Chem 202

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Technicalities

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Learning Resources

Main text books:
 Chemistry, by Chang, 9th. ed., 2007, McGraw-Hill.

Subsidiary books:
 Chemistry, by Mortimer, 6th ed., 1986, Wadsworth Inc.
 Chemistry, by Steven S. Zumdahl, 6th ed., Houghton Mifflin College Div.
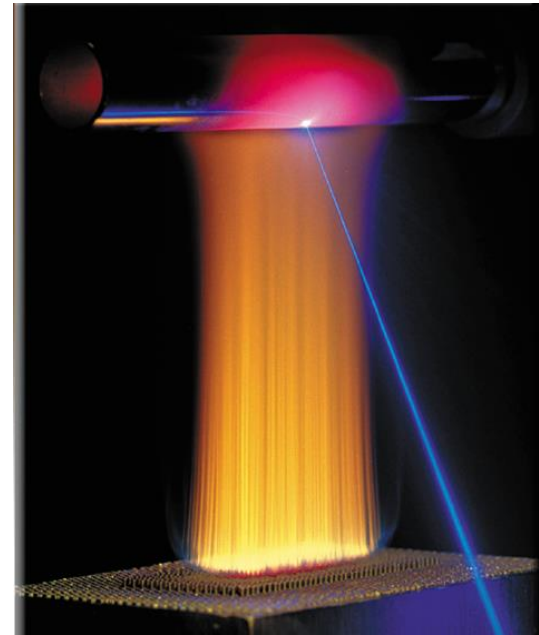
Course Grading:

|	
First exams	15 marks (Chapters 6,18)
Second exam	15 marks (Chapters 19,12)
Assignments	5 marks
Labs	25 marks
Final exam	40 marks
Total	100 marks
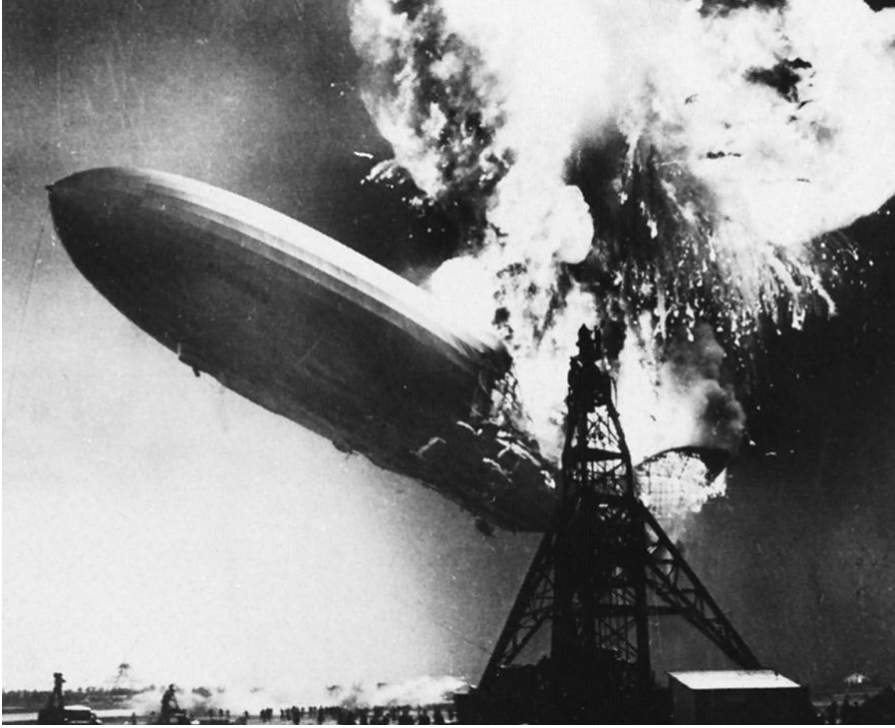
Thermochemistry

*Chapter 6*

Energy is the capacity to do work

- **_Radiant energy_** comes from the sun and is earth's primary energy source

- **_Thermal energy_** is the energy associated with the random motion of atoms and molecules

- **_Chemical energy_** is the energy stored within the bonds of chemical substances

- **_Nuclear energy_** is the energy stored within the collection of neutrons and protons in the atom

- **_Potential energy_** is the energy available by virtue of an object's position
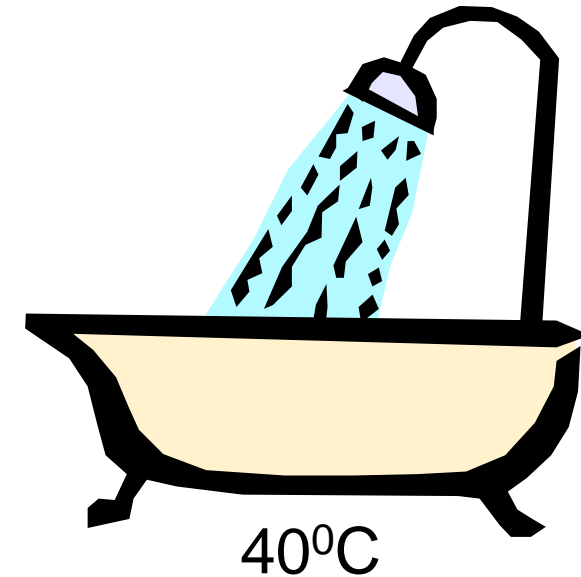
6.1
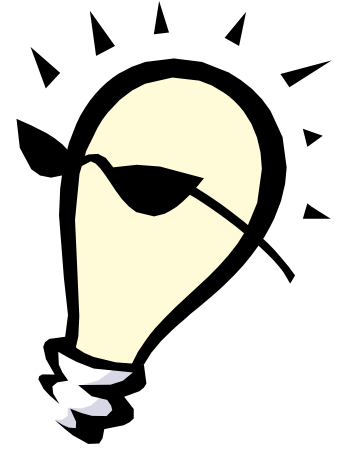
Energy Changes in Chemical Reactions

Heat is the transfer of **thermal energy** between two bodies that are at different temperatures.

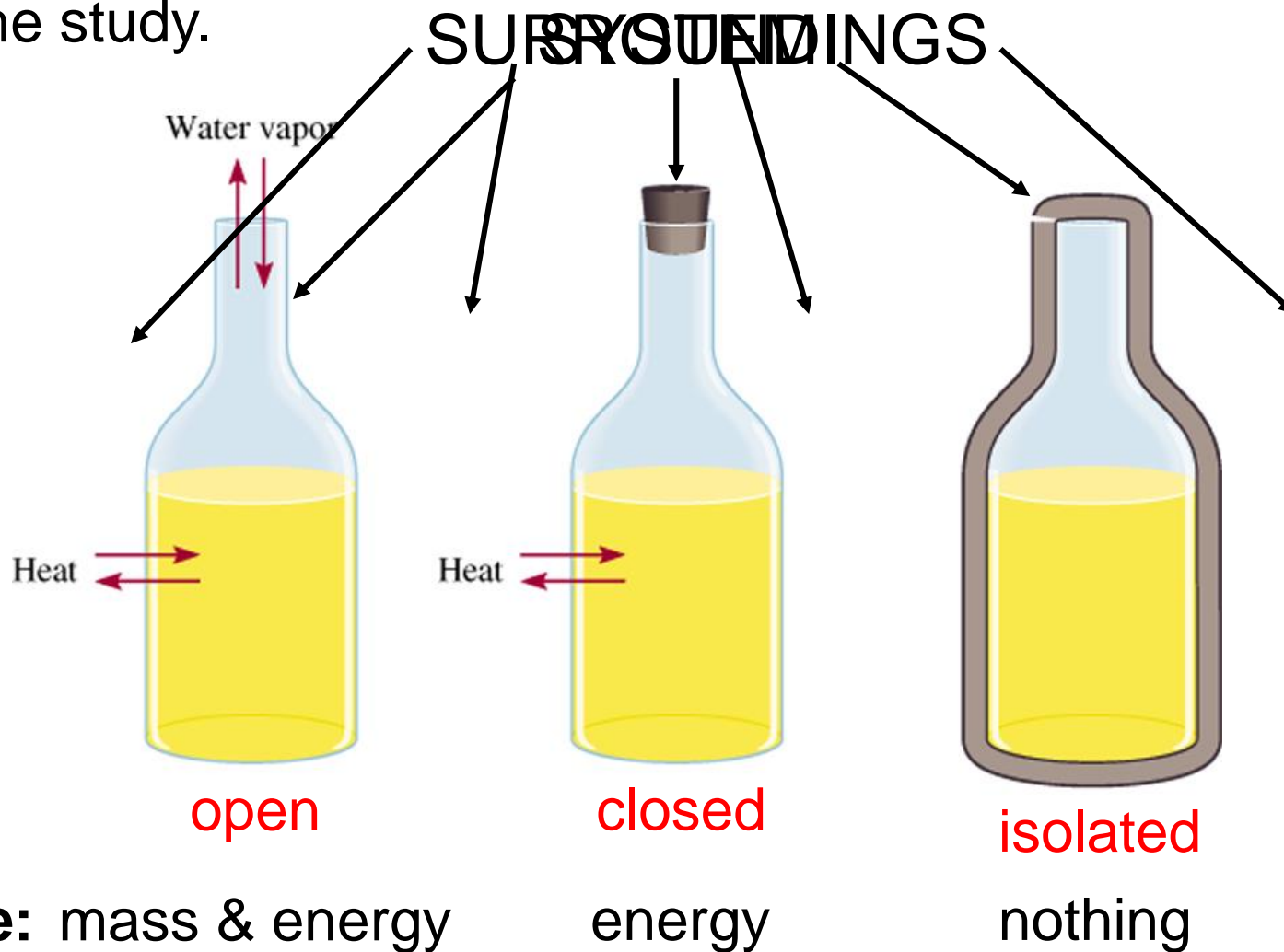*Temperature* is a measure of the **thermal energy**.
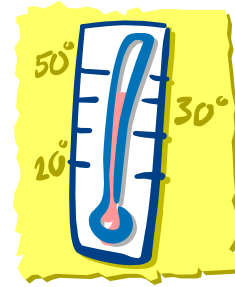
Temperature ̶X̶ Thermal Energy

90⁰C

40⁰C

greater thermal energy

6.2

Thermochemistry is the study of heat change in chemical reactions.

The *system* is the specific part of the universe that is of interest in the study.

SURROUNDINGS

SYSTEM

Water vapor

Heat

Heat

open

closed

isolated

Exchange: mass & energy   energy   nothing

6.2

Exothermic process is any process that gives off heat – transfers thermal energy from the system to the surroundings.

$$2H_2\ (g) + O_2\ (g) \longrightarrow 2H_2O\ (l) + \text{energy}$$

$$H_2O\ (g) \longrightarrow H_2O\ (l) + \text{energy}$$
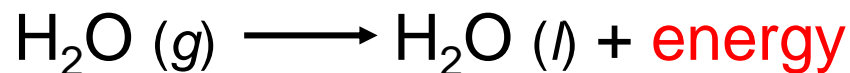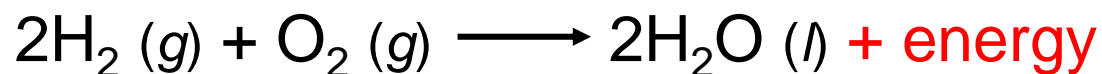
Endothermic process is any process in which heat has to be supplied to the system from the surroundings.

$$\text{energy} + 2HgO\ (s) \longrightarrow 2Hg\ (l) + O_2\ (g)$$

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

6.2

Exothermic

2H₂ (g) + O₂ (g)

Heat given off by the system to the surroundings

2H₂O (l)

Endothermic

2Hg (l) + O₂ (g)

Heat absorbed by the system from the surroundings

2HgO (s)

6.2
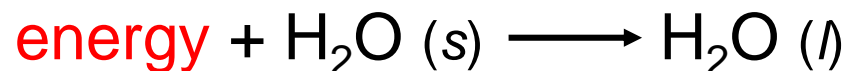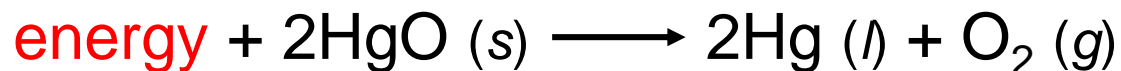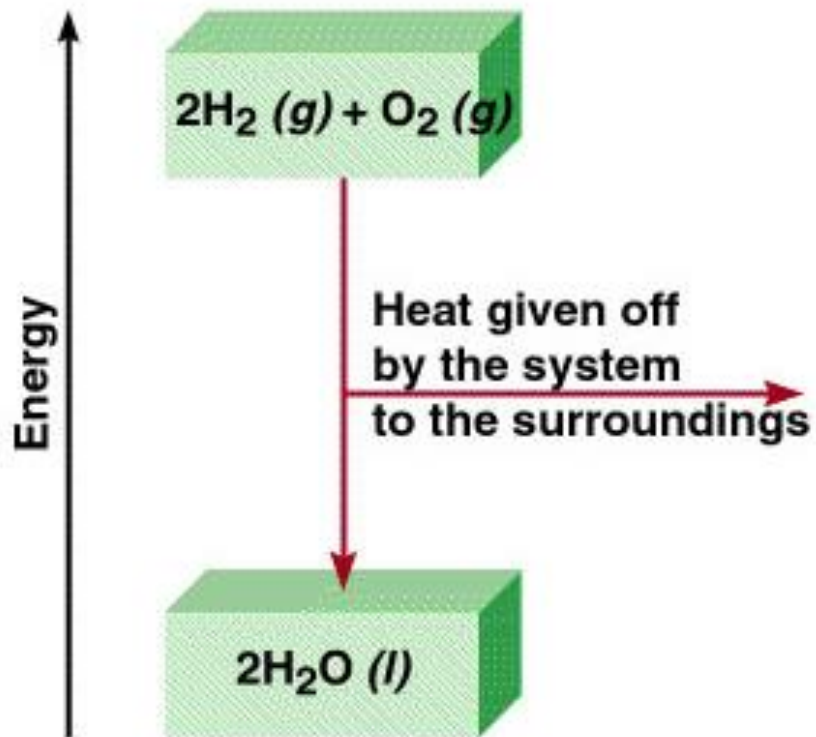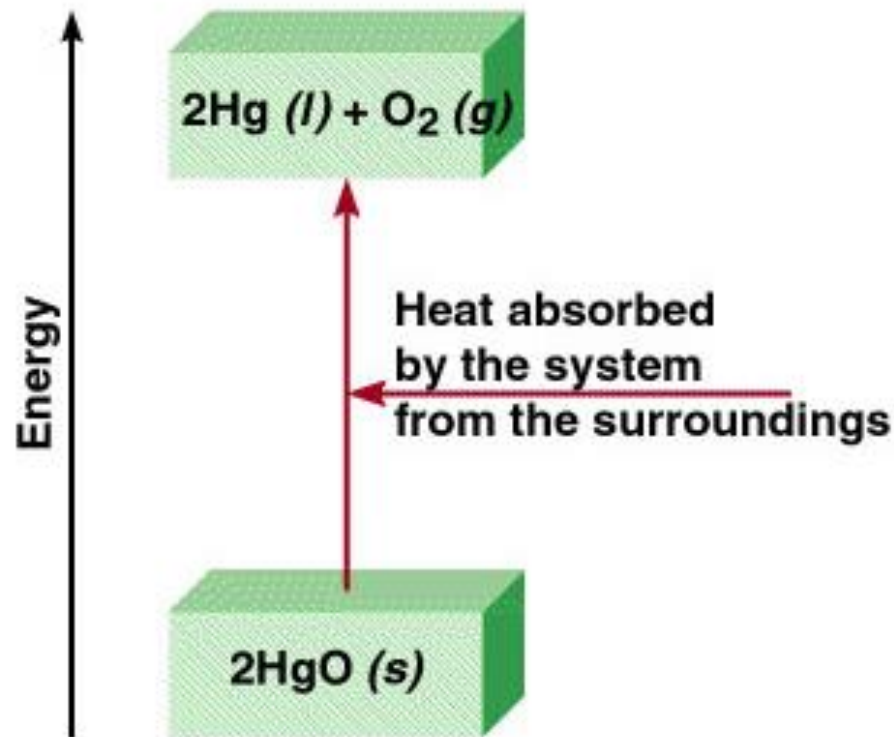
Thermodynamics

State functions are properties that are determined by the state of the system, regardless of how that condition was achieved.

energy, pressure, volume, temperature
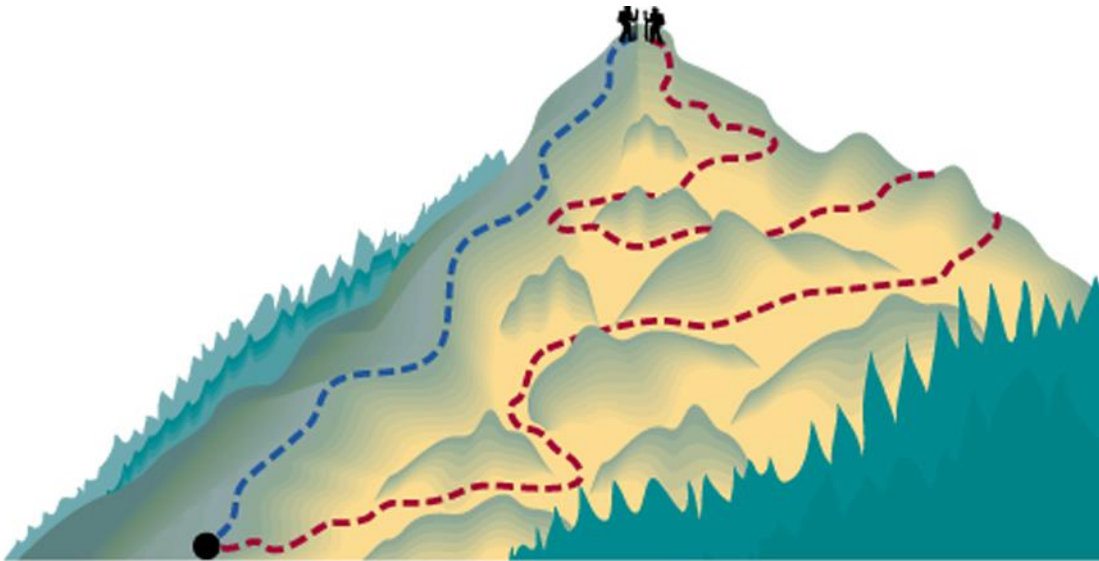
$$\Delta E = E_{final} - E_{initial}$$

$$\Delta P = P_{final} - P_{initial}$$

$$\Delta V = V_{final} - V_{initial}$$

$$\Delta T = T_{final} - T_{initial}$$

Potential energy of hiker 1 and hiker 2 is the same even though they took different paths.

6.3

First law of thermodynamics – energy can be converted from one form to another, but cannot be created or destroyed.

$$\Delta E_{system} + \Delta E_{surroundings} = 0$$

or

$$\Delta E_{system} = -\Delta E_{surroundings}$$

$$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$$
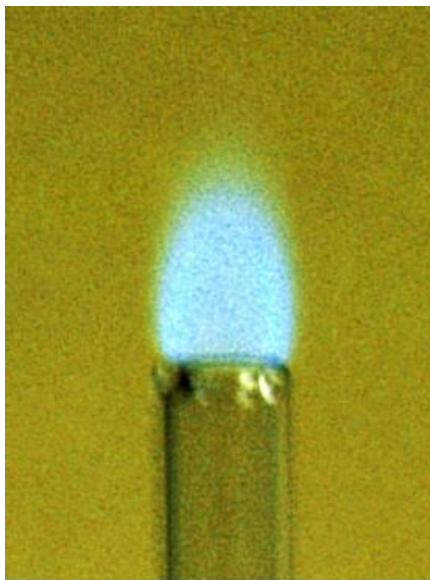
Exothermic chemical reaction!

Chemical energy **lost** by combustion = Energy **gained** by the surroundings
  system   **surroundings**

6.3

Another form of the *first law* for ΔE_{system}

$\Delta E = q + w$

ΔE is the change in internal energy of a system

q is the heat exchange between the system and the surroundings

w is the work done on (or by) the system

$w = -P\Delta V$ when a gas expands against a constant external pressure

TABLE 6.1

Sign Conventions for Work and Heat	
Process	**Sign**
Work done by the system on the surroundings	−
Work done on the system by the surroundings	+
Heat absorbed by the system from the surroundings (endothermic process)	+
Heat absorbed by the surroundings from the system (exothermic process)	−

Work Done On the System

$w = F\,d$

$w = -P\,\Delta V$

$P \times V = \dfrac{F}{d^2} \times d^3 = Fd = w$
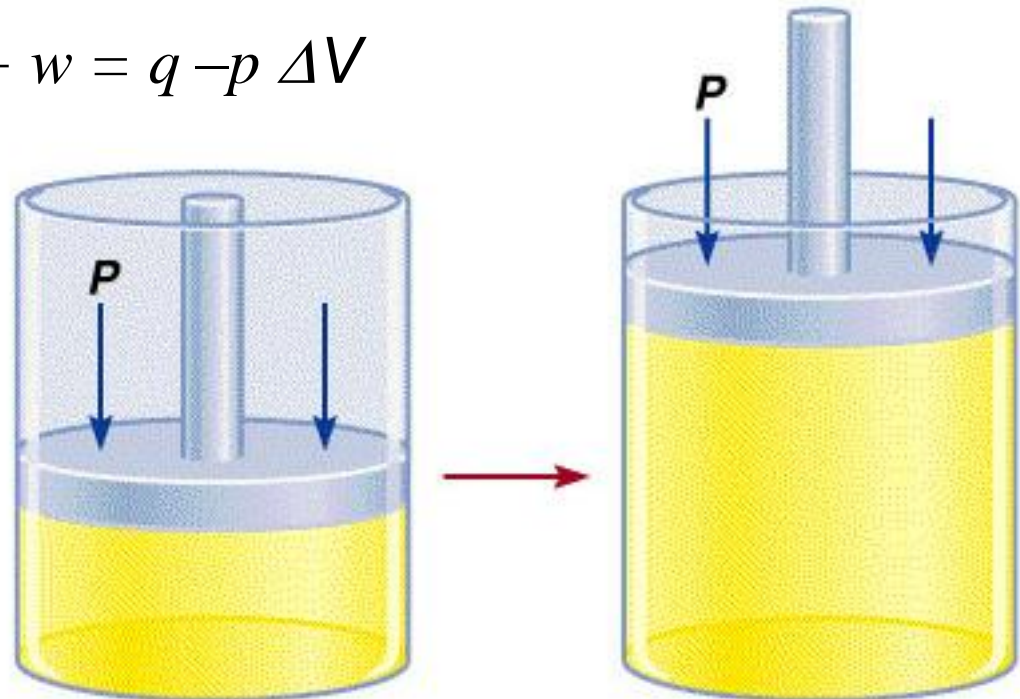
$\Delta V > 0$

$-P\Delta V < 0$

$w_{sys} < 0$

$\Delta E = q + w = q - p\,\Delta V$

Work is not a state function!

$\Delta w \neq w_{final} - w_{initial}$

initial

final

A sample of nitrogen gas expands in volume from 1.6 L to 5.4 L at constant temperature. What is the work done in joules if the gas expands (a) against a vacuum and (b) against a constant pressure of 3.7 atm?

$$w = -P \Delta V$$

(a) $\Delta V = 5.4 \text{ L} - 1.6 \text{ L} = 3.8 \text{ L}$ $P = 0 \text{ atm}$

$W = -0 \text{ atm} \times 3.8 \text{ L} = 0 \text{ L} \cdot \text{atm} = 0 \text{ joules}$

(b) $\Delta V = 5.4 \text{ L} - 1.6 \text{ L} = 3.8 \text{ L}$ $P = 3.7 \text{ atm}$

$w = -3.7 \text{ atm} \times 3.8 \text{ L} = -14.1 \text{ L} \cdot \text{atm}$

$w = -14.1 \text{ L} \cdot \text{atm} \times \dfrac{101.3 \text{ J}}{1 \text{L} \cdot \text{atm}} = -1430 \text{ J}$

6.3

Enthalpy and the First Law of Thermodynamics

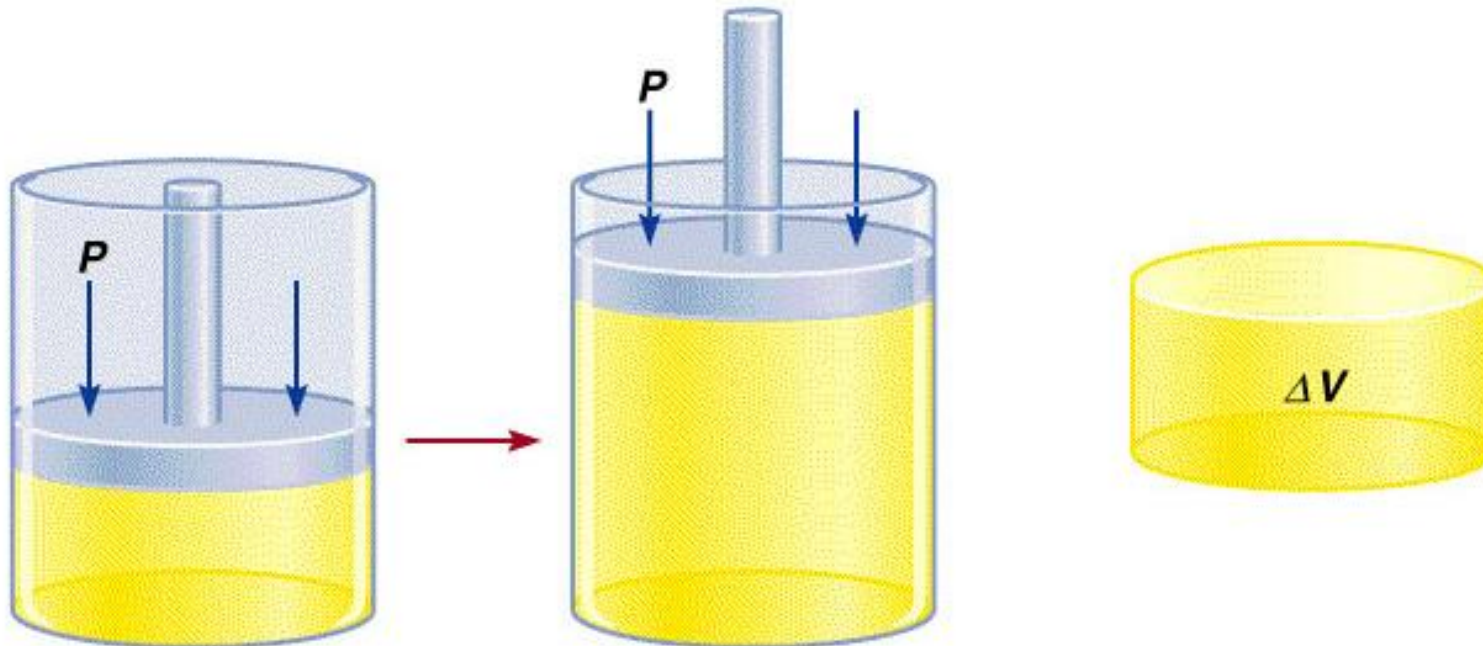$$\Delta E = q + w \text{ At Constant Temperature}$$

At constant pressure:

$$q_p = \Delta H \text{ and } w = -P\Delta V$$

$$\Delta E = \Delta H - P\Delta V \text{ At Constant Pressure}$$

$$\Delta H = \Delta E + P\Delta V$$

6.4

Enthalpy (H) is used to quantify the heat flow into or out of a system in a process that occurs at constant pressure.

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

ΔH = heat given off or absorbed during a reaction **at constant pressure**

Energy

$2H_2\,(g) + O_2\,(g)$

Exothermic:
heat given off
by the system
to the surroundings

$2H_2O\,(l)$

$H_{products} < H_{reactants}$
$\Delta H < 0$

Energy

$2Hg\,(l) + O_2\,(g)$

Endothermic:
heat absorbed
by the system
from the surroundings

$2HgO\,(s)$

$H_{products} > H_{reactants}$
$\Delta H > 0$

6.4
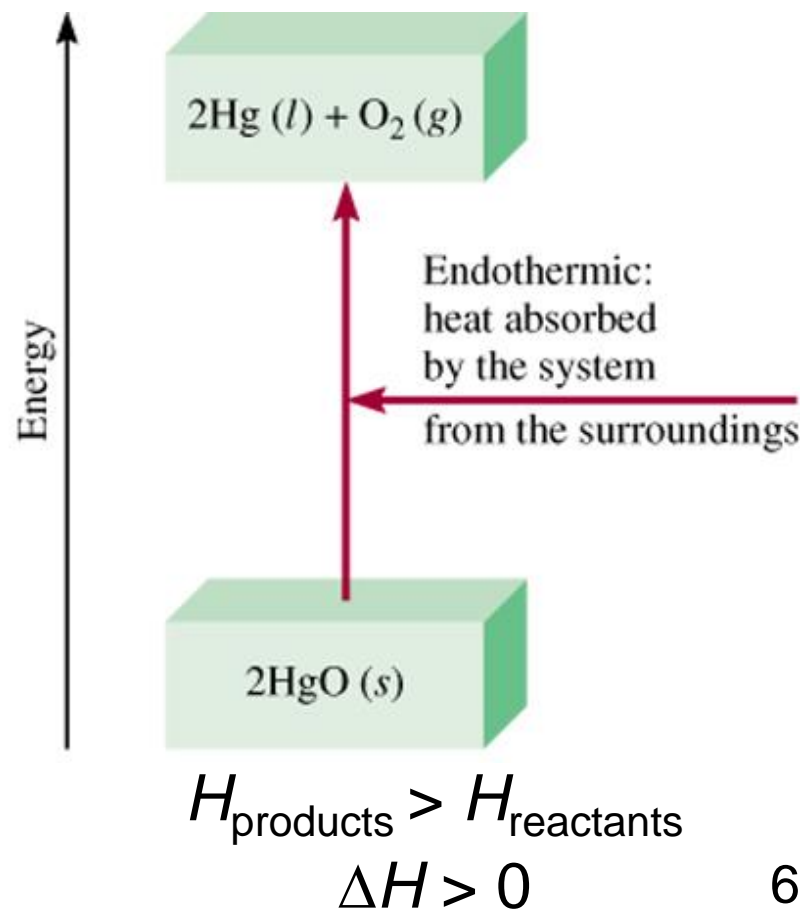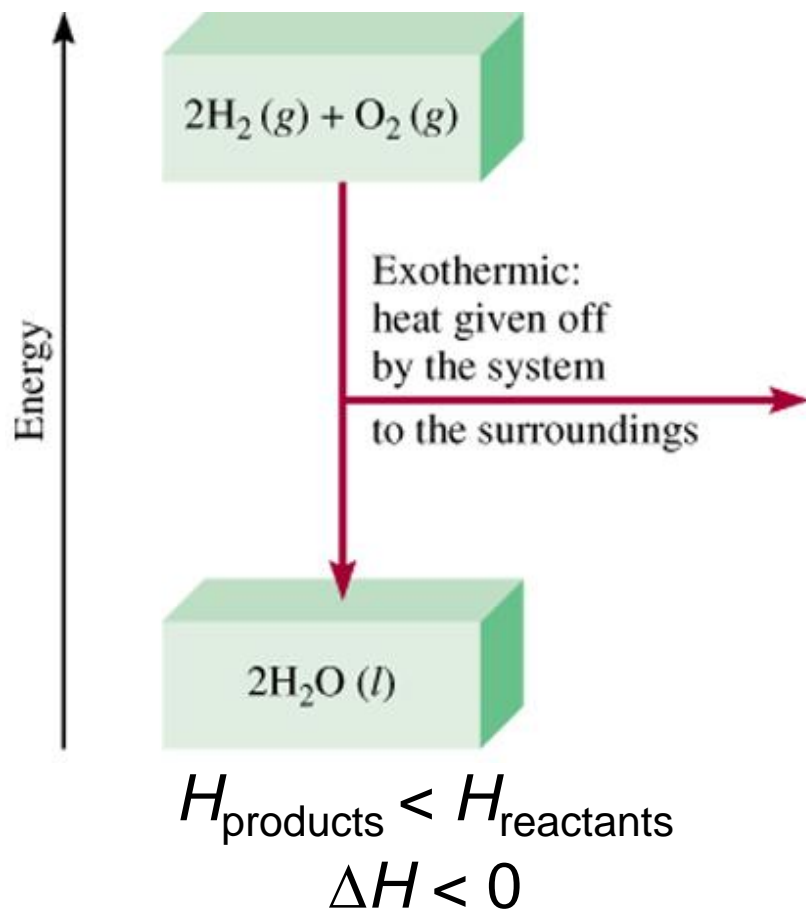
Thermochemical Equations
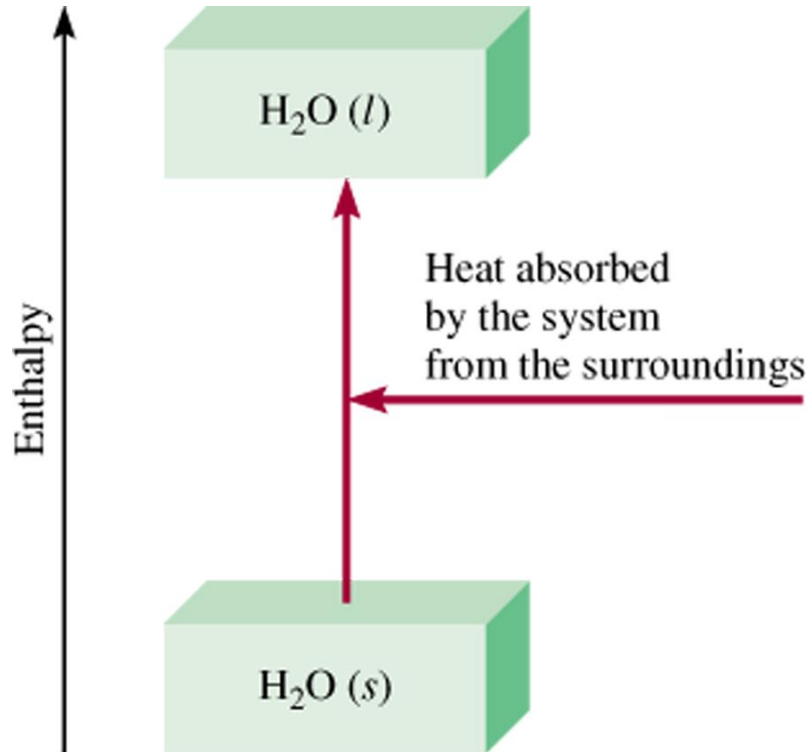
Is ΔH negative or positive?

System absorbs heat

Endothermic

$\Delta H > 0$

Enthalpy

H_2O (*l*)

Heat absorbed by the system from the surroundings

H_2O (*s*)

6.01 kJ are absorbed for every 1 mole of ice that melts at 0^0C and 1 atm.

$$H_2O \ (s) \longrightarrow H_2O \ (l) \quad \Delta H = 6.01 \ kJ$$

6.4
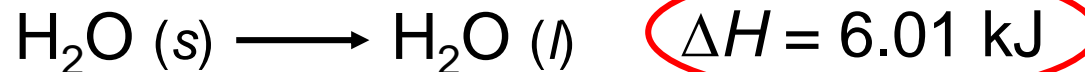
Thermochemical Equations
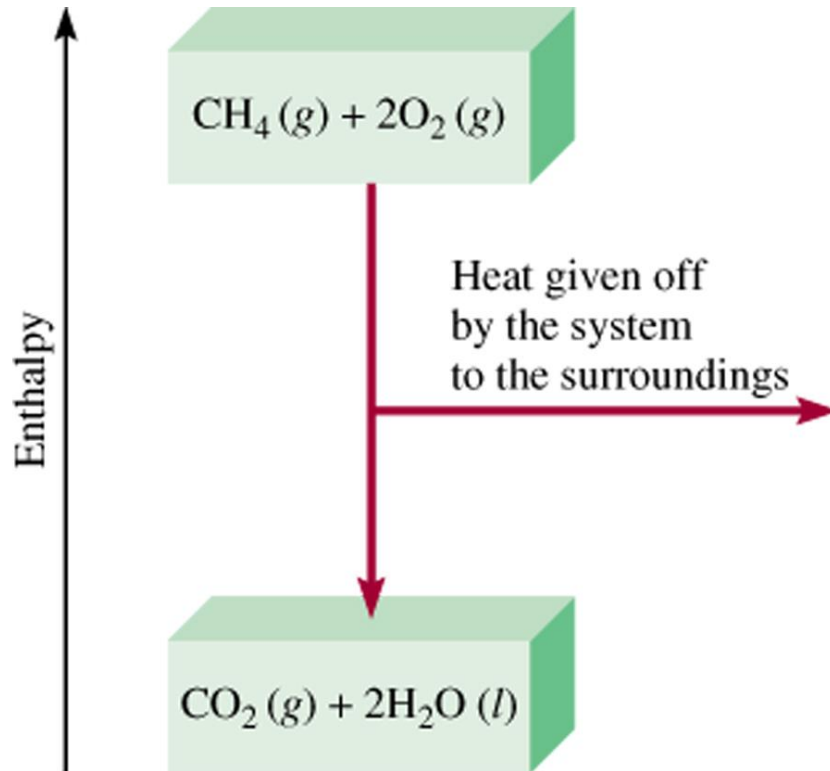
Is ΔH negative or positive?

System gives off heat

Exothermic

$\Delta H < 0$

890.4 kJ are released for every 1 mole of methane that is combusted at 25^0C and 1 atm.

$CH_4\ (g) + 2O_2\ (g) \longrightarrow CO_2\ (g) + 2H_2O\ (l)$ $\Delta H = -890.4$ kJ

6.4
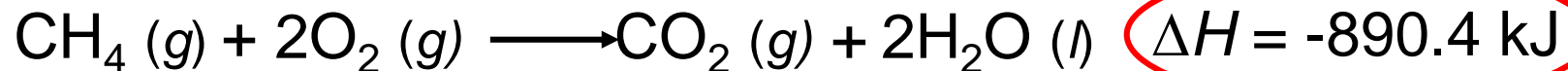
Thermochemical Equations

- The stoichiometric coefficients always refer to the number of moles of a substance

$$H_2O \ (s) \longrightarrow H_2O \ (l) \qquad \Delta H = 6.01 \text{ kJ}$$
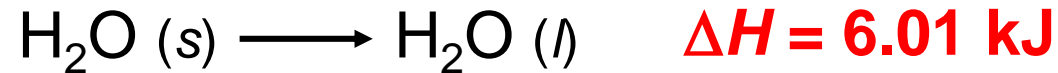
- If you reverse a reaction, the sign of ΔH changes

$$H_2O \ (l) \longrightarrow H_2O \ (s) \qquad \Delta H = \text{-6.01 kJ}$$

- If you multiply both sides of the equation by a factor n, then ΔH must change by the same factor n.

$$2H_2O \ (s) \longrightarrow 2H_2O \ (l) \qquad \Delta H = 2 \times 6.01 = 12.0 \text{ kJ}$$

Thermochemical Equations

- The physical states of all reactants and products must be specified in thermochemical equations.

$$H_2O \, (s) \longrightarrow H_2O \, (l) \qquad \Delta H = 6.01 \text{ kJ}$$

$$H_2O \, (l) \longrightarrow H_2O \, (g) \qquad \Delta H = 44.0 \text{ kJ}$$
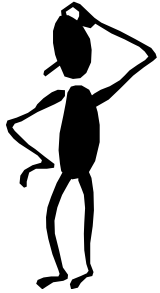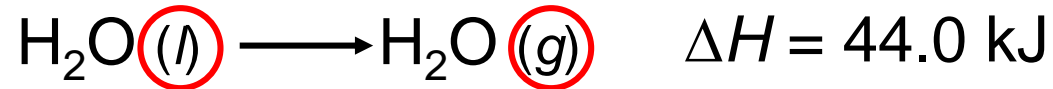
How much heat is evolved when 266 g of white phosphorus (P_4) burn in air?

$$P_4 \, (s) + 5O_2 \, (g) \longrightarrow P_4O_{10} \, (s) \qquad \Delta H = -3013 \text{ kJ}$$
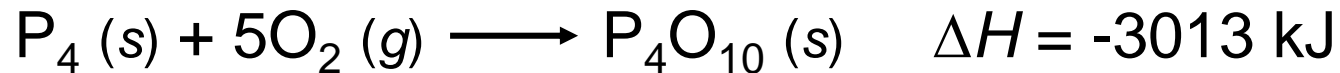
$$266 \text{ g } P_4 \times \frac{1 \text{ mol } P_4}{123.9 \text{ g } P_4} \times \frac{3013 \text{ kJ}}{1 \text{ mol } P_4} = 6470 \text{ kJ}$$

6.4

A Comparison of ΔH and ΔE

Find ΔE for the reaction:

$$2Na\ (s) + 2H_2O\ (l) \longrightarrow 2NaOH\ (aq) + H_2\ (g) \quad \Delta H = -367.5 \text{ kJ/mol}$$
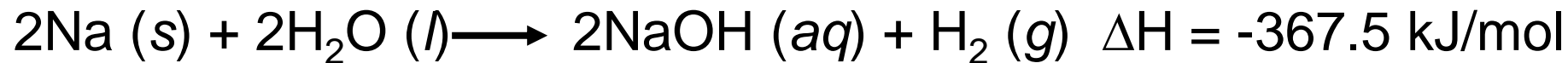
$\Delta E = \Delta H - P\Delta V$ At 25 ^{0}C, 1 mole H_2 = 24.5 L at 1 atm

$P\Delta V$ = 1 atm x 24.5 L = 2.5 kJ

$= 1\ atm\ x\ 24.5\ Lx\ 101.3\ /\ 1000\ = 2.5\ kJ$

ΔE = -367.5 kJ/mol – 2.5 kJ/mol = -370.0 kJ/mol

P

Air + water vapor

P

Air + water vapor +
H_2 gas

6.4
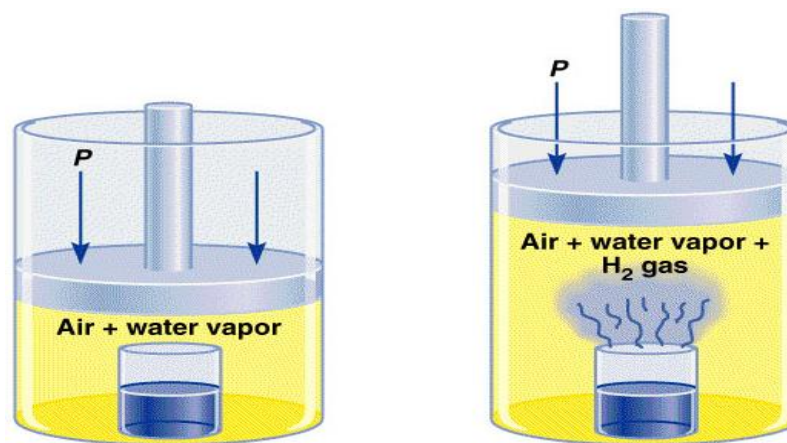
A Comparison of ΔH and ΔE

o the total energy of a chemical system at **constant pressure**

o (conditions of most reactions)

o cannot measure enthalpy directly, but can measure changes in enthalpy

$$\Delta H = H_{products} - H_{reactant}$$

$$\Delta E = \Delta H - \Delta PV \qquad \text{and PV = nRT, so}$$

$$\Delta E = \Delta H - RT \, \Delta n$$

$\Delta n = 0 \qquad \qquad \Delta E = \Delta H$

$\Delta n > 0 \qquad \qquad \Delta E = \Delta H - \Delta n \, RT$

$\Delta n < 0 \qquad \qquad \Delta E = \Delta H + RT \, \Delta n$

$\Delta n = $ n of product gases – n of reactant gases

Example 6-4

- Calculate the change in internal energy when 2 moles of CO are converted to 2 moles of CO_2 at 1 atm and 25 $^\circ$C

$$2CO\ (g) +\ O_2\ (g) \rightarrow 2CO_2\ (g) \quad \Delta H = \text{-566 kJ/mol}$$

$$\Delta E = \Delta H - \Delta n\ RT$$

$$\Delta n = 2 - 3 = -1$$

$$\Delta E = \text{-566} - (-1)\ (8.314)\ /1000\ (298) = \text{-563.5 kJ}$$

Calculate the change in internal energy for the formation of 1 mole of CO at 1 atm and 25 $^\circ$C

$$C\ (graphite) +\ \tfrac{1}{2}O_2\ (g) \rightarrow\ CO\ (g) \quad \Delta H = \text{-110.5 kJ/mol}$$

$$\Delta E = \Delta H - \Delta n\ RT \qquad \Delta n = 1 - \tfrac{1}{2} = \tfrac{1}{2}$$

$$\Delta E = \text{-110.5} - (\tfrac{1}{2})\ (8.314)\ /1000\ (298) = \text{-111.7 kJ}$$

The *specific heat (s)* of a substance is the amount of heat (*q*) required to raise the temperature of **one gram** of the substance by **one degree** Celsius.

The *heat capacity* (*C*) of a substance is the amount of heat (*q*) required to raise the temperature of a given quantity (*m*) of the substance by **one degree** Celsius.

The Specific Heats of Some Common Substances	
Substance	**Specific Heat (J/g · °C)**
Al	0.900
Au	0.129
C (graphite)	0.720
C (diamond)	0.502
Cu	0.385
Fe	0.444
Hg	0.139
H_2O	4.184
C_2H_5OH (ethanol)	2.46

TABLE 6.2

$$C = ms$$

Heat (*q*) absorbed or released:

$$q = ms \, \Delta t$$

$$q = C \, \Delta t$$

$$\Delta t = t_{final} - t_{initial}$$

6.5

How much heat is given off when an 869 g iron bar cools from 94^0C to 5^0C?

s of Fe = 0.444 J/g • ^{0}C

$\Delta t = t_{final} - t_{initial} = 5^0$C $- 94^0$C = -89^0C

$q = ms\Delta t = 869$ g̸ x 0.444 J/g̸ • ^{0}C̸ x -89^0C̸ = -34,000 J

Find the final temperature when 34000 j of
heat evolved (given off) on cooling 869 g of Iron bar at 94 ^{o}C?
s of Fe = 0.444 J/g • ^{0}C
$q = m x s x \Delta T$
$-34000 = 869$ g x 0.444 J/g • ^{0}C x ΔT
$\Delta T = -34000 / 869$ x 0.444 = $-89 \, ^o$C
$T_f = T_i + \Delta T = 94 - 89 = 5 \, ^o$C

6.5

Constant-Volume Calorimetry

Thermometer

Stirrer

Ignition wire

- Calorimeter bucket
- Insulated jacket
- Water
- O_2 inlet
- Bomb
- Sample cup

No heat enters or leaves!
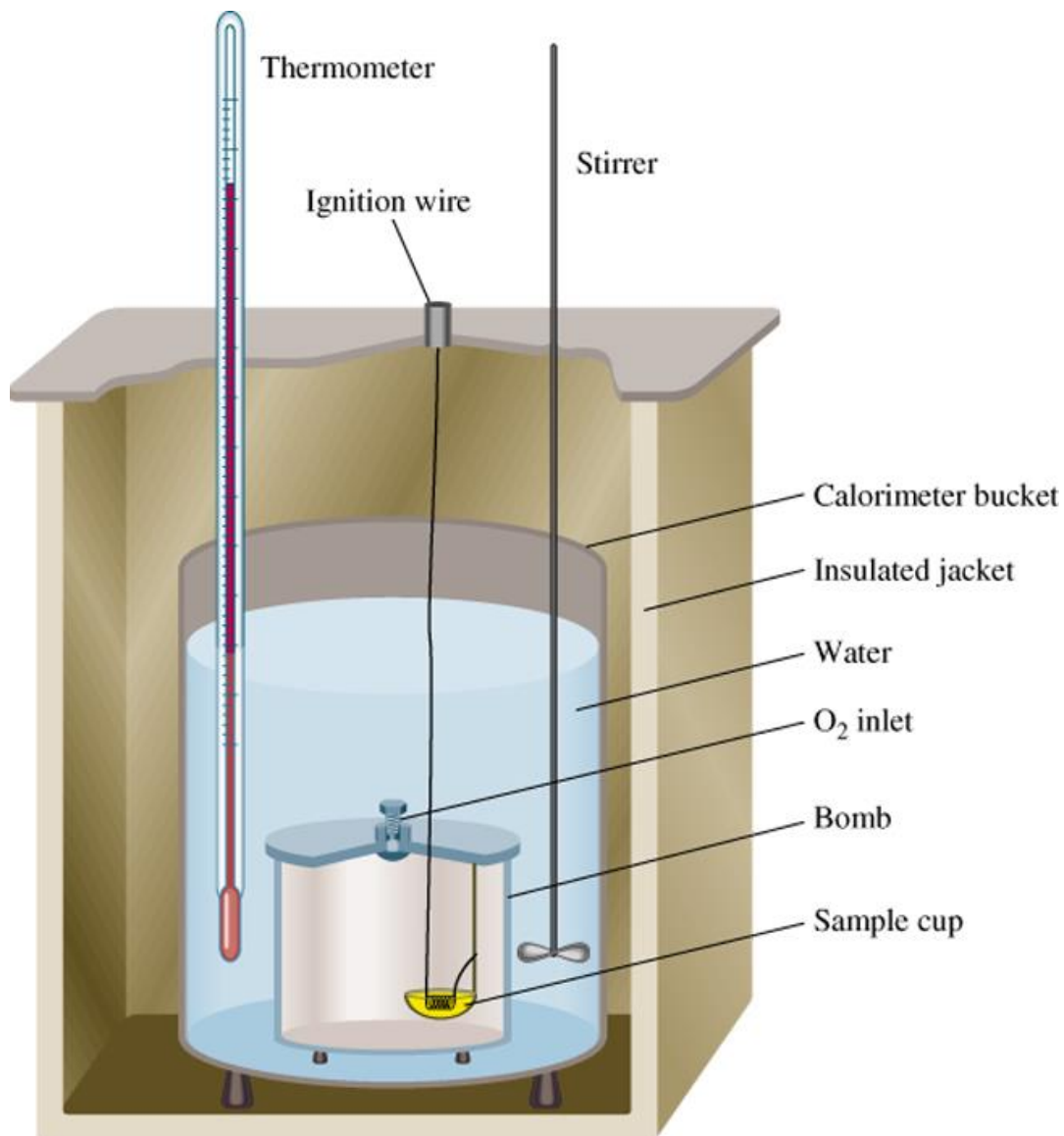
$q_{sys} = q_{water} + q_{bomb} + q_{rxn}$

$q_{sys} = 0$

$q_{rxn} = - (q_{water} + q_{bomb})$

$q_{water} = m\,s\Delta t$

$q_{bomb} = C_{bomb}\Delta t$

Reaction at Constant V

$\Delta H \neq q_{rxn}$

$\Delta H \sim q_{rxn}$

6.5

Constant-Pressure Calorimetry

Thermometer

Stirrer

Styrofoam cups
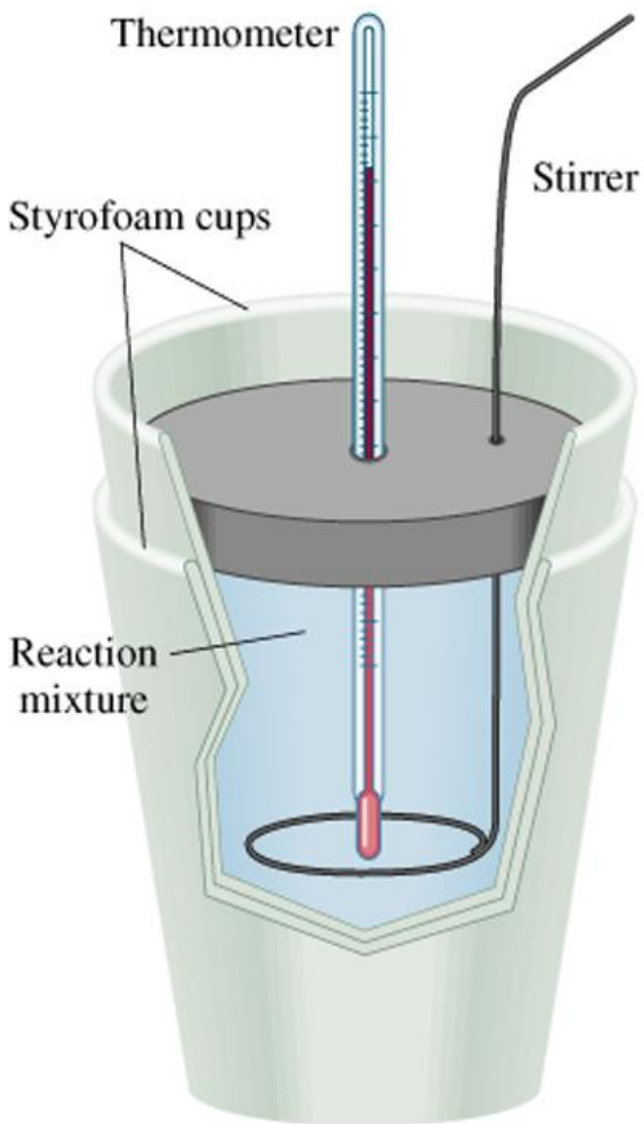
Reaction
mixture

$q_{sys} = q_{water} + q_{cal} + q_{rxn}$

$q_{sys} = 0$

$q_{rxn} = -(q_{water} + q_{cal})$

$q_{water} = ms\Delta t$

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

Reaction at Constant P

$\Delta H = q_{rxn}$

No heat enters or leaves!

6.5

TABLE 6.3

Heats of Some Typical Reactions Measured at Constant Pressure

Type of Reaction	Example	ΔH (kJ/mol)
Heat of neutralization	$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$	-56.2
Heat of ionization	$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq)$	56.2
Heat of fusion	$H_2O(s) \longrightarrow H_2O(l)$	6.01
Heat of vaporization	$H_2O(l) \longrightarrow H_2O(g)$	$44.0*$
Heat of reaction	$MgCl_2(s) + 2Na(l) \longrightarrow 2NaCl(s) + Mg(s)$	-180.2

*Measured at 25°C. At 100°C, the value is 40.79 kJ.

6.5

Chemistry in Action:

Fuel Values of Foods and Other Substances

$$C_6H_{12}O_6 \ (s) + 6O_2 \ (g) \longrightarrow 6CO_2 \ (g) + 6H_2O \ (l) \quad \Delta H = -2801 \ kJ/mol$$
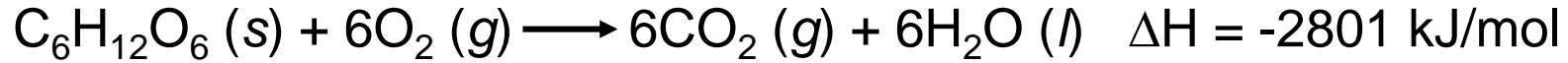
1 cal = 4.184 J

1 Cal = 1000 cal = 4184 J

Nutrition Facts

Serving Size 6 cookies (28g)
Servings Per Container about 11

Amount Per Serving

Calories 120	Calories from Fat 30

% Daily Value*

Total Fat 4g	**6%**
Saturated Fat 0.5g	**4%**
Polyunsaturated Fat 0g	
Monounsaturated Fat 1g	
Cholesterol 5mg	**2%**
Sodium 105mg	**4%**
Total Carbohydrate 20g	**7%**
Dietary Fiber Less than 1gram	**2%**
Sugars 7g	
Protein 2g	

Because there is no way to measure the absolute value of the enthalpy of a substance, must I measure the enthalpy change for every reaction of interest?

Establish an arbitrary scale with the **standard enthalpy of formation** (ΔH_f^0) as a reference point for all enthalpy expressions.

Standard enthalpy of formation (ΔH_f^0) is the heat change that results when **one mole** of a compound is formed from its **elements** at a pressure of 1 atm.
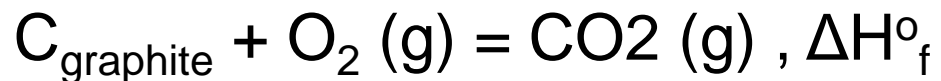
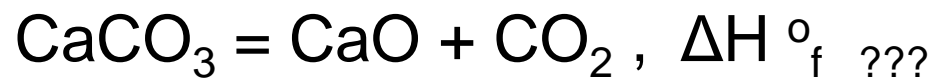The standard enthalpy of formation of any element in its most stable form is zero.

$$\Delta H_f^0 (O_2) = 0 \qquad\qquad \Delta H_f^0 (C, graphite) = 0$$

$$\Delta H_f^0 (O_3) = 142 \text{ kJ/mol} \qquad \Delta H_f^0 (C, diamond) = 1.90 \text{ kJ/mol}$$

$$CaCO_3 = CaO + CO_2, \quad \Delta H^{\circ}_f \; ???$$

$$C_{graphite} + O_2\,(g) = CO2\,(g), \quad \Delta H^{\circ}_f$$

Which of the following reactions represent heat
of formation of nitric acid HNO3 ?
H (g) + N (g)+ O3 (g) = HNO3 (l)
H2 (g) + N2 (g) + O2 (g) = HNO3(l)
H2 (g) + N2 (g) + 3O2 (g) = 2HNO3 (l)
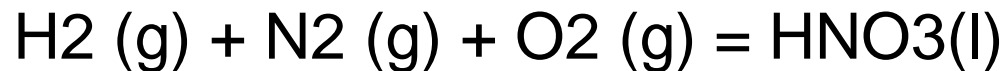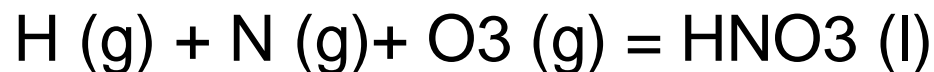
The **standard enthalpy of reaction** (ΔH_{rxn}^0) is the enthalpy of a reaction carried out at 1 atm.

$$aA + bB \longrightarrow cC + dD$$

$$\Delta H_{rxn}^0 = [c\Delta H_f^0 (C) + d\Delta H_f^0 (D)] - [a\Delta H_f^0 (A) + b\Delta H_f^0 (B)]$$

$$\Delta H_{rxn}^0 = \Sigma n\Delta H_f^0 \text{ (products)} - \Sigma n\Delta H_f^0 \text{ (reactants)}$$

Hess's Law: When reactants are converted to products, the **change in enthalpy is the same** whether the reaction takes place in **one step or in a series of steps**.

(**Enthalpy is a state function**. It doesn't matter how you get there, only where you start and end.)

6.6
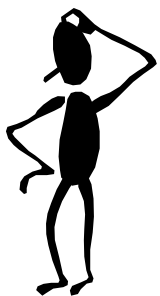
Calculate the standard enthalpy of formation of CS_2 (l) given that:

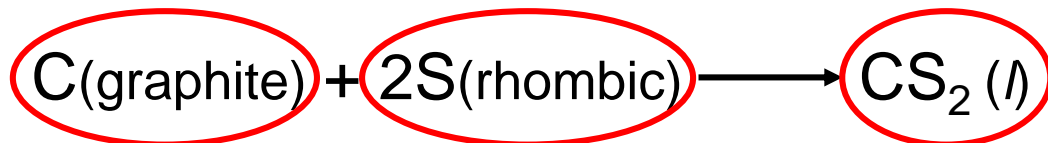$$C(graphite) + O_2 (g) \longrightarrow CO_2 (g) \quad \Delta H^0_{rxn} = -393.5 \text{ kJ}$$

$$S(rhombic) + O_2 (g) \longrightarrow SO_2 (g) \quad \Delta H^0_{rxn} = -296.1 \text{ kJ}$$

$$CS_2(l) + 3O_2 (g) \longrightarrow CO_2 (g) + 2SO_2 (g) \quad \Delta H^0_{rxn} = -1072 \text{ kJ}$$
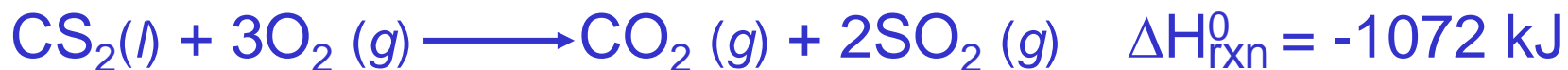
1. Write the enthalpy of formation reaction for CS_2

$$C(graphite) + 2S(rhombic) \longrightarrow CS_2 (l)$$

2. Add the given rxns so that the result is the desired rxn.

$$C(graphite) + O_2 (g) \longrightarrow CO_2 (g) \quad \Delta H^0_{rxn} = -393.5 \text{ kJ}$$

$$2S(rhombic) + 2O_2 (g) \longrightarrow 2SO_2 (g) \quad \Delta H^0_{rxn} = -296.1 \text{x2 kJ}$$

$$+ \quad CO_2(g) + 2SO_2 (g) \longrightarrow CS_2 (l) + 3O_2 (g) \quad \Delta H^0_{rxn} = +1072 \text{ kJ}$$

$$C(graphite) + 2S(rhombic) \longrightarrow CS_2 (l)$$

$$\Delta H^0_{rxn} = -393.5 + (2\text{x}-296.1) + 1072 = 86.3 \text{ kJ}$$

6.6
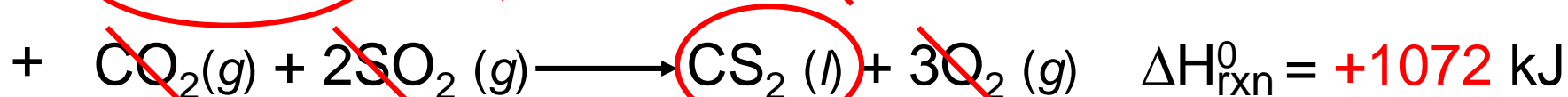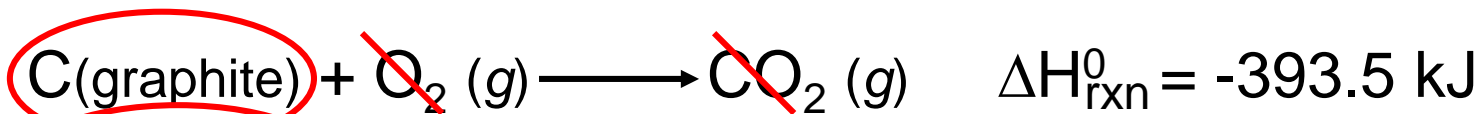
Benzene (C_6H_6) burns in air to produce carbon dioxide and liquid water. How much heat is released per mole of benzene combusted? The standard enthalpy of formation of benzene is 49.04 kJ/mol.

$$2C_6H_6 \text{ (l)} + 15O_2 \text{ (g)} \longrightarrow 12CO_2 \text{ (g)} + 6H_2O \text{ (l)}$$

$$\Delta H^0_{rxn} = \Sigma n \, \Delta H^0_f \text{ (products)} - \Sigma n \, \Delta H^0_f \text{ (reactants)}$$

$$\Delta H^0_{rxn} = [12\Delta H^0_f (CO_2) + 6\Delta H^0_f (H_2O)] - [2\Delta H^0_f (C_6H_6)]$$

$$\Delta H^0_{rxn} = [12 \times -393.5 + 6 \times -187.6] - [2 \times 49.04] = -5946 \text{ kJ}$$

$$\frac{-5946 \text{ kJ}}{2 \text{ mol}} = -2973 \text{ kJ/mol } C_6H_6$$

The ***enthalpy of solution*** (ΔH_{soln}) is the heat generated or absorbed when a certain amount of solute dissolves in a certain amount of solvent.

$$\Delta H_{soln} = H_{soln} - H_{components}$$

Heats of Solution of Some Ionic Compounds

Compound	ΔH_{soln} (kJ/mol)
LiCl	−37.1
$CaCl_2$	−82.8
NaCl	4.0
KCl	17.2
NH_4Cl	15.2
NH_4NO_3	26.2

TABLE 6.5

Which substance(s) could be used for melting ice?

Which substance(s) could be used for a cold pack?

The Solution Process for NaCl

Na⁺ and Cl⁻ ions in the gaseous state

Step 1
Lattice energy
$U = 788 \text{ kJ/mol}$

Step 2
Heat of hydration
$\Delta H_{hydr} = -784 \text{ kJ/mol}$

Heat of solution
$\Delta H_{soln} = 4 \text{ kJ/mol}$

Na⁺ and Cl⁻ ions
in the solid state

Hydrated Na⁺ and Cl⁻ ions

$\Delta H_{soln} = \text{Step 1} + \text{Step 2} = 788 - 784 = 4 \text{ kJ/mol}$

6.7