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

Energy Changes in Chemical Reactions

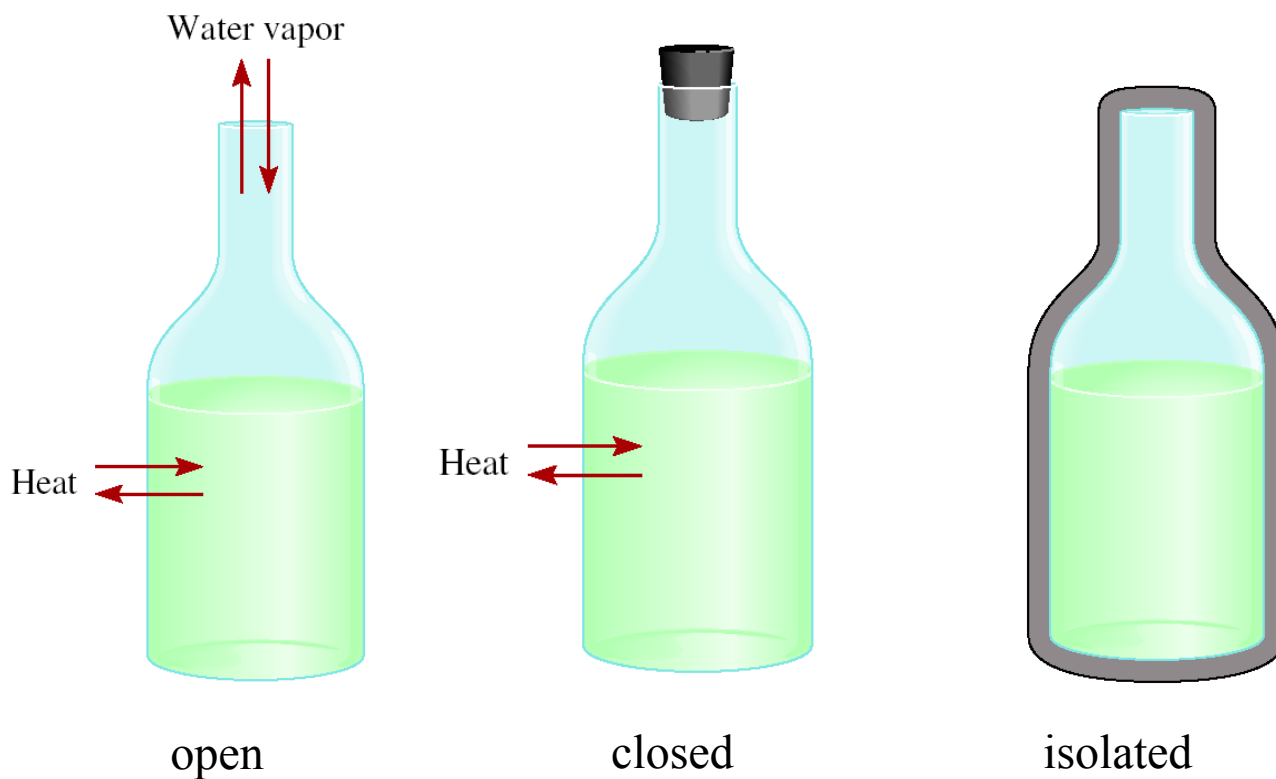*Heat* is the transfer of thermal energy between two bodies that are at different temperatures.

Temperature is a measure of the thermal energy.

Temperature = Thermal Energy

100°C

37°C

25°C

0°C
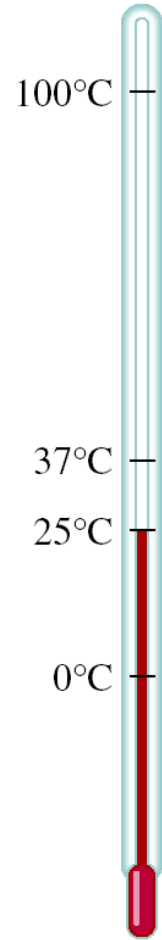
Thermochemistry is the study of heat change in chemical reactions.

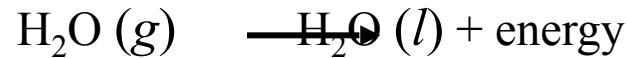The *system* is the specific part of the universe that is of interest in the study.

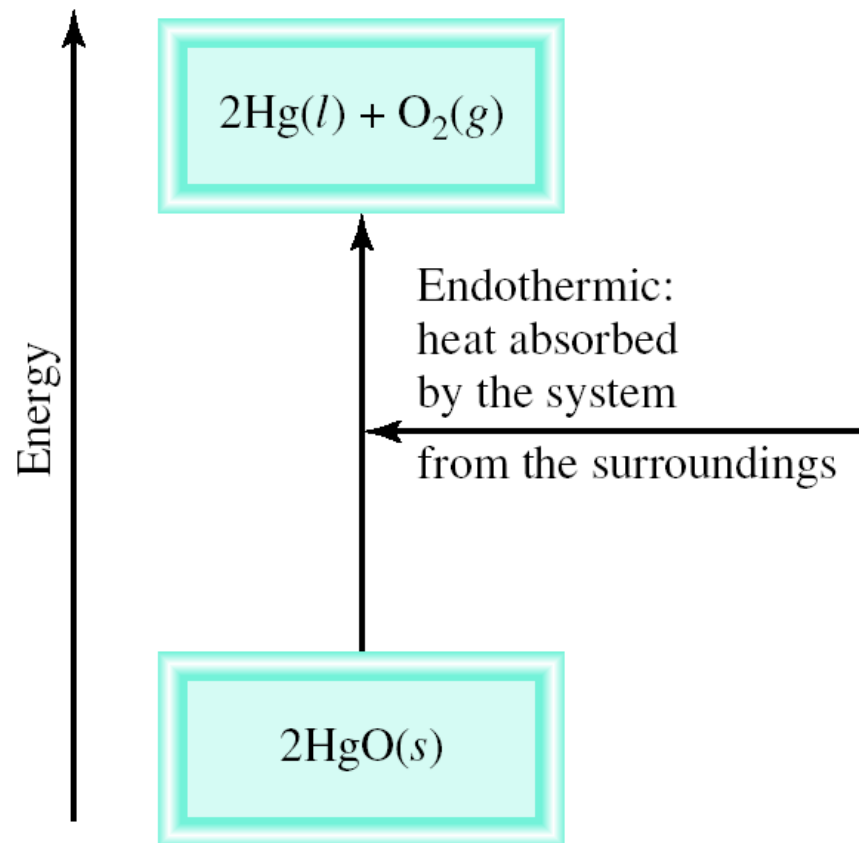| open	closed	isolated

Exchange: mass & energy   energy   nothing

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

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

$$H_2O\ (g) \longrightarrow H_2O\ (l) + energy$$

Endothermic process is any process in which heat has to be supplied to the system from the surroundings.

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

$$energy + H_2O\ (s) \longrightarrow H_2O\ (l)$$

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Schematic of Exothermic and Endothermic Processes

Energy

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

Exothermic:
heat given off
by the system
to the surroundings

$2H_2O(l)$

Energy

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

Endothermic:
heat absorbed
by the system
from the surroundings

$2HgO(s)$
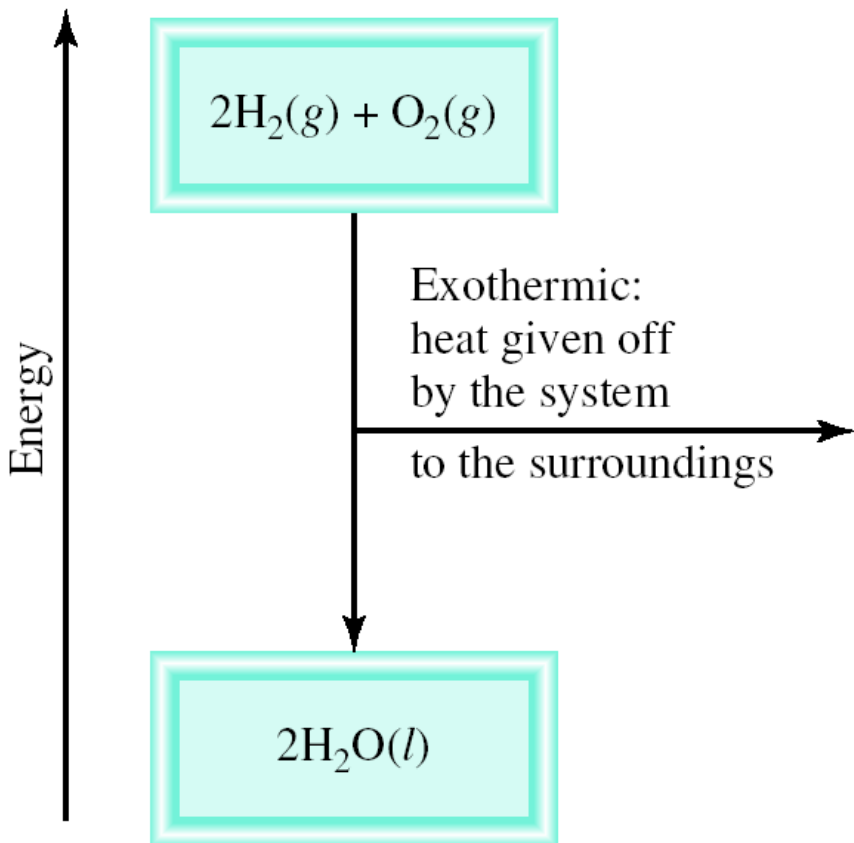
Thermodynamics is the scientific study of the interconversion of heat and other kinds of energy.

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

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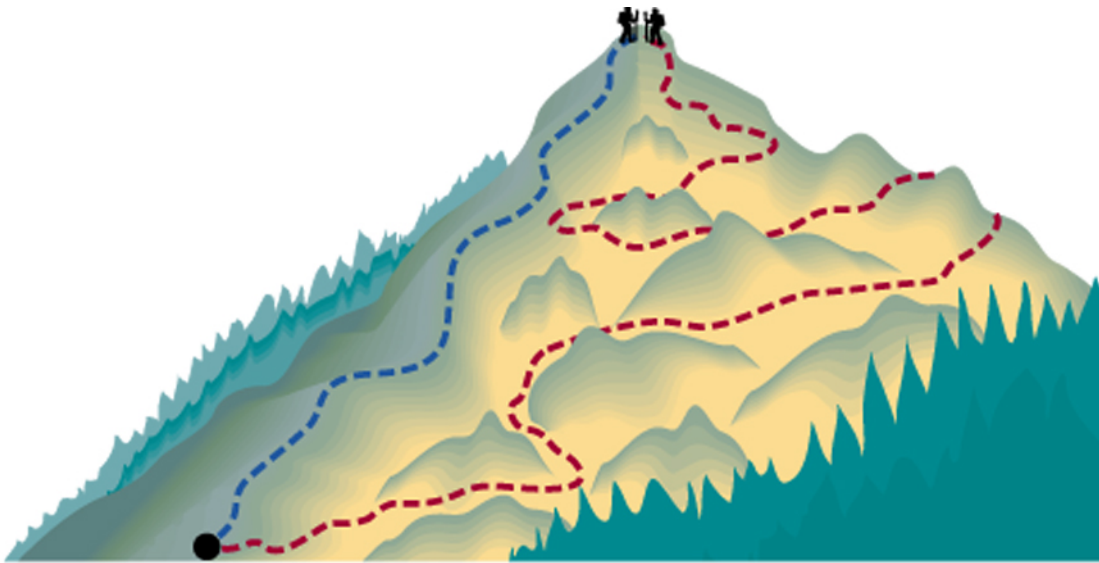
$$\Delta E = E_{final} - E_{initial}$$

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

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

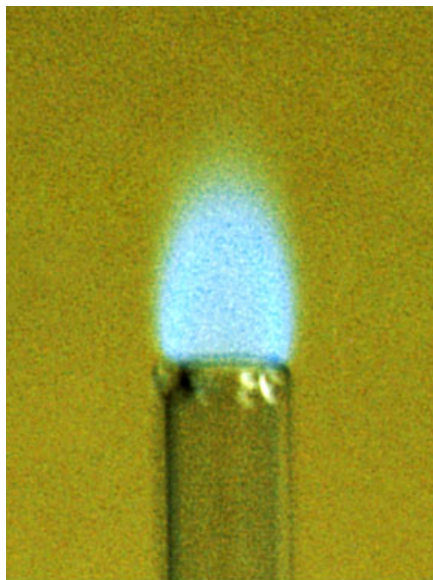$$\Delta T = T_{final} - T_{initial}$$

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

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

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

$$C_3H_8 + 5O_2 \quad \xcancel{3CO_2} + 4H_2O$$

Exothermic chemical reaction!

Chemical energy lost by combustion = Energy gained by the surroundings
$\qquad\qquad$ system $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ surroundings

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

$w = F \times d$

$w = -P \, \Delta V$

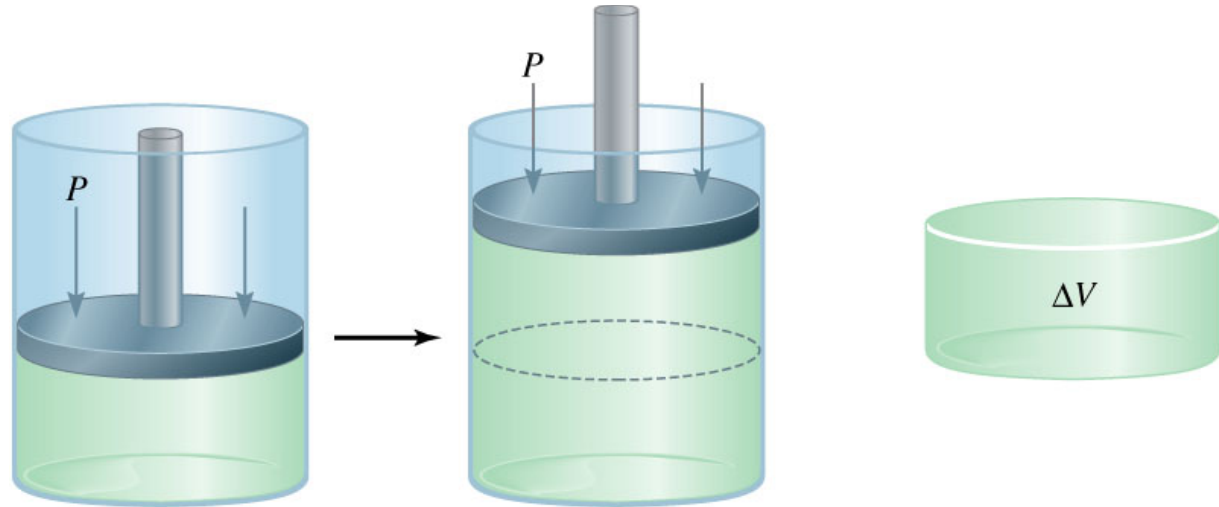$P \times V = \dfrac{F}{d^2} \times d^3 = F \times d = w$

$\Delta V > 0$

$-P\Delta V < 0$

$w_{sys} < 0$

Work is not a state function.

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

initial

final

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

$W = -0 \text{ atm x } 3.8 \text{ L} = 0 \text{ L•atm} = 0 \text{ joules}$

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

$w = -3.7 \text{ atm x } 3.8 \text{ L} = -14.1 \text{ L•atm}$

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

Chemistry in Action: Making Snow

$\Delta E = q + w$

$q = 0$

$w < 0, \Delta E < 0$

$\Delta E = C\Delta T$

$\Delta T < 0$, SNOW!

Enthalpy and the First Law of Thermodynamics

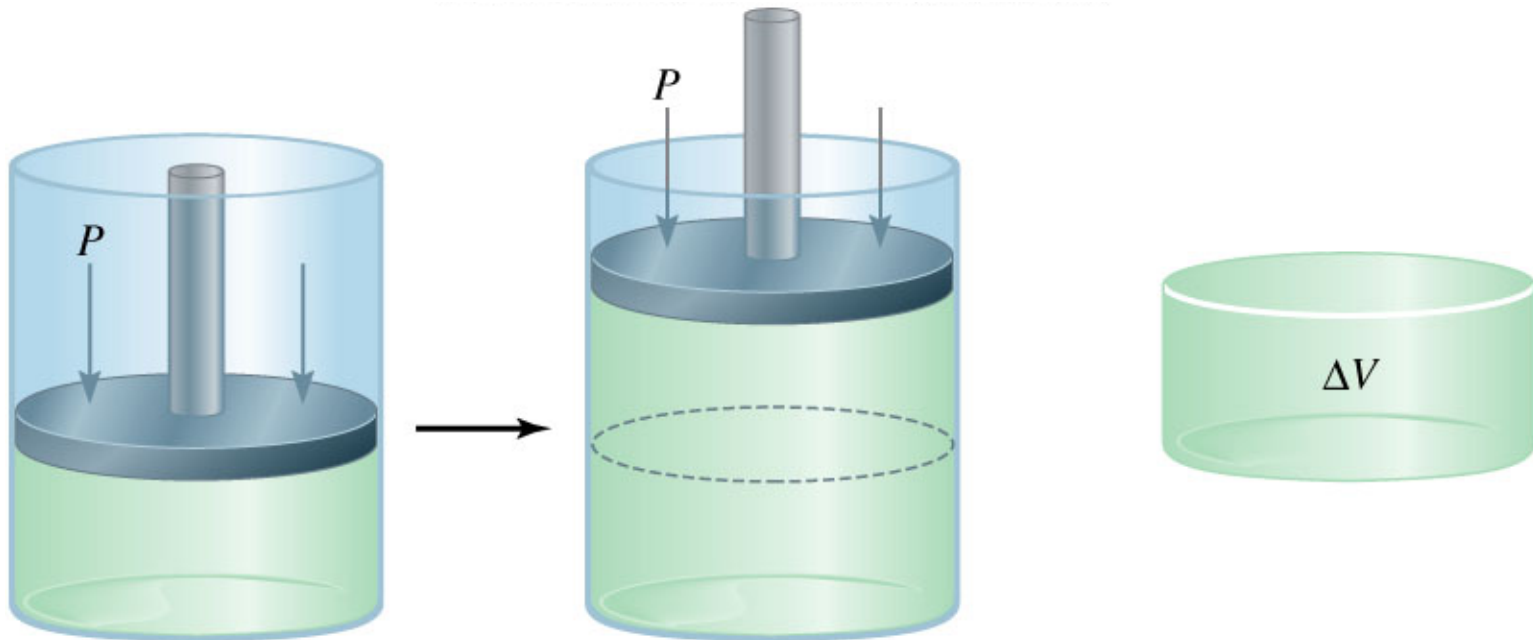$$\Delta E = q + w$$

At constant pressure:

$q = \Delta H$ and $w = -P\Delta V$

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

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

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

Enthalpy

H$_2$O(*l*)

Heat absorbed
by the system
from the surroundings
$\Delta H = 6.01$ kJ/mol

H$_2$O(*s*)

$H_{products} < H_{reactants}$

$\Delta H < 0$

Enthalpy

CH$_4$(*g*) + 2O$_2$(*g*)

Heat given off
by the system
to the surroundings
$\Delta H = -890.4$ kJ/mol

CO$_2$(*g*) + 2H$_2$O(*l*)

$H_{products} > H_{reactants}$

$\Delta H > 0$

Thermochemical Equations

Enthalpy

$H_2O(l)$

Heat absorbed
by the system
from the surroundings

$\Delta H = 6.01$ kJ/mol

$H_2O(s)$
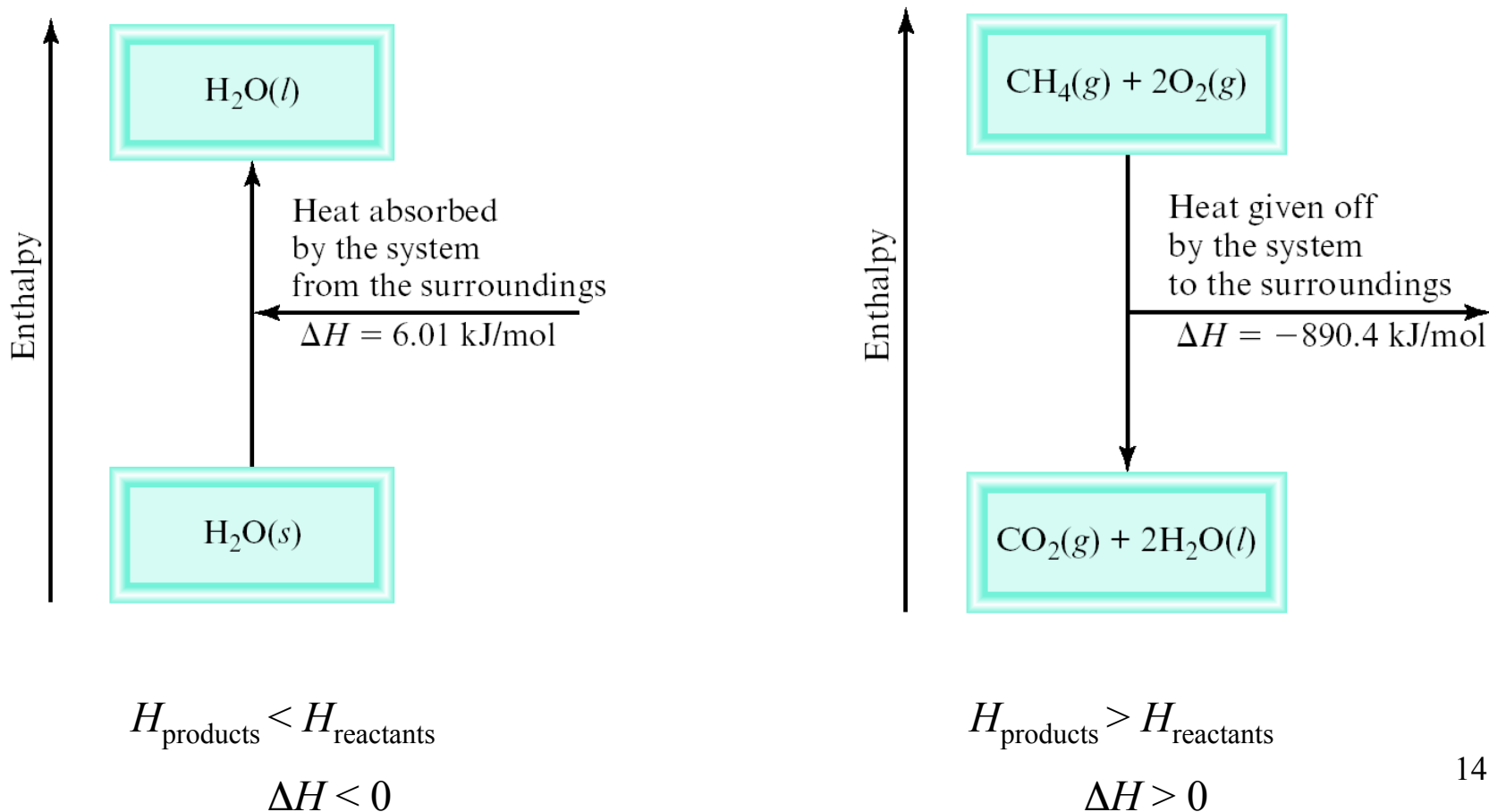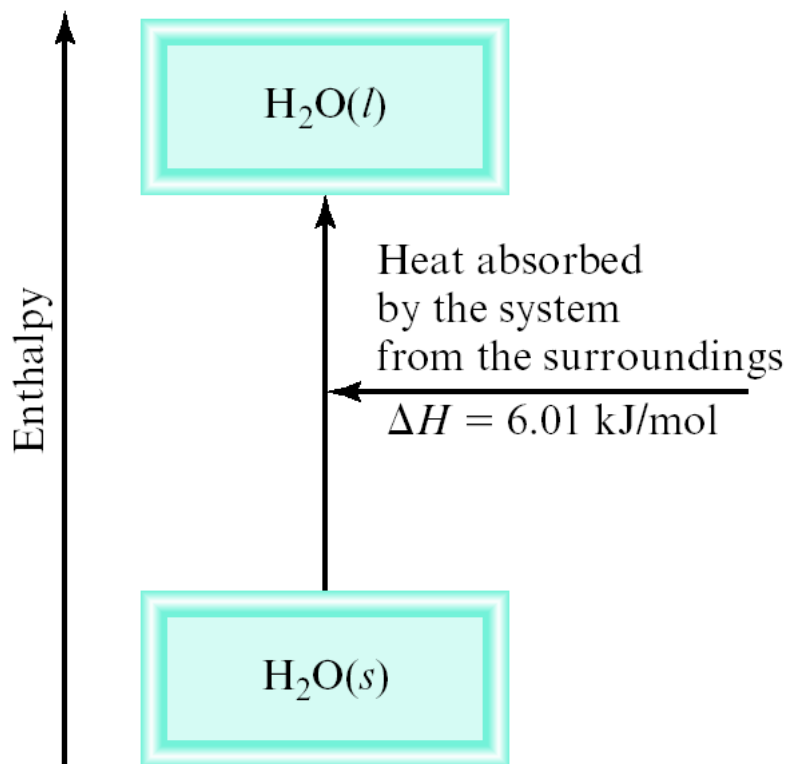
Is ΔH negative or positive?

System absorbs heat

Endothermic

$\Delta H > 0$

6.01 kJ are absorbed for every 1 mole of ice that melts at 0⁰C and 1 atm.

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

Thermochemical Equations

Enthalpy

$CH_4(g) + 2O_2(g)$

Heat given off
by the system
to the surroundings

$\Delta H = -890.4$ kJ/mol

$CO_2(g) + 2H_2O(l)$
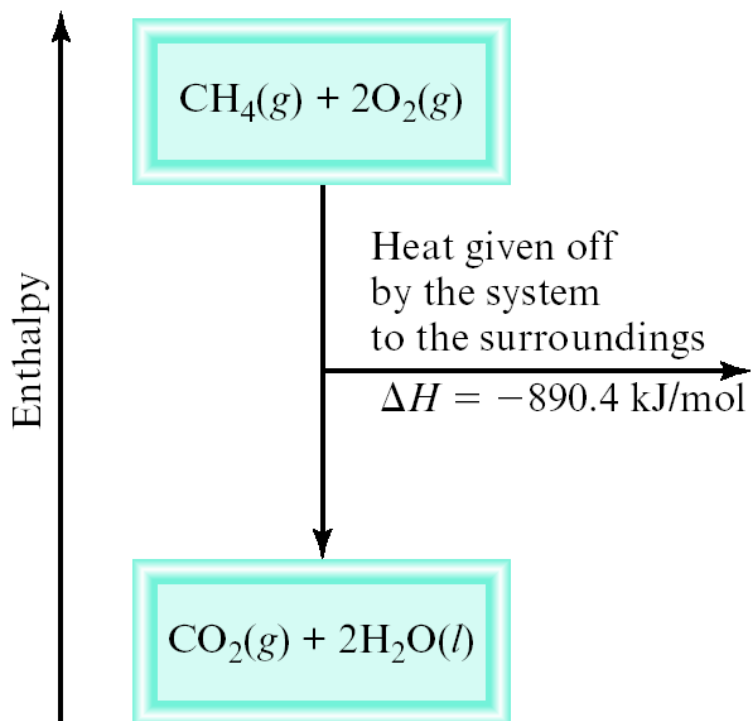
Is ΔH negative or positive?

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/mol

Thermochemical Equations

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

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

- If you reverse a reaction, the sign of ΔH changes

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

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

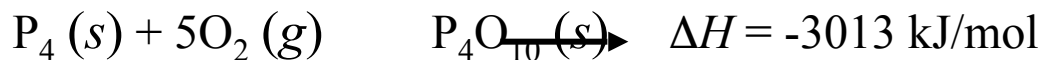$$2H_2O \ (s) \longrightarrow 2H_2O \ (l) \qquad \Delta H = 2 \ x \ 6.01 = 12.0 \ \text{kJ}$$

Thermochemical Equations

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

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

$$H_2O \ (l) \longrightarrow H_2O \ (g) \qquad \Delta H = 44.0 \ \text{kJ/mol}$$

How much heat is evolved when 266 g of white phosphorus (P_4) burn in air?

$$P_4 \ (s) + 5O_2 \ (g) \longrightarrow P_4O_{10} \ (s) \qquad \Delta H = -3013 \ \text{kJ/mol}$$

$$266 \ \text{g } P_4 \times \frac{1 \ \text{mol } P_4}{123.9 \ \text{g } P_4} \times \frac{3013 \ \text{kJ}}{1 \ \text{mol } P_4} = 6470 \ \text{kJ}$$

A Comparison of ΔH and ΔE

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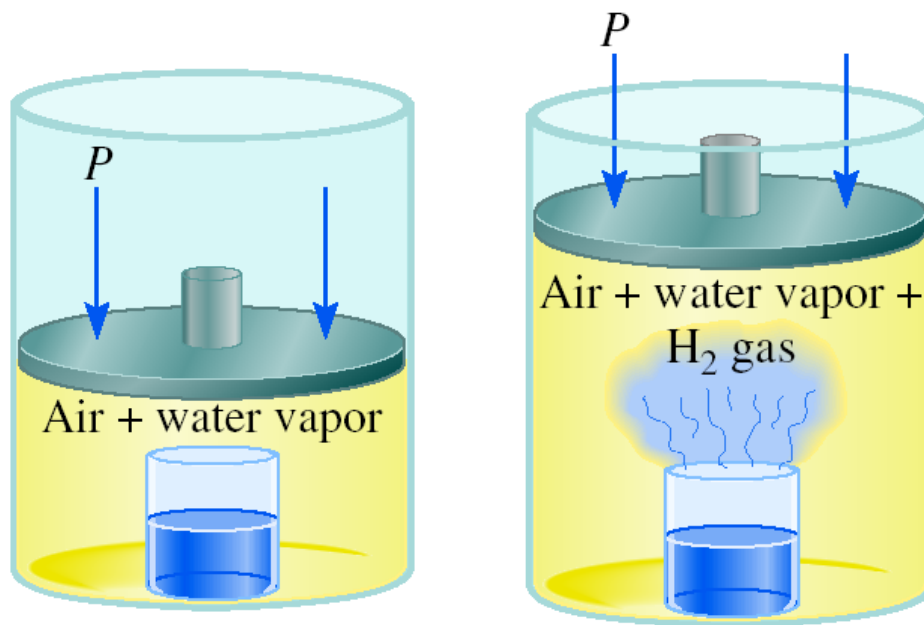
$\Delta E = \Delta H - P\Delta V$ At 25 °C, 1 mole H_2 = 24.5 L at 1 atm

$P\Delta V = 1\ \text{atm} \times 24.5\ \text{L} = 2.5\ \text{kJ}$

$\Delta E = -367.5\ \text{kJ/mol} - 2.5\ \text{kJ/mol} = -370.0\ \text{kJ/mol}$

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.

$$C = m \times s$$

TABLE 6.2

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

Heat (*q*) absorbed or released:

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

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

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

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

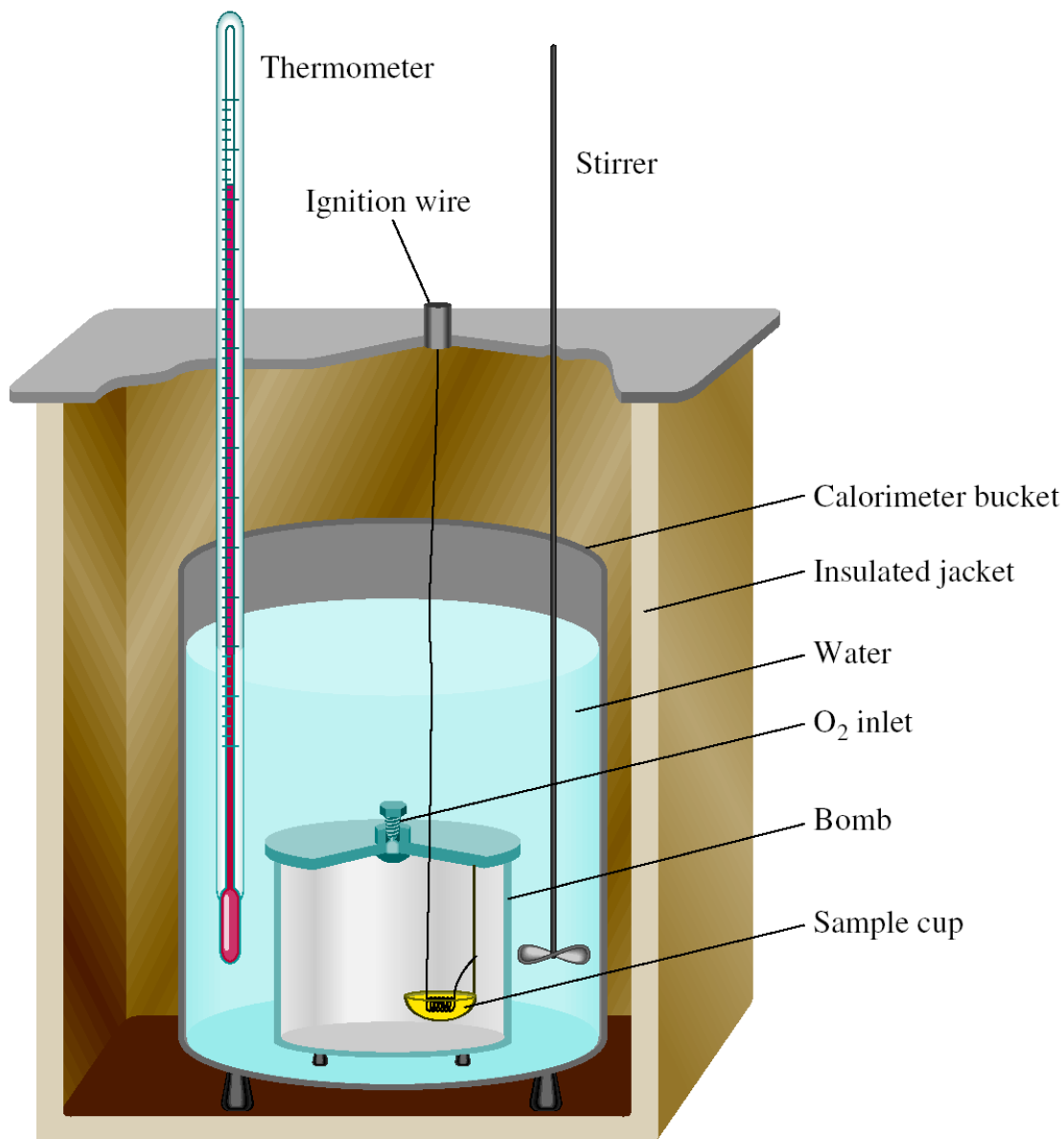s of Fe = 0.444 J/g • °C

$\Delta t = t_{final} - t_{initial}$ = 5°C − 94°C = -89°C

$q = ms\Delta t$ = 869 g x 0.444 J/g • °C x −89°C   = -34,000 J

Constant-Volume Calorimetry

Thermometer

Stirrer

Ignition wire

Calorimeter bucket

Insulated jacket

Water

O_2 inlet

Bomb

Sample cup

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

$$q_{sys} = 0$$

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

$$q_{water} = m \text{ x s x } \Delta t$$

$$q_{bomb} = C_{bomb} \, x \, \Delta t$$
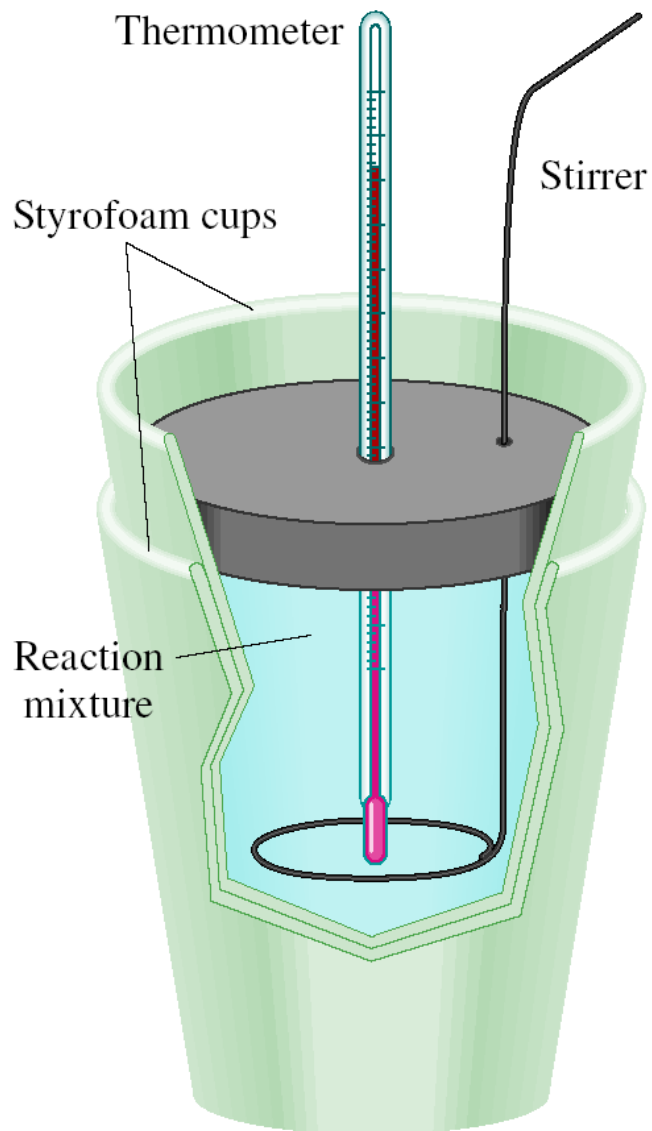
Reaction at Constant V

$$\Delta H = q_{rxn}$$

$$\Delta H \sim q_{rxn}$$

No heat enters or leaves!

Constant-Pressure Calorimetry

Thermometer

Stirrer

Styrofoam cups

Reaction mixture

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

$q_{sys} = 0$

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

$q_{water} = m \text{ x } s \text{ x } \Delta t$

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

Reaction at Constant P

$$\Delta H = q_{rxn}$$

No heat enters or leaves!

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.

Chemistry in Action:

Fuel Values of Foods and Other Substances

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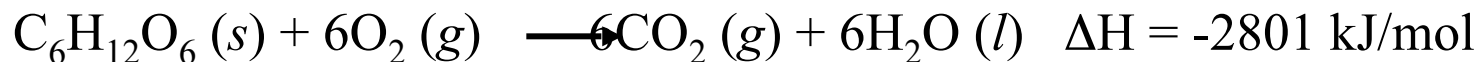
1 cal = 4.184 J

1 Cal = 1000 cal = 4184 J

Substance	$\Delta H_{combustion}$ (kJ/g)
Apple	-2
Beef	-8
Beer	-1.5
Gasoline	-34

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^0_f) as a reference point for all enthalpy expressions.

Standard enthalpy of formation (ΔH^0_f) 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.

$$\Delta H^0_f (O_2) = 0$$

$$\Delta H^0_f (O_3) = 142 \text{ kJ/mol}$$

$$\Delta H^0_f (C, \text{graphite}) = 0$$

$$\Delta H^0_f (C, \text{diamond}) = 1.90 \text{ kJ/mol}$$

Substance	ΔH_f°(kJ/mol)	Substance	ΔH_f°(kJ/mol)
Ag(s)	0	$H_2O_2(l)$	−187.6
AgCl(s)	−127.0	Hg(l)	0
Al(s)	0	$I_2(s)$	0
$Al_2O_3(s)$	−1669.8	HI(g)	25.9
$Br_2(l)$	0	Mg(s)	0
HBr(g)	−36.2	MgO(s)	−601.8
C(graphite)	0	$MgCO_3(s)$	−1112.9
C(diamond)	1.90	$N_2(g)$	0
CO(g)	−110.5	$NH_3(g)$	−46.3
$CO_2(g)$	−393.5	NO(g)	90.4
Ca(s)	0	$NO_2(g)$	33.85
CaO(s)	−635.6	$N_2O(g)$	81.56
$CaCO_3(s)$	−1206.9	$N_2O_4(g)$	9.66
$Cl_2(g)$	0	O(g)	249.4
HCl(g)	−92.3	$O_2(g)$	0
Cu(s)	0	$O_3(g)$	142.2
CuO(s)	−155.2	S(rhombic)	0
$F_2(g)$	0	S(monoclinic)	0.30
HF(g)	−271.6	$SO_2(g)$	−296.1
H(g)	218.2	$SO_3(g)$	−395.2
$H_2(g)$	0	$H_2S(g)$	−20.15
$H_2O(g)$	−241.8	Zn(s)	0
$H_2O(l)$	−285.8	ZnO(s)	−348.0

TABLE 6.4 Standard Enthalpies of Formation of Some Inorganic Substances at 25°C

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The standard enthalpy of reaction (ΔH^0_{rxn}) is the enthalpy of a reaction carried out at 1 atm.

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

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

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

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.)

C(graphite) + $O_2(g)$

$\Delta H^\circ = -110.5$ kJ

CO(g) + $\frac{1}{2}O_2(g)$

Enthalpy

$\Delta H^\circ = -393.5$ kJ

$\Delta H^\circ = -283.0$ kJ

$CO_2(g)$

C (graphite) + 1/2O_2 (g) $\longrightarrow$ CO (g)

CO (g) + 1/2O_2 (g) $\longrightarrow$ CO_2 (g)

C (graphite) + O_2 (g) $\longrightarrow$ CO_2 (g)

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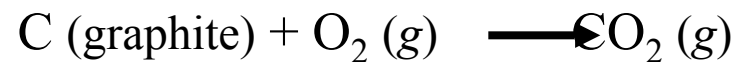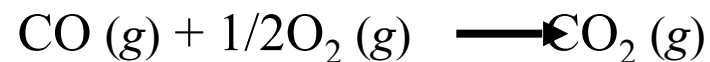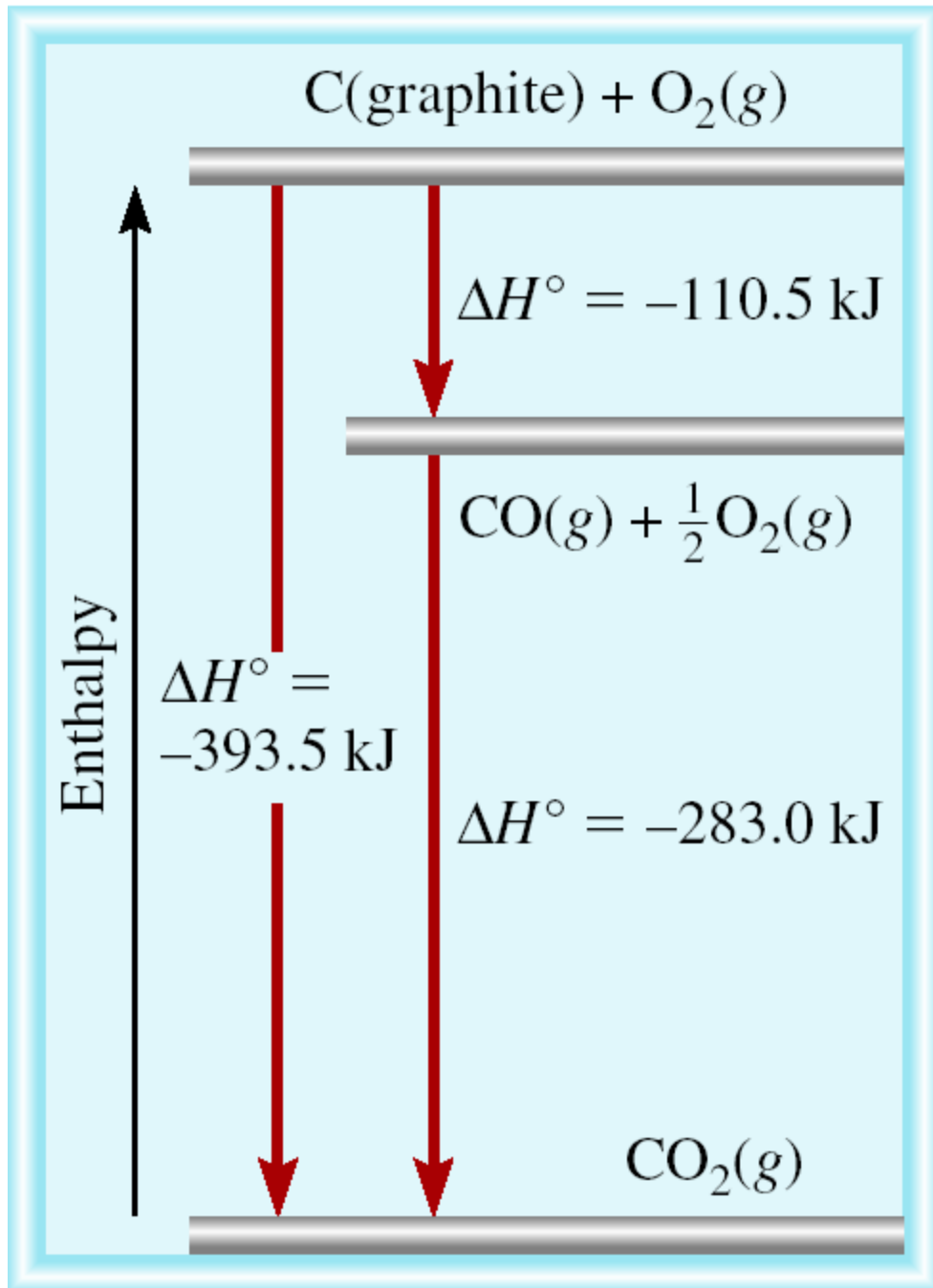
Calculate the standard enthalpy of formation of CS_2 (l) given that:

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

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

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

1. Write the enthalpy of formation reaction for CS_2

$C(\text{graphite}) + 2S(\text{rhombic}) \longrightarrow CS_2 (l)$
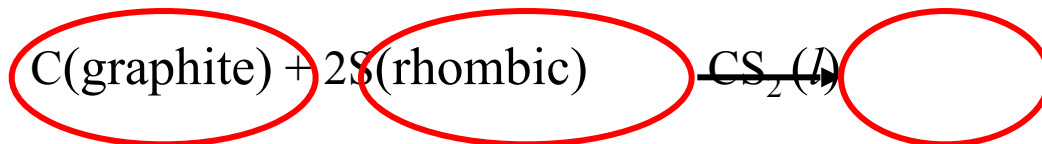
2. Add the given rxns so that the result is the desired rxn.

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

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

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

_____

$C(\text{graphite}) + 2S(\text{rhombic}) \longrightarrow CS_2 (l)$
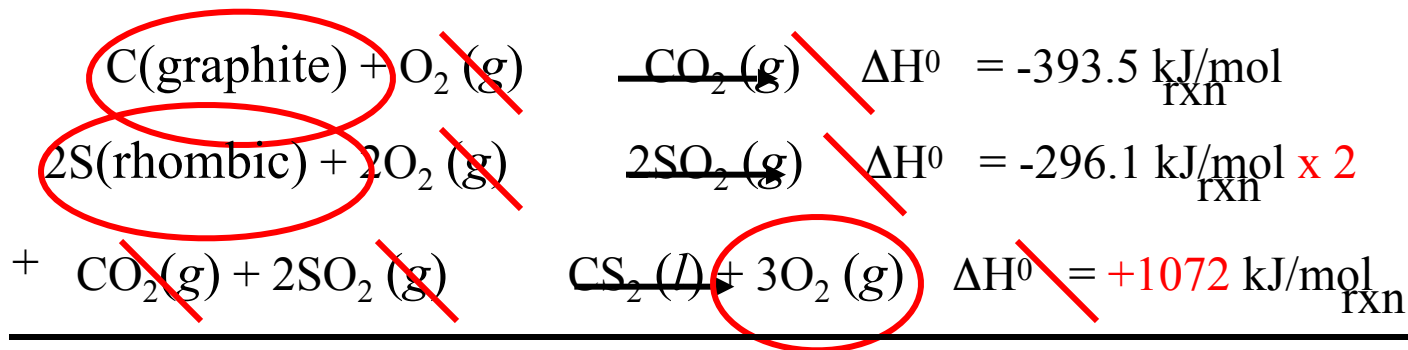
$\Delta H^0_{rxn} = -393.5 + (2 \times -296.1) + 1072 = 86.3 \text{ kJ/mol}$

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.
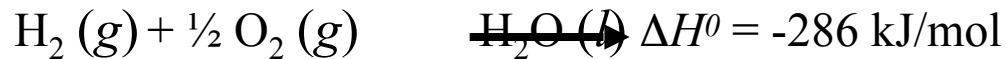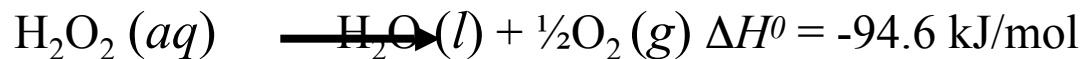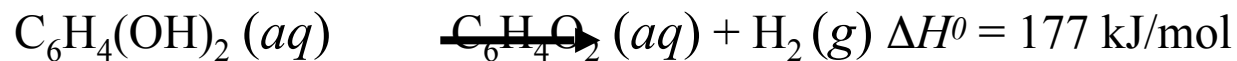
$$2C_6H_6 \; (l) + 15O_2 \; (g) \qquad 12CO_2 \; (g) + 6H_2O \; (l)$$

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

$$\Delta H^0_{rxn} = [\quad 12\Delta H^0_f \text{ (CO}_2) + \quad 6\Delta H^0_f \text{ (H}_2\text{O)] } - [\quad 2\Delta H^0_f \text{ (C}_6\text{H}_6)]$$

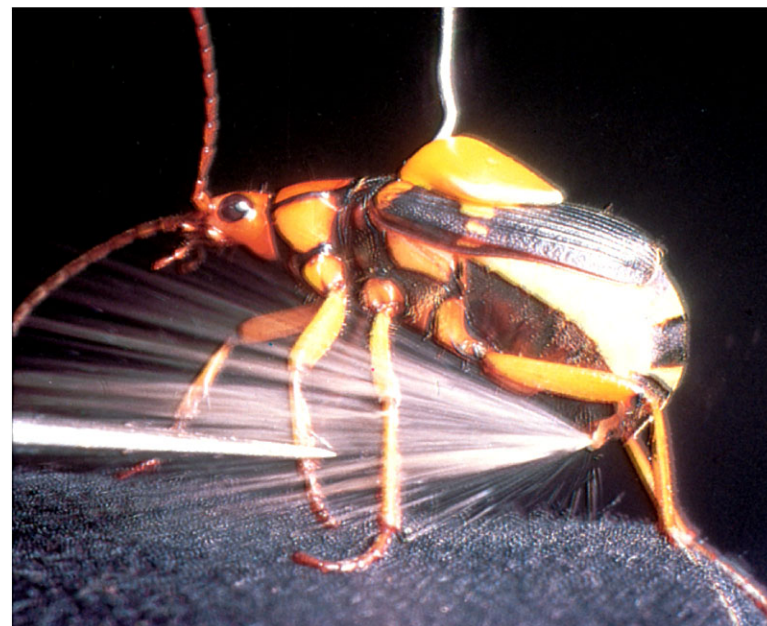$$\Delta H^0_{rxn} = [\, 12\text{x}{-}393.5 + 6\text{x}{-}187.6 \,] - [\, 2\text{x}49.04 \,] = -5946 \text{ kJ}$$

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

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Chemistry in Action: Bombardier Beetle Defense

$C_6H_4(OH)_2\ (aq) + H_2O_2\ (aq) \longrightarrow C_6H_4O_2\ (aq) + 2H_2O\ (l)\ \Delta H^0 = ?$

$C_6H_4(OH)_2\ (aq) \longrightarrow C_6H_4O_2\ (aq) + H_2\ (g)\ \Delta H^0 = 177\ kJ/mol$

$H_2O_2\ (aq) \longrightarrow H_2O\ (l) + \frac{1}{2}O_2\ (g)\ \Delta H^0 = -94.6\ kJ/mol$

$H_2\ (g) + \frac{1}{2}\ O_2\ (g) \longrightarrow H_2O\ (l)\ \Delta H^0 = -286\ kJ/mol$

$\Delta H^0 = 177 - 94.6 - 286 = -204\ kJ/mol$

Exothermic!

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.

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

TABLE 6.5

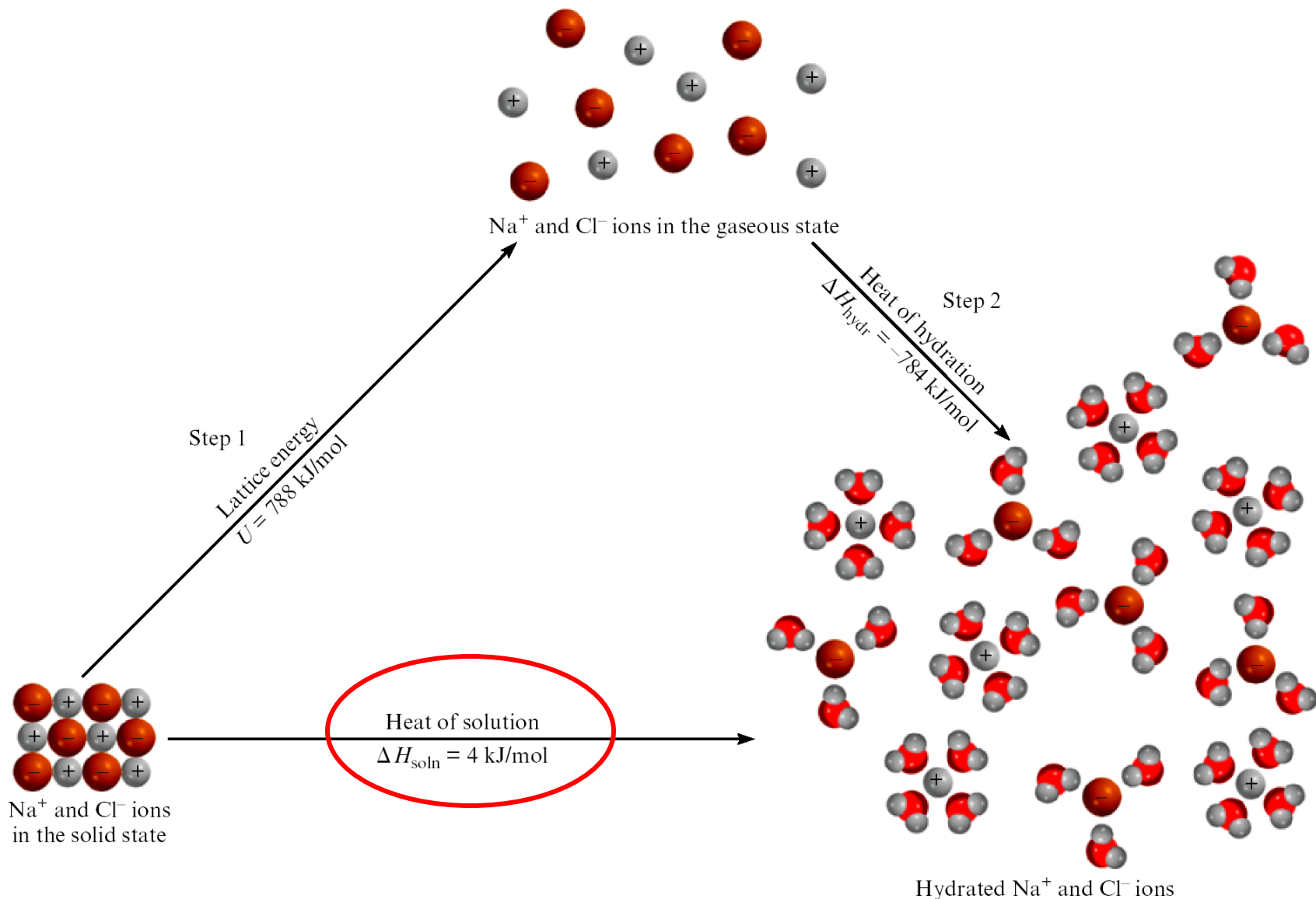**Heats of Solution of Some Ionic Compounds**

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

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 kJ/mol

Step 2

Heat of hydration
ΔH_{hydr} = −784 kJ/mol

Na$^+$ and Cl$^-$ ions
in the solid state

Heat of solution
ΔH_{soln} = 4 kJ/mol

Hydrated Na$^+$ and Cl$^-$ ions

ΔH_{soln} = Step 1 + Step 2 = 788 − 784 = 4 kJ/mol