

# Chapter 6

## Thermochemistry

### I) Energy

Energy - the capacity to do work

Work: involves moving something

#### A) Forms of energy

1) **Kinetic Energy**: energy due to the motion of an object

$$E_k = 1/2 mv^2$$

m - mass  
v - velocity or speed

example: water going down a waterfall

2) **Potential Energy**: energy due to the position of an object in the field of a force.  
stored energy

$$E_p = mgh$$

m - mass  
g - gravitational acceleration  
h - height

example: water at the top of a waterfall

Potential energy can be converted into kinetic energy and kinetic energy can be converted into potential energy.

example: a weight raised above the ground has potential energy which is converted into kinetic energy when it falls to the ground.

## B) Units of Energy

SI units: Joules (J) =  $\frac{\text{Kg m}^2}{\text{s}^2}$

(joule is an extremely small unit)

Commonly used: calorie (cal)

**Calorie** is the amount of energy needed to raise one gram of water by one degree Celsius.

1 cal = 4.184 J (exact)

## C) Internal Energy (U)

**Internal Energy**: Sum of kinetic energy and potential energy at the atomic level (particles making up the system)

**potential energy**: attraction of  $e^-$  and atomic nucleus in molecules  
positive and negative charges at small distances apart

**kinetic energy**: vibration of bonds, rotational energy of the molecules, and motion of the  $e^-$  in the molecule.

When studying a chemical reaction, the energy involved in these reactions is internal energy

## II) Energy Changes in Chemical Reactions

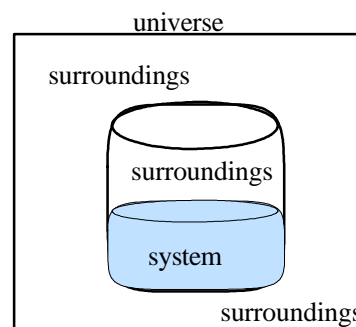
Chemical reactions can *absorb* or *release* energy in the form of *heat*

### A) What is heat?

**heat**: the transfer of thermal energy between two bodies that are at different temperatures.

Define two bodies

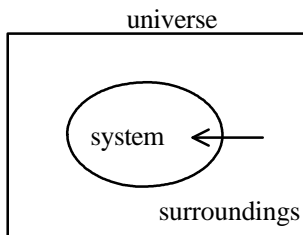
- 1) **system**
  - specific part of the universe we wish to study
  - includes substances involved in chemical and physical reactions
- 2) **surrounding**
  - rest of the universe outside of system



Define: **Heat (q)**

energy flow into and out of the system due to the difference in temperature between the system and the surroundings.

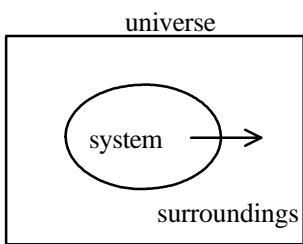
## B) Define the flow of heat



- heat flows into the system from the surrounds
- heat is being absorbed by the system from the surroundings

**Endothermic** process  
("endo" means in)

defined as +q (positive heat)



- heat flows out of the system into the surrounds
- heat is being released to the surroundings from the system

**Exothermic** process  
("exo" means out)

defined as -q (negative heat)

## C) Heat of reaction

**Heat of a reaction:** heat required to return a system to a given temperature after a reaction has been completed.

**endothermic reaction:** a system is cool; need to add heat to obtain original temperature of the reaction  
heat is absorbed

**exothermic reaction:** a system is warm; need to remove heat to obtain original temperature of the reaction  
heat is released

example:



this reaction evolves 1170 kJ of heat

## D) Another form of Energy Transfer

**work:** energy transferred when an object is moved by a force

**Pressure-Volume Work** ( most useful in this chapter)

- expanding and contracting of a gas at constant pressure

$\omega = -P\Delta V$           minus sign defines that the system loses energy

## E) Internal Energy defined

in summary:

Energy transfers between the system and the surrounds

- heat    (results in a difference in temperatures)
- work    (object moved by a force)

The Law of Conservation of Energy:

- energy cannot be created or destroyed
- (first law of thermodynamics)
- energy can be converted but the total energy remains constant

Defined the change in the system's internal energy ( $\Delta U$ ) as

$$\Delta U = q + \omega$$

### III) Enthalpy

#### A) Define

Enthalpy (H): used to quantify the heat flow into and out of a system in a *constant pressure* process

$$H = U + PV$$

H - enthalpy  
U - internal work  
PV - pressure-volume work

#### B) Change in enthalpy

In this chapter, we are more interested in the change in enthalpy ( $\Delta H$ ) at const. P

Derive from the difference between a system in the initial and final states.

$$\Delta H = H_f - H_i$$

substitute definition of  $H_f$  and  $H_i$

$$\Delta H = (U_f + PV_f) - (U_i + PV_i)$$

gather like terms

$$\Delta H = (U_f - U_i) + (PV_f - PV_i)$$

take out P

$$\Delta H = (U_f - U_i) + P(V_f - V_i)$$

simplify

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

Change in enthalpy

#### C) Relating heat of a reaction to change in enthalpy

rearrange above equation in order to solve for the change in internal energy ( $\Delta U$ )

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

- energy leaves or enters the system as heat ( $\Delta H$ )
- the system  $\uparrow$  or  $\downarrow$  in volume at constant  $P_{\text{atm}}$  which requires energy ( $-P\Delta V$ )

we defined earlier that  $\Delta U = q_p + \omega$  at constant P

- know  $\omega = -P\Delta V$  at const. P
- q at const P is  $q_p$

Substitute the definition of  $\Delta U$  into eqn.  $\Delta U = \Delta H - P\Delta V$

$$q_p + \omega = \Delta H - P\Delta V$$

substitute in the definition of work;  $\omega = -P\Delta V$

$$q_p + -P\Delta V = \Delta H - P\Delta V$$

simplify

$$q_p = \Delta H$$

- endothermic process:  $+q_p$  and  $\Delta H > 0$
- exothermic process:  $-q_p$  and  $\Delta H < 0$

example:



$$\Delta U = q_p + P\Delta V$$

- reaction is exothermic ( $-q_p$ )
- work  $P\Delta V$ ; is small but not negligible

observation: water is pushed out of the tube by the  $\text{H}_2$  gas.

## D) State Function

- extensive property (depends on the quantity of material)
- state function

State function

- depends only on the beginning state and final state
- does *not* depend on the path (or route) from point A to point B

Example:

You book a flight from Peoria to San Francisco. The starting point and final point are important.

- 1) start: Peoria to Chicago to Minnesota to San Francisco :finish
- 2) start: Peoria to St. Louis to Colorado to San Francisco :finish
- 3) start: Peoria to Chicago to Texas to San Francisco :finish

## E) Summary

at const. pressure,  $\Delta H = q_p$

Heat flows from system into the surroundings, exothermic process

$$-q_p \text{ and } \Delta H < 0$$

Heat flows into the system from the surroundings, endothermic process

$$+q_p \text{ and } \Delta H > 0$$

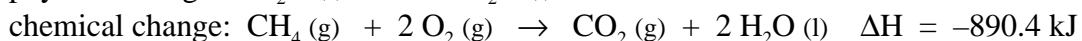
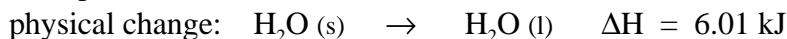
### III) Thermal Chemical Equations and Applications

#### A) Thermal chemical equation

is a chemical reaction which includes

- 1) phase labels
- 2) heat of reaction:  $\Delta H$  written after the chemical reaction

examples:



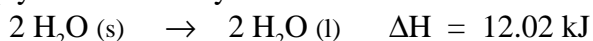
Two important rules for manipulating thermochemical equations:

- 1)  $\Delta H$  is an extensive property

When a thermochemical equation is multiplied by any factor, the value of  $\Delta H$  for the new equation is obtained by multiplying the value of  $\Delta H$  in the original equation by that same factor.



multiply the reaction by 2

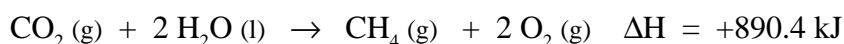


- 2)  $\Delta H = q_p$

When a chemical equation is reversed, the value of  $\Delta H$  is reversed in sign.



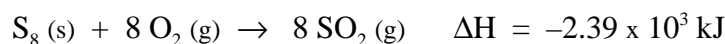
reverse the reaction



#### B) Apply stoichiometry to heats of reactions

According to rule one above the amount of heat produced or absorbed in a reaction depends on the moles of reactants used or products produced.

If 15.0 g of sulfur is burned in air, how much heat evolves from this amount of sulfur?



$$15.0 \text{ g} \left( \frac{1 \text{ mol S}_8}{256.8 \text{ g S}_8} \right) \left( \frac{-2.39 \times 10^3 \text{ kJ}}{1 \text{ mol S}_8} \right) = -1.40 \times 10^2 \text{ kJ}$$

The heat evolved;  $q_p = -1.40 \times 10^2 \text{ kJ}$

## C) Measuring heats of reaction

### 1) Specific heat (s)

quantity of heat needed to raise the temperature of one gram of any substance by 1 °C at constant pressure

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

where m = mass

s - specific heat (Table 6.1 in Ebbing)

$\Delta T$  - change in Temp ( $T_{\text{final}} - T_{\text{initial}}$ )

$$s = 4.184 \frac{\text{J}}{\text{g } ^\circ\text{C}} \quad \text{or} \quad 1.00 \frac{\text{cal}}{\text{g } ^\circ\text{C}}$$

specific heat of water

example:

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

Calculate the heat involved when a 5.5 g iron nail is

$$q = (5.5 \text{ g}) \left( 0.449 \frac{\text{J}}{\text{g } ^\circ\text{C}} \right) (25 - 37 ^\circ\text{C})$$

cooled from 37 °C to 25 °C?

(s = 0.449 J/g °C)

$$q = -3.0 \times 10^1 \text{ J}$$

### 2) Heat Capacity (C)

amount of heat required to change a sample of substance by 1 °C (or 1 K)

$$q = C \Delta T \quad C - \text{given in Table 6.1 Ebbing}$$

$$C = 75.3 \frac{\text{J}}{\text{mol } ^\circ\text{C}}$$

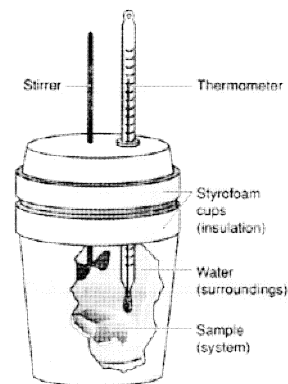
heat capacity of water

## D) How is heat of a reaction measured?

Calorimeter: device used to measure the heat released (or absorbed) by a physical or chemical process.

### 1) Coffee-cup calorimeter

- constant pressure
- used to measure heat flow involved in neutralization reactions; heats of solution or dilutions
- information needed to use this apparatus
  - heat capacity of the calorimeter
  - temperature change of the solution
  - mass of the solution in the calorimeter



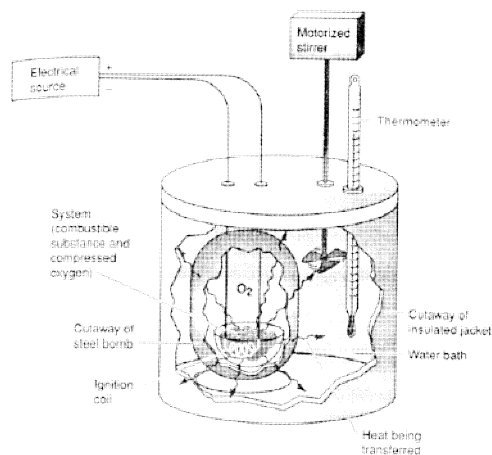
### 2) Bomb calorimeter

- constant volume
- used to measure heats of combustion

Measuring the heat of combustion  
 a sample is placed in a small cup  
 container is filled with  $O_2$   
 sample is ignited electrically  
 the heat released raises the temp. of  
 water surrounding the bomb.

Since the reaction vessel is closed  
 the volume is constant and  
 the pressure does not remain  
 constant.

Under these conditions the small  
 correction is needed for  $\Delta H$



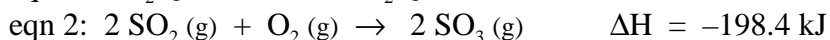
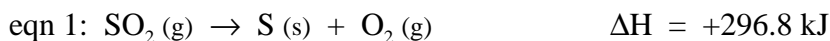
## IV) Hess's Law

Hess's law of heat summation is the enthalpy change of an overall process is the sum of the enthalpy changes of its individual steps

This method of finding the heat of reaction is useful for reactions that are very difficult or impossible.  $\Delta H_{\text{rxn}}$ , heat of reaction, is a state function. It only depends on the initial reactants and final products and not on the path from the reactants to the products. Therefore, we can take  $\Delta H_{\text{rxn}}$  from several other reactions to determine  $\Delta H_{\text{rxn}}$  for the reaction of interest. We can manipulate chemical reactions using the two rules above (page 7) to help create the reaction of interest.

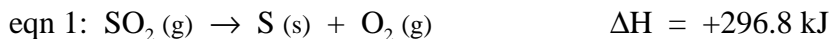
For example:

Find the heat of reaction for  $\text{S (s)} + 3/2 \text{O}_2 \rightarrow \text{SO}_3 \text{(g)}$ , using the following information.

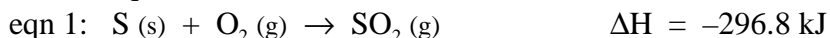


The object in finding the  $\Delta H_{\text{rxn}}$  for the reaction of interest is to sum up equations 1 and 2 to give the eqn of interest. But before summing up the reactions, they may have to adjusted to provide the desired result.

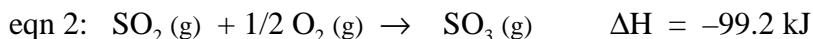
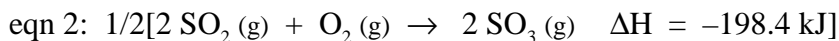
In this example the desired rxn has S as a reactant, eqn 1 has S as a product. We will need to reverse eqn 1. When a reaction is reversed the sign on  $\Delta H$  is changed.



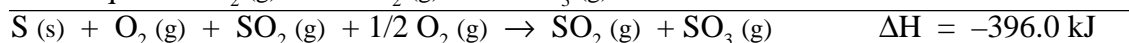
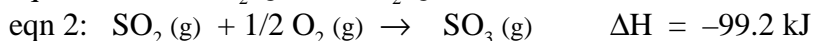
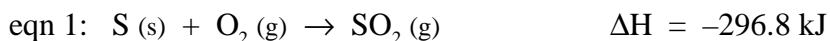
reverse eqn 1



The desired eqn has 1 mole of  $\text{SO}_3$ , whereas eqn 2 produces 2 moles of  $\text{SO}_3$ . Eqn 2 can be divided by 2 to give the desired amount of product. If the reaction is divided by two so is  $\Delta H$ .



Now, eqns 1 and 2 are summed to obtain the desired reaction.



In the new eqn, remove molecules that appear on both sides of the reaction.

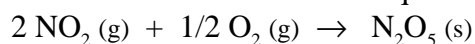


and combine like species

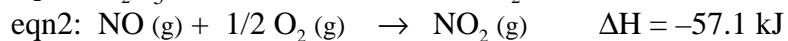
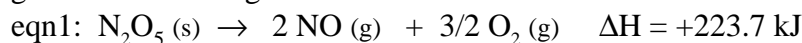


Example:

Calculate  $\Delta\text{H}$  for the overall equation



given the following



reverse eqn 1:



reverse eqn 2 and multiply by 2:

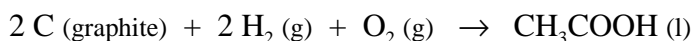


add the two eqns together.

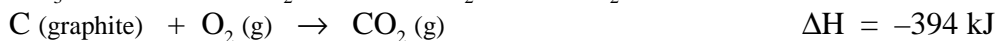
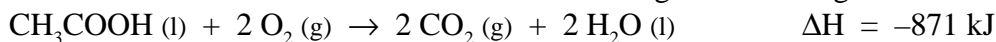


Example:

Hydrogen cyanide is highly poisonous, volatile liquid. It can be prepared by the reaction .



Calculate the heat of reaction for this reaction using the following information.



## V) Standard Heats of Formation

### A) Standard State

Because  $\Delta H$  varies slightly with conditions, a standard temperature and pressure were defined so that data can easily be compared.

Standard State for thermodynamics is

- 1 atm pressure
- 25 °C (298K)

The enthalpy of a reaction at standard state is designated as  $\Delta H^\circ$  (or  $\Delta H_{\text{rxn}}^\circ$ )

### B) Standard Enthalpy of formation ( $\Delta H_f^\circ$ )

Standard enthalpy of formation is the enthalpy change for the formation of 1 mole of a substance in its standard state from its elements in their standard states.

The standard enthalpy of formation is tabulated in [Table 6.2](#) or [Appendix C](#) in Ebbing.

The tabulated data must specify the exact form of the element.

**Allotrope:** one of two or more distinct forms of an element in the same physical state.

example: O<sub>2</sub> (g) oxygen and O<sub>3</sub> (g) ozone  
C (diamond) and C (graphite)

the reference form is the stablest form of the element under standard conditions.  
which is O<sub>2</sub> (g) for oxygen at 25 °C and 1 atm pressure  
and C (graphite) for carbon at 25 °C and 1 atm pressure.

### C) Calculating $\Delta H_{\text{rxn}}^\circ$ using heat of formations

$$\Delta H_{\text{rxn}}^\circ = \sum n\Delta H_f^\circ(\text{products}) - \sum m\Delta H_f^\circ(\text{reactants})$$

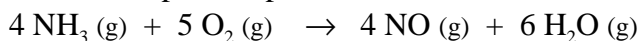
where S = 'sum of'

m is the coefficients on the product side of the reaction

n is the coefficients on the reactant side of the reaction

Example:

The first step in the production of nitric acid is the oxidation of ammonia



Calculate the  $\Delta H_{\text{rxn}}^\circ$  from  $\Delta H_f^\circ$  values.

$$\Delta H_{\text{rxn}}^{\circ} = \sum n \Delta H_f^{\circ}(\text{products}) - \sum m \Delta H_f^{\circ}(\text{reactants})$$

$$\Delta H_{\text{rxn}}^{\circ} = 4\Delta H_f^{\circ}[\text{NO}_2(\text{g})] + 6\Delta H_f^{\circ}[\text{H}_2\text{O}(\text{g})] - 4\Delta H_f^{\circ}[\text{NH}_3(\text{g})] - 5\Delta H_f^{\circ}[\text{O}_2(\text{g})]$$

$$\Delta H_{\text{rxn}}^{\circ} = 4(90.3 \text{ kJ/mol}) + 6(-241.8 \text{ kJ/mol}) - 4(-45.9 \text{ kJ/mol}) - 5(0 \text{ kJ/mol})$$

$$\Delta H_{\text{rxn}}^{\circ} = -906 \text{ kJ}$$