

WILEY

Chapter 6
Energy and
Chemical Change

Chemistry, 7th Edition
International Student Version
Brady/Jespersen/Hyslop

Chapter in Context

- Explore the difference between potential and kinetic energy
- Apply the principle of the conservation of energy
- Examine the connection between energy, heat, and temperature
- Learn about state functions
- Determine the amount of heat exchanged from the temperature change of an object
- Understand exo- and endothermic reactions

Chapter in Context, cont'd

- Learn and apply the first law of thermodynamics
- Understand the difference between the heat of reaction under constant pressure versus constant volume
- Explore the utility of and assumptions in thermochemical equations
- Uses Hess's law to predict enthalpies of reaction
- Determine and use standard heats of reaction to solve problems

Thermochemistry

- Study of energies given off by or absorbed by reactions

Thermodynamics

- Study of heat transfer or heat flow

Energy (E)

- Ability to do work or to transfer heat

Kinetic Energy (KE)

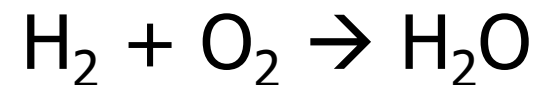
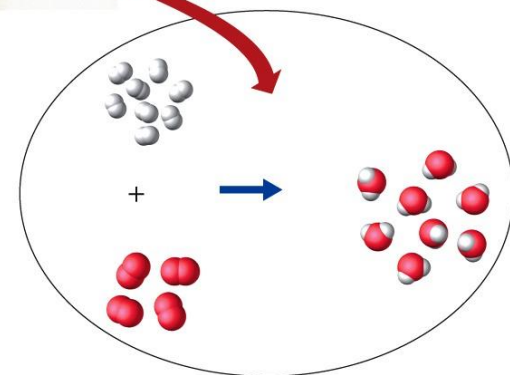
- Energy of motion
- $KE = \frac{1}{2}mv^2$

Potential Energy (PE)

- Stored energy
- Exists in natural attractions and repulsions
 - Gravity
 - Positive and negative charges
 - Springs



Corbis Images



Chemical Energy

- PE possessed by chemicals
- Stored in chemical bonds
- Breaking bonds requires energy
- Forming bonds releases energy

Your Turn!

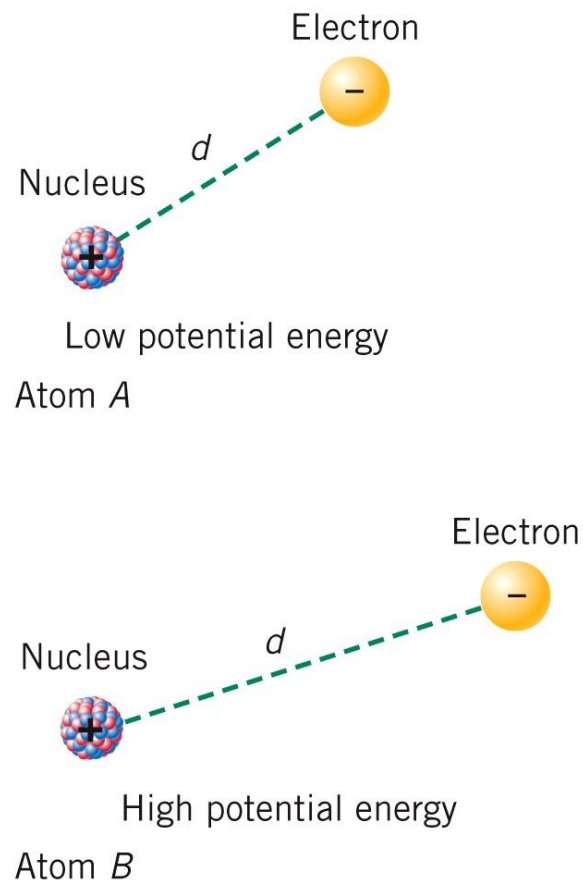
Which of the following is **not** a form of kinetic energy?

- A. A pencil rolls across a desk
- B. A pencil is sharpened
- C. A pencil is heated
- D. A pencil rests on a desk
- E. A pencil falls to the floor

Factors Affecting Potential Energy

Increase Potential Energy

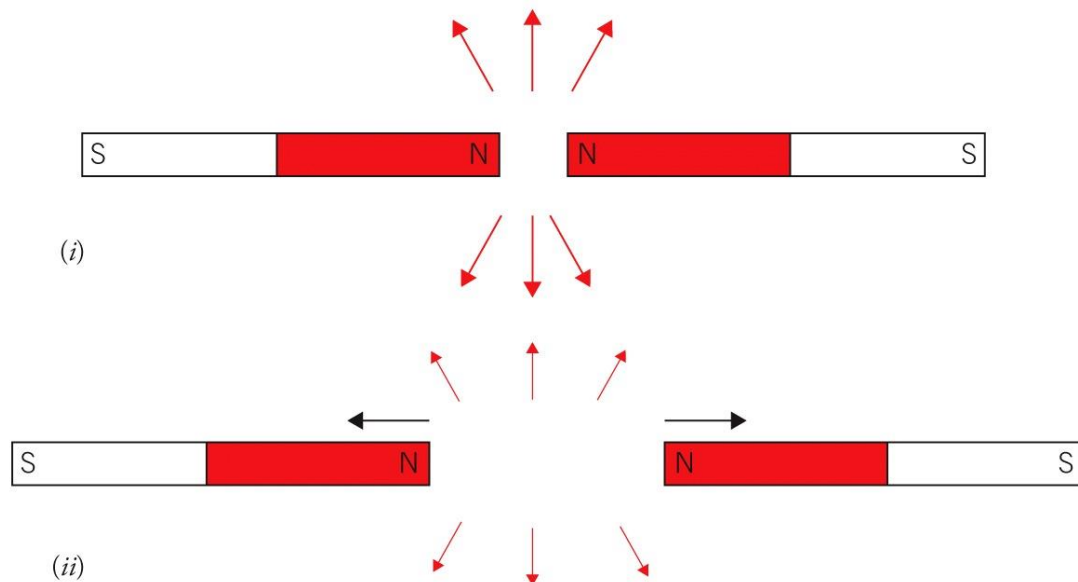
- Pull apart objects that attract each other
 - A book is attracted to the earth by gravity
 - North and south poles of magnets
 - Positive and negative charges
- Push together objects that repel each other
 - Spring compressed
 - Same poles on two magnets
 - Two like charges



Factors Affecting Potential Energy

Decrease Potential Energy

- Objects that attract each other come together
 - Book falls
 - North and south poles of two magnets
 - Positive and negative charges
- Objects that repel each other move apart
 - North poles on two magnets
 - Spring released
 - Two like charges



Your Turn!

Which of the following represents a **decrease** in the potential energy of the system?

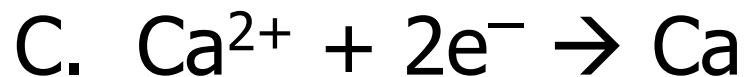
- A. A book is raised six feet above the floor
- B. A ball rolls downhill
- C. Two electrons come close together
- D. A spring is stretched completely
- E. Two atomic nuclei approach each other

Your Turn!

Which of the following represents an **increase** in the potential energy of the system?



B. A periodic table falls off the wall



D. A firecracker explodes

E. Gasoline is burned and creates CO_2 and H_2O

Law of Conservation of Energy

- Energy can neither be created nor destroyed
- Can only be converted from one form to another
- Total energy of universe is constant

$$\text{Total Energy} = \text{Potential Energy} + \text{Kinetic Energy}$$

Units of Energy

Joule (J)

- KE possessed by 2 kg object moving at speed of 1 m/s.

$$1 \text{ J} = \frac{1}{2} (2 \text{ kg}) \left(\frac{1 \text{ m}}{1 \text{ s}} \right)^2 \qquad 1 \text{ J} = \frac{1 \text{ kg} \cdot \text{m}^2}{\text{s}^2}$$

- If calculated value is greater than 1000 J, use kilojoules (kJ)
- 1 kJ = 1000 J

Units of Energy

A calorie (cal)

- Energy needed to raise the temperature of 1 g H₂O by 1 ° C
 - **1 cal = 4.184 J (exactly)**
 - 1 kcal = 1000 cal
 - 1 kcal = 4.184 kJ

A nutritional Calorie (Cal)

- note capital C
- 1 Cal = 1000 cal = 1 kcal
- 1 kcal = 4.184 kJ

Your Turn!

Which is a unit of energy?

- A. Pascal
- B. Newton
- C. Joule
- D. Watt
- E. Ampere

Your Turn!

Convert 175.2 kJ into nutritional Calories

A. $41.87 \times 10^3 \text{ Cal}$

B. 41.87 cal

C. 733.0 Cal

D. 41.87 Cal

E. $733.0 \times 10^3 \text{ Cal}$

$$\frac{175.2 \text{ kJ}}{1} \times \frac{1 \text{ kcal}}{4.184 \text{ kJ}} \times \frac{1 \text{ Cal}}{1 \text{ kcal}} = 41.87 \text{ Cal}$$

Your Turn!

Convert 57.9 kJ into calories

A. 13800 Cal

B. 13.8 cal

C. 242 kcal

D. 242 Cal

E. 13.8 kcal

$$\frac{57.9 \cancel{\text{kJ}}}{1} \times \frac{1000 \cancel{\text{J}}}{1 \cancel{\text{kJ}}} \times \frac{1 \text{ cal}}{4.184 \cancel{\text{J}}} =$$

$$13800 \cancel{\text{ cal}} \times \frac{\text{kcal}}{1000 \cancel{\text{ cal}}} = \mathbf{13.8 \text{ kcal}}$$

Temperature vs. Heat

Temperature

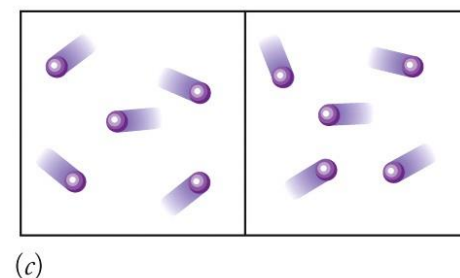
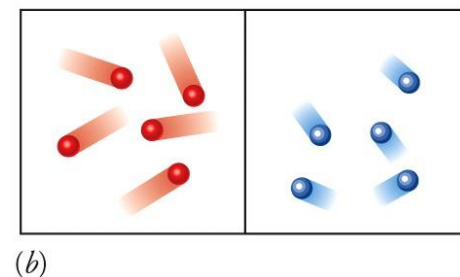
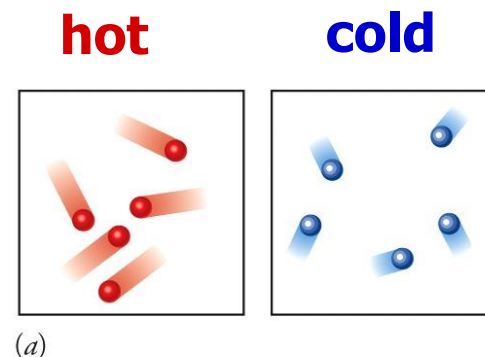
- Proportional to **average** kinetic energy of object's particles
- Higher average kinetic energy means
 - Higher temperature
 - Faster moving molecules

Heat

- Total amount of energy transferred between objects
- Heat transfer is caused by a temperature difference
- Always passes spontaneously from warmer objects to colder objects
- Transfers until both are the same temperature

Heat Transfer

- Hot and cold objects placed in contact
 - Molecules in hot object moving faster
- KE transfers from hotter to colder object
 - A decrease in average KE of hotter object
 - An increase in average KE of colder object
- Over time
 - Average KEs of both objects becomes the same
 - Temperature of both becomes the same



Heat

- Pour hot coffee into cold cup
 - Heat flows from hot coffee to cold cup
 - Faster coffee molecules bump into wall of cup
 - Transfer kinetic energy
 - Eventually, the cup and the coffee reach the same temperature

Thermal Equilibrium

- When both cup and coffee reach same average kinetic energy and same temperature
- Energy transferred through heat comes from object's **internal energy**

Internal Energy (E)

- Sum of energies of all particles in system

E = total energy of system

E = potential + kinetic = $PE + KE$

Change in Internal Energy

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

- Δ means change
- final – initial
- What we can actually measure
- Want to know change in E associated with given process

ΔE , Change in Internal Energy

- For reaction: **reactants** \longrightarrow **products**
- $\Delta E = E_{\text{products}} - E_{\text{reactants}}$
 - Can use to do something useful
 - Work
 - Heat
- If system absorbs energy during reaction
 - Energy coming into system has a positive sign (+)
 - Final energy $>$ initial energy

Example: Photosynthesis *or* charging battery

- As system absorbs energy
 - Increase potential energy
 - Available for later use

Kinetic Molecular Theory

- Kinetic Molecular Theory tells us

Temperature

- Related to average kinetic energy of particles in object

Internal energy

- Related to average total molecular kinetic energy
- Includes molecular potential energy

Average kinetic energy

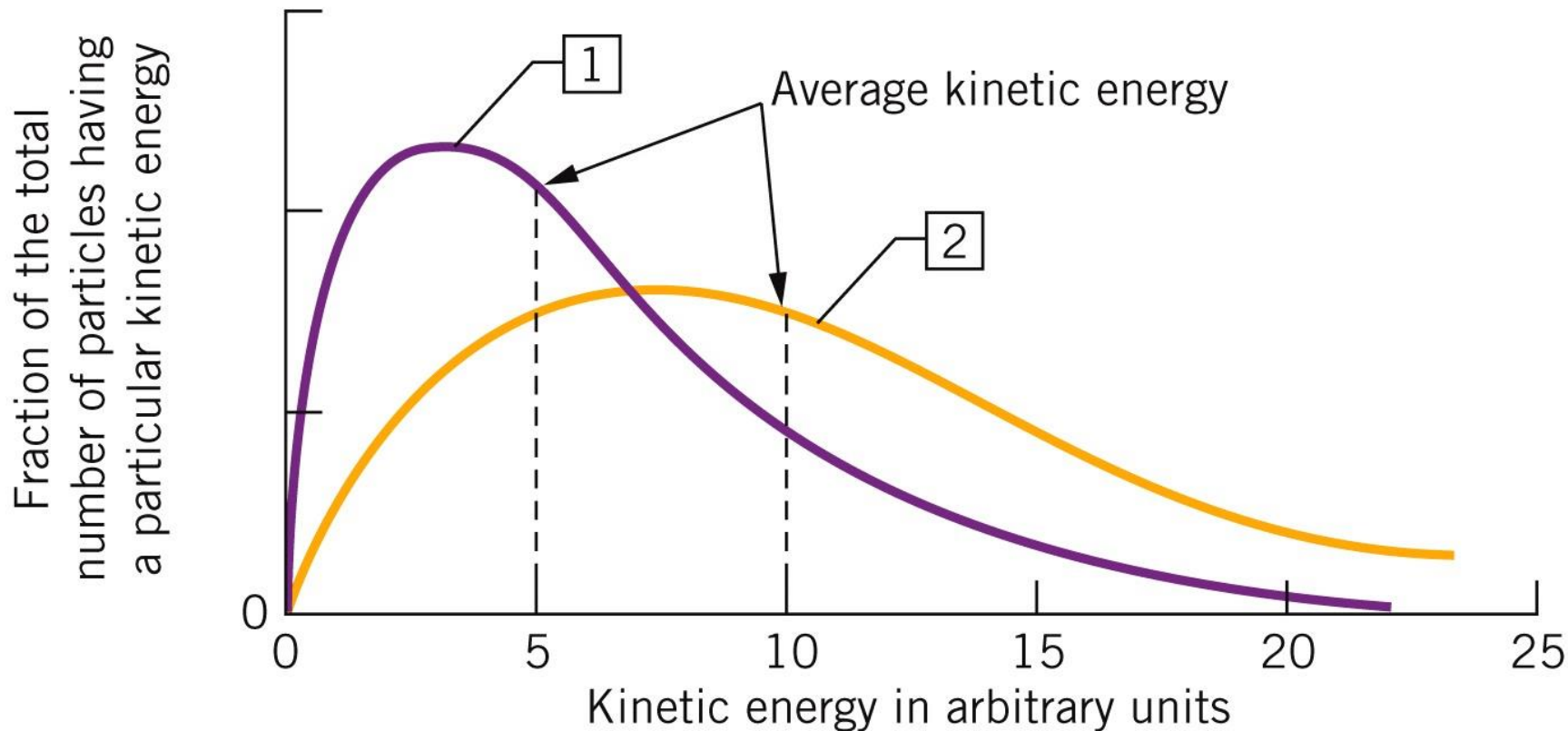
- Implies distribution of kinetic energies among molecules in object

Temperature and Average Kinetic Energy^{6.2}

In a large collection of gas molecules

- Wide distribution of kinetic energy (KE)
- Small number with $KE = 0$
 - Collisions can momentarily stop a molecule's motion
- Very small number with very high KE
- Most molecules intermediate KEs
- Collisions tend to average kinetic energies
 - **Result** is a distribution of energies

Distribution of Kinetic Energy



1: lower temperature

2: higher temperature

At higher temperature, distribution shifts to higher kinetic energy

Distribution of Kinetic Energy

Temperature

- Average KE of all atoms and molecules in object
- Average speed of particles
- Kelvin temperature of sample
 - $T(\text{K}) \propto \text{Avg KE} = \frac{1}{2} m v_{\text{avg}}^2$
- At higher temperature
 - Most molecules moving at higher average speed
- **Cold** object = Small average KE
- **Hot** object = Large average KE

Note: At 0 K KE = 0 so $v = 0$

Kinetic Theory: Liquids and Solids ^{6.2}

- Atoms and molecules in liquids and solids also constantly moving
- Particles of solids jiggle and vibrate in place
- Distributions of KEs of particles in gas, liquid and solid are the same at same temperatures
- At **same temperature**, gas, liquid, and solid have
 - **Same** average kinetic energy
 - But very **different** potential energy

Your Turn!

Which statement about kinetic energy (KE) is true?

- A. Atoms and molecules in gases, liquids and solids possess KE since they are in constant motion.
- B. At the same temperature, gases, liquids and solids all have different KE distributions.
- C. Molecules in gases are in constant motion, while molecules in liquids and solids are not.
- D. Molecules in gases and liquids are in constant motion, while molecules in solids are not.
- E. As the temperature increases, molecules move more slowly.

ΔE , Change in Internal Energy

- $\Delta E = E_{\text{products}} - E_{\text{reactants}}$
 - Energy change can appear entirely as heat
 - Can measure heat
 - Can't measure E_{product} or E_{reactant}
 - Importantly, we can measure ΔE
 - Energy of system depends only on its current condition
 - DOES NOT depend on:
 - How system got it
 - What energy the system might have sometime in future

State of Object or System

- Complete list of properties that specify object's current condition

For Chemistry

- Defined by physical properties
 - Chemical composition
 - Substances
 - Number of moles
 - Pressure
 - Temperature
 - Volume

State Functions

- Any property that **only** depends on object's current state or condition
- Independence from method, path or mechanism by which change occurs is important feature of all state functions
- Some State functions, E , P , t , and V :
 - Internal energy E
 - Pressure P
 - Temperature t
 - Volume V

State of an object

- If $t_c = 25^\circ \text{C}$, tells us all we need to know
 - Don't need to know **how** system got to that temperature, just that this is where it currently is
- If temperature increases to 35°C , then change in temperature is simply:
 - $\Delta t = t_{\text{final}} - t_{\text{initial}}$
 - Don't need to know how this occurred, just need to know initial and final values
- What does Δt tell us?
 - Change in average KE of particles in object
 - Change in object's total KE
 - Heat energy

Defining the System

System

- What we are interested in studying
 - Reaction in beaker

Surroundings

- Everything else
 - Room in which reaction is run

Boundary

- Separation between system and surroundings
 - Visible **Example:** Walls of beaker
 - Invisible **Example:** Line separating warm and cold fronts

Three Types of Systems

Open System

- Open to atmosphere
- Gain or lose mass and energy across boundary
- Most reactions done in open systems



Open system

Closed System

- Not open to atmosphere
- Energy can cross boundary, but mass **cannot**



Closed system

Three Types of Systems

Isolated System

- No energy or matter can cross boundary
- Energy and mass are constant

Example: Thermos bottle



Isolated system

Adiabatic Process

Adiabatic Process

- Process that occurs in isolated system
- Process where neither energy nor matter crosses the system/surrounding boundary

Your Turn!

A closed system can _____

- A. include the surroundings
- B. absorb energy and mass
- C. not change its temperature
- D. not absorb or lose energy and mass
- E. absorb or lose energy, but not mass

Heat (q)

- Cannot measure heat directly
- Heat (q) gained or lost by an object
 - Directly proportional to temperature change (Δt) it undergoes
 - Adding heat, increases temperature
 - Removing heat, decreases temperature
- Measure changes in temperature to quantify amount of heat transferred

$$q = C \times \Delta t$$

- C = heat capacity

Heat Capacity (C)

- Amount of heat (q) required to raise temperature of object by 1°C

$$\text{Heat Exchanged} = \text{Heat Capacity} \times \Delta t$$

$$q = C \times \Delta t$$

- **Units for C = $\text{J}/^\circ\text{C}$ or $\text{J}\cdot^\circ\text{C}^{-1}$**
- **Extensive property**
- Depends on two factors
 1. Sample size or amount (mass)
 - Doubling amount doubles heat capacity
 2. Identity of substance
 - Water vs. iron

Learning Check: Heat Capacity

A cup of water is used in an experiment. Its heat capacity is known to be $720 \text{ J}/^\circ\text{C}$. How much heat will it absorb if the experimental temperature changed from 19.2°C to 23.5°C ?

$$q = C \times \Delta t$$

$$q = 720 \frac{\text{J}}{^\circ\text{C}} \times (23.5 - 19.2^\circ\text{C})$$

$$q = 720 \frac{\text{J}}{\cancel{^\circ\text{C}}} \times (4.3 \cancel{^\circ\text{C}})$$

$$q = 3.1 \times 10^3 \text{ J}$$

Learning Check: Heat Capacity

If it requires 4.184 J to raise the temperature of 1.00 g of water by 1.00 C, calculate the heat capacity of 1.00 g of water.

$$C = \frac{q}{\Delta t}$$

$$C_{1.00 \text{ g water}} = \frac{4.184 \text{ J}}{1.00 \text{ }^\circ\text{C}} = \mathbf{4.18 \text{ J/}^\circ\text{C}}$$

Your Turn!

What is the heat capacity of 300. g of an object if it requires 2510. J to raise the temperature of the object by 2.00°C ?

A. $4.18\text{ J}/^{\circ}\text{C}$

B. $418\text{ J}/^{\circ}\text{C}$

C. $837\text{ J}/^{\circ}\text{C}$

D. $1.26 \times 10^3\text{ J}/^{\circ}\text{C}$

E. $2.51 \times 10^3\text{ J}/^{\circ}\text{C}$

$$C_{\text{object}} = \frac{2510\text{ J}}{2.00^{\circ}\text{C}} = \mathbf{1255\text{ J}/^{\circ}\text{C}}$$

Your Turn!

A copper mug has a heat capacity of $77.5 \text{ J}/^\circ\text{C}$. After adding hot water to the mug, the temperature of the mug changed from 77.0°F to 185°F . How much heat did the mug absorb from the water?

A. $4.65 \times 10^3 \text{ J}$ $q = C \times \Delta t = 77.5 \text{ J}/^\circ\text{C} \times \Delta t$

B. 1.29 J Note units: temps. must be in $^\circ\text{C}$

C. $8.37 \times 10^3 \text{ J}$ $t_i = 25.0^\circ\text{C}$, $t_f = 85.0^\circ\text{C}$,

D. $5.97 \times 10^3 \text{ J}$ So $\Delta t = 85.0^\circ\text{C} - 25.0^\circ\text{C} = 60.0^\circ\text{C}$

E. $1.43 \times 10^4 \text{ J}$ $q = \frac{77.5 \text{ J}}{^\circ\text{C}} \times 60.0^\circ\text{C}$

$= 4.65 \times 10^3 \text{ J}$

Specific Heat (s)

- Amount of heat energy needed to raise temperature of 1 g substance by 1 ° C

$$C = s \times m \quad \text{or} \quad s = \frac{C}{m}$$

- **Intensive property**

- Ratio of two extensive properties

- **Units**

- **J/(g °C)** or **J g⁻¹ °C⁻¹**

- Unique to each substance

- Large specific heat means substance releases large amount of heat as it cools

Learning Check

- Calculate the specific heat of water if the heat capacity of 100. g of water is 418 J/° C.

$$s = \frac{C}{m} \quad s = \frac{418 \text{ J/}^\circ\text{C}}{100. \text{ g}} = \mathbf{4.18 \text{ J/g}^\circ\text{C}}$$

- What is the specific heat of water if heat capacity of 1.00 g of water is 4.18 J/° C?

$$s = \frac{4.18 \text{ J/}^\circ\text{C}}{1.00 \text{ g}} = \mathbf{4.18 \text{ J/g}^\circ\text{C}}$$

- Thus, heat capacity is independent of amount of substance

Your Turn!

The specific heat of silver $0.235 \text{ J g}^{-1} \text{ } ^\circ \text{ C}^{-1}$. What is the heat capacity of a $100. \text{ g}$ sample of silver?

A. $0.235 \text{ J/}^\circ \text{ C}$

$$C = s \cdot m$$

B. $2.35 \text{ J/}^\circ \text{ C}$

C. $23.5 \text{ J/}^\circ \text{ C}$

$$C = 0.235 \frac{\text{J}}{\cancel{\text{g}} \text{ } ^\circ \text{C}} \cdot 100. \cancel{\text{g}}$$

D. $235 \text{ J/}^\circ \text{ C}$

E. $2.35 \times 10^3 \text{ J/}^\circ \text{ C}$

$$C = 23.5 \frac{\text{J}}{^\circ \text{C}}$$

Specific Heats of Some Substances

6.3

TABLE 6.1 Specific Heats

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

Using Specific Heat

Heat Exchanged = (Specific Heat × mass) × Δt

$$q = s \times m \times \Delta t$$

Units = $\text{J}/(\text{g } ^\circ \text{C}) \times \text{g} \times ^\circ \text{C} = \text{J}$

- Substances with high specific heats resist changes in temperature when heat is applied
- Water has unusually high specific heat
 - Important to body (~60% water)
 - Used to cushion temperature changes
 - Why coastal temperatures are different from inland temperatures

Learning Check: Specific Heat

Calculate the specific heat of a metal if it takes 235 J to raise the temperature of a 32.91 g sample by 2.53 ° C.

$$q = m \times s \times Dt$$

$$s = \frac{q}{m \times Dt} = \frac{235 \text{ J}}{32.91 \text{ g} \times 2.53 \text{ }^\circ\text{C}}$$

$$s = 2.82 \frac{\text{J}}{\text{g } ^\circ\text{C}}$$

Your Turn!

The specific heat of copper metal is $0.385 \text{ J}/(\text{g } ^\circ\text{C})$. How many J of heat are necessary to raise the temperature of a 1.42 kg block of copper from $25.0 \text{ } ^\circ\text{C}$ to $88.5 \text{ } ^\circ\text{C}$?

A. 547 J

B. $1.37 \times 10^4 \text{ J}$

C. $3.47 \times 10^4 \text{ J}$

D. 34.7 J

E. $4.74 \times 10^4 \text{ J}$

$$q = m \times s \times \Delta t$$

$$\Delta t = (88.5 - 25.0) \text{ } ^\circ\text{C}$$

$$q = 1420 \text{ g} \cdot 0.385 \frac{\text{J}}{\text{g } ^\circ\text{C}} \cdot 63.5 \text{ } ^\circ\text{C}$$

$$q = 3.47 \times 10^4 \text{ J}$$

Direction of Heat Flow

- Heat is the energy transferred between two objects
 - Heat lost by one object has the same magnitude as heat gained by other object
- Sign of q indicates direction of heat flow
 - Heat is gained, q is positive (+)
 - Heat is lost, q is negative (−)

$$q_1 = -q_2$$

Example: A piece of warm iron is placed into beaker of cool water. Iron loses 10.0 J of heat, water gains 10.0 J of heat

$$q_{\text{iron}} = -10.0 \text{ J} \qquad q_{\text{water}} = +10.0 \text{ J}$$

Your Turn!

A cast iron skillet is moved from a hot oven to a sink full of water. Which of the following is false?

- A. The water heats
- B. The skillet cools
- C. The heat transfer for the skillet has a negative (–) sign
- D. The heat transfer for the skillet has the same sign as the heat transfer for the water

Example 1: Using Heat Capacity

A ball bearing at 260.0 °C is dropped into a cup containing 250. g of water. The water warms from 25.0 to 37.3 °C. What is the heat capacity of the ball bearing in J/°C?

Heat capacity of the cup of water = 1046 J / °C

$$q_{\text{lost by ball bearing}} = -q_{\text{gained by water}}$$

1. Determine temperature change of water

$$\Delta t_{\text{water}} = (37.3 \text{ °C} - 25.0 \text{ °C}) = 12.3 \text{ °C}$$

2. Determine how much heat gained by water

$$\begin{aligned} q_{\text{water}} &= C_{\text{water}} \times \Delta t_{\text{water}} = 1046 \text{ J/°C} \times 12.3 \text{ °C} \\ &= 12.87 \times 10^3 \text{ J} \end{aligned}$$

Ex. 1: Using Heat Capacity (cont)

A ball bearing at 260.0 °C is dropped into a cup containing 250. g of water. The water warms from 25.0 to 37.3 °C. What is the heat capacity of the ball bearing in J/°C? C of the cup of water = 1046 J /° C

3. Determine how much heat ball bearing lost

$$q_{\text{ball bearing}} = -q_{\text{water}} = -12.87 \times 10^3 \text{ J}$$

4. Determine T change of ball bearing

$$\Delta t_{\text{ball bearing}} = (37.3 \text{ °C} - 260.0 \text{ °C}) = -222.7 \text{ °C}$$

5. Calculate C of ball bearing

$$C = \frac{q}{\Delta t} = \frac{-12.87 \times 10^3 \text{ J}}{-222.7 \text{ °C}} = 57.8 \text{ J/°C}$$

Ex. 2: Specific Heat Calculation

How much heat energy must you lose from a 250. mL cup of coffee for the temperature to fall from 65.0 °C to 37.0 °C? (Assume density of coffee = 1.00 g/mL, $s_{\text{coffee}} = s_{\text{water}} = 4.18 \text{ J/g}^\circ\text{C}$)

$$q = s \times m \times \Delta t$$

$$\Delta t = 37.0 - 65.0 \text{ }^\circ\text{C} = -28.0 \text{ }^\circ\text{C}$$

$$q = 4.18 \text{ J/g}^\circ\text{C} \times 250. \text{ mL} \times 1.00 \text{ g/mL} \times (-28.0 \text{ }^\circ\text{C})$$

$$q = (-29.3 \times 10^3 \text{ J}) = \mathbf{-29.3 \text{ kJ}}$$

Ex. 3: Using Specific Heat

If a 38.6 g piece of gold absorbs 297 J of heat, what will the final temperature of the gold be if the initial temperature is 24.5 °C? The specific heat of gold is 0.129 J/g °C.

Need to find t_{final} $\Delta t = t_f - t_i$

First use $q = s \times m \times \Delta t$ to calculate Δt

$$\Delta t = \frac{q}{s \times m} = \frac{297 \cancel{\text{J}}}{0.129 \cancel{\text{J/g}} \text{ } ^\circ\text{C} \times 38.6 \cancel{\text{g}}} = 59.6 \text{ } ^\circ\text{C}$$

Next calculate t_{final}

$$59.6 \text{ } ^\circ\text{C} = t_f - 24.5 \text{ } ^\circ\text{C}$$

$$t_f = 59.6 \text{ } ^\circ\text{C} + 24.5 \text{ } ^\circ\text{C} = 84.1 \text{ } ^\circ\text{C}$$

Your Turn!

What is the heat capacity of a container if 100. g of water ($s = 4.18 \text{ J/g } ^\circ\text{C}$) at $100. ^\circ\text{C}$ are added to 100. g of water at $25.0 ^\circ\text{C}$ in the container and the final temperature is $61.0 ^\circ\text{C}$?

- A. $35 \text{ J/}^\circ\text{C}$
- B. $4.12 \times 10^3 \text{ J/}^\circ\text{C}$
- C. $21 \text{ J/}^\circ\text{C}$
- D. $4.53 \times 10^3 \text{ J/}^\circ\text{C}$
- E. $50. \text{ J/}^\circ\text{C}$

Your Turn! - Solution

What is the heat capacity of a container if 100. g of water ($s = 4.18 \text{ J/g } ^\circ\text{C}$) at $100. ^\circ\text{C}$ are added to 100. g of water at $25.0 ^\circ\text{C}$ in the container and the final temperature is $61.0 ^\circ\text{C}$?

$$q_{\text{lost by hot water}} = m \times \Delta t \times s$$

$$= (100. \text{ g}) (61.0 ^\circ\text{C} - 100. ^\circ\text{C}) (4.18 \text{ J/g } ^\circ\text{C}) = -1.63 \times 10^4 \text{ J}$$

$$q_{\text{gained by cold water}} = (100. \text{ g}) (61.0 ^\circ\text{C} - 25.0 ^\circ\text{C}) (4.18 \text{ J/g } ^\circ\text{C})$$

$$= \mathbf{1.50 \times 10^4 \text{ J}}$$

$$q_{\text{lost by system}} = 1.50 \times 10^4 \text{ J} + (-1.63 \times 10^4 \text{ J}) = -1.3 \times 10^3 \text{ J}$$

$$q_{\text{container}} = -q_{\text{lost by system}} = \mathbf{+1.3 \times 10^3 \text{ J}}$$

$$C = \frac{q}{\Delta t} = \frac{1.3 \times 10^3 \text{ J}}{(61.0 - 25.0) ^\circ\text{C}} = \mathbf{36 \text{ J/}^\circ\text{C}}$$

Chemical Bonds and Energy

Chemical bond

- Attractive forces that bind
 - Atoms to each other in molecules, or
 - Ions to each other in ionic compounds
 - Give rise to compound's potential energy

Chemical energy

- Potential energy stored in chemical bonds

Chemical reactions

- Generally involve both breaking and making chemical bonds

Chemical Reactions

Forming Bonds

- Atoms that are attracted to each other are moved closer together
- Decrease the potential energy of reacting system
- Releases energy

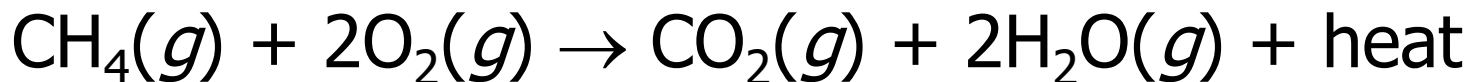
Breaking Bonds

- Atoms that are attracted to each other are forced apart
- Increase the potential energy of reacting system
- Requires energy

Exothermic Reaction

- Reaction where products have less chemical energy than reactants
 - Some chemical heat energy converted to kinetic energy
 - Reaction releases heat energy to surroundings
 - Heat leaves the system; q is negative (-)
 - Heat energy is a ***product***
 - Reaction gets warmer, temperature increases

Example:



Endothermic Reaction

- Reaction where products have more chemical energy than reactants
 - Some kinetic energy converted to chemical energy
 - Reaction absorbs heat from surroundings
 - Heat added to system; q is positive (+)
 - Heat energy is a ***reactant***
 - Reaction becomes colder, temperature decreases

Example: Photosynthesis



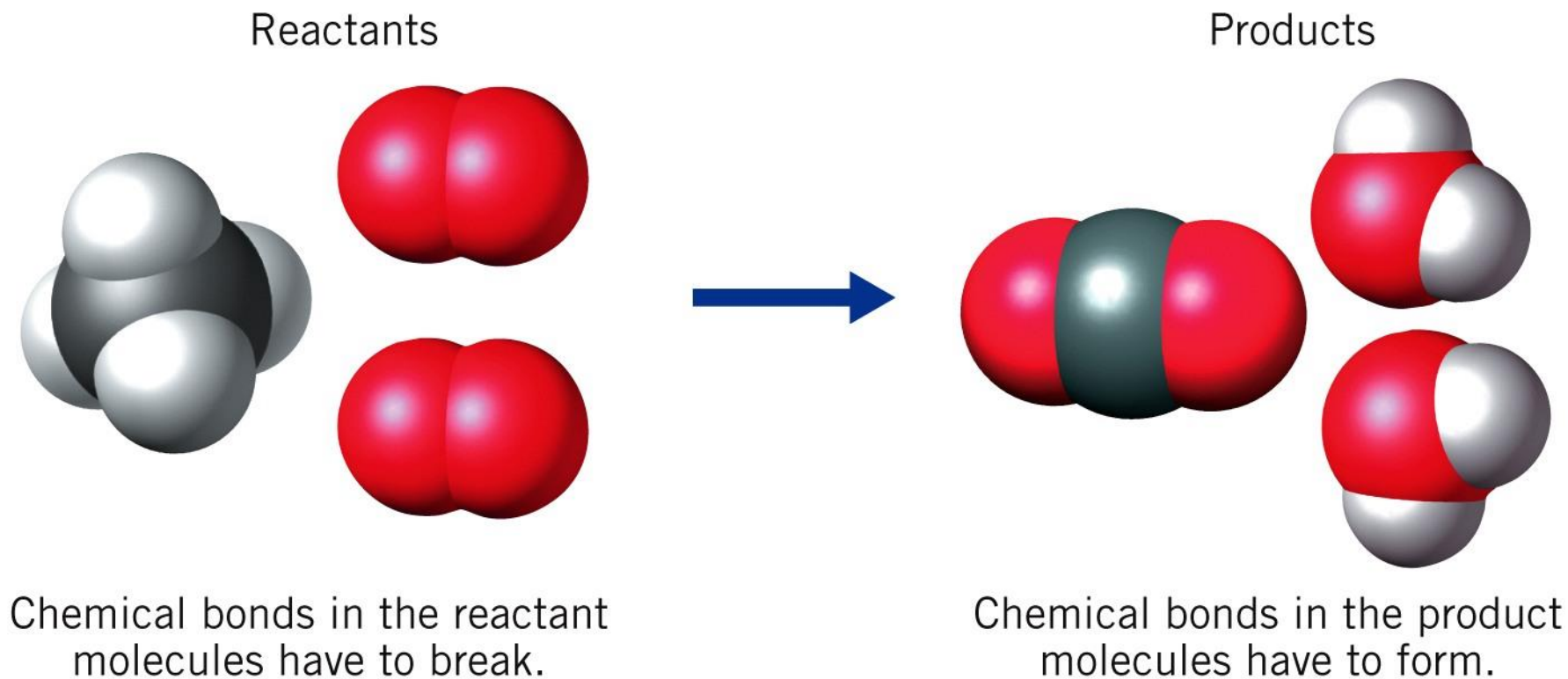
Bond Strength

- Measure of how much **energy** is needed to break bond or how much energy is released when bond is formed.
- Larger amount of energy equals a stronger bond
 - Weak bonds require less energy to break than strong bonds
- Key to understanding reaction energies

Example: If reaction has

- Weak bonds in reactants and
- Stronger bonds in products
- Heat released

Why Fuels Release Heat



- Methane and oxygen have weaker bonds
- Water and carbon dioxide have stronger bonds

Your Turn!

Chemical energy is

- A. the kinetic energy resulting from violent decomposition of energetic chemicals
- B. the heat energy associated with combustion reactions
- C. the electrical energy produced by fuel cells
- D. the potential energy which resides in chemical bonds
- E. the energy living plants receive from solar radiation

Your Turn!

Which of the following is an endothermic process?

- A. $\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$ Attraction of charges releases heat
- B. wood burning Produces heat (i.e., heat released)
- C. $\text{CH}_4(\text{g}) \rightarrow \text{C}(\text{g}) + 4\text{H}(\text{g})$ Breaking bonds requires heat
- D. a bomb exploding Produces heat (i.e., heat released)
- E. water condensing Heat must be released

Heat of Reaction

- Amount of heat absorbed or released in chemical reaction
- Determined by measuring temperature change they cause in surroundings

Calorimeter

- Instrument used to measure temperature changes
- Container of known heat capacity
- Use results to calculate heat of reaction

Calorimetry

- Science of using calorimeter to determine heats of reaction

Heats of Reaction

- Calorimeter design not standard
 - Depends on
 - Type of reaction
 - Precision desired
- Usually measure heat of reaction under one of two sets of conditions
 - **Constant volume, q_V**
 - Closed, rigid container
 - **Constant pressure, q_P**
 - Open to atmosphere

What is Pressure?

- Amount of force acting on unit area

$$\text{Pressure} = \frac{\text{force}}{\text{area}}$$

Atmospheric Pressure

- Pressure exerted by Earth's atmosphere by virtue of its weight.
 - $\sim 14.7 \text{ lb/in}^2$
- Container open to atmosphere
 - Under constant P conditions
 - $P \sim 14.7 \text{ lb/in}^2 \sim 1 \text{ atm} \sim 1 \text{ bar}$

Comparing q_V and q_P

- Difference between q_V and q_P can be significant
- Reactions involving large volume changes,
 - Consumption or production of gas
- Consider gas phase reaction in cylinder immersed in bucket of water
 - Reaction vessel is cylinder topped by piston
 - Piston can be locked in place with pin
 - Cylinder immersed in insulated bucket containing weighed amount of water
 - Calorimeter consists of piston, cylinder, bucket, and water

Comparing q_V and q_P

- Heat capacity of calorimeter = 8.101 kJ/°C
- Reaction run twice, identical amounts of reactants

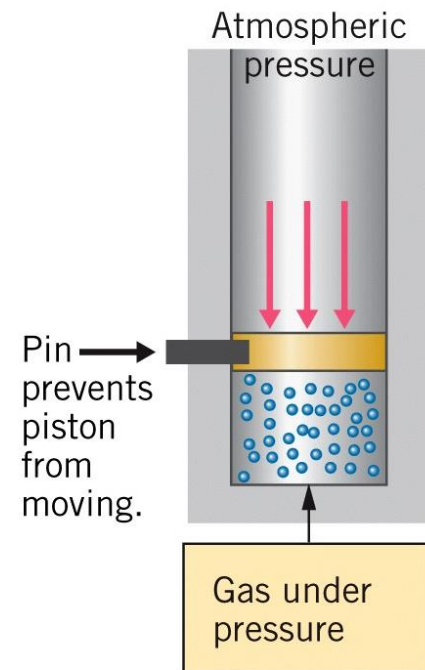
Run 1: q_V - Constant Volume

- Same reaction run once at constant volume and once at constant pressure
- Pin locked
- $t_i = 24.00$ °C; $t_f = 28.91$ °C

$$q_{cal} = C\Delta t$$

$$= 8.101 \text{ J/}^\circ\text{C} \times (28.91 - 24.00)^\circ\text{C} = 39.8 \text{ kJ}$$

$$q_V = -q_{cal} = -39.8 \text{ kJ}$$



Comparing q_V and q_P

Run 2: q_P

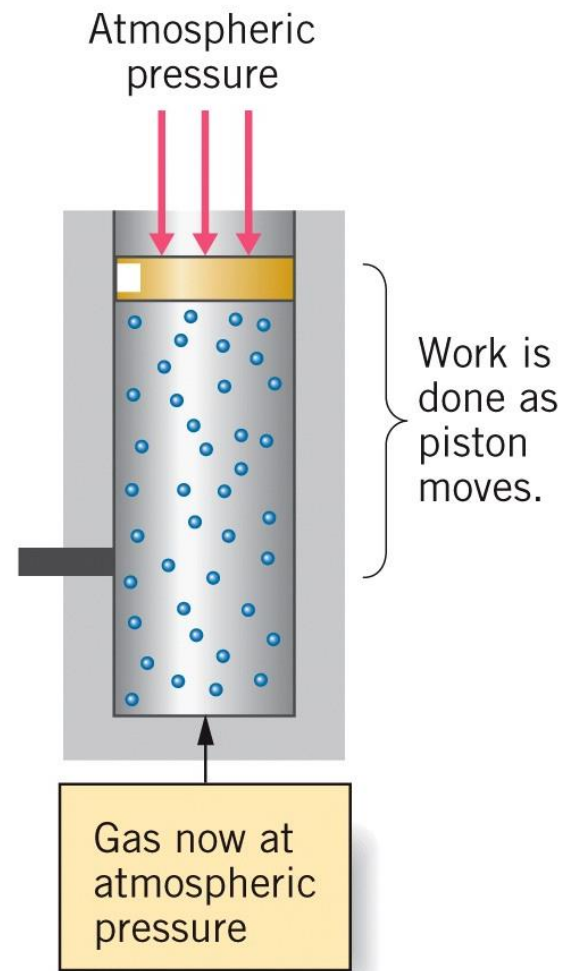
- Run at atmospheric pressure
- Pin unlocked
- $t_i = 27.32\text{ }^\circ\text{C}$; $t_f = 31.54\text{ }^\circ\text{C}$
- Heat absorbed by calorimeter is

$$q_{cal} = C\Delta t$$

$$= 8.101\text{ J}/\cancel{^\circ\text{C}} \times (31.54 - 27.32)\cancel{^\circ\text{C}}$$

$$= 34.2\text{ kJ}$$

$$q_P = -q_{cal} = -34.2\text{ kJ}$$



Comparing q_V and q_P

- $q_V = -39.8 \text{ kJ}$
- $q_P = -34.2 \text{ kJ}$
- System (reacting mixture) expands, pushes against atmosphere, does ***work***
 - Uses up some energy that would otherwise be heat
 - **Work** = $(-39.8 \text{ kJ}) - (-34.2 \text{ kJ}) = -5.6 \text{ kJ}$
- Expansion work or pressure volume work
 - **Minus sign means energy leaving system**

Work Convention

$$\text{Work} = -P \times \Delta V$$

- P = opposing pressure against which piston pushes
- ΔV = change in volume of gas during expansion
- $\Delta V = V_{\text{final}} - V_{\text{initial}}$
- For expansion
 - Since $V_{\text{final}} > V_{\text{initial}}$
 - ΔV must be positive
 - So expansion work is negative
 - Work done **by** system

Your Turn!

Calculate the work associated with the expansion of a gas from 152.0 L to 189.0 L at a constant pressure of 17.0 atm.

A. 629 L atm

B. -629 L atm

C. -315 L atm

D. 171 L atm

E. 315 L atm

$$\text{Work} = -P \times \Delta V$$

$$\Delta V = 189.0 \text{ L} - 152.0 \text{ L} = 37.0 \text{ L}$$

$$W = -17.0 \text{ atm} \times 37.0 \text{ L}$$

Your Turn!

A chemical reaction took place in a 6 liter cylindrical enclosure fitted with a piston. Over the course of the reaction, the system underwent a volume change from 0.400 liters to 3.20 liters. Which statement below is always **true**?

- A. Work was performed on the system.
- B. Work was performed by the system.
- C. The internal energy of the system increased.
- D. The internal energy of the system decreased.
- E. The internal energy of the system remained unchanged.

First Law of Thermodynamics

- In an isolated system, the change in internal energy (ΔE) is constant:

$$\Delta E = E_f - E_i = 0$$

- Can't measure internal energy of anything
- Can measure changes in energy

E is state function

$\Delta E = \text{heat} + \text{work}$

$\Delta E = q + w$

$\Delta E = \text{heat input} + \text{work input}$

First Law of Thermodynamics

- Energy of system may be transferred as heat or work, but not lost or gained
- If we monitor heat transfers (q) of all materials involved and all work processes, can predict that their sum will be zero
 - Some energy transfers will be positive, gain in energy
 - Some energy transfers will be negative, a loss in energy
- By monitoring surroundings, we can predict what is happening to system

First Law of Thermodynamics

- $\Delta E = q + w$

q is (+)	Heat absorbed by system (IN)
q is (-)	Heat released by system (OUT)
w is (+)	Work done on system (IN)
w is (-)	Work done by system (OUT)

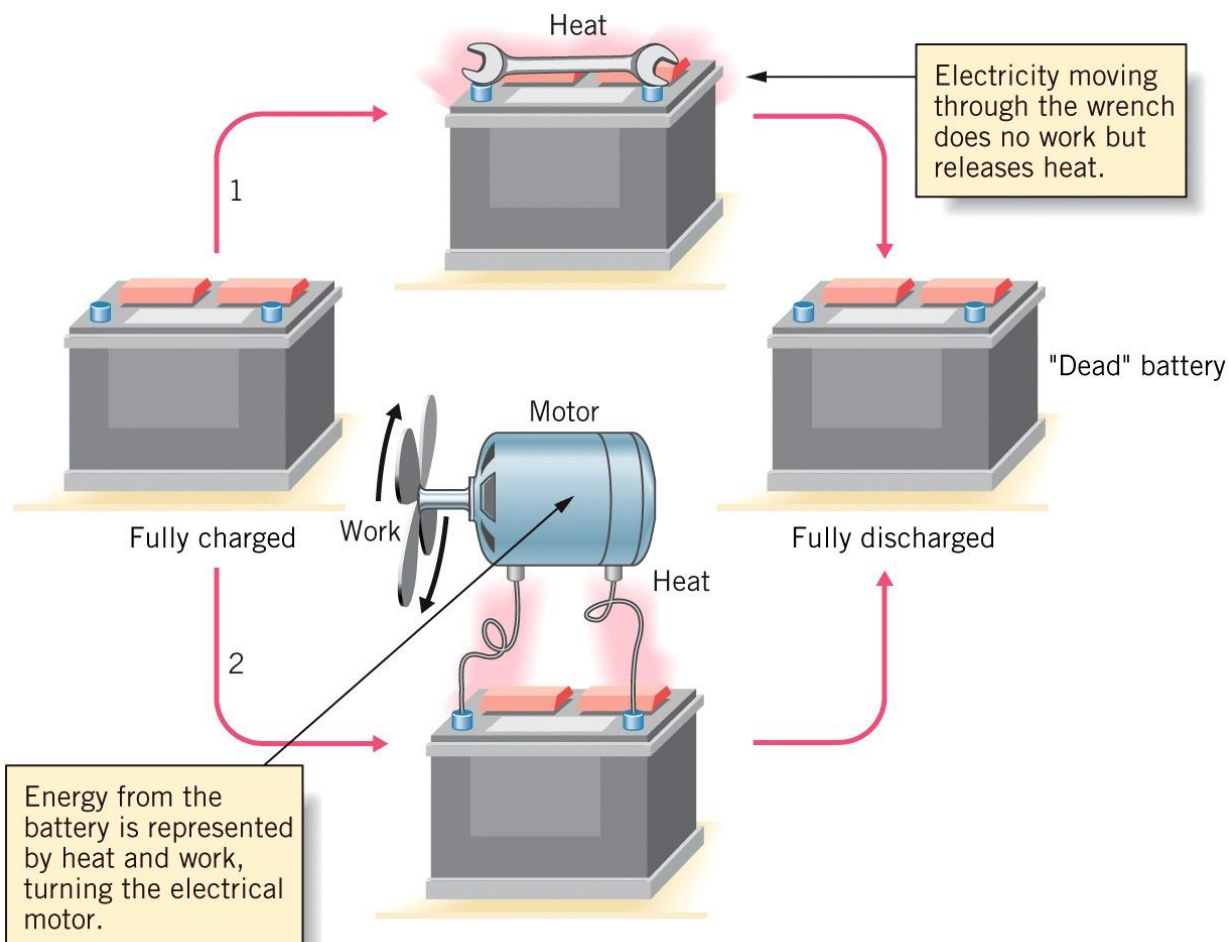
Endothermic reaction

- $\Delta E = +$

Exothermic reaction

- $\Delta E = -$

ΔE is Independent of Path



q and w

- NOT path independent
- NOT state functions
- Depend on how change takes place

Discharge of Car Battery

Path *a*

- Short out with wrench
- All energy converted to heat, no work
 - $\Delta E = q$ ($w = 0$)

Path *b*

- Run motor
- Energy converted to work and little heat
 - $\Delta E = w + q$ ($w \gg q$)
- ΔE is same for each path
 - Partitioning between two paths differs

Your Turn!

A gas releases 3.0 J of heat and then performs 12.2 J of work. What is the change in internal energy of the gas?

A. -15.2 J

B. 15.2 J

C. -9.2 J

D. 9.2 J

E. 3.0 J

$$E = q + w$$

$$E = -3.0 \text{ J} + (-12.2 \text{ J})$$

Your Turn!

Which of the following is **not** an expression for the First Law of Thermodynamics?

- A. Energy is conserved
- B. Energy is neither created nor destroyed
- C. The energy of the universe is constant
- D. Energy can be converted from work to heat
- E. The energy of the universe is increasing

Your Turn!

A reaction contracts by 1.534 L under a constant pressure of 2.134 atm while releasing 200.7 J of heat to the surrounding. What is the change in internal energy of the system? 1.000 Latm = 101.3 J

$$E = q + w = -200.7 \text{ J} + w$$

A. 131.0 J

$$\text{Work} = -P \times \Delta V$$

B. 532.4 J

$$= -2.134 \text{ atm} \times 1.534 \text{ L} = 3.274 \text{ Latm}$$

C. -131.0 J

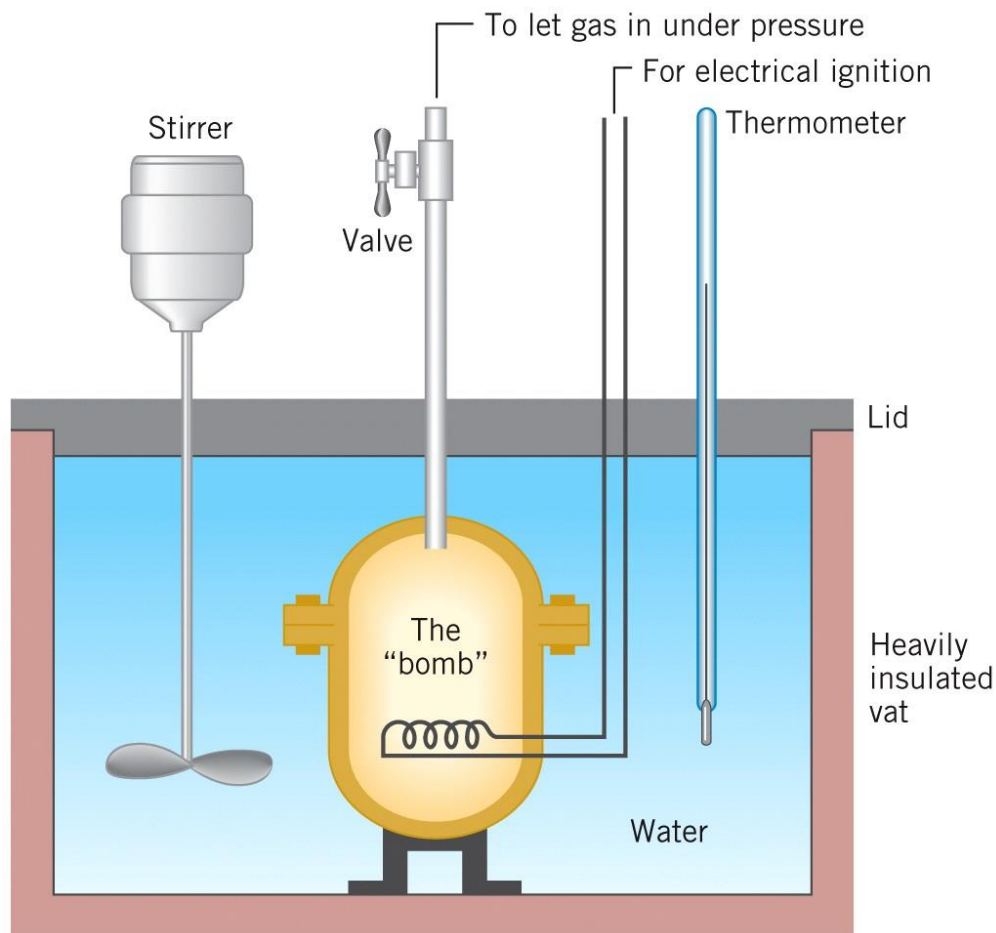
$$= 3.274 \text{ Latm} \times \frac{101.3 \text{ J}}{1.000 \text{ Latm}} = 331.7 \text{ J}$$

D. -532.4 J

E. 331.6 J

$$E = q + w = -200.7 \text{ J} + 331.7 \text{ J} = 131.0 \text{ J}$$

Bomb Calorimeter (Constant V)



- Apparatus for measuring ΔE in reactions at constant volume
- Vessel in center with rigid walls
- No change in volume, so $\Delta V = 0$ so $P\Delta V = 0$
- Heavily insulated vat
 - Water bath
 - No heat escapes
- $\Delta E = q - P\Delta V$
- $\Delta E = q + 0 = q_v$
- subscript ' v ' emphasizes constant **volume**

Example 4: Calorimeter Problem

When 1.000 g of olive oil is completely burned in pure oxygen in a bomb calorimeter, the temperature of the water bath increases from 22.000 °C to 26.049 °C.

a) How many Calories are in olive oil, per gram? The heat capacity of the calorimeter is 9.032 kJ/°C.

$$\Delta t = 26.049 \text{ }^\circ\text{C} - 22.000 \text{ }^\circ\text{C} = 4.049 \text{ }^\circ\text{C}$$

$$q_{\text{absorbed by calorimeter}} = C\Delta t = 9.032 \text{ kJ}/\cancel{\text{ }^\circ\text{C}} \times 4.049 \cancel{\text{ }^\circ\text{C}}$$

$$= 36.57 \text{ kJ}$$

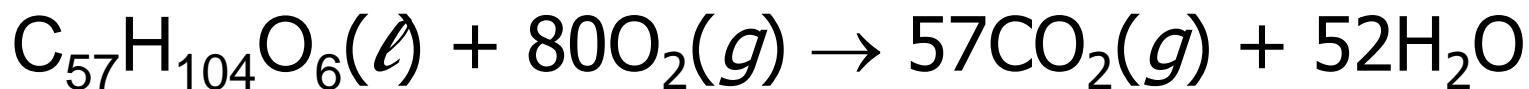
$$q_{\text{released by oil}} = -q_{\text{calorimeter}} = -36.57 \text{ kJ}$$

$$q_{\text{oil}} \text{ (in cal/g)} = \frac{-36.57 \cancel{\text{ kJ}}}{1.000 \text{ g}} \times \frac{1 \cancel{\text{ kcal}}}{4.184 \cancel{\text{ kJ}}} \times \frac{1 \text{ Cal}}{1 \cancel{\text{ kcal}}}$$

-8.740 Cal/g oil

Ex. 4 Calorimeter Problem (cont)^{6.6}

b) Olive oil is almost pure glyceryl trioleate, $C_{57}H_{104}O_6$. The equation for its combustion is



What is ΔE for the combustion of one mole of glyceryl trioleate (MM = 885.4 g/mol)? Assume the olive oil burned in part a) was pure glyceryl trioleate.

$$\frac{-36.57 \text{ kJ}}{1.000 \text{ g } C_{57}H_{104}O_6} \times \frac{885.4 \text{ g } C_{57}H_{104}O_6}{1 \text{ mol } C_{57}H_{104}O_6}$$

$$\Delta E = q_V = -3.238 \times 10^4 \text{ kJ/mol oil}$$

Your Turn!

A bomb calorimeter has a heat capacity of 2.47 kJ/K. When a 3.74×10^{-3} mol sample of ethylene was burned in this calorimeter, the temperature increased by 2.14 K. Calculate the energy of combustion for one mole of ethylene.

- A. -5.29 kJ/mol
- B. 5.29 kJ/mol
- C. -148 kJ/mol
- D. -1410 kJ/mol
- E. 1410 kJ/mol

$$q_{\text{cal}} = C\Delta t$$

$$= 2.47 \text{ kJ/K} \times 2.14 \text{ K} = 5.286 \text{ kJ}$$

$$q_{\text{ethylene}} = -q_{\text{cal}} = -5.286 \text{ kJ}$$

$$\Delta E_{\text{ethylene}} = \frac{-5.286 \text{ kJ}}{3.74 \times 10^{-3} \text{ mol}}$$

$$\Delta E_{\text{ethylene}} = -1410 \text{ kJ/mol}$$

Enthalpy (H)

- Heat of reaction at constant **pressure** (q_p)

$$H = E + PV$$

- Similar to E , but for systems at constant P
- Now have $P\Delta V$ work + heat transfer
- H = state function
- At constant pressure

$$\Delta H = \Delta E + P\Delta V = (q_p + w) + P\Delta V$$

If only work is P–V work, $w = -P\Delta V$

$$\Delta H = (q_p + w) - w = q_p$$

Enthalpy Change (ΔH)

H is a state function

- $\Delta H = H_{\text{final}} - H_{\text{initial}}$
- $\Delta H = H_{\text{products}} - H_{\text{reactants}}$
- Significance of sign of ΔH

Endothermic reaction

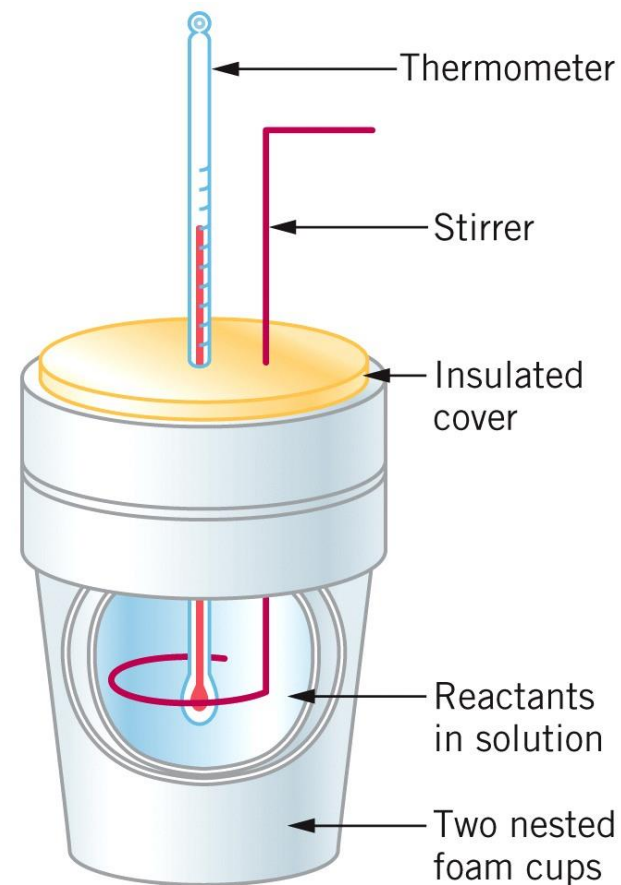
- System absorbs energy from surroundings
- ΔH positive

Exothermic reaction

- System loses energy to surroundings
- ΔH negative

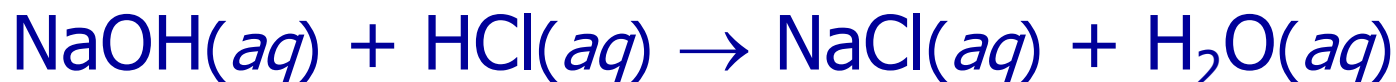
Coffee Cup Calorimeter

- Simple
- Measures q_p
- Open to atmosphere
 - Constant P
- Let heat be exchanged between reaction and water, and measure change in temperature
 - Very little heat lost
- Calculate heat of reaction
 - $q_p = C\Delta t$



Ex. 5: Coffee Cup Calorimetry

NaOH and HCl undergo rapid and exothermic reaction when you mix 50.0 mL of 1.00 *M* HCl and 50.0 mL of 1.00 *M* NaOH. The initial $t = 25.5$ °C and final $t = 32.2$ °C. What is ΔH in kJ/mole of HCl? Assume for these solutions $s = 4.184$ J g⁻¹°C⁻¹. Density: 1.00 *M* HCl = 1.02 g mL⁻¹; 1.00 *M* NaOH = 1.04 g mL⁻¹.



$$q_{\text{absorbed by solution}} = \text{mass} \times s \times \Delta t$$

$$\text{mass}_{\text{HCl}} = 50.0 \text{ mL} \times 1.02 \text{ g/mL} = 51.0 \text{ g}$$

$$\text{mass}_{\text{NaOH}} = 50.0 \text{ mL} \times 1.04 \text{ g/mL} = 52.0 \text{ g}$$

$$\text{mass}_{\text{final solution}} = 51.0 \text{ g} + 52.0 \text{ g} = 103.0 \text{ g}$$

$$\Delta t = (32.2 - 25.5) \text{ °C} = 6.7 \text{ °C}$$

Ex. 5: Coffee Cup Calorimetry

$$q_{cal} = 103.0 \text{ g} \times 4.184 \text{ J g}^{-1} \text{ } ^\circ\text{C}^{-1} \times 6.7 \text{ } ^\circ\text{C} = 2890 \text{ J}$$

Rounds to $q_{cal} = 2.9 \times 10^3 \text{ J} = 2.9 \text{ kJ}$

$$q_{rxn} = -q_{calorimeter} = -2.9 \text{ kJ}$$

$$0.0500 \text{ L HCl soln} \times \frac{1 \text{ mol HCl}}{1 \text{ L HCl soln}}$$

$$= 0.0500 \text{ mol HCl}$$

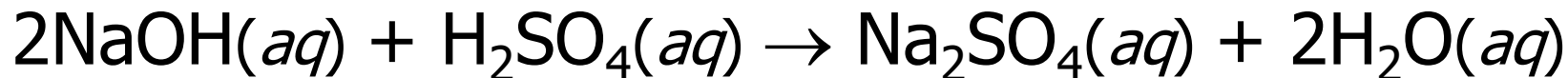
Heat evolved per mol HCl =

$$\Delta H = \frac{-2.9 \text{ kJ}}{0.0500 \text{ mol HCl}} = -58 \text{ kJ/mol}$$

Ex. 6: Coffee Cup Calorimetry

When 50.0 mL of 0.987 M H_2SO_4 is added to 25.0 mL of 2.00 M $NaOH$ at 25.0 ° C in a calorimeter, the temperature of the aqueous solution increases to 33.9 ° C. Calculate ΔH in kJ/mole of limiting reactant. Assume: specific heat of the solution is 4.184 J/g ° C, density is 1.00 g/mL, and the calorimeter absorbs a negligible amount of heat.

Write balanced equation



Determine heat absorbed by calorimeter

$$\text{mass}_{\text{soln}} = (25.0 \text{ mL} + 50.0 \text{ mL}) \times 1.00 \text{ g/mL} = 75.0 \text{ g}$$

$$q_{\text{soln}} = 75.0 \text{ g} \times (33.9 - 25.0)^\circ\text{C} \times 4.184 \text{ J/g}^\circ\text{C} = \mathbf{2.8 \times 10^3 \text{ J}}$$

Ex. 6: Determine Limiting Reagent

$$50.0 \text{ mL } \cancel{\text{H}_2\text{SO}_4} \times \frac{1 \text{ L } \cancel{\text{H}_2\text{SO}_4}}{1000 \text{ mL } \cancel{\text{H}_2\text{SO}_4}} \times \frac{0.987 \text{ mol H}_2\text{SO}_4}{1 \text{ L } \cancel{\text{H}_2\text{SO}_4}}$$

$$= 0.04935 \text{ mol H}_2\text{SO}_4 \text{ present}$$

$$0.04935 \text{ mol } \cancel{\text{H}_2\text{SO}_4} \times \frac{2 \text{ mol NaOH}}{1 \text{ mol } \cancel{\text{H}_2\text{SO}_4}} = 0.0987 \text{ mol NaOH}$$

needed

$$25.0 \text{ mL } \cancel{\text{NaOH}} \times \frac{1 \text{ L } \cancel{\text{NaOH}}}{1000 \text{ mL } \cancel{\text{NaOH}}} \times \frac{2 \text{ mol NaOH}}{1 \text{ L } \cancel{\text{NaOH}}}$$

$$= 0.0500 \text{ mol NaOH present}$$

NaOH is limiting

$$\Delta H = \frac{-2.8 \times 10^3 \cancel{\text{ J}}}{0.0500 \text{ mol NaOH}} \times \frac{1 \text{ kJ}}{1000 \cancel{\text{ J}}} = \mathbf{-56 \text{ kJ/mol}}$$

Your Turn!

A 43.29 g sample of solid is transferred from boiling water ($t = 99.8\text{ }^{\circ}\text{C}$) to 152 g water at $22.5\text{ }^{\circ}\text{C}$ in a coffee cup. The temperature of the water rose to $24.3\text{ }^{\circ}\text{C}$. Calculate the specific heat of the solid.

A. $-1.1 \times 10^3\text{ J g}^{-1}\text{ }^{\circ}\text{C}^{-1}$

B. $1.1 \times 10^3\text{ J g}^{-1}\text{ }^{\circ}\text{C}^{-1}$

C. $1.0\text{ J g}^{-1}\text{ }^{\circ}\text{C}^{-1}$

D. $0.35\text{ J g}^{-1}\text{ }^{\circ}\text{C}^{-1}$

E. $0.25\text{ J g}^{-1}\text{ }^{\circ}\text{C}^{-1}$

$$q = m \times s \times \Delta t$$

$$q_{\text{water}} = 152\text{ g} \cdot \frac{4.184\text{ J}}{\text{g }^{\circ}\text{C}} \cdot (24.3 - 22.5)\text{ }^{\circ}\text{C}$$

$$= 1.1 \times 10^3\text{ J}$$

$$q_{\text{sample}} = -q_{\text{water}} = -1.1 \times 10^3\text{ J}$$

$$s = \frac{-1.1 \times 10^3\text{ J}}{43.29\text{ g} \times (24.3 - 99.8)\text{ }^{\circ}\text{C}}$$

Enthalpy Changes in Chemical Reactions

- Focus on systems
- Endothermic
 - Reactants + *heat* \longrightarrow products
- Exothermic
 - Reactants \longrightarrow products + *heat*
- Want convenient way to use enthalpies to calculate reaction enthalpies
- Need way to tabulate enthalpies of reactions

The Standard State

- A **standard state** specifies all the necessary parameters to describe a system. Generally this includes the pressure, temperature, and amount and state of the substances involved
- **Standard state in thermochemistry**
 - Pressure = 1 atmosphere
 - Temperature = 25 °C = 298 K
 - Amount of substance = 1 mol (for formation reactions and phase transitions)
 - Amount of substance = moles in an equation (balanced with the smallest whole number coefficients)

Thermodynamic Quantities

- E and H are state functions and are also extensive properties
- ΔE and ΔH are measurable changes but still extensive properties
 - Often used where n is not standard, or specified
 - ΔE° and ΔH° are standard changes and intensive properties
 - Units of kJ /mol for formation reactions and phase changes (e.g., ΔH°_f or $\Delta H^\circ_{\text{vap}}$)
 - Units of kJ for balanced chemical equations ($\Delta H^\circ_{\text{reaction}}$)

ΔH in Chemical Reactions

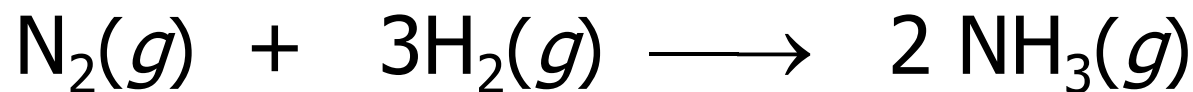
Standard Conditions for ΔH 's

- 25 °C and 1 atm and 1 mole

Standard Heat of Reaction (ΔH°)

- Enthalpy change for reaction at 1 atm and 25 °C

Example:

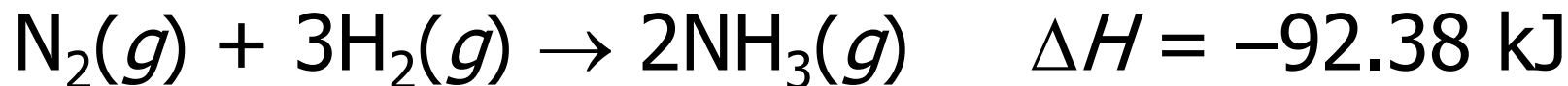


1.000 mol 3.000 mol 2.000 mol

- When N_2 and H_2 react to form NH_3 at 25 °C and 1 atm 92.38 kJ released
- $\Delta H = -92.38 \text{ kJ}$

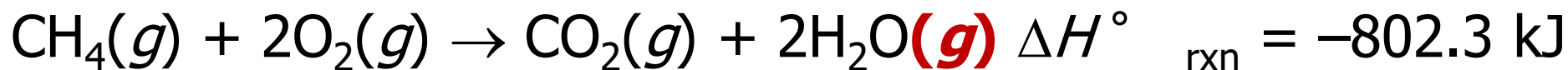
Thermochemical Equation

- Write ΔH immediately after equation



- Must give physical states of products and reactants**

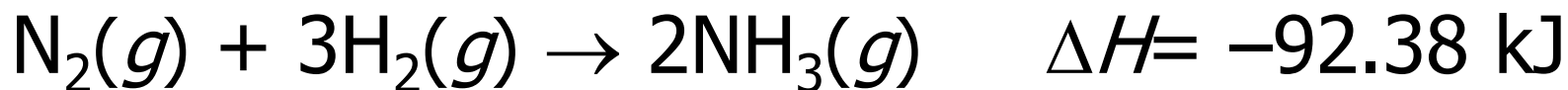
- ΔH different for different states



- Difference is equal to the energy to vaporize water

Thermochemical Equation

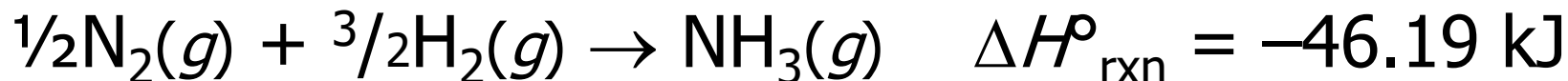
- Write ΔH immediately after equation



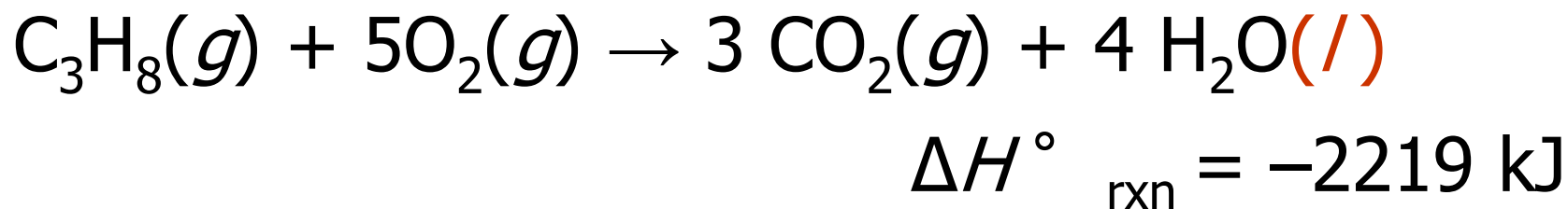
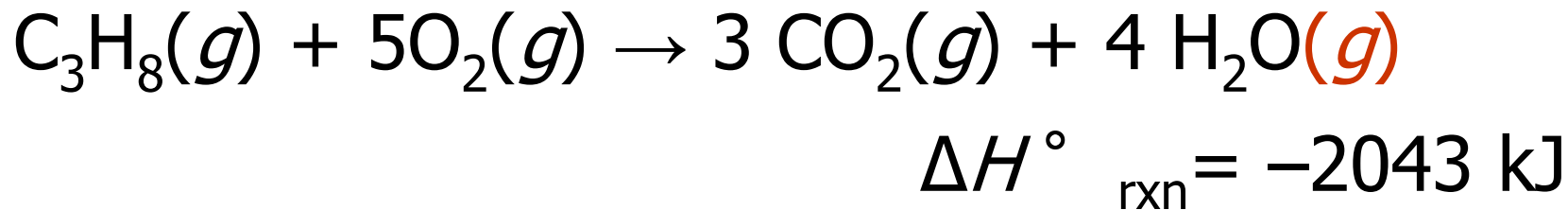
- Assumes coefficients is the number of moles
 - 92.38 kJ released when 2 moles of NH_3 formed
 - If 10 mole of NH_3 formed



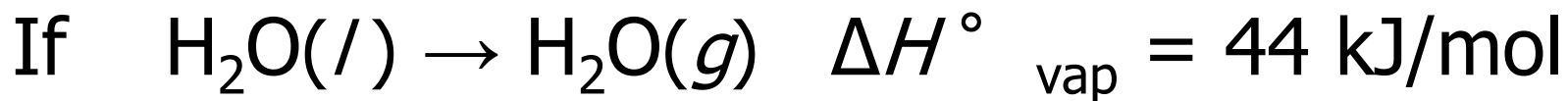
- $\Delta H^\circ = (5 \times -92.38 \text{ kJ}) = -461.9 \text{ kJ}$
- Can have fractional coefficients
 - Fraction of mole, NOT fraction of molecule



State Matters!



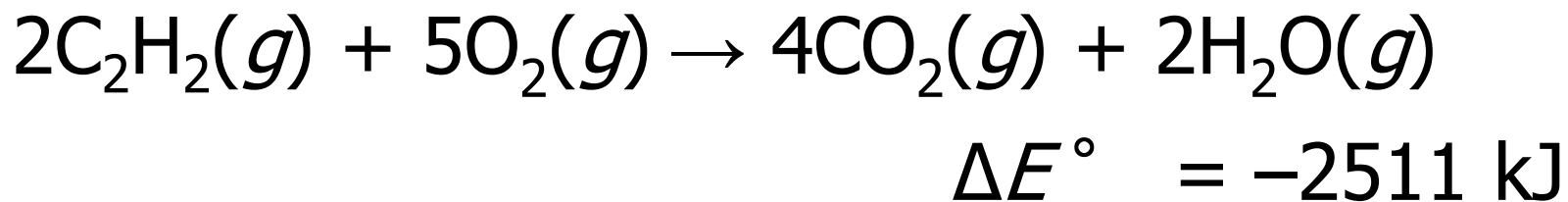
Note: there is difference in energy because states do not match



$$\text{Or } -2219 \text{ kJ} + 176 \text{ kJ} = -2043 \text{ kJ}$$

Learning Check:

Consider the following reaction:

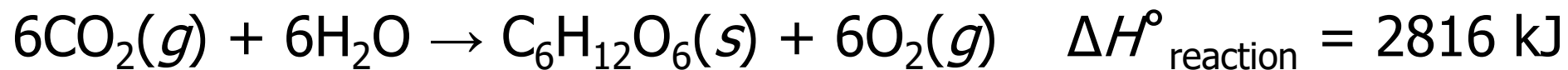


The reactants (acetylene and oxygen) have 2511 kJ more energy than products. How many kJ are released for 1 mol C_2H_2 ?

$$\frac{-2511 \text{ kJ}}{2 \text{ mol C}_2\text{H}_2} \cdot 1 \text{ mol C}_2\text{H}_2 = -1,256 \text{ kJ}$$

Learning Check:

Given the equation below, how many kJ are required for 44 g CO₂ (MM = 44.01 g/mol) to react with H₂O?



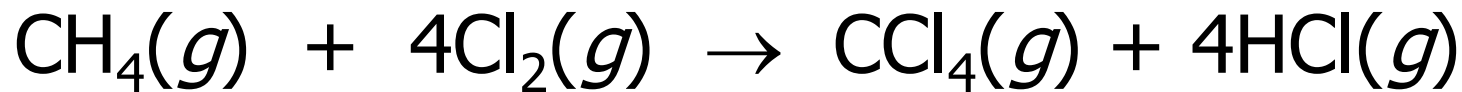
$$44 \cancel{\text{g CO}_2} \times \frac{1 \cancel{\text{mol CO}_2}}{44.01 \cancel{\text{g CO}_2}} \times \frac{2816 \text{ kJ}}{6 \cancel{\text{mol CO}_2}} = \mathbf{470 \text{ kJ}}$$

▪ If 100. kJ are provided, what mass of CO₂ can be converted to glucose?

$$100 \cancel{\text{kJ}} \times \frac{6 \cancel{\text{mol CO}_2}}{2816 \cancel{\text{kJ}}} \times \frac{44 \text{ g CO}_2}{1 \cancel{\text{mol CO}_2}} = \mathbf{9.4 \text{ g}}$$

Your Turn!

Based on the reaction



$$\Delta H^\circ_{\text{reaction}} = -434 \text{ kJ/mol CH}_4$$

What energy change occurs when 1.2 moles of methane reacts?

A. $-3.6 \times 10^2 \text{ kJ}$

~~$\Delta H = -434 \text{ kJ/mol} \times 1.2 \text{ mol}$~~

B. $5.2 \times 10^2 \text{ kJ}$

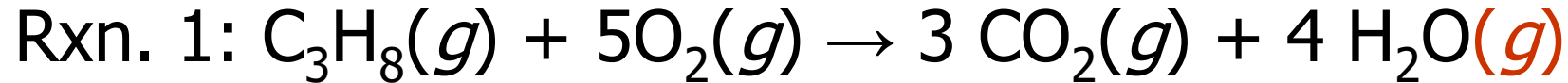
$\Delta H = -520.8 \text{ kJ} = 5.2 \times 10^2 \text{ kJ}$

C. $-4.3 \times 10^2 \text{ kJ}$

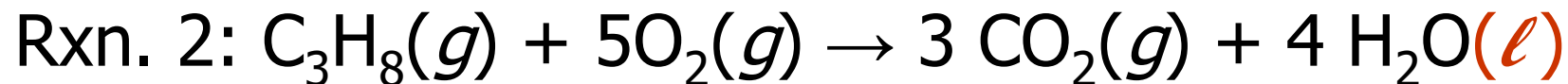
D. $3.6 \times 10^2 \text{ kJ}$

E. $-5.2 \times 10^2 \text{ kJ}$

Your Turn!



$$\Delta H^\circ_{\text{rxn}} = -2043 \text{ kJ}$$



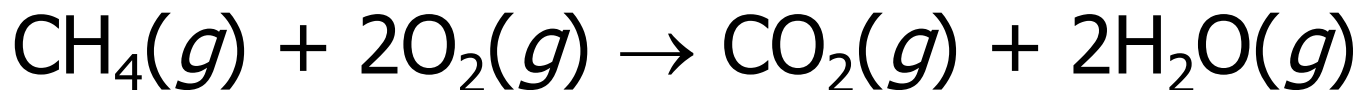
$$\Delta H^\circ_{\text{rxn}} = -2219 \text{ kJ}$$

Why does rxn. 2 release more heat than rxn. 1?

- A. It shouldn't, and the ΔH values should be equal
- B. More reactants must have been used in rxn. 2
- C. In rxn. 1 some of the heat of the reaction is used up converting liquid water to gas, so less heat can be given off.
- D. Liquids always have lower temperatures than gases

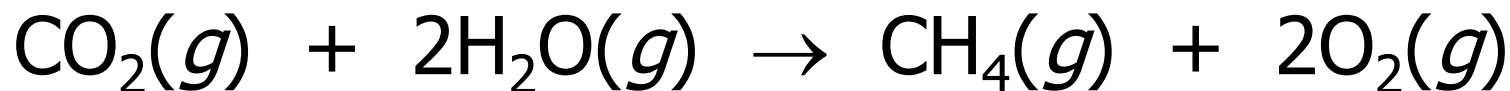
Reversing Thermochemical Equations

Consider



$$\Delta H^\circ_{\text{reaction}} = -802.3 \text{ kJ}$$

- Reverse thermochemical equation
- Must change sign of ΔH



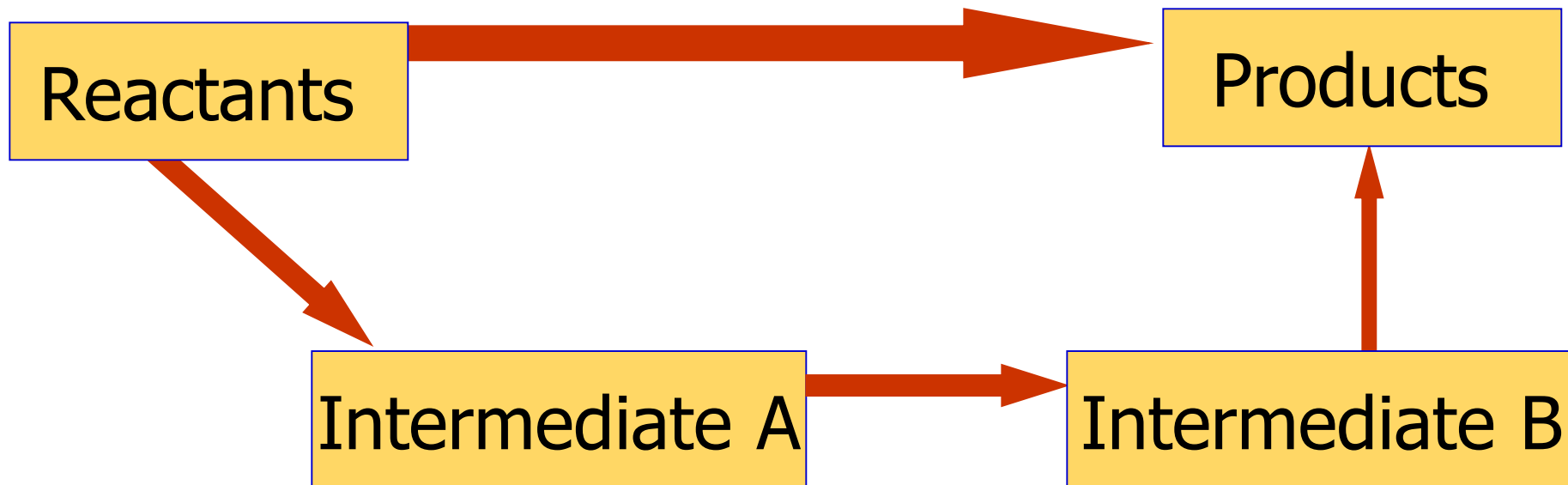
$$\Delta H^\circ_{\text{reaction}} = 802.3 \text{ kJ}$$

Reversing Thermochemical Equations Changes sign of ΔH

- Makes sense:
 - Get energy ***out*** when form products
 - Must put energy ***in*** to go back to reactants
- **Consequence of Law of Conservation of Energy**
 - Like mathematical equation
 - If you know ΔH° for reaction, you also know ΔH° for the reverse

Multiple Paths; Same ΔH°

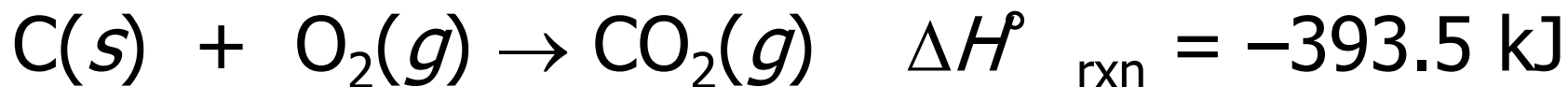
- Can often get from reactants to products by several different paths



- Should get same ΔH°
- Enthalpy is state function and path independent
- Let's see if this is true

Ex. 7: Multiple Paths; Same ΔH°

Path a: Single step

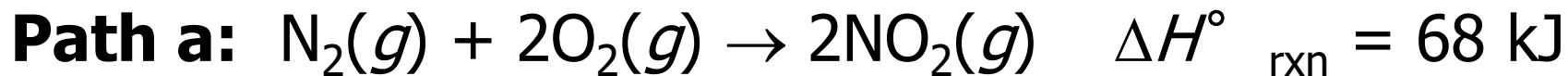


Path b: Two step

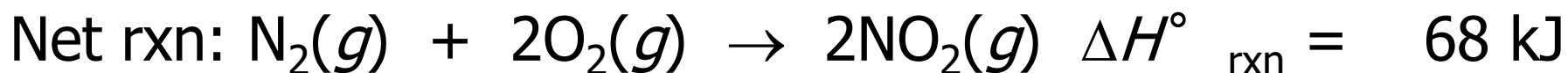
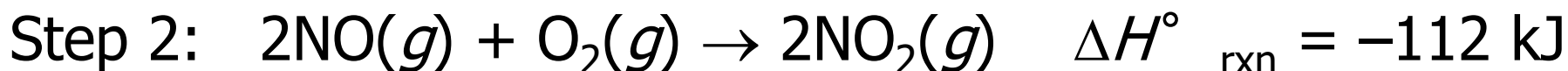


- Chemically and thermochemically, identical results
- True for exothermic and endothermic reactions

Ex. 8: Multiple Paths; Same ΔH_{rxn} ^{6.8}



Path b:

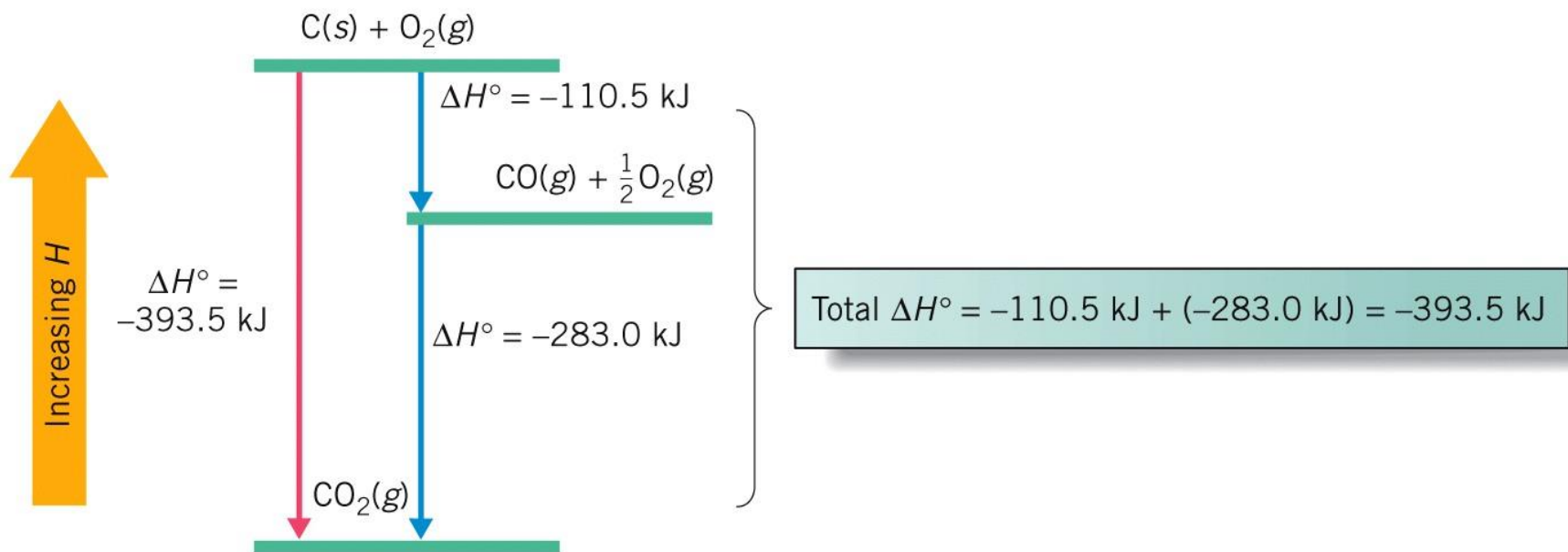


Hess' s Law of Heat Summation

- For any reaction that can be written into steps, value of $\Delta H^\circ_{\text{rxn}}$ for reactions = sum of $\Delta H^\circ_{\text{rxn}}$ values of each individual step

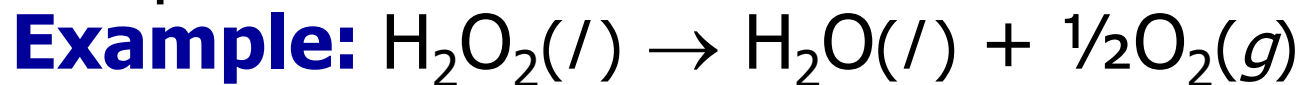
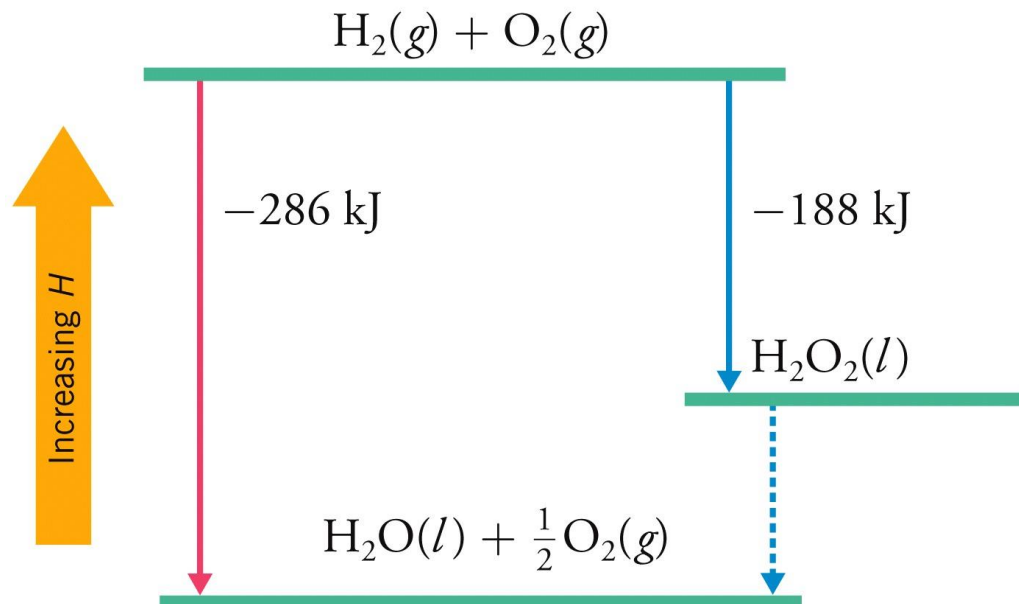
Enthalpy Diagrams

- Graphical description of Hess' Law
 - Vertical axis = enthalpy scale
 - Horizontal line = various states of reactions
 - Higher up = larger enthalpy
 - Lower down = smaller enthalpy



Enthalpy Diagrams

- Use to measure ΔH_{rxn}
 - Arrow down $\Delta H_{\text{rxn}} =$ negative
 - Arrow up $\Delta H_{\text{rxn}} =$ positive
- Calculate cycle
 - One step process = sum of two step process



$$-286 \text{ kJ} = -188 \text{ kJ} + \Delta H_{\text{rxn}}$$

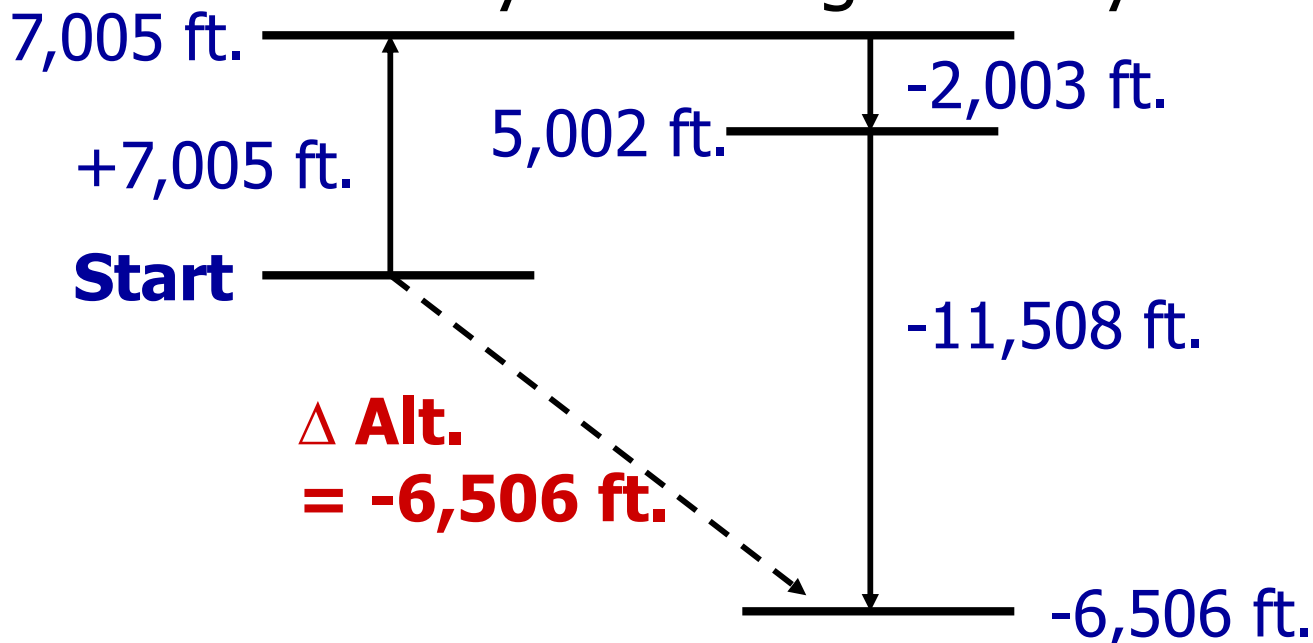
$$\Delta H_{\text{rxn}} = -286 \text{ kJ} - (-188 \text{ kJ})$$

$$\Delta H_{\text{rxn}} = \mathbf{-98 \text{ kJ}}$$

Your Turn!

What is your change in altitude if you climb up a 7,005 ft. mountain, drive a car from that spot down 2,003 ft, then parachute down another 11,508 ft. into a canyon?

Draw a diagram that reflects your changes and your calculation.



- A. -6506 ft.
- B. 20516 ft.
- C. 16310 ft.
- D. -20516 ft.
- E. No change

Note: Change is negative because altitude *decreased*
Final state is lower than initial state

Hess' s Law

Hess' s Law of Heat Summation

- Going from reactants to products
- Enthalpy change is same whether reaction takes place in one step or many
- **Chief Use**
 - Calculation of $\Delta H^{\circ}_{\text{rxn}}$ for reaction that can't be measured directly
 - Thermochemical equations for individual steps of reaction sequence may be combined to obtain thermochemical equation of overall reaction

Rules for Manipulating Thermochemical Equations

1. When equation is reversed, sign of $\Delta H^{\circ}_{\text{rxn}}$ must also be reversed.
2. If all coefficients of equation are multiplied or divided by same factor, value of $\Delta H^{\circ}_{\text{rxn}}$ must likewise be multiplied or divided by that factor
3. Formulas canceled from both sides of equation must be for substance in ***same*** physical states

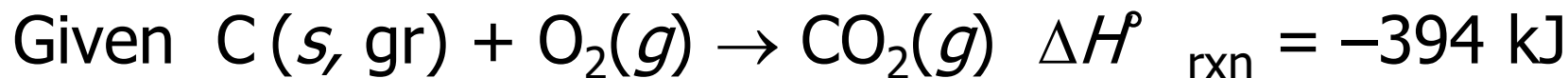
Strategy for Adding Reactions Together:

1. Choose most complex compound in equation for one-step path
2. Choose equation in multi-step path that contains that compound
3. Write equation down so that compound
 - is on appropriate side of equation
 - has appropriate coefficient for our reaction
4. Repeat steps 1 – 3 for next most complex compound, etc.

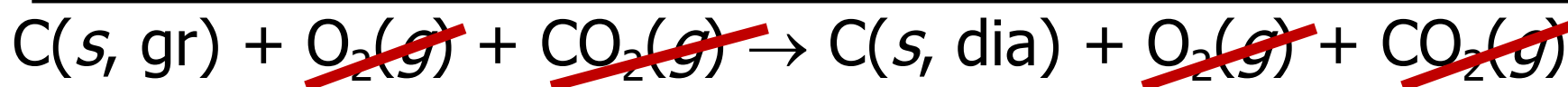
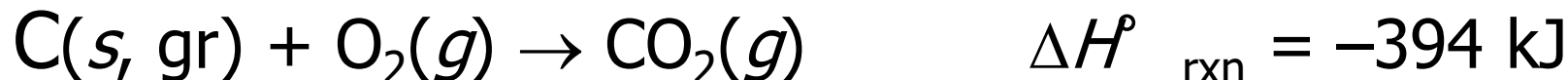
Strategy for Adding Reactions (Cont.)

5. Choose equation that allows you to
 - cancel intermediates
 - multiply by appropriate coefficient
6. Add reactions together and cancel like terms
7. Add energies together, modifying enthalpy values in same way equation modified
 - If reversed equation, change sign on enthalpy
 - If doubled equation, double energy

Example 9: Calculate $\Delta H^\circ_{\text{rxn}}$ for



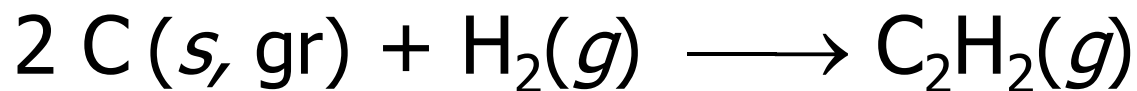
- To get desired equation, must reverse second equation and add resulting equations



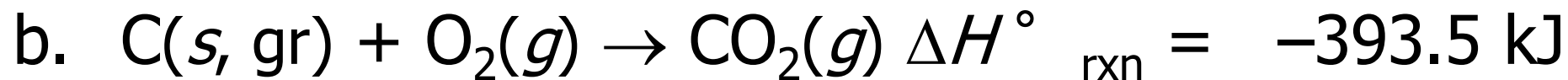
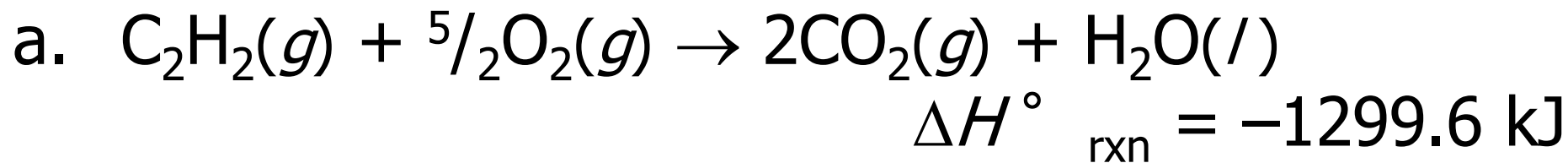
$$\Delta H^\circ = -394 \text{ kJ} + 396 \text{ kJ} = \boxed{+ 2 \text{ kJ}}$$

Learning Check: Example 10

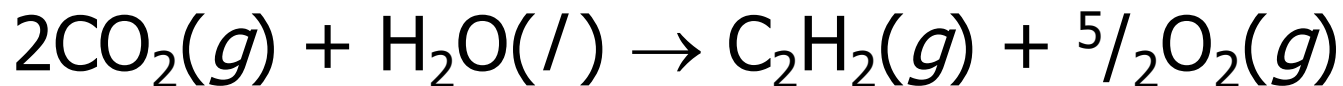
Calculate $\Delta H^\circ_{\text{rxn}}$ for



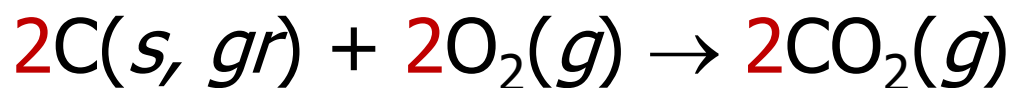
Given the following:



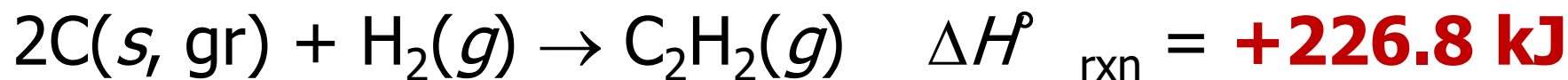
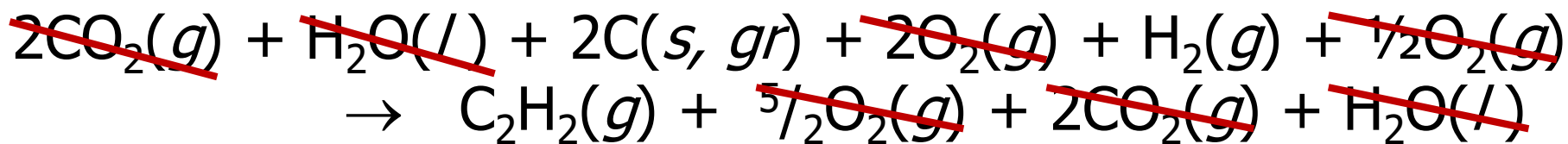
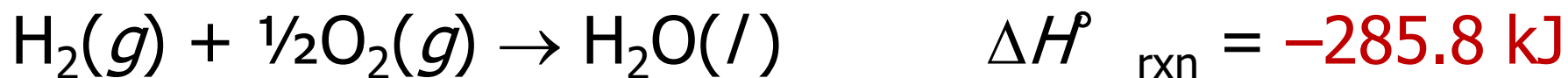
Example 10: Calculate $\Delta H^\circ_{\text{rxn}}$ for



$$\Delta H^\circ_{\text{rxn}} = -(-1299.6 \text{ kJ}) = +1299.6 \text{ kJ}$$



$$\Delta H^\circ_{\text{rxn}} = (2 \times -393.5 \text{ kJ}) = -787.0 \text{ kJ}$$



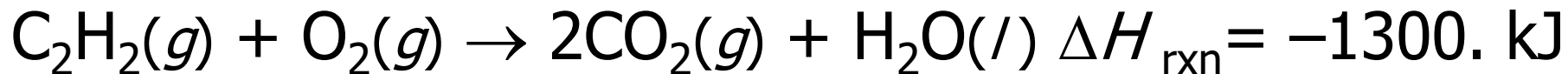
Your Turn!

Which of the following is a statement of Hess's Law?

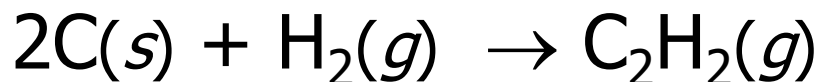
- A. ΔH for a reaction in the forward direction is equal to ΔH for the reaction in the reverse direction.
- B. ΔH for a reaction depends on the physical states of the reactants and products.
- C. If a reaction takes place in steps, ΔH for the reaction will be the sum of ΔH s for the individual steps.
- D. If you multiply a reaction by a number, you multiply ΔH by the same number.
- E. ΔH for a reaction in the forward direction is equal in magnitude and opposite in sign to ΔH for the reaction in the reverse direction.

Your Turn!

Given the following data:



Calculate for the reaction



A. 226 kJ

B. -1980 kJ

C. -620 kJ $\Delta H_{\text{rxn}} = +1300. \text{ kJ} + 2(-394 \text{ kJ}) + (-286 \text{ kJ})$

D. -226 kJ

E. 620 kJ

Tabulating ΔH° values

- Need to Tabulate ΔH° values
- Major problem is vast number of reactions
- Define standard reaction and tabulate these
- Use Hess's Law to calculate ΔH° for any other reaction

Standard Enthalpy of Formation, ΔH_f°

- Amount of heat absorbed or evolved when one mole of substance is formed at 1 atm (1 bar) and 25 °C (298 K) from elements in their standard states
- Standard heat of formation

Standard State

- Most stable form and physical state of element at 1 atm (1 bar) and 25 ° C (298 K)

Element	Standard state
O	O ₂ (g)
C	C (s, gr)
H	H ₂ (g)
Al	Al(s)
Ne	Ne(g)

Note: **All ΔH_f° of elements in their standard states = 0**

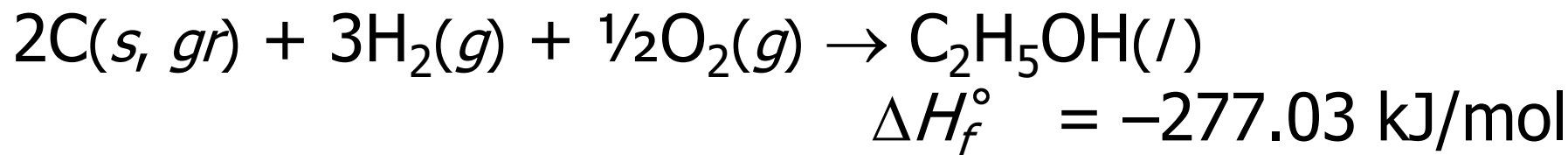
Forming element from itself.

- See Appendix in back of textbook and Table 6.2

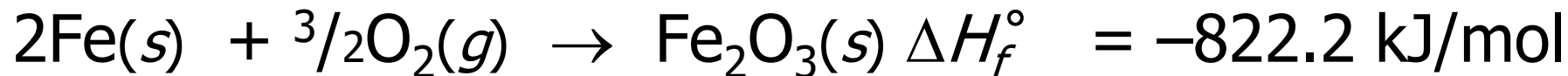
Uses of Standard Enthalpy (Heat)^{6.9} of Formation, ΔH_f°

1. From definition of ΔH_f° , can write balanced equations directly

ΔH_f° of $\text{C}_2\text{H}_5\text{OH}(l)$



ΔH_f° of $\text{Fe}_2\text{O}_3(s)$



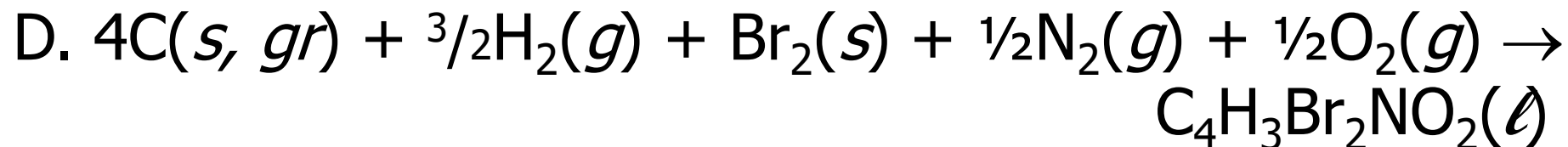
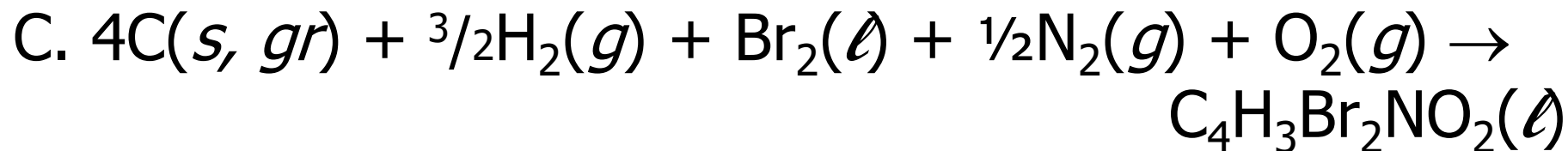
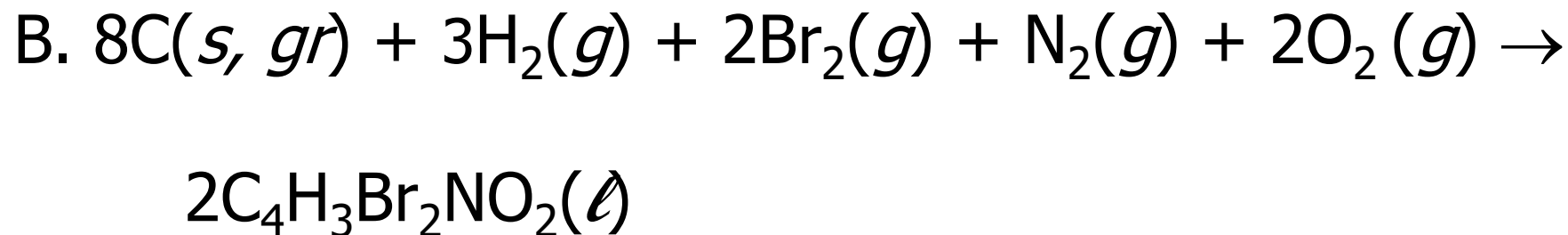
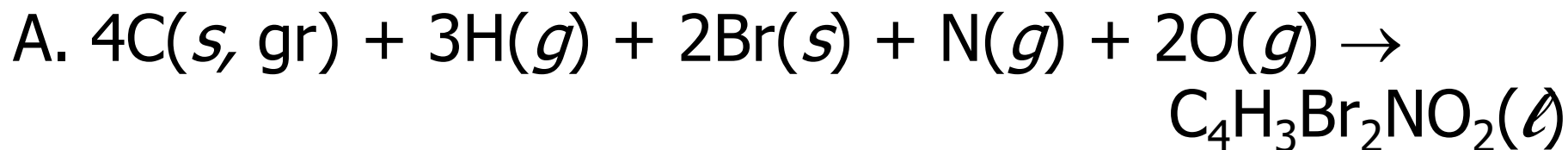
Your Turn!

Which reaction corresponds to the standard enthalpy of formation of $\text{NaHCO}_3(s)$, $\Delta H_f^\circ = -947.7 \text{ kJ/mol}$?

- A. $\text{Na}(s) + \frac{1}{2}\text{H}_2(g) + \frac{3}{2}\text{O}_2(g) + \text{C}(s, gr) \rightarrow \text{NaHCO}_3(s)$
- B. $\text{Na}^+(g) + \text{H}^+(g) + 3\text{O}^{2-}(g) + \text{C}^{4+}(g) \rightarrow \text{NaHCO}_3(s)$
- C. $\text{Na}^+(aq) + \text{H}^+(aq) + 3\text{O}^{2-}(aq) + \text{C}^{4+}(aq) \rightarrow \text{NaHCO}_3(s)$
- D. $\text{NaHCO}_3(s) \rightarrow \text{Na}(s) + \frac{1}{2}\text{H}_2(g) + \frac{3}{2}\text{O}_2(g) + \text{C}(s, gr)$
- E. $\text{Na}^+(aq) + \text{HCO}_3^-(aq) \rightarrow \text{NaHCO}_3(s)$

Your Turn!

Which reaction corresponds to the standard enthalpy of formation of $\text{C}_4\text{H}_3\text{Br}_2\text{NO}_2(\ell)$?



Your Turn!

The standard enthalpy of formation of sulfur dioxide is -296.9 kJ. What is ΔH for the formation of 16.03 g of sulfur dioxide in its standard state from its elements in their standard states?

- A. 148.4 kJ
- B. -296.9 kJ
- C. -4,759 kJ
- D. -148.4 kJ
- E. 593.6 kJ

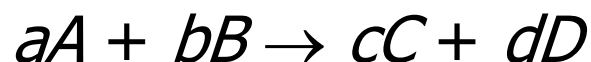
$$16.03 \text{ g SO}_2 \times \frac{\text{mol SO}_2}{32.07 \text{ g SO}_2} \times \frac{-296.9 \text{ kJ}}{\text{mol SO}_2} = \mathbf{-148.4 \text{ kJ}}$$

Using ΔH_f°

2. Way to apply Hess's Law without needing to manipulate thermochemical equations

$$\Delta H^\circ_{\text{reaction}} = \left(\begin{array}{l} \text{Sum of all } \Delta H^\circ_f \\ \text{of all of the} \\ \text{products} \end{array} \right) - \left(\begin{array}{l} \text{Sum of all} \\ \Delta H^\circ_f \text{ of all of} \\ \text{the reactants} \end{array} \right)$$

Consider the reaction:



$$\Delta H^\circ_{\text{reaction}} = c \times \Delta H^\circ_f(C) + d \times \Delta H^\circ_f(D) - \{a \times \Delta H^\circ_f(A) + b \times \Delta H^\circ_f(B)\}$$

- $\Delta H^\circ_{\text{rxn}}$ has units of kJ because
- Coefficients \times heats of formation have units of mol \times kJ/mol

$$\Delta H^\circ_{\text{rxn}} = \sum \left[\Delta H^\circ_f(\text{products}) \times (\text{moles of product}) \right] -$$

$$\sum \left[\Delta H^\circ_f(\text{reactants}) \times (\text{moles of reactant}) \right]$$

$\Delta H^\circ_{\text{rxn}}$ has units of kJ ΔH°_f has units of kJ/mol

Ex. 11: Calculate $\Delta H^\circ_{\text{rxn}}$ Using ΔH_f°

Calculate $\Delta H^\circ_{\text{rxn}}$ using ΔH_f° data for the reaction



1. Multiply each ΔH_f° (in kJ/mol) by the number of moles in the equation
2. Add the ΔH_f° (in kJ/mol) multiplied by the number of moles in the equation of each product
3. Subtract the ΔH_f° (in kJ/mol) multiplied by the number of moles in the equation of each reactant

$$\Delta H^\circ_{\text{rxn}} = \sum \left[\Delta H_f^\circ (\text{products}) \times (\text{moles of product}) \right] - \sum \left[\Delta H_f^\circ (\text{reactants}) \times (\text{moles of reactant}) \right]$$

$\Delta H^\circ_{\text{rxn}}$ has units of kJ

ΔH_f° has units of kJ/mol

$$\Delta H^\circ_{\text{rxn}} = \Delta H_f^\circ (\text{SO}_2(g)) + \frac{1}{2} \Delta H_f^\circ (\text{O}_2(g)) - \Delta H_f^\circ (\text{SO}_3(g))$$

$$\Delta H^\circ_{\text{rxn}} = -297 \text{ kJ/mol} + \frac{1}{2} (0 \text{ kJ/mol}) - (-396 \text{ kJ/mol})$$

$$\Delta H^\circ_{\text{rxn}} = 99 \text{ kJ}$$

Learning Check

Calculate $\Delta H^\circ_{\text{rxn}}$ using ΔH°_f for the reaction



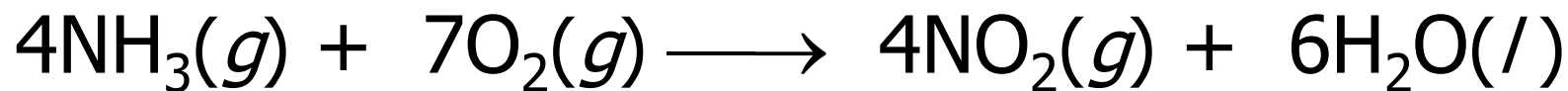
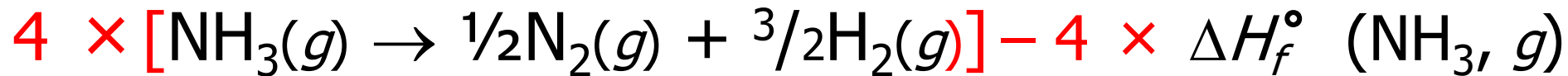
$$\Delta H^\circ_{\text{rxn}} = 4\Delta H^\circ_f \text{NO}_2(g) + 6\Delta H^\circ_f \text{H}_2\text{O}(l) - 4\Delta H^\circ_f \text{NH}_3(g) - 7\Delta H^\circ_f \text{O}_2(g)$$

$$\Delta H^\circ_{\text{rxn}} = 4 \text{ mol} (34 \text{ kJ/mol}) + 6 \text{ mol} (-285.9 \text{ kJ/mol}) - 4 \text{ mol} (-46.0 \text{ kJ/mol}) - 7 \text{ mol} (0 \text{ kJ/mol})$$

$$\Delta H^\circ_{\text{rxn}} = [136 - 1715.4 + 184] \text{ kJ}$$

$$\Delta H^\circ_{\text{rxn}} = -1395 \text{ kJ}$$

Check Using Hess' s Law



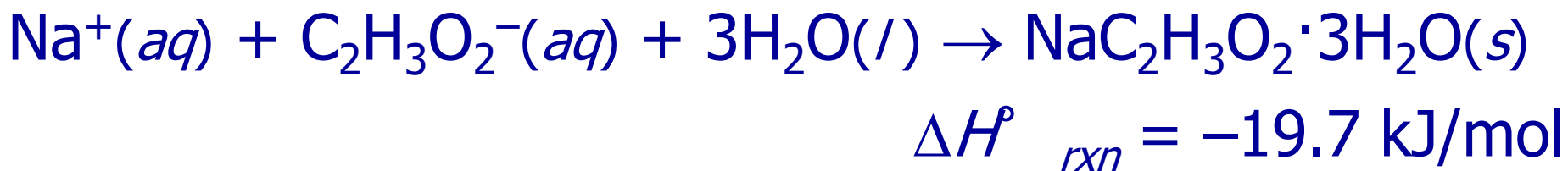
$$\Delta H_{\text{rxn}}^\circ = 4\Delta H_f^\circ \text{NO}_2(g) + 6\Delta H_f^\circ \text{H}_2\text{O}(l) - 4\Delta H_f^\circ \text{NH}_3(g) - 7\Delta H_f^\circ \text{O}_2(g)$$

Same as before

Example 12: Other Calculations

- Don't always want to know ΔH°_{rxn}
- Can use Hess's Law and ΔH°_{rxn} to calculate ΔH°_f for compound where not known

Example: Given the following data, what is the value of ΔH°_f ($\text{C}_2\text{H}_3\text{O}_2^-, aq$)?



Example 12 cont.

$$\Delta H^\circ_{rxn} = \Delta H_f^\circ (\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}, s) - \Delta H_f^\circ (\text{Na}^+, aq) - \Delta H_f^\circ (\text{C}_2\text{H}_3\text{O}_2^-, aq) - 3\Delta H_f^\circ (\text{H}_2\text{O}, l)$$

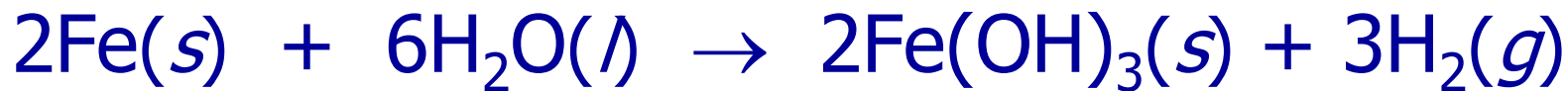
Rearranging

$$\Delta H_f^\circ (\text{C}_2\text{H}_3\text{O}_2^-, aq) = \Delta H_f^\circ (\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}, s) - \Delta H_f^\circ (\text{Na}^+, aq) - \Delta H^\circ_{rxn} - 3\Delta H_f^\circ (\text{H}_2\text{O}, l)$$

$$\begin{aligned} \Delta H_f^\circ (\text{C}_2\text{H}_3\text{O}_2^-, aq) &= \\ &-710.4 \text{ kJ/mol} - (-239.7 \text{ kJ/mol}) - (-19.7 \\ &\text{kJ/mol}) - 3(-285.9 \text{ kJ/mol}) \\ &= +406.7 \text{ kJ/mol} \end{aligned}$$

Learning Check

Calculate ΔH for this reaction using ΔH_f° data.



$$\Delta H_f^\circ \quad 0 \qquad -285.8 \qquad -696.5 \qquad 0$$

$$\Delta H^\circ_{\text{rxn}} = 2 \times \Delta H_f^\circ (\text{Fe}(\text{OH})_3, s) + 3 \times \Delta H_f^\circ (\text{H}_2, g) \\ - 2 \times \Delta H_f^\circ (\text{Fe}, s) - 6 \times \Delta H_f^\circ (\text{H}_2\text{O}, l)$$

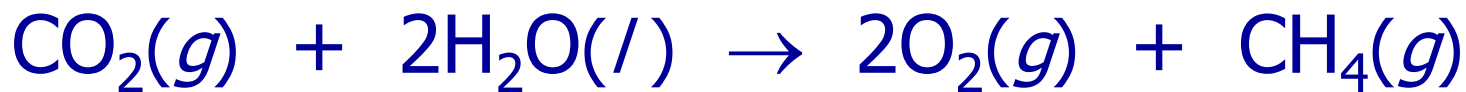
$$\Delta H^\circ_{\text{rxn}} = \cancel{2 \text{ mol}} \times (\cancel{-696.5 \text{ kJ/mol}}) + 3 \times 0 - 2 \times 0 \\ - \cancel{6 \text{ mol}} \times (\cancel{-285.8 \text{ kJ/mol}})$$

$$\Delta H^\circ_{\text{rxn}} = -1393 \text{ kJ} + 1714.8 \text{ kJ}$$

$$\Delta H^\circ_{\text{rxn}} = \mathbf{321.8 \text{ kJ}}$$

Learning Check

Calculate $\Delta H^\circ_{\text{rxn}}$ for this reaction using ΔH_f° data.



$$\Delta H_f^\circ \quad -393.5 \quad -285.8 \quad 0 \quad -74.8$$

$$\Delta H^\circ_{\text{rxn}} = 2 \times \Delta H_f^\circ (\text{O}_2, g) + \Delta H_f^\circ (\text{CH}_4, g) - \Delta H_f^\circ (\text{CO}_2, g) - 2 \times \Delta H_f^\circ (\text{H}_2\text{O}, l)$$

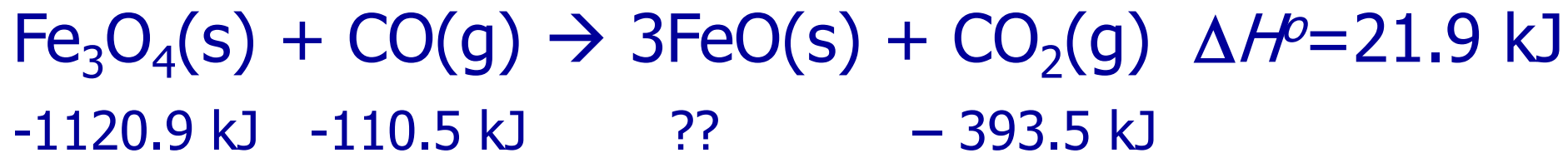
$$\Delta H^\circ_{\text{rxn}} = 2 \times 0 + 1 \text{ mol} \times (-74.8 \text{ kJ/mol}) - 1 \text{ mol} \times (-393.5 \text{ kJ/mol}) - 2 \text{ mol} \times (-285.8 \text{ kJ/mol})$$

$$\Delta H^\circ_{\text{rxn}} = -74.8 \text{ kJ} + 393.5 \text{ kJ} + 571.6 \text{ kJ}$$

$$\Delta H^\circ_{\text{rxn}} = 890.3 \text{ kJ}$$

Your Turn!

Calculate ΔH_f° for FeO(s) using the information below. ΔH_f° values are shown below each substance.



- A. 272.0 kJ
- B. -816.0 kJ
- C. -272.0 kJ
- D. 26.00 J
- E. -38.60 kJ

Your Turn! sol'n

$$\Delta H_{\text{rxn}}^{\circ} = \sum \left[\Delta H_f^{\circ} (\text{products}) \times (\text{moles of product}) \right] - \sum \left[\Delta H_f^{\circ} (\text{reactants}) \times (\text{moles of reactant}) \right]$$

Important



$$\Delta H_{\text{rxn}}^{\circ} = [3\Delta H_f^{\circ} (\text{FeO}, s) + \Delta H_f^{\circ} (\text{O}_2, g)] - [\Delta H_f^{\circ} (\text{Fe}_3\text{O}_4, s) + \Delta H_f^{\circ} (\text{CO}, g)]$$

$$+21.9 \text{ kJ} = [3\Delta H_f^{\circ} (\text{FeO}, s) + -393.5 \text{ kJ}] - [-1120.9 \text{ kJ} + -110.5 \text{ kJ}]$$

$$+21.9 \text{ kJ} = [3\Delta H_f^{\circ} (\text{FeO}, s) + 837.9 \text{ kJ}]$$

$$-816.0 \text{ kJ} = 3\Delta H_f^{\circ} (\text{FeO}, s)$$

$$-272.0 \text{ kJ} = \Delta H_f^{\circ} (\text{FeO}, s)$$