

# **CHEMISTRY - DMKC1033** THERMOCHEMISTRY Chapter

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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



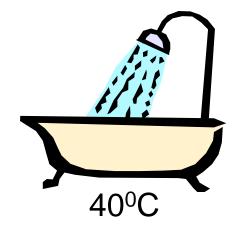
#### **Energy Changes in Chemical Reactions**

**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





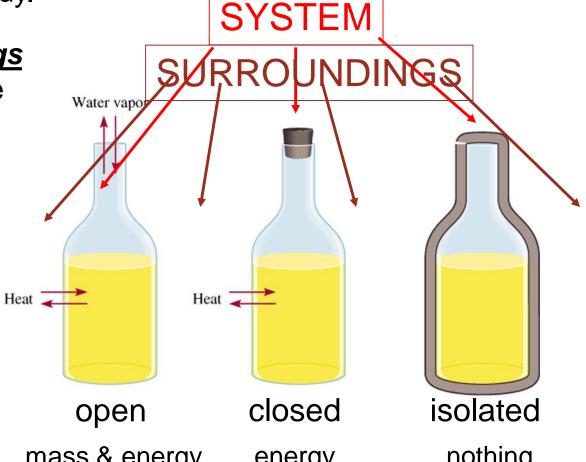
greater thermal energy

*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.



**Exchange:** 

mass & energy

energy

nothing

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

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

**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<sub>2</sub> (g)

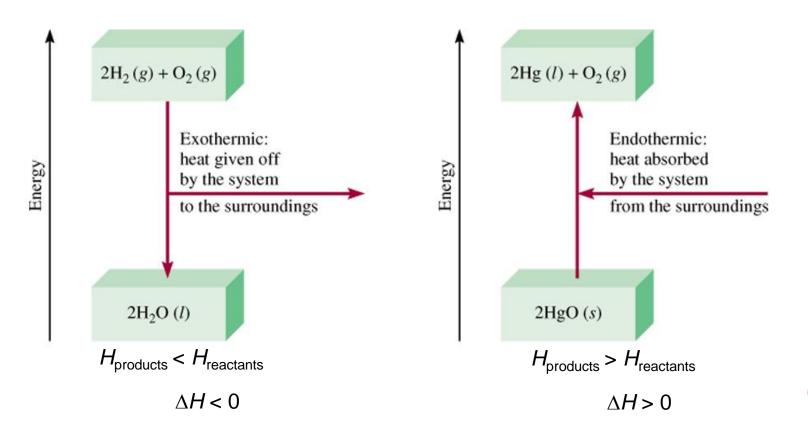
energy + 
$$H_2O$$
 (s)  $\longrightarrow$   $H_2O$  ( $\hbar$ )

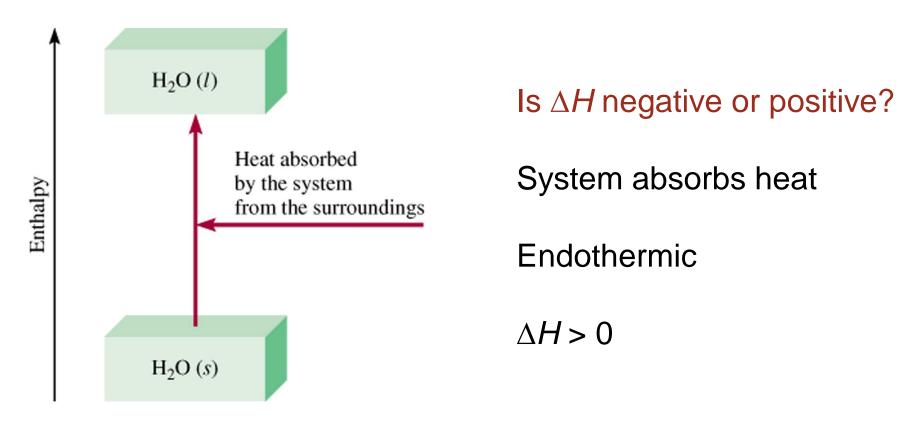
#### **Enthalpy**

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

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

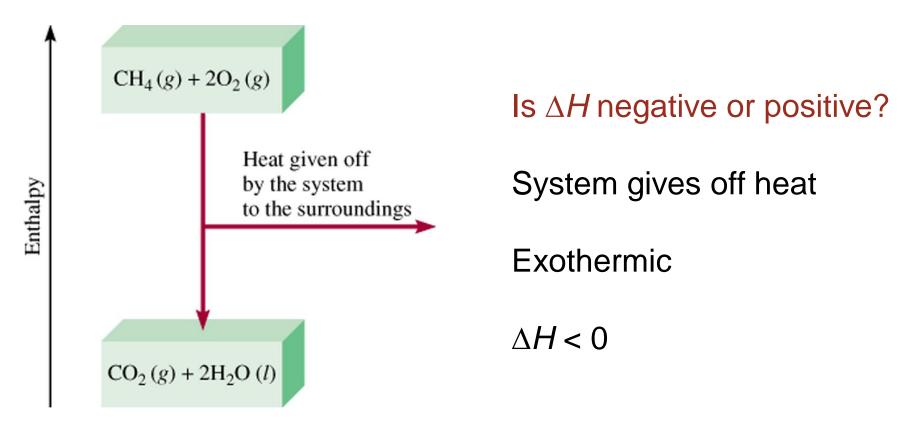
 $\Delta H$  = heat given off or absorbed during a reaction at constant pressure





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

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



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

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(f) \Delta H = -890.4 \text{ kJ}$$

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

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

• If you reverse a reaction, the sign of  $\Delta H$  changes

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

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

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

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

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

$$H_2O(h) \longrightarrow H_2O(g)$$
  $\Delta H = 44.0 \text{ kJ}$ 



How much heat is evolved when 266 g of white phosphorus (P<sub>4</sub>) burn in air?

#### **Calorimetry**

The **specific heat** ( $\mathbf{s}$ ) of a substance is the amount of heat ( $\mathbf{q}$ ) 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:

$$q = ms\Delta t$$

$$q = C\Delta t$$

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

### **Table 6.1** The Specific Heats of Some Common Substances

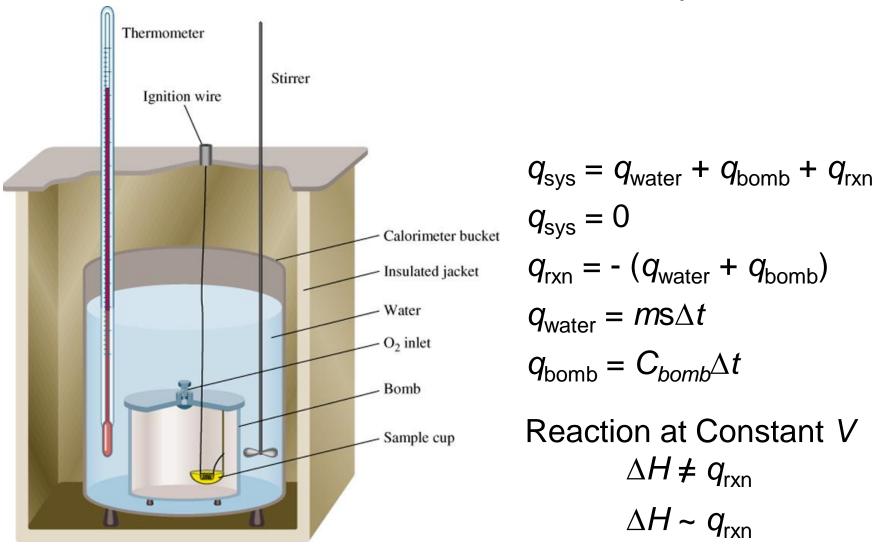
Substance	Specific heat (J/g·°C)
Al	0.900
Au	0.129
C (graphite)	0.720
C (diamond)	0.502
Cu	0.385
Fe	0.444
Hg	0.139
H <sub>2</sub> O	4.184
C <sub>2</sub> H <sub>5</sub> OH (ethanol)	2.46



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

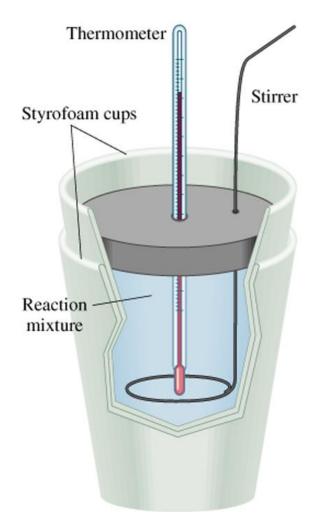


### **Constant-Volume Calorimetry**



No heat enters or leaves!

#### **Constant-Pressure Calorimetry**



$$q_{
m sys} = q_{
m water} + q_{
m cal} + q_{
m rxn}$$
 $q_{
m sys} = 0$ 
 $q_{
m rxn} = -(q_{
m water} + q_{
m cal})$ 
 $q_{
m water} = m_{
m S} \Delta t$ 
 $q_{
m cal} = C_{
m cal} \Delta t$ 

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**  $(\Delta H^0_f)$  as a reference point for all enthalpy expressions.

**Standard enthalpy of formation** ( $\Delta H_f^0$ ) 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.

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

$$\Delta H_f^0$$
 (O<sub>3</sub>) = 142 kJ/mol  $\Delta H_f^0$  (C, diamond) = 1.90 kJ/mol

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

Substance	ΔH <sub>f</sub> (kJ/mol)	Substance	ΔH° <sub>f</sub> (kJ/mol)
Ag(s)	0	H <sub>2</sub> O <sub>2</sub> (I)	-187.6
AgCl(s)	-127.04	Hg(/)	0
Al(s)	0	I <sub>2</sub> (s)	0
$AI_2O_3(s)$	-1669.8	HI(g)	25.94
Br <sub>2</sub> (/)	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 <sub>3</sub> (s)	-1206.9	$N_2O(g)$	81.56
$Cl_2(g)$	0	O(g)	249.4
HCI(g)	-92.3	$O_2(g)$	0
Cu(s)	0	O₃(g)	142.2
CuO(s)	-155.2	S(rhombic)	0
F <sub>2</sub> (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 <sub>2</sub> O(/)	-285.8		





The **standard enthalpy of reaction** ( $\Delta H_{rxn}^0$ ) is the enthalpy of a reaction carried out at 1 atm.

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

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

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



Benzene (C<sub>6</sub>H<sub>6</sub>) 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  $CS_2$  (I) given that:

C(graphite) + O<sub>2</sub> (g) 
$$\longrightarrow$$
 CO<sub>2</sub> (g)  $\Delta H_{rxn}^0 = -393.5 \text{ kJ}$ 

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

$$CS_2(I) + 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g)$$
  $\Delta H_{rxn}^0 = -1072 \text{ kJ}$ 

## Q&A session







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<sub>4</sub> with oxygen gas to yield carbon dioxide and water.

$$\Delta H_f^0 \text{CH4(g)} = -74.5 \text{ kJ}$$



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

$$C_2H_2(g) + 2H_2(g) \rightarrow C_2H_6(g)$$

$$\Delta H = ?$$

$$C_2H_2(g) + 2.5 O_2(g) \rightarrow 2 CO_2(g) + H_2O(l)$$

$$\Delta H = -1305 \text{ kJ}$$

$$H_2(g) + 0.5 O_2(g) \rightarrow H_2O(l)$$

$$\Delta H = -286 \text{ kJ}$$

$$C_2H_6(g) + 3.5 O_2(g) \rightarrow 2 CO_2(g) + 3 H_2O(l)$$

$$\Delta H = -1560 \text{ kJ}$$