1 Q_2}{d}$$

- $\kappa = 8.99 \times 10^9 \text{ J}\cdot\text{m}/\text{C}^2$

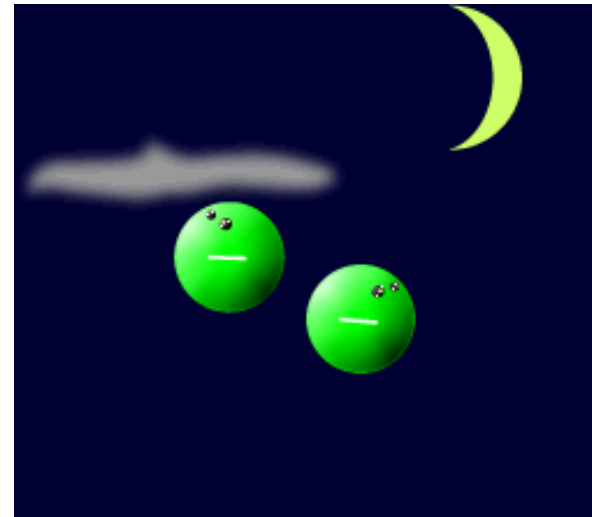
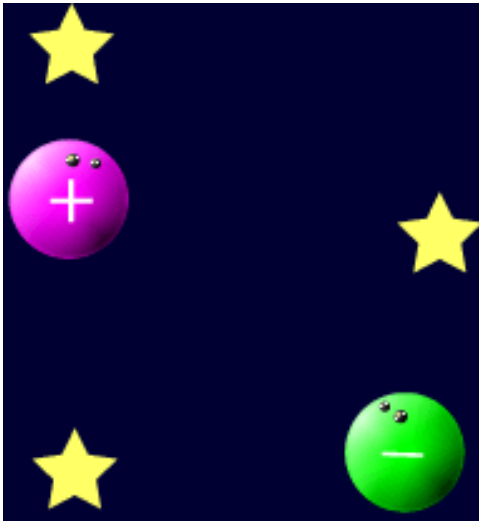
- $Q_1$  and  $Q_2 =$  a multiple of  $1.60 \times 10^{-19} \text{ C}$  (the charge of an electron)

- $d =$  distance (m)



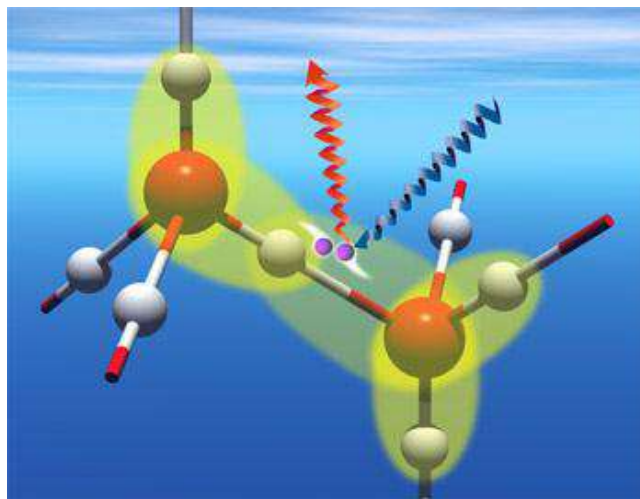
# Electrostatic Potential Energy

- If  $Q_1$  and  $Q_2$  have the same charge, then  $E_{el}$  is positive and the charges repel.
- If  $Q_1$  and  $Q_2$  have opposite charges, then  $E_{el}$  is negative and the charges attract.
- $E_{el}$  decreases with increasing distance.



# Chemical Energy

- Chemical energy is due to the potential energy stored in the arrangement of atoms.
- Thermal energy is the energy a substance possesses due to its temperature.
- Chemical energy and thermal energy are both important in chemical reactions.



# Unit of Energy

● A calorie is the quantity of heat that raises the temperature of 1 gram of pure water 1°C.

● The SI unit for energy is the joule (J).

$$1\text{J} = 1\text{kg}\cdot\text{m}^2/\text{s}^2$$

● A calorie is another unit for energy.

$$1\text{cal} = 4.184\text{J}$$

● A Calorie (nutrition) is used in the food industry.

$$1\text{Cal} = 1000\text{cal}$$

<b>Nutrition Facts</b>	
Serving Size 172 g	
Amount Per Serving	
<b>Calories</b> 200	Calories from Fat 8
% Daily Value*	
<b>Total Fat</b> 1g	1%
Saturated Fat 0g	1%
Trans Fat	
<b>Cholesterol</b> 0mg	0%
<b>Sodium</b> 7mg	0%
<b>Total Carbohydrate</b> 36g	12%
Dietary Fiber 11g	45%
Sugars 6g	
<b>Protein</b> 13g	
Vitamin A 1%	Vitamin C 1%
Calcium 4%	Iron 24%
*Percent Daily Values are based on a 2,000 calorie diet. Your daily values may be higher or lower depending on your calorie needs.	
NutritionData.com	

# Practice Problems

Make the following conversions.

1. 444 calories to Joules

2. 850 Joules to calories



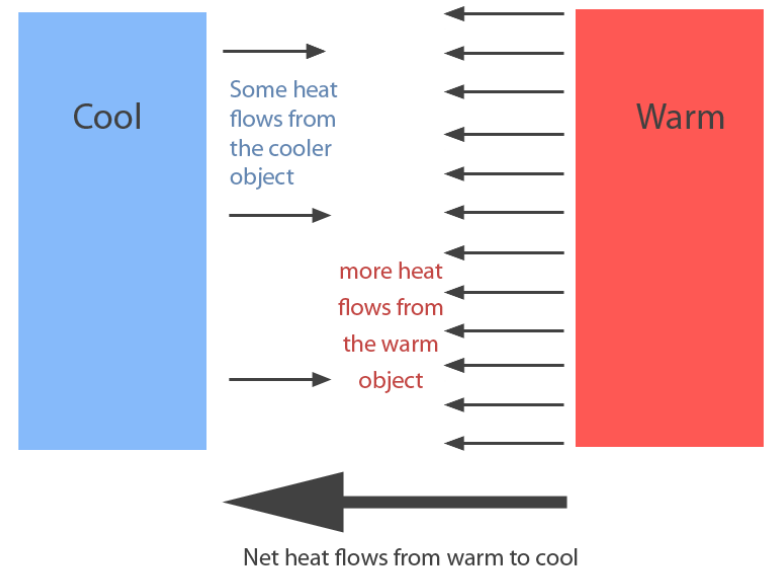
# Work and Heat

- Work is energy used to move an object against a force.

$$W = F \times d$$

- Heat is energy transferred from a hotter object to a colder one.

A cooler body can reduce net heat loss from a warmer one



# Sample Exercise

- A bowler lifts a 5.4kg (12 lb.) bowling ball from ground level to a height of 1.6m (5.2 feet) and then drops the ball back to the ground.
  - a. What happens to the potential energy of the bowling ball as it is raised from the ground?
  
  
  
  
  
  
  
  
  
  
  - b. What quantity of work, in J, is used to raise the ball?  
(Note:  $F = m \times g$ )

## Sample Exercise con't

c. After the ball is dropped, it gains kinetic energy. If we assume that all the work done in part b has been converted to kinetic energy by the time the ball strikes the ground, what is the speed of the ball at the instant just before it hits the ground? (Note:  $g = 9.8 \text{ m/s}^2$ )

# Practice Exercise

- What is the kinetic energy, in J, of
- a. an Ar atom moving with a speed of 650 m/s? (1 amu =  $1.66 \times 10^{-24}$  g)
- b. a mole of Ar atoms moving with a speed of 650 m/s?

# The Great Debate

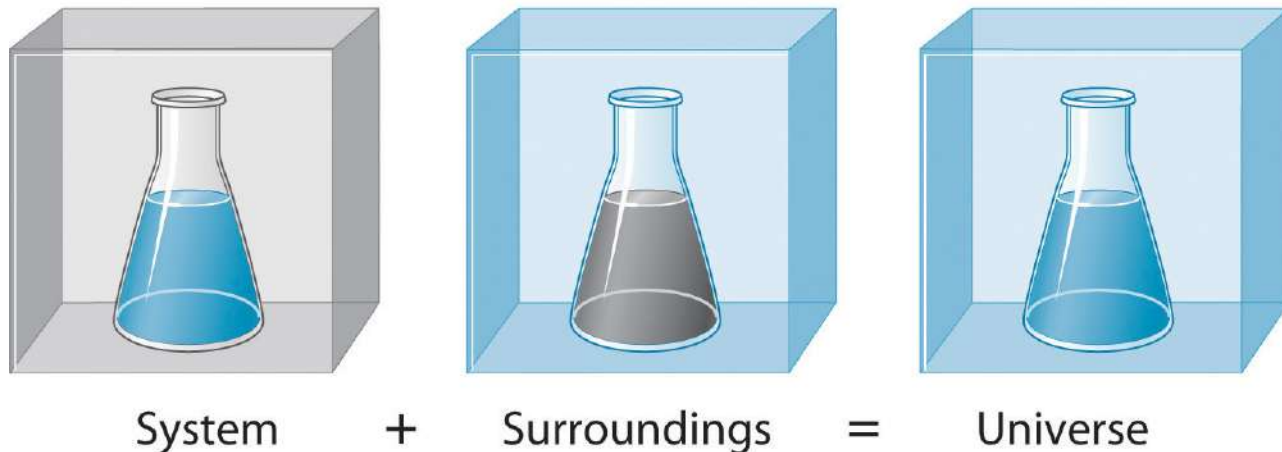
1. Exothermic reactions lose heat.
2. Endothermic reactions absorb heat.

# Exothermic and Endothermic

- Thermochemistry is concerned with the flow of heat between a chemical system (reaction) and its surroundings.
- A system is the specific part of the universe on which you focus your attention.
- The surroundings include everything outside the system.
- The system and the surroundings constitute the universe.

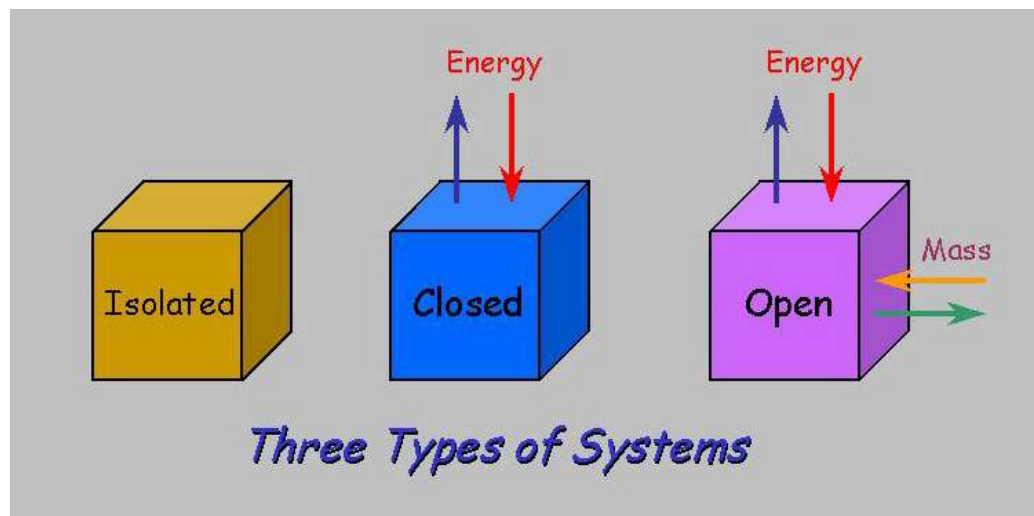
# System vs. Surroundings

- The system is the part of the universe in which we focus our attention (the reaction).
- The surrounding are anything that is not the system (the beaker, our hands, a solvent, a thermometer, etc.)



# Systems

- An open system is one in which matter and energy can be exchanged with the surroundings.
- A closed system can exchange energy but not matter with its surroundings.
- An isolated system does not exchange energy or matter with the surroundings.



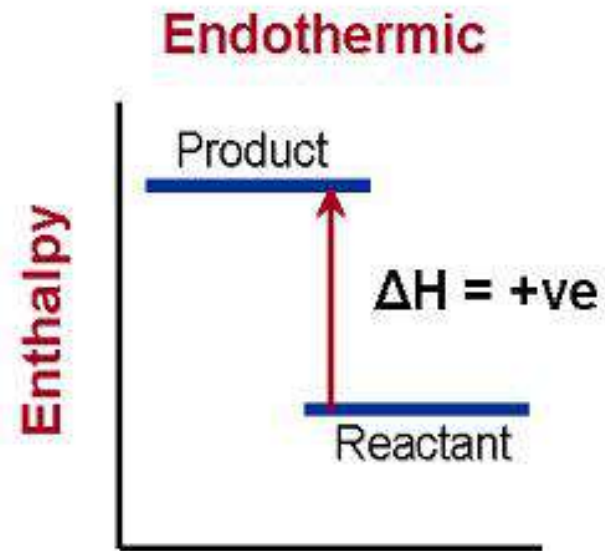
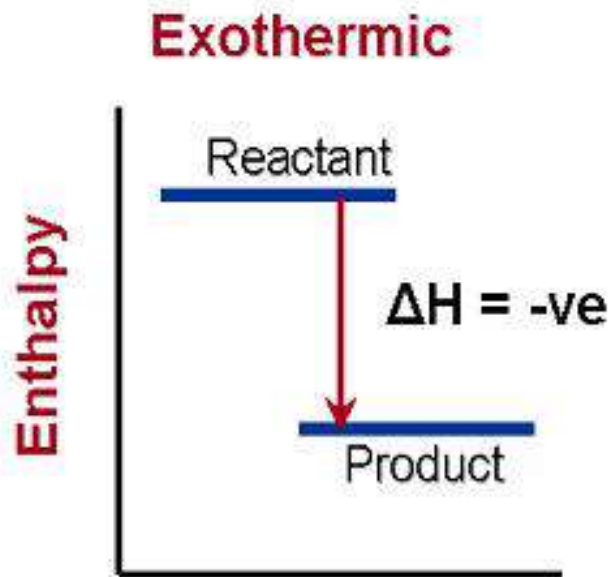


# Exothermic and Endothermic

- In thermochemical calculations the direction of the heat flow is given from the point of view of the system.
- A process that absorbs heat from the surroundings is called an endothermic process.
- A process that loses heat to the surroundings is called an exothermic process.



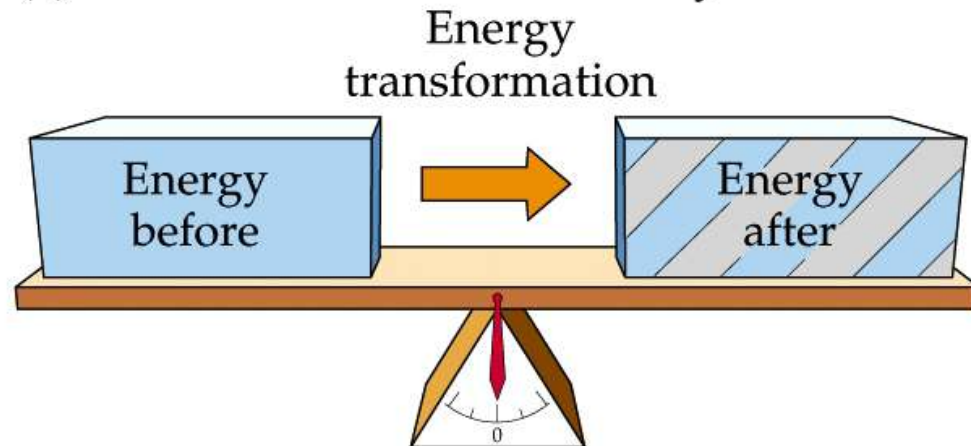
# Exothermic and Endothermic



# The First Law of Thermodynamics

- The first law of thermodynamics states that energy is conserved.
- Energy can transform from one form to another and can move to different places, but the overall energy must remain constant.

(a) The First Law of Thermodynamics



# Internal Energy

- The internal energy ( $E$ ) of a system is the sum of all the kinetic and potential energy of all of its components.
- Calculating  $E$  is difficult, but calculating  $\Delta E$  is easier and more useful.

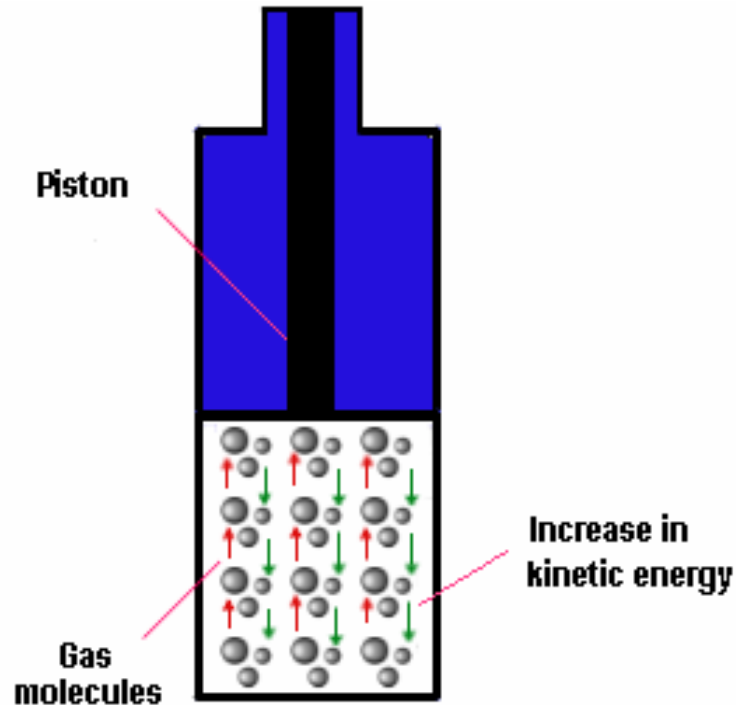
$$\Delta E = E_f - E_i$$

- If  $\Delta E$  is positive, then the system has gained energy.
- If  $\Delta E$  is negative, then the system has lost energy.

$\Delta E$

$$\Delta E = q + w$$

● When heat is added to a system or work is done on a system, its internal energy increases.



# Sample Exercise

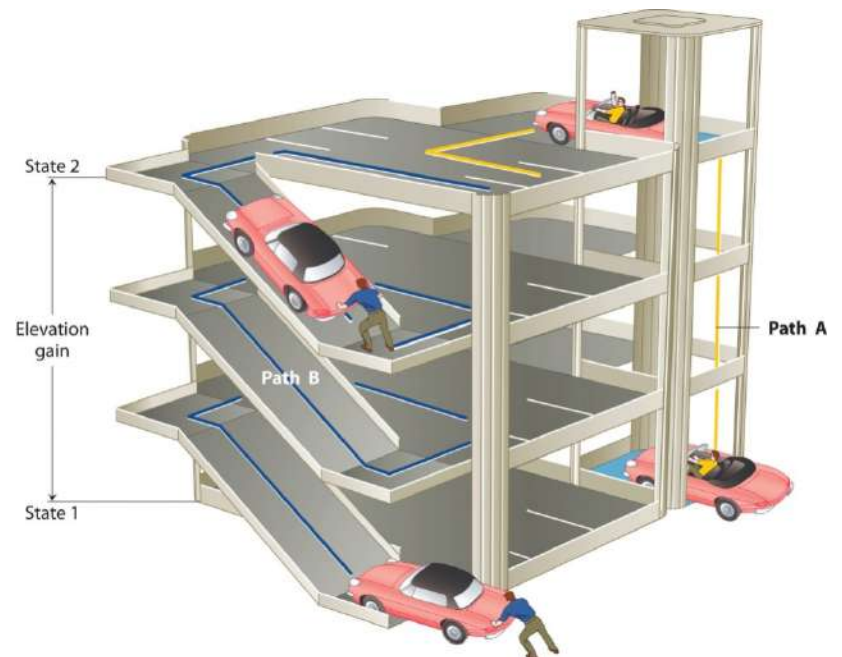
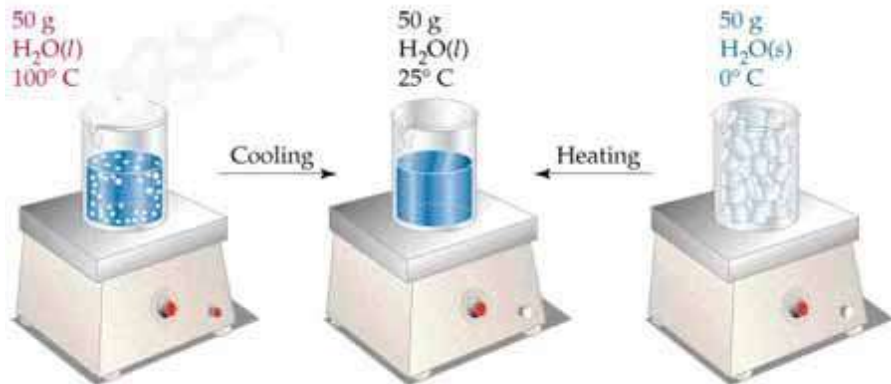
- Two gases,  $A_{(g)}$  and  $B_{(g)}$ , are confined in a cylinder-and-piston arrangement like that in Figure 5.3. Substances A and B react to form a solid product:  $A_{(g)} + B_{(g)} \rightarrow C_{(s)}$ . As the reaction occurs, the system loses 1150J of heat to the surroundings. The piston moves downward as the gases react to form a solid. As the volume of the gas decreases under the constant pressure of the atmosphere, the surroundings do 480J of work on the system. What is the change in the internal energy of the system?

# Practice Exercise

- Calculate the change in the internal energy of the system for a process in which the system absorbs 140J of heat from the surroundings and does 85J of work on the surroundings.

# State Function

- A state function is a property of a system that is determined by a system's present state and not affected by the path taken to get there.
- $\Delta E$  is a state function. (Ex: 50g of hot water cooling to 25°C vs. 50g of ice warming to 25°C)





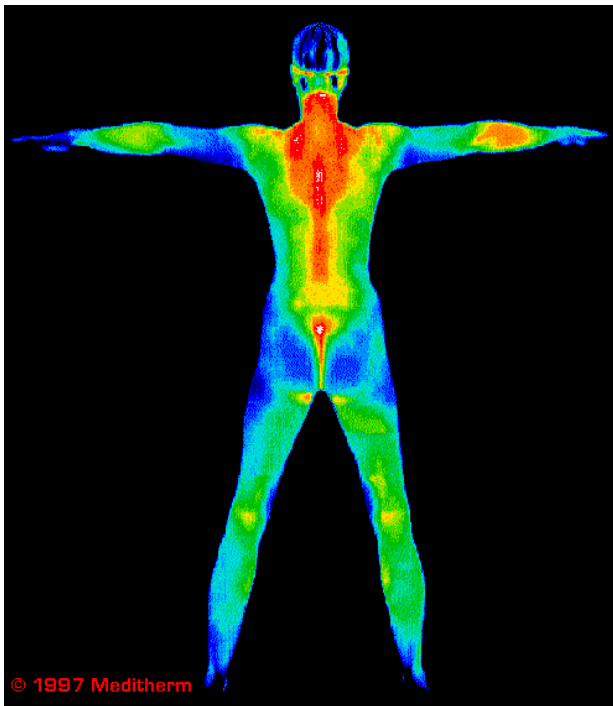
# Energy



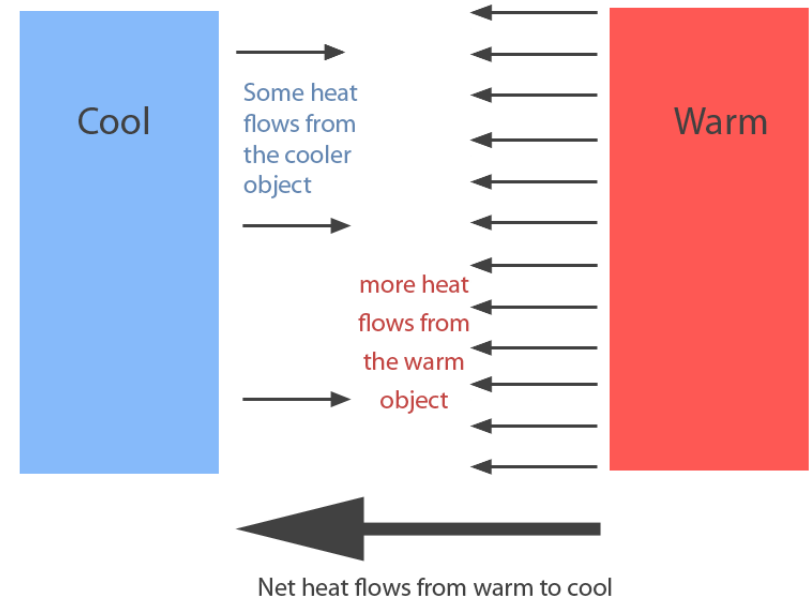
- Energy is the capacity to do work or supply heat.
- Energy has no mass or volume.
- Chemical potential energy is energy stored in chemicals.
- The kinds of atoms and the arrangement of the atoms in a substance determine the amount of energy stored in the substance.

# Heat

- Heat is a form of energy that always flows from a warmer object to a cooler object.
- Heat is represented by  $q$ .

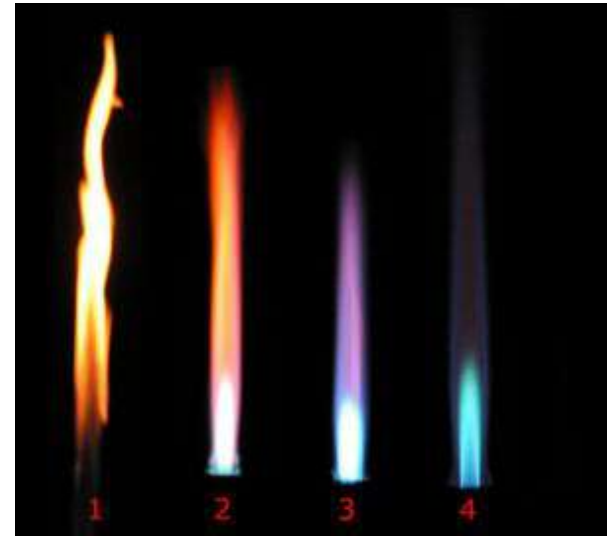


A cooler body can reduce net heat loss from a warmer one



# Thermochemistry

- Thermochemistry is the study of the heat changes that occur during chemical reactions and physical changes of state.
- The law of conservation of energy states that in any chemical or physical process, energy is neither created nor destroyed.



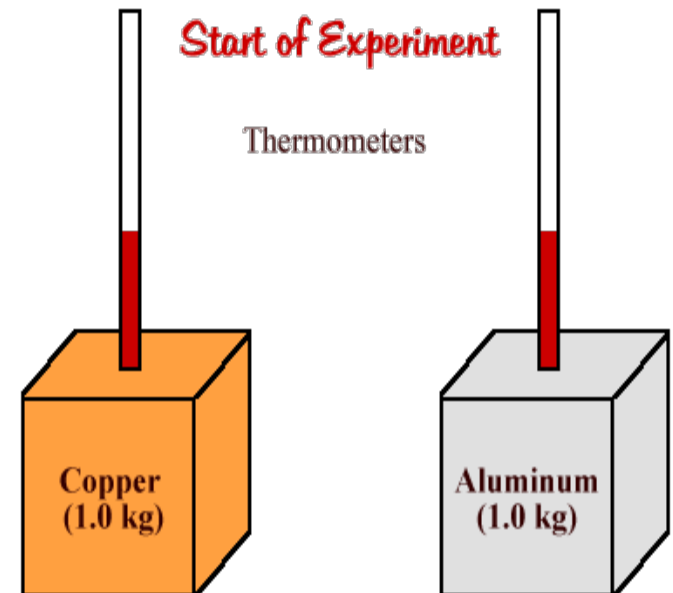
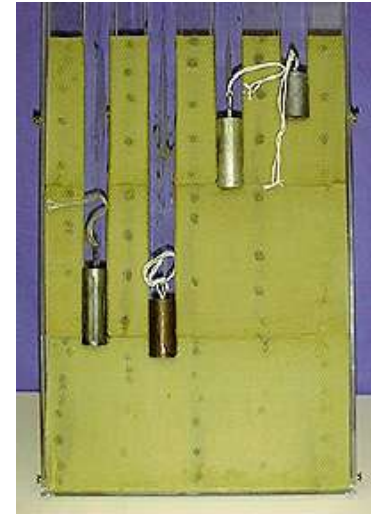
# Heat Capacity

- The heat capacity of an object is the amount of heat it takes to change an object's temperature by exactly  $1^{\circ}\text{C}$ .
- The greater the mass of an object, the greater the heat capacity.
- The heat capacity of an object also depends on its chemical composition.



# Specific Heat

- The specific heat capacity of a substance is the amount of heat it takes to raise the temperature of 1 gram of the substance  $1^{\circ}\text{C}$ .
- Specific heat is represented by  $C$ .
- The units of specific heat are  $\text{J}/\text{g}^{\circ}\text{C}$ .
- Water has a higher specific heat than most substances.



# Heat

Heat = mass x specific heat x change in temp

$$q = m \cdot C \cdot \Delta T$$

Mass is in grams

Specific heat is in  $\text{J/g}^\circ\text{C}$

Change in temp is in  $^\circ\text{C}$



## Sample Problem

- The temperature of a 95.4g piece of copper increases from 25°C to 48°C when the copper absorbs 849J of heat. What is the specific heat of copper?

## Practice Problems

1. When 435J of heat is added to 3.4g of olive oil at 21°C, the temperature increases to 85°C. What is the specific heat of the olive oil?



## Practice Problems

2. How much heat is required to raise the temperature of 250g of mercury 52°C? (specific heat of mercury = 0.14 J/g°C)

## Section 17.1 Assessment

1. In what direction does heat flow between two objects?
2. How do endothermic processes differ from exothermic processes?
3. On what factors does the heat capacity of an object depend?
4. How many kilojoules of heat are absorbed when 1000g of water is heated from 18°C to 85°C?  
(specific heat of water = 4.184 J/g°C)

## Section 17.1 Assessment

5. Using calories, calculate how much heat 32.0g of water absorbs when it is heated from 25°C to 80°C. How many joules is this? (specific heat of water = 4.184 J/g°C)

## Section 17.1 Assessment

6. How much heat is needed to warm 250g of water (about 1 cup) from 22°C (about room temperature) to near its boiling point, 98°C? The specific heat of water is 4.18 J/gK

What is the molar heat capacity of water?

## Section 17.1 Assessment

7. Large beds of rock are used in some solar-heated homes to store heat. Assume that the specific heat of the rocks is  $0.82 \text{ J/g}\cdot\text{K}$ . Calculate the quantity of heat absorbed by  $50.0\text{kg}$  of rocks if their temperature increases by  $12.0^\circ\text{C}$ .

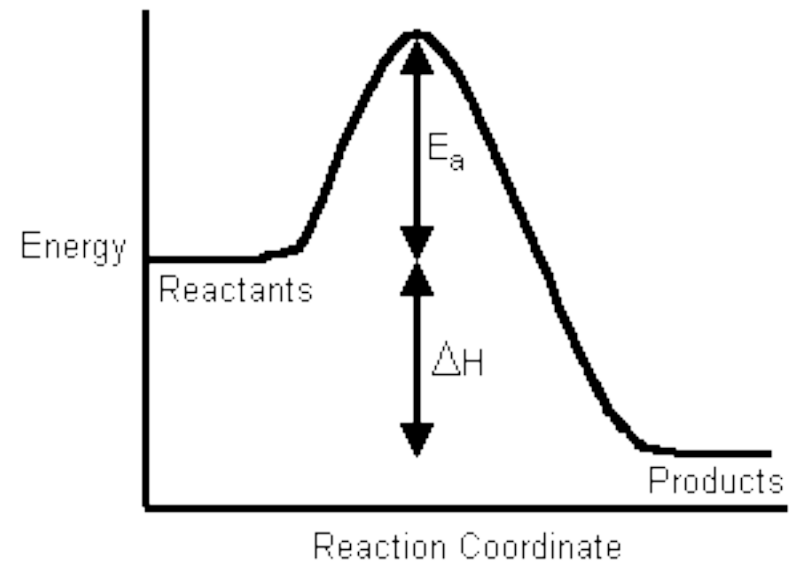
What temperature change would these rocks undergo if they emitted  $450\text{kJ}$  of heat?

## Section 17.2 – Measuring and Expressing Enthalpy Changes

- Calorimetry is the accurate and precise measurement of heat change for chemical and physical processes.
- Calorimeters are devices used to measure the amount of heat absorbed or released during chemical and physical processes.
- Enthalpy is the heat content of a system at constant pressure.
- Enthalpy is represented by  $H$ .

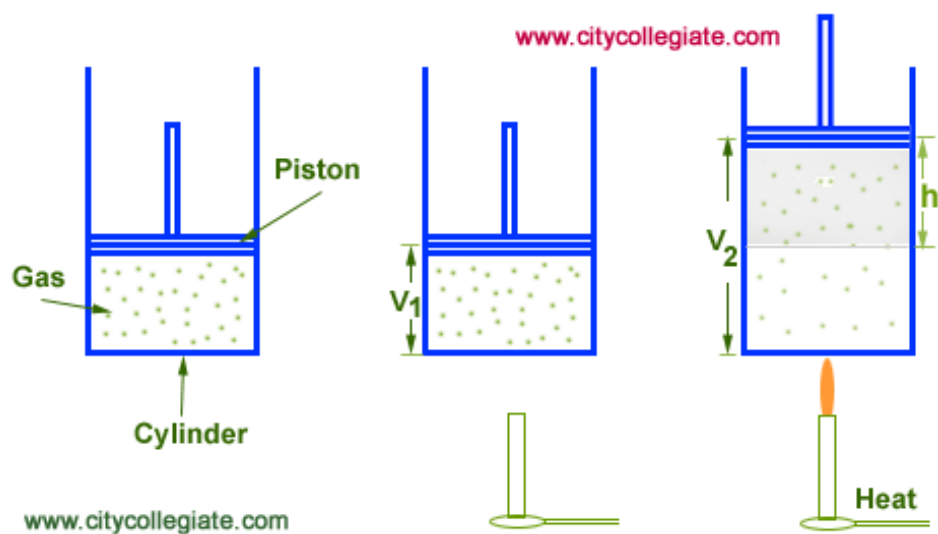
# $\Delta H$

- Enthalpy is an extensive property which means that it depends on the amount of substance.
- The enthalpy change for a reaction is equal in magnitude, but opposite in sign, to  $\Delta H$  for the reverse reaction.
- The enthalpy change for a reaction depends on the state of the reactants and products.



# Enthalpy

- The work done by a chemical reaction consists of a volume change in the system.
- The work involved in the expansion or compression of gases is called pressure-volume work.
- Enthalpy is the heat flow of a system at constant pressure.





# Sample Exercise

● Indicate the sign of the enthalpy change,  $\Delta H$ , in each of the following processes carried out under atmospheric pressure, and indicate whether the process is endothermic or exothermic:

a. An ice cube melts

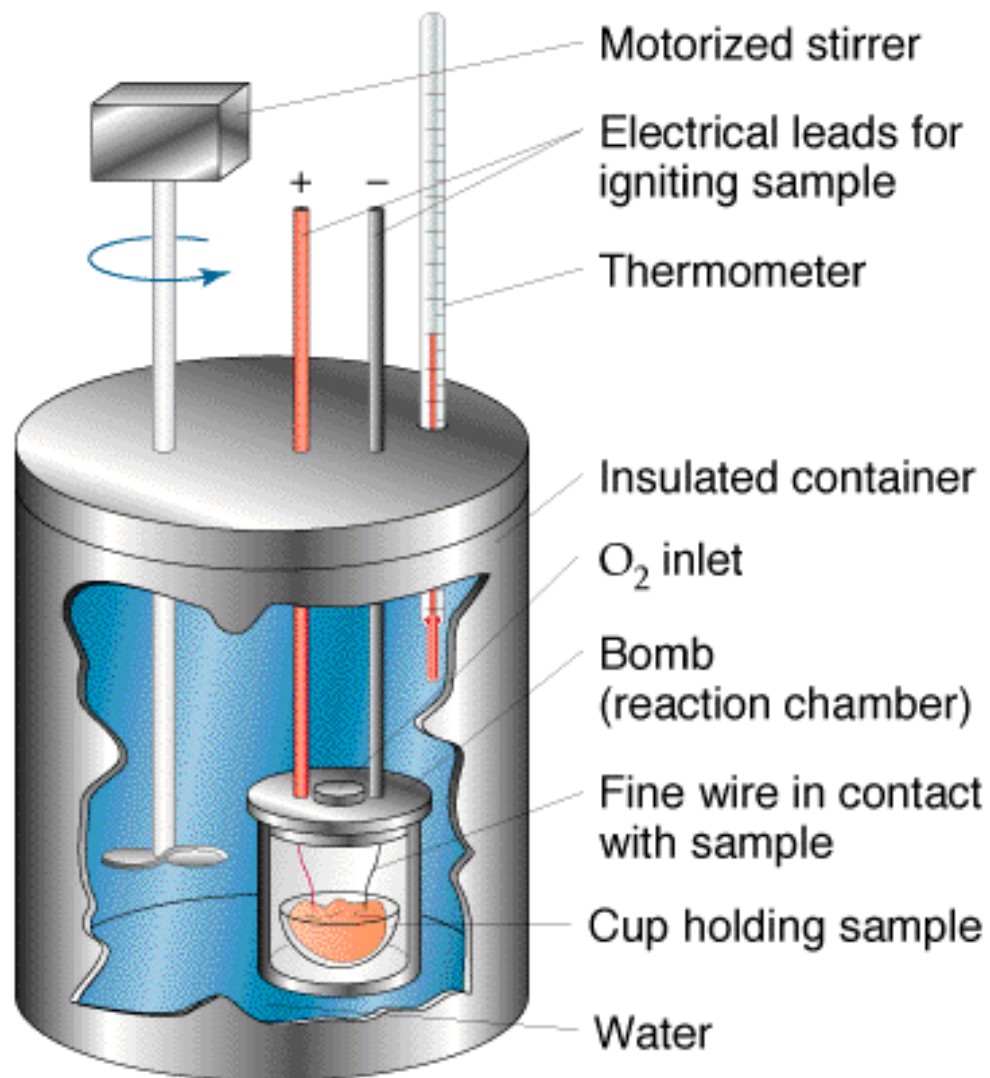
b. 1g of butane ( $C_4H_{10}$ ) is combusted in sufficient oxygen to give complete combustion to  $CO_2$  and  $H_2O$ .

# Practice Exercise

- Suppose we confine 1g of butane and sufficient oxygen to completely combust it in a cylinder with a piston. The cylinder is perfectly insulating, so no heat can escape to the surroundings. A spark initiates combustion of the butane, which forms carbon dioxide and water vapor. If we used this apparatus to measure the enthalpy change in the reaction, would the piston rise, fall, or stay the same?

# Calorimeter

$$q = \Delta H = m \cdot C \cdot \Delta T$$

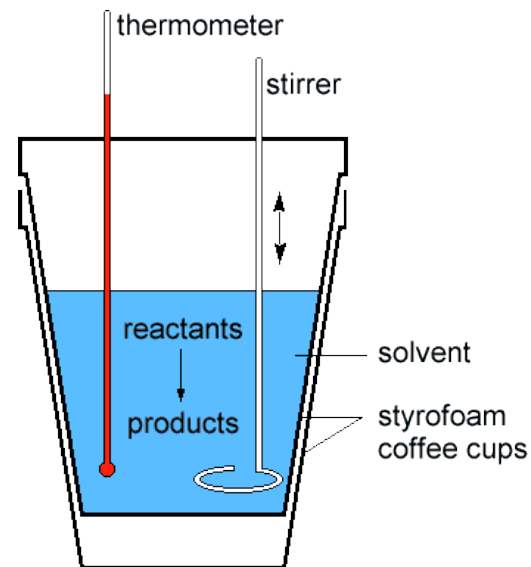


# Heat Change Sign Convention

Direction of Heat Flow	Sign	Reaction Type
Heat Flows Out of the System	$-\Delta H$	Exothermic
Heat Flows Into the System	$+\Delta H$	Endothermic

# Constant-Pressure Calorimetry

- The reactants and the products of a reaction are the system.
- Even a solvent (Ex. H<sub>2</sub>O) is considered the surroundings.
- In a calorimeter the heat change of the water equals the heat change of the reaction, but with the opposite sign.



$$q_{\text{soln}} = -q_{\text{rxn}}$$

# Sample Exercise

- When a student mixes 50mL of 1.0M HCl and 50mL of 1.0M NaOH in a coffee-cup calorimeter, the temperature of the resultant solution increases from 21.0°C to 27.5°C. Calculate the enthalpy change for the reaction in kJ/mol HCl, assuming that the calorimeter loses only a negligible quantity of heat, that the total volume of the solution is 100mL, that its density is 1.0g/mL, and that its specific heat is 4.18 J/gK.

# Practice Exercise

- When 50.0mL of 0.100M AgNO<sub>3</sub> and 50.0mL of 0.100M HCl are mixed in a constant-pressure calorimeter, the temperature of the mixture increases from 22.30°C to 23.11°C. The temperature increase is caused by the following reaction:



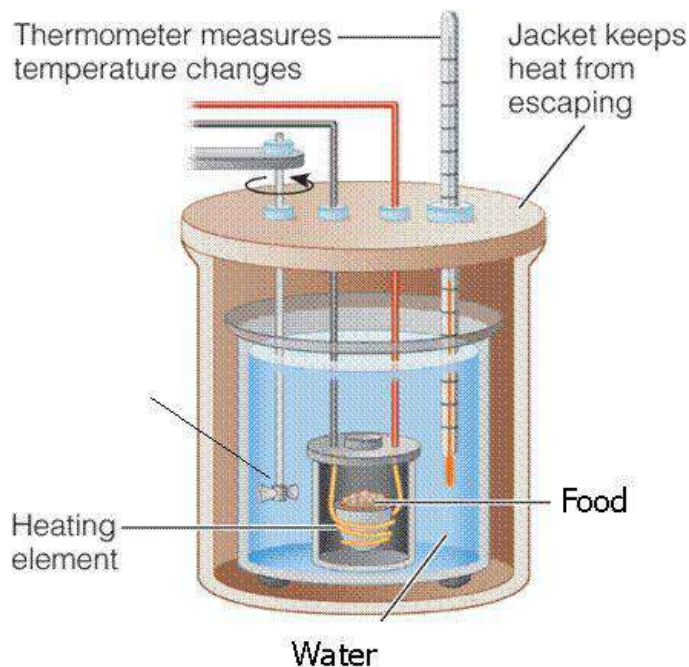
Calculate  $\Delta H$  for this reaction in kJ/mol AgNO<sub>3</sub>, assuming that the combined solution has a mass of 100.0g and a specific heat of 4.18J/g°C.

# Bomb Calorimeter

- A bomb calorimeter is used for constant volume calorimetry.

$$q_{\text{rxn}} = -C_{\text{cal}} \times \Delta T$$

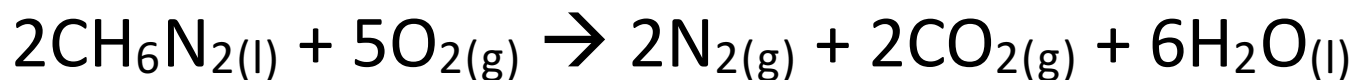
- $C_{\text{cal}}$  is the heat capacity of the water in the calorimeter.





# Sample Exercise

- Methylhydrazine ( $\text{CH}_6\text{N}_2$ ) is used as a liquid rocket fuel. The combustion of methylhydrazine with oxygen produces  $\text{N}_{2(g)}$ ,  $\text{CO}_{2(g)}$ , and  $\text{H}_2\text{O}_{(l)}$ :



When 4.00g of methylhydrazine is combusted in a bomb calorimeter, the temperature of the calorimeter increases from  $25.00^\circ\text{C}$  to  $39.50^\circ\text{C}$ . In a separate experiment the heat capacity of the calorimeter is measured to be  $7.794 \text{ kJ}/^\circ\text{C}$ . Calculate the heat of reaction for the combustion of a mole of  $\text{CH}_6\text{N}_2$ .

# Practice Exercise

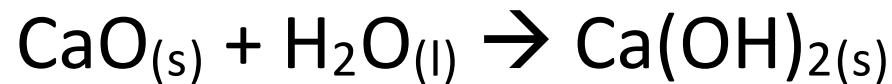
- A 0.5865g sample of lactic acid ( $\text{HC}_3\text{H}_5\text{O}_3$ ) is burned in a calorimeter whose heat capacity is  $4.812 \text{ kJ}/^\circ\text{C}$ . The temperature increases from  $23.10^\circ\text{C}$  to  $24.95^\circ\text{C}$ . Calculate the heat of combustion of lactic acid

a. Per gram

b. Per mole

# Thermochemical Equations

- An equation that included the heat change is a thermochemical equation.
- A heat of reaction is the heat change for the equation exactly as written.
- Ex:



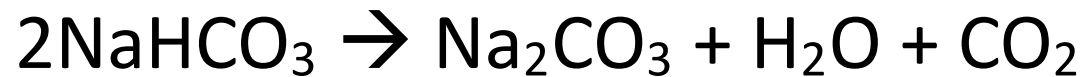
$$\Delta H = -65.2 \text{ KJ}$$



$$\Delta H = +129 \text{ KJ}$$

## Sample Problem

- Calculate the amount of heat (in kJ) required to decompose 2.24 moles of  $\text{NaHCO}_3$ .



$$\Delta H = 129\text{kJ}$$

## Practice Problems

1. Calculate the amount of heat (in kJ) absorbed when 5.66g of carbon disulfide is formed.



## Practice Problems

2. How many kilojoules of heat are produced when 3.40 mole  $\text{Fe}_2\text{O}_3$  reacts with an excess of CO?



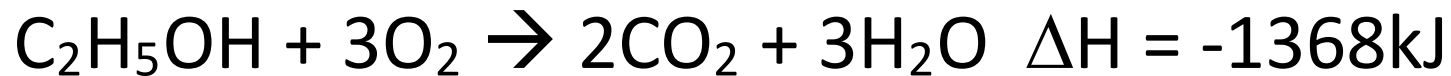
$$\Delta H = -26.33 \text{ kJ}$$

## Section 17.2 Assessment

1. When 2 mol of solid magnesium combines with 1 mol of oxygen gas, 2 mol of solid magnesium oxide is formed and 1204kJ of heat is released. Write the thermochemical equation for this combustion reaction.

## Section 17.2 Assessment

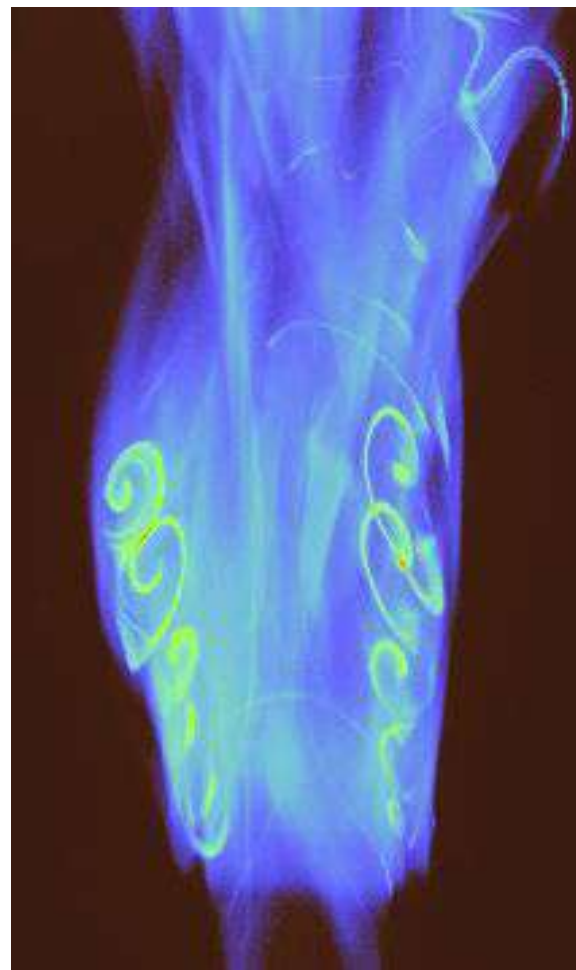
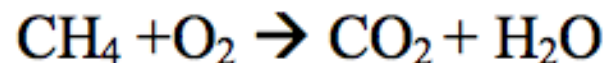
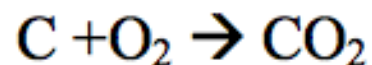
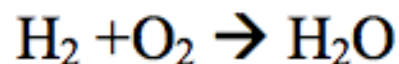
2. How much heat is released when 12.5g of ethanol burns?





# Section 17.3 – Heat in Changes of State

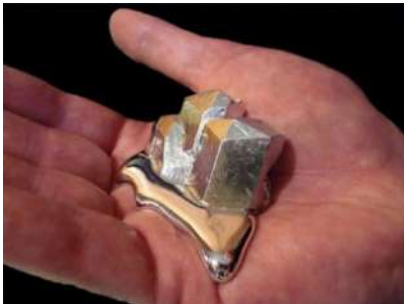
- The heat of combustion is the heat of reaction for the complete burning of one mole of a substance.



## $\Delta H$ (fusion and solidification)

- The heat absorbed by one mole of a substance melting from a solid to a liquid at constant temperature is the molar heat of fusion.
- The heat lost when one mole of a liquid changes to a solid at a constant temperature is the molar heat of solidification.

$$\Delta H_{\text{fus}} = - \Delta H_{\text{solid}}$$



# $\Delta H$ (vaporization and condensation)

- The heat absorbed by one mole of a substance changing from a liquid to a vapor is the molar heat of vaporization.
- The heat released by one mole of a substance changing from a vapor to a liquid is the molar heat of condensation.

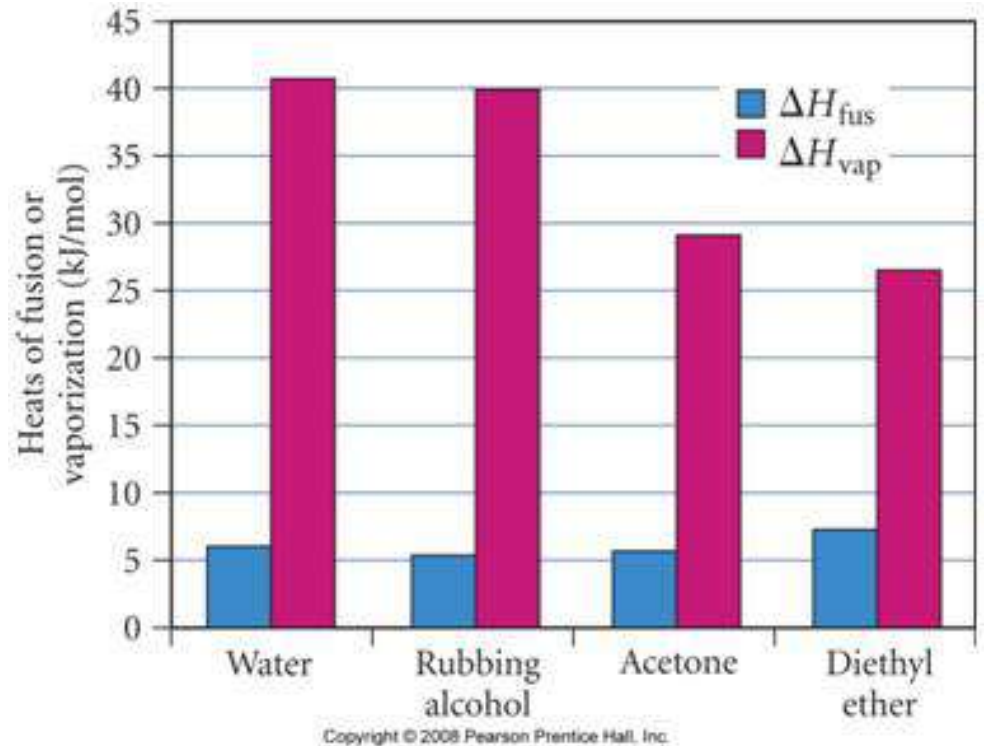


$$\Delta H_{\text{vap}} = - \Delta H_{\text{cond}}$$



## Practice Problems

1. What is the  $\Delta H_{\text{vap}}$  of acetone?
2. What is the  $\Delta H_{\text{cond}}$  of water?
3. What is the  $\Delta H_{\text{fus}}$  of rubbing alcohol?
4. What is the  $\Delta H_{\text{solid}}$  of diethyl ether?

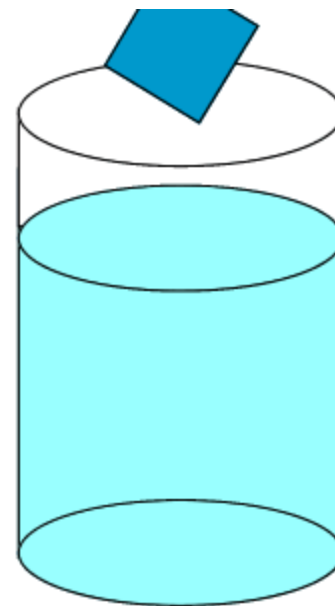
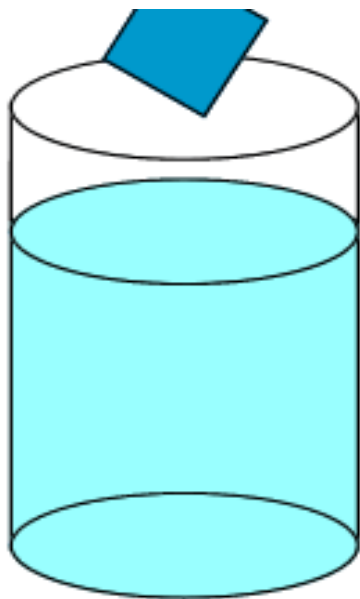


## $\Delta H$ (solution)

- The heat change caused by dissolution of one mole of a substance is the molar heat of solution.
- Ex.

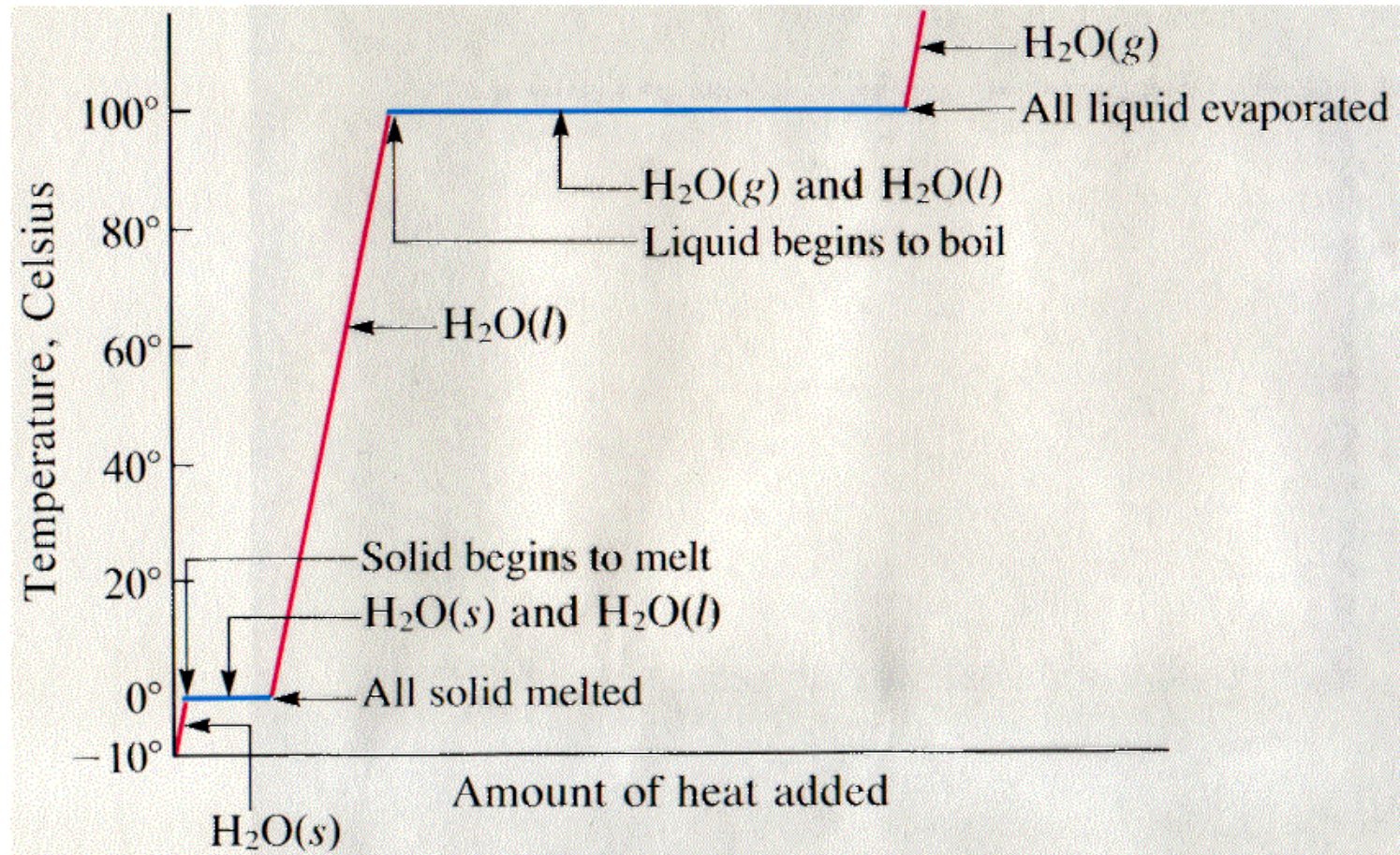


$$\Delta H_{\text{soln}} = -445.1 \text{ KJ}$$





# Heating Curve for Water



## Sample Problem

- How much heat (in kJ) is absorbed when 24.8g  $\text{H}_2\text{O}_{(s)}$  at  $0^\circ\text{C}$  and 101.3kPa is converted to liquid at  $0^\circ\text{C}$ .

## Practice Problems

1. How much heat is absorbed when 63.7g  $\text{H}_2\text{O}_{(l)}$  at  $100^\circ\text{C}$  and 101.3kPa is converted to steam at  $100^\circ\text{C}$ ?



## Practice Problems

2. How many kilojoules of heat are absorbed when 0.46g of chloroethane ( $\text{C}_2\text{H}_5\text{Cl}$ ) vaporizes at its boiling point? (The molar heat of vaporization for chloroethane is 26.4 kJ/mol.)

## Practice Problems

3. How much heat (in kJ) is released when 2.5 mol of NaOH is dissolved in water? (The molar heat of solution is  $-445.1$  kJ/mol.)

## Practice Problems

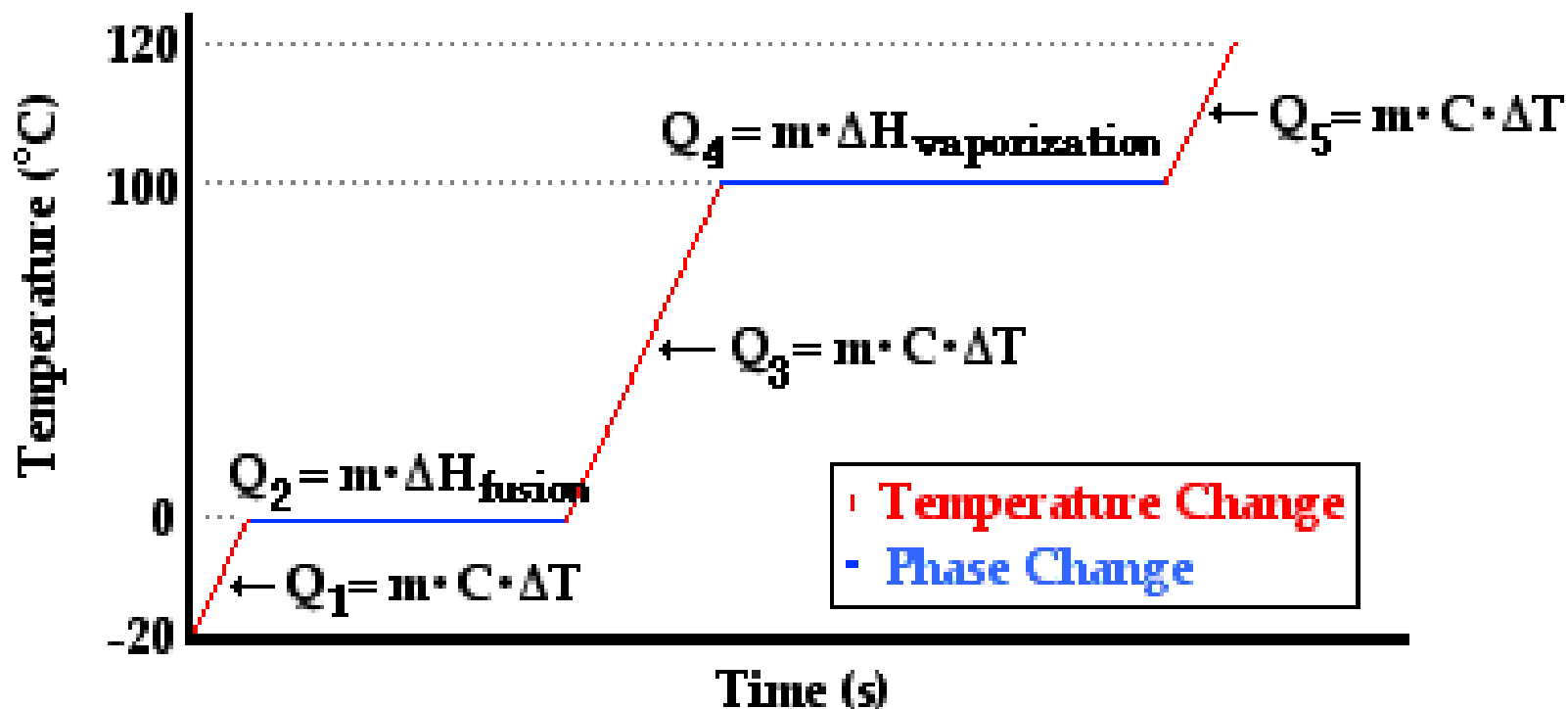
4. How many moles of  $\text{NH}_4\text{NO}_3$  must be dissolved in water so that 88kJ of heat is absorbed from the water? (The molar heat of solution 25.7 kJ/mol.)

# Heating Curve Problems

- Sometimes a question might ask you about a physical change that involves a temperature change and a phase change.
- You will have to do these problems in multiple steps.
- You have to work your way through the heating curve.

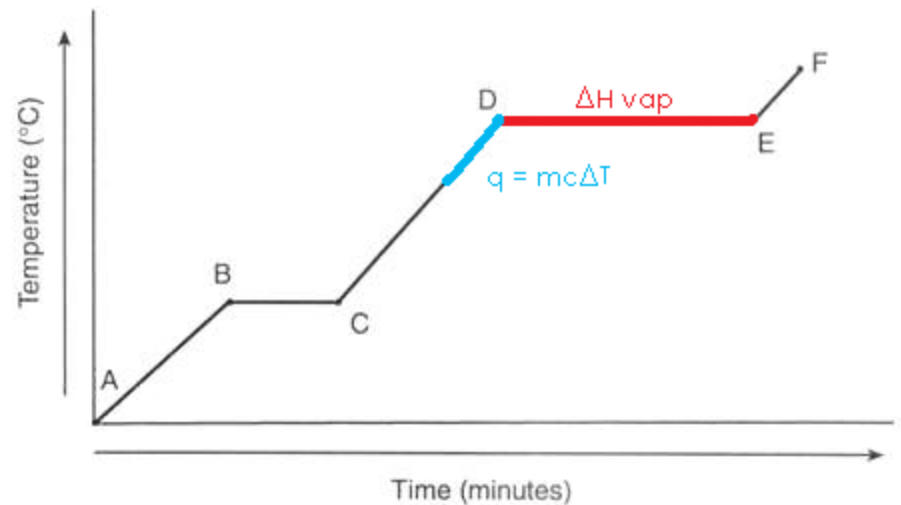
# Heating Curve

## Heating Curve for Water



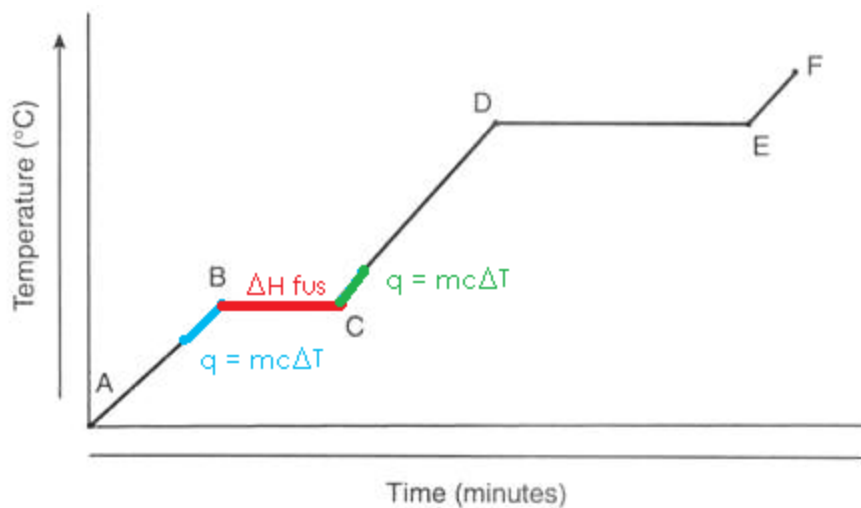
# Sample Problem

- Calculate the amount of heat required to change 50g of water at 75°C to steam.



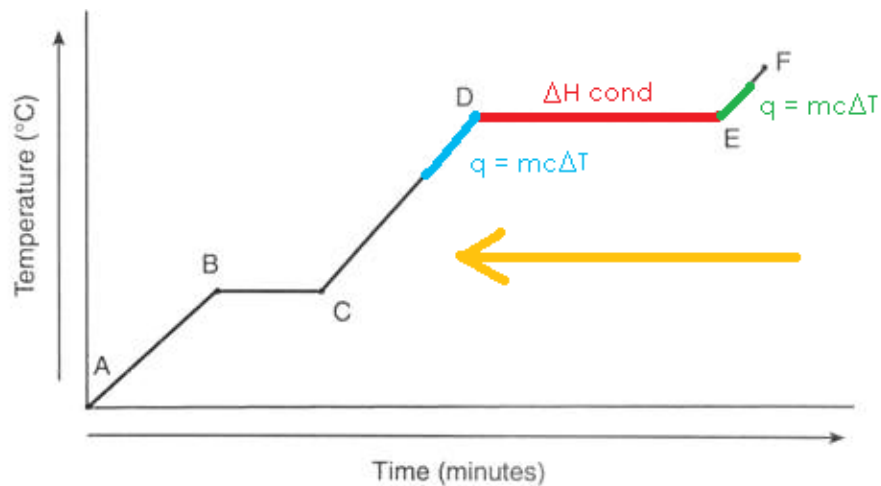
# Practice Problems

1. Calculate the amount of heat needed to change 175g of ice at  $-20^{\circ}\text{C}$  to water at  $15^{\circ}\text{C}$ .



# Practice Problems

2. Calculate the amount of heat released when 100g of steam at 130°C is cooled to water at 60°C.



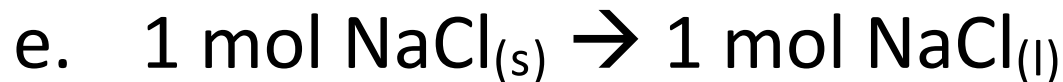
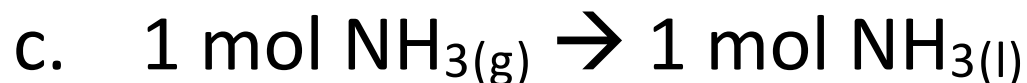
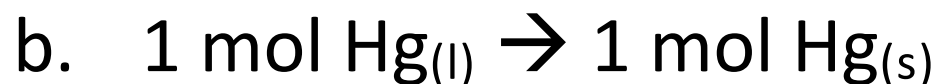
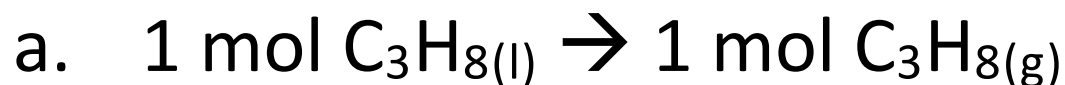


## Section 17.3 Assessment

1. How does the molar heat of fusion of a substance compare to its molar heat of solidification?
2. How does the molar heat of vaporization of a substance compare to its molar heat of condensation?

## Section 17.3 Assessment

3. Identify each enthalpy change by name and classify each change as exothermic or endothermic.



## Section 17.4 – Calculating Heats of Reaction

- Hess' Law of heat summation states that if you add two or more thermochemical equations to give a final equation, then you can also add the heat changes to give the final heat change.



## Sample Problem

- Calculate the enthalpy change for the following reaction given the following information:



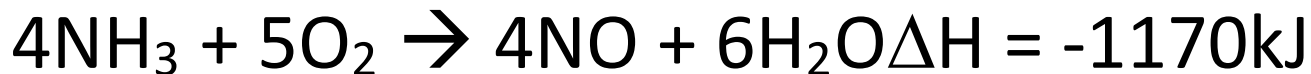
## Practice Problems

1. Find the enthalpy change for the reaction using the following information.



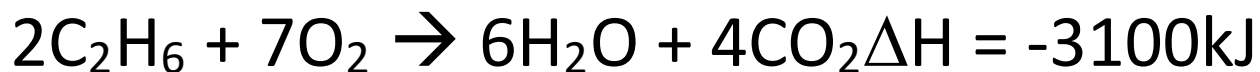
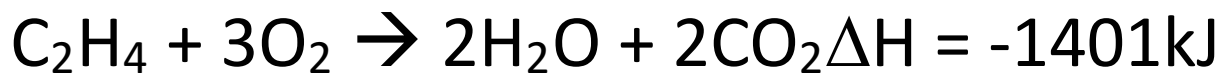
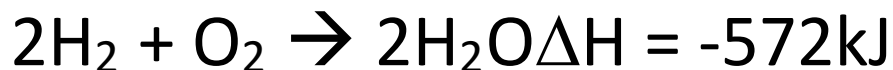
## Practice Problems

2. Calculate the enthalpy change for the reaction using the following information:



## Practice Problems

3. Calculate the enthalpy change for the reaction using the following information.



# Standard Heat of Formation

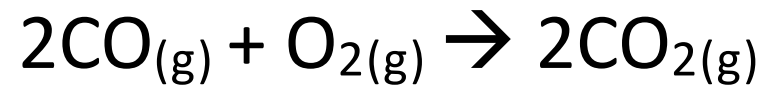
- The standard heat of formation of a compound is the change in enthalpy that accompanies the formation of one mole of the compound from its element with all substances in their standard states at 25°C.
- The  $\Delta H_f^\circ$  of a free element in its standard state is zero.

$$\Delta H^\circ = \Delta H_f^\circ (\text{products}) - \Delta H_f^\circ (\text{reactants})$$



## Sample Problem

- Calculate the standard heat of formation for the following reaction.



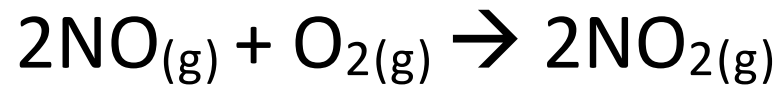
# Practice Problems

1. Calculate the standard heat of formation for the following reaction.



## Practice Problems

2. Calculate the standard heat of formation for the following reaction.

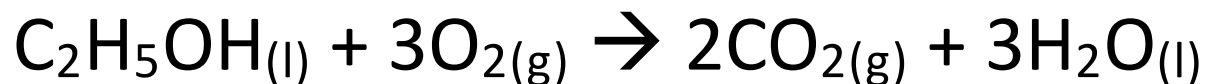


# Sample Exercise

- a. Calculate the standard enthalpy change for the combustion of 1 mol of benzene,  $\text{C}_6\text{H}_6(\text{l})$ , to form  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$ .
  
  
  
  
  
  
  
  
  
  
- b. Compare the quantity of heat produced by combustion of 1.00g propane to that produced by 1.00g benzene.

# Practice Exercise

- Using the standard enthalpies of formation listed in Table 5.3, calculate the enthalpy change for the combustion of 1 mol of ethanol:



# Sample Exercise

- The standard enthalpy change for the reaction



is 178.1 kJ. From the values for the standard enthalpies of formation of  $\text{CaO}_{(s)}$  and  $\text{CO}_{2(g)}$  given in Table 5.3, calculate the standard enthalpy of formation of  $\text{CaCO}_{3(s)}$ .

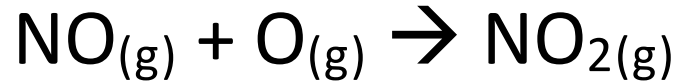
# Practice Exercise

- Given the following standard enthalpy change, use the standard enthalpies of formation in Table 5.3 to calculate the standard enthalpy of formation of  $\text{CuO}_{(s)}$ .

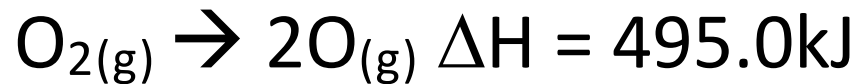
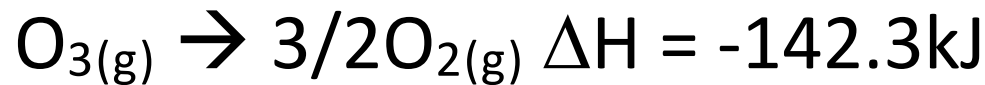
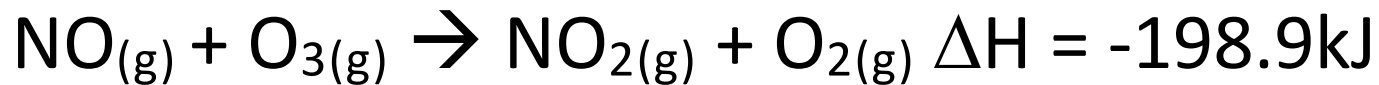


## Section 17.4 Assessment

- Calculate  $\Delta H$  for the reaction



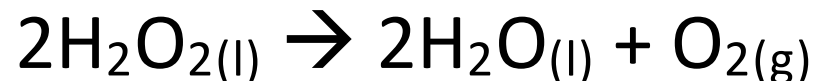
Given the following information:





## Section 17.4 Review

2. What is the standard heat of reaction for the decomposition of hydrogen peroxide?



# Sample Integrative Exercise

- Trinitroglycerin,  $C_3H_5N_3O_9$  (usually referred to simply as nitroglycerin), has been widely used as an explosive. Alfred Nobel used it to make dynamite in 1866. Rather surprisingly, it also is used as a medication, to relieve angina (chest pains resulting from partially blocked arteries to the heart) by dilating the blood vessels. The enthalpy of decomposition at 1atm pressure of trinitroglycerin to form nitrogen gas, carbon dioxide gas, liquid water, and oxygen gas at  $25^\circ C$  is  $-1541.4 \text{ kJ/mol}$ .

# Sample Integrative Exercise con't

a. Write a balanced chemical equation for the decomposition of trinitroglycerin.

b. Calculate the standard heat of formation of trinitroglycerin.

# Sample Integrative Exercise con't

c. A standard dose of trinitroglycerin for relief of angina is 0.60mg. If the sample is eventually oxidized in the body (not explosively, though!) to nitrogen gas, carbon dioxide gas, and liquid water, what number of calories is released?

d. One common form of trinitroglycerin melts at about  $3^{\circ}\text{C}$ . From this information and the formula for the substance, would you expect it to be a molecular or ionic compound? Explain.

# Sample Integrative Exercise con't

- e. Describe the various conversions of forms of energy when trinitroglycerin is used as an explosive to break rockfaces in highway construction.