Thermochemistry
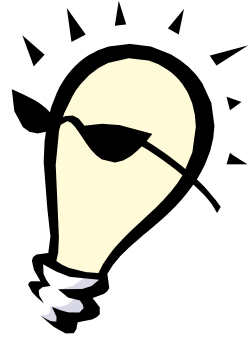
Chapter 7

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The Nature & Types of Energy

___*Energy* is the capacity to do work___

- ***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

- ***Electrical energy*** is the energy associated with the flow of electrons

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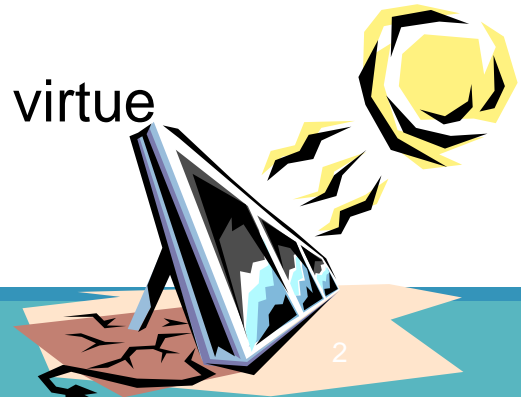
Energy Changes in Chemical Reactions

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

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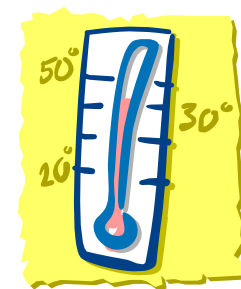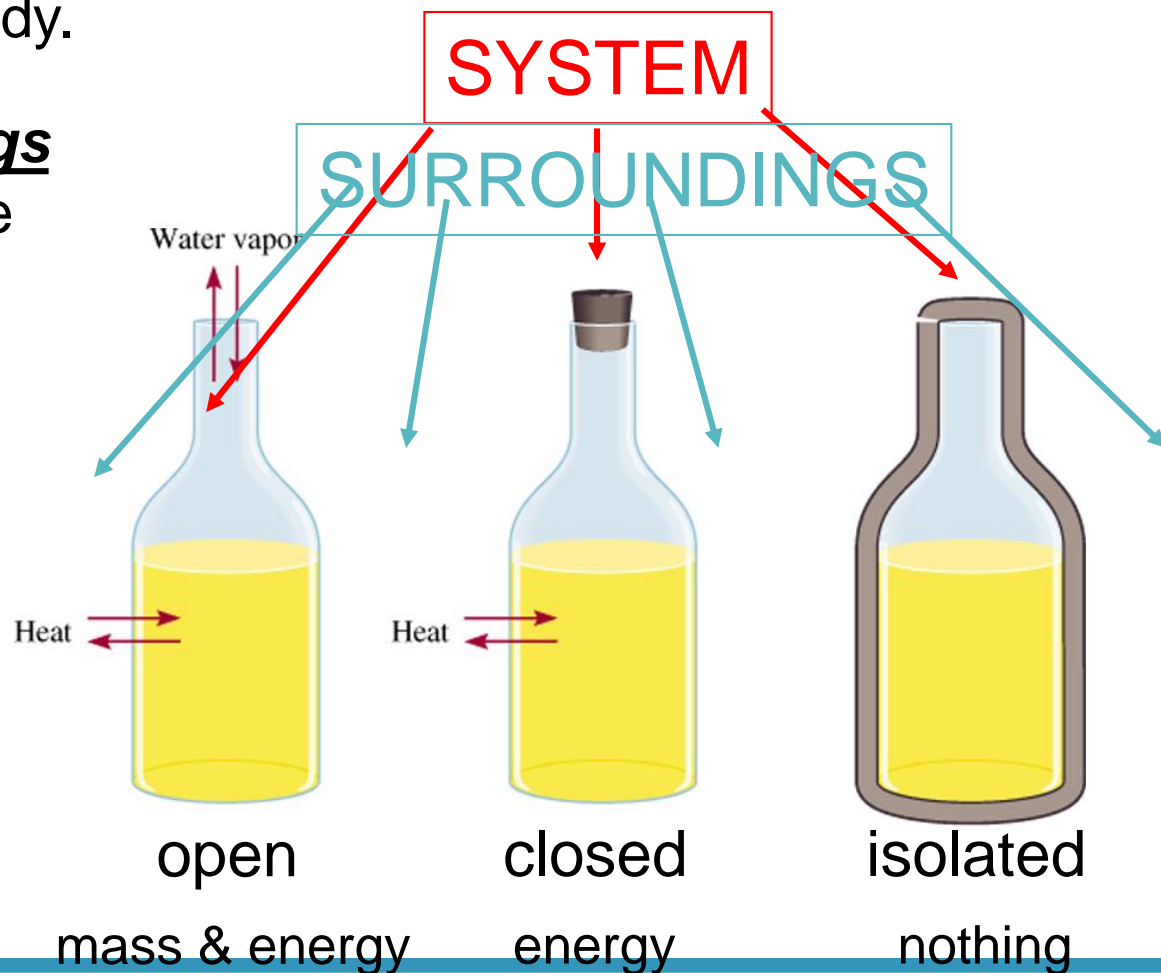
Temperature ≠ Thermal Energy

90⁰C

40⁰C

greater thermal energy

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.

The ***surroundings*** are the rest of the universe outside the system.

SYSTEM

SURROUNDINGS

Water vapor

Heat

Heat

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.

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

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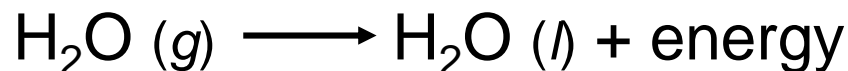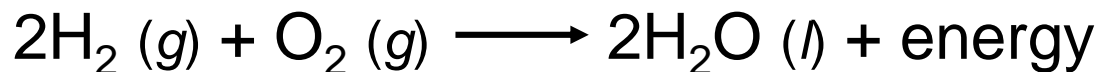
Endothermic process is any process in which heat has to be supplied to the system from the surroundings.

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

$$energy + H_2O\,(s) \longrightarrow H_2O\,(l)$$
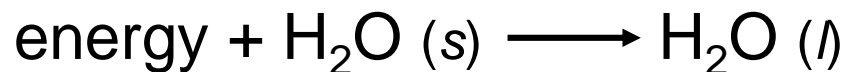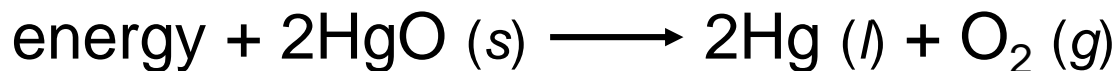
Enthalpy
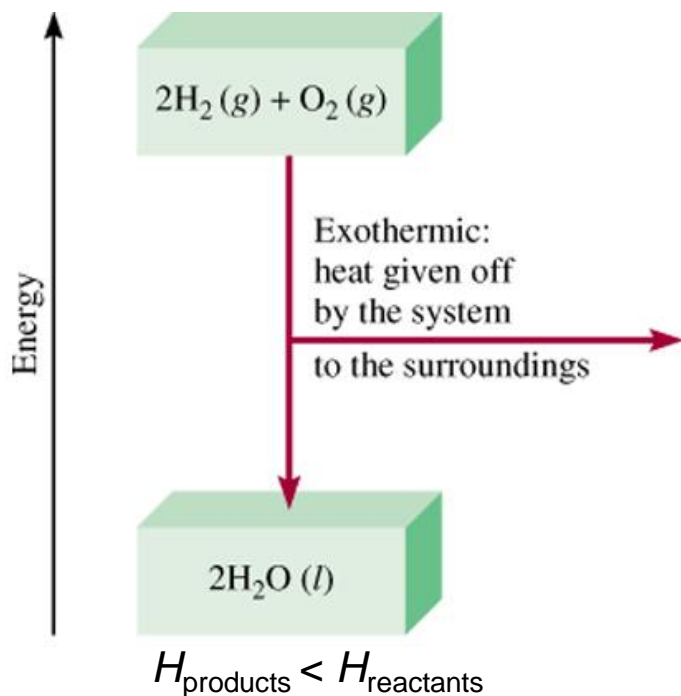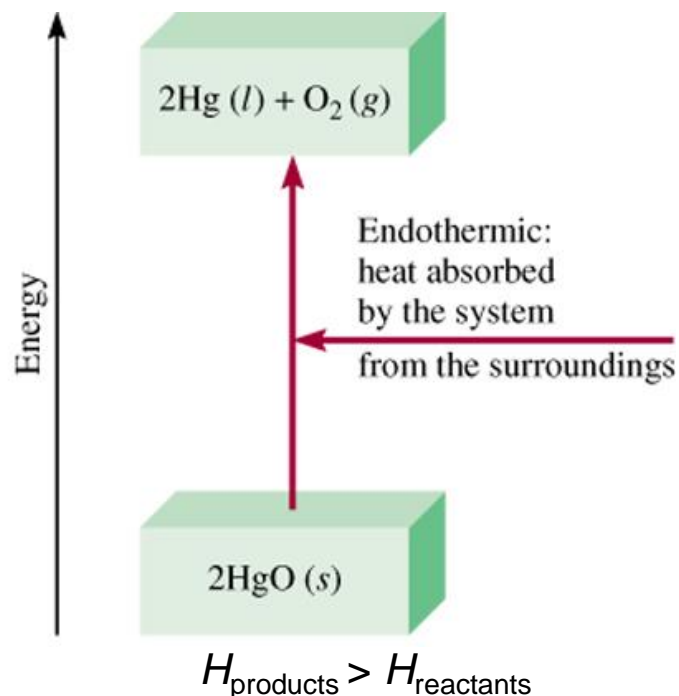
Enthalpy (H) is used to quantify the heat flow into or out of a system in a process that occurs at constant pressure.

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

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

$H_{products} < H_{reactants}$

$\Delta H < 0$

$H_{products} > H_{reactants}$

$\Delta H > 0$
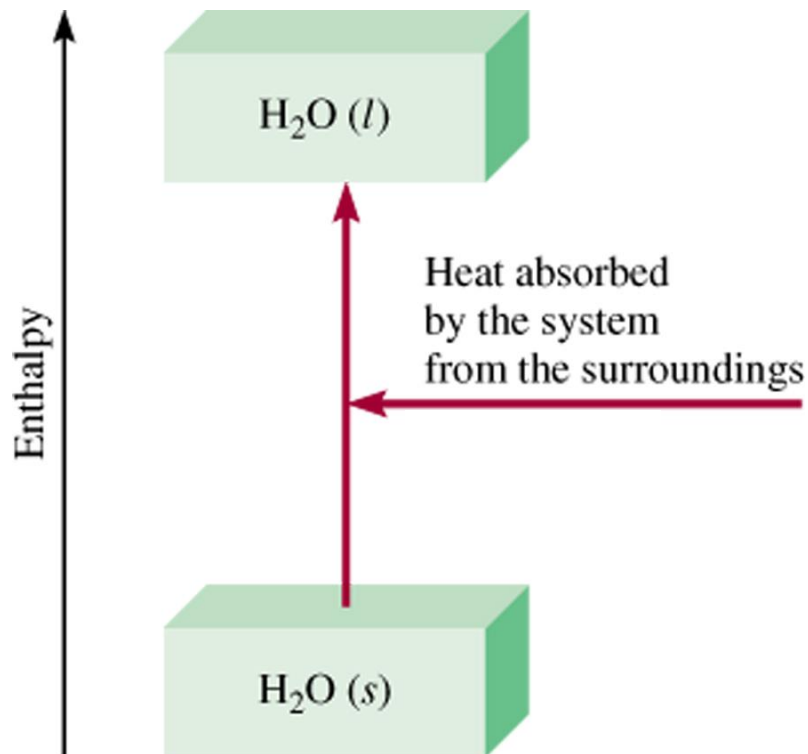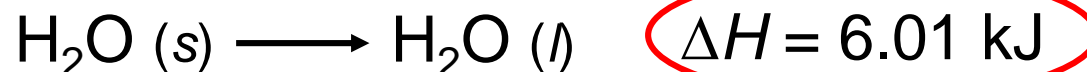
6

Thermochemical Equations

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 0^0C and 1 atm.

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

Thermochemical Equations

Enthalpy

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

Heat given off
by the system
to the surroundings

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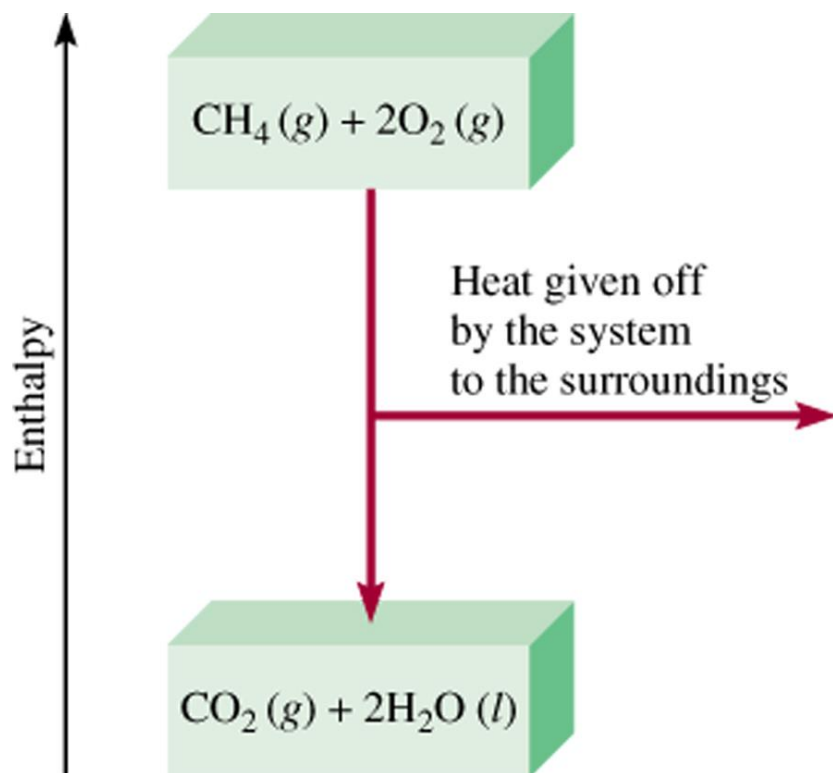
Is ΔH negative or positive?

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

Thermochemical Equations

- The stoichiometric coefficients always refer to the number of moles of a substance
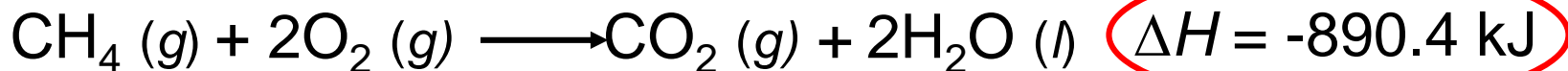
$$H_2O \ (s) \longrightarrow H_2O \ (l) \qquad \Delta H = 6.01 \ kJ$$
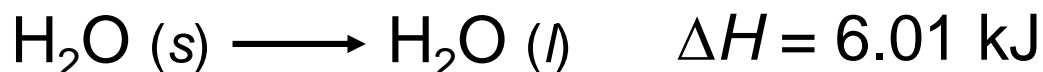
- If you reverse a reaction, the sign of ΔH changes

$$H_2O \ (l) \longrightarrow H_2O \ (s) \qquad \Delta H = \text{-6.01} \ kJ$$
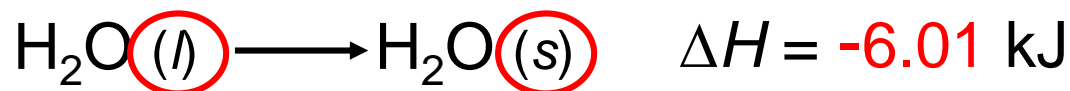
- If you multiply both sides of the equation by a factor n, then ΔH must change by the same factor n.

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

Thermochemical Equations

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

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

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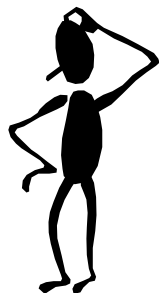
How much heat is evolved when 266 g of white phosphorus (P_4) burn in air?

Calorimetry

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.

$C = ms$

Heat (*q*) absorbed or released:

$q = ms\Delta t$

$q = C\Delta t$

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

Table 6.1 The Specific Heats of Some Common Substances

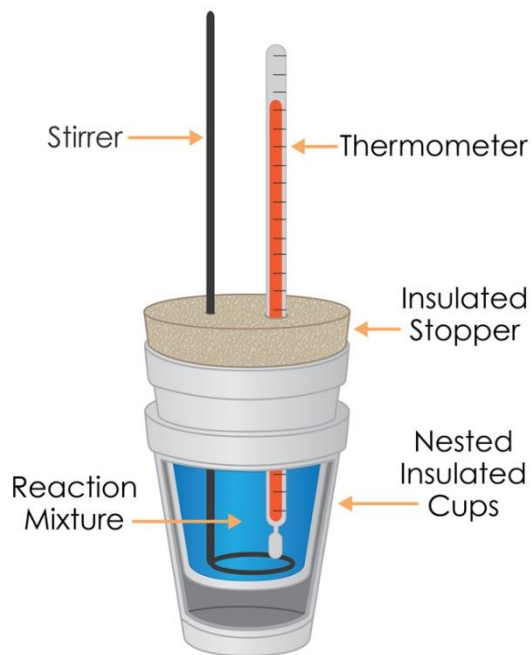| Substance	Specific heat (J/g · °C)
Al	0.900
Au	0.129
C (graphite)	0.720
C (diamond)	0.502
Cu	0.385
Fe	0.444
Hg	0.139
H_2O	4.184
C_2H_5OH (ethanol)	2.46

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

Types of Calorimeter

Constant Pressure
(coffee cup)

Constant Volume
(bomb)
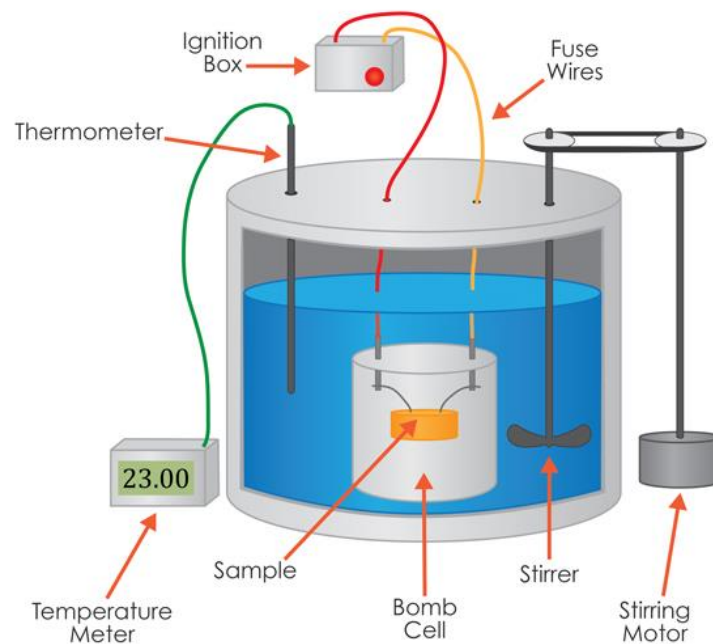
Constant-Volume Calorimetry

Thermometer
Ignition wire
Stirrer
Calorimeter bucket
Insulated jacket
Water
O_2 inlet
Bomb
Sample cup
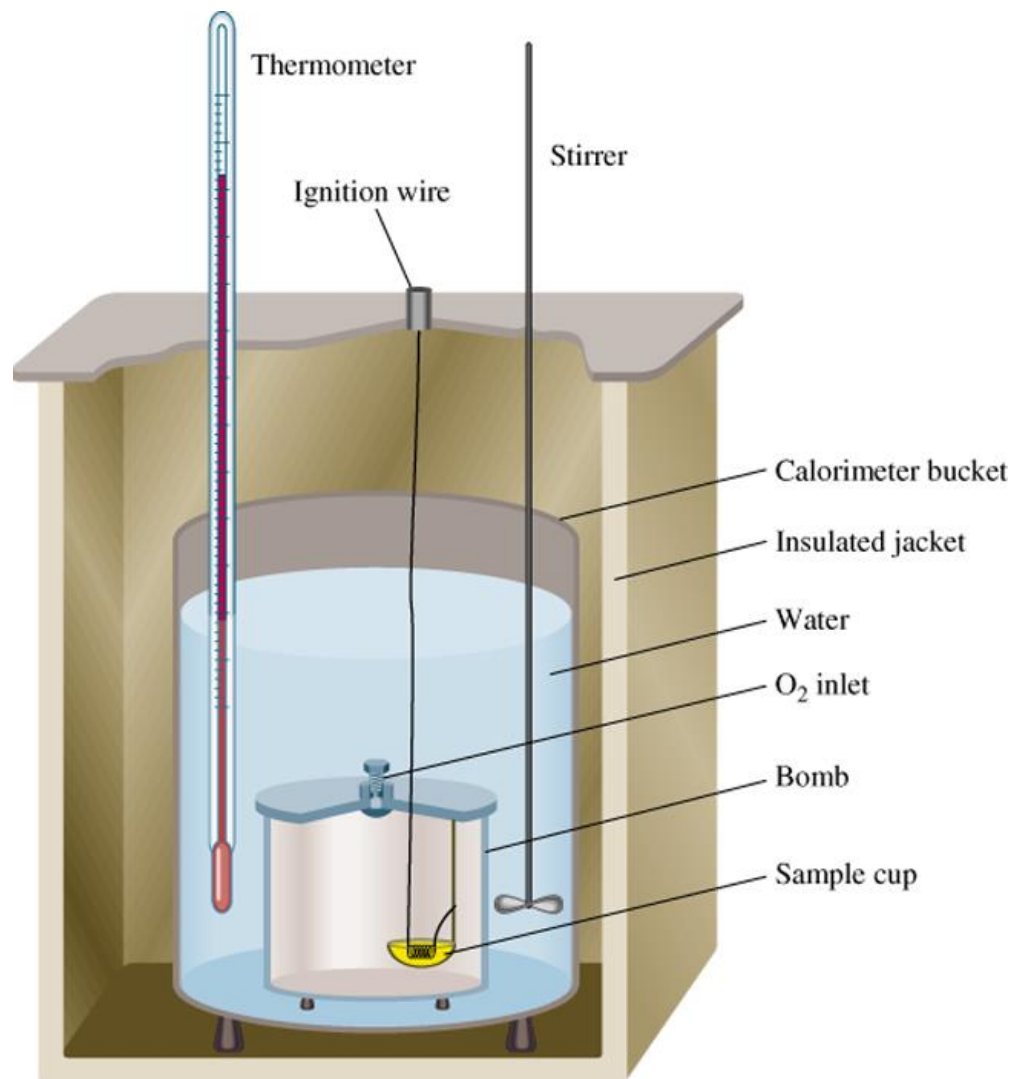
$q_{sys} = q_{water} + q_{bomb} + q_{rxn}$

$q_{sys} = 0$

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

$q_{water} = ms\Delta t$

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

Reaction at Constant V

$\Delta H \neq q_{rxn}$

$\Delta H \sim q_{rxn}$

No heat enters or leaves!

Constant-Pressure Calorimetry

Thermometer

Stirrer

Styrofoam cups

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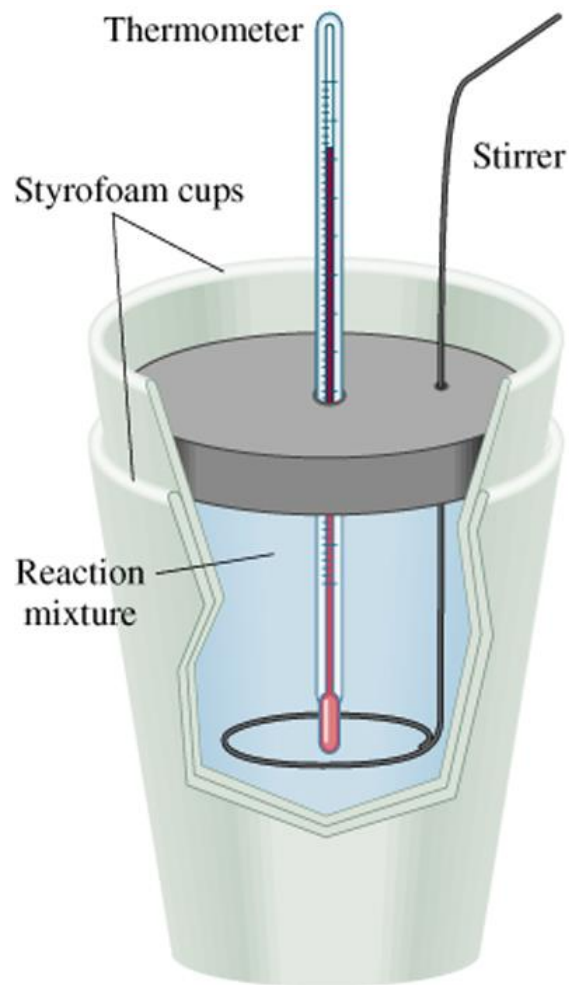
$q_{sys} = q_{water} + q_{cal} + q_{rxn}$

$q_{sys} = 0$

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

$q_{water} = ms\Delta t$

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

Reaction at Constant P
$$\Delta H = q_{rxn}$$

No heat enters or leaves!

Standard Enthalpy of Formation & Reaction

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.

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

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

Table 6.3 Standard Enthalpies of Formation of Some Inorganic Substances at 25°C

Substance	ΔH_f° (kJ/mol)	Substance	ΔH_f° (kJ/mol)
$Ag(s)$	0	$H_2O_2(l)$	-187.6
$AgCl(s)$	-127.04	$Hg(l)$	0
$Al(s)$	0	$I_2(s)$	0
$Al_2O_3(s)$	-1669.8	$HI(g)$	25.94
$Br_2(l)$	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	$N_2O_4(g)$	9.66
$CaCO_3(s)$	-1206.9	$N_2O(g)$	81.56
$Cl_2(g)$	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
$HF(g)$	-268.61	$SO_2(g)$	-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	$ZnO(s)$	-347.98
$H_2O(l)$	-285.8		
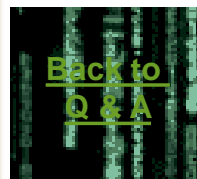
The **standard enthalpy of reaction** (ΔH^0_{rxn}) is the enthalpy of a reaction carried out at 1 atm.

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

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

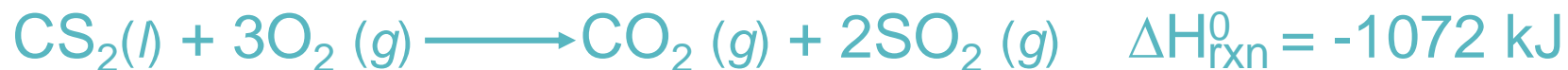$$\Delta H^0_{rxn} = \Sigma n\Delta H^0_f(\text{products}) - \Sigma m\Delta H^0_f(\text{reactants})$$

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.

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.
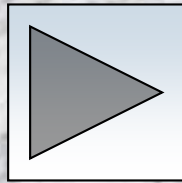
(Enthalpy is a state function. It doesn't matter how you get there, only where you start and end.)
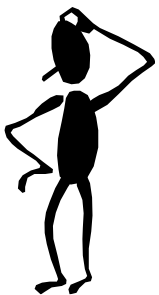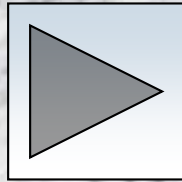
Calculate the standard enthalpy of formation of CS_2 (l) given that:

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

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

$CS_{2(l)} + 3O_2\ (g) \longrightarrow CO_2\ (g) + 2SO_2\ (g)$ $\Delta H^0_{rxn} = -1072$ kJ
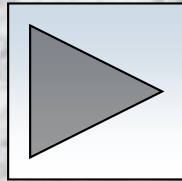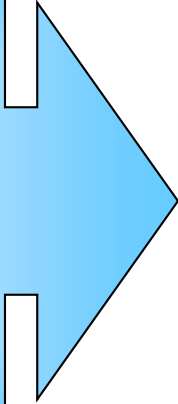
Q & A session

▶ Question 1

▶ Question 2

▶ Question 3

Calculate the quantity of heat required to raise the temperature of 2.10 gram of water from 2.0 °C to 6.0 °C.

Calculate the specific heat if a 36.9 gram sample of a metal at 57.2 °C is immersed in 50.1 gram of water at 16.0 °C, warming the water to 20.5 °C.

Calculate the enthalpy change for the reaction of one mole of CH_4 with oxygen gas to yield carbon dioxide and water.

ΔH^o_f $CH4(g)$ = - 74.5 kJ

Table 6.3

Calculate the enthalpy of the following reaction based on the enthalpies of combustion in equation given:

$$C_2H_2 (g) + 2 H_2 (g) \rightarrow C_2H_6 (g) \qquad \Delta H = ?$$

$C_2H_2 (g) + 2.5 O_2 (g) \rightarrow 2 CO_2 (g) + H_2O (l)$ $\Delta H = -1305$ kJ

$H_2 (g) + 0.5 O_2 (g) \rightarrow H_2O (l)$ $\Delta H = -286$ kJ

$C_2H_6 (g) + 3.5 O_2 (g) \rightarrow 2 CO_2 (g) + 3 H_2O (l)$ $\Delta H = -1560$ kJ