Chapter 6: Thermochemistry

These Notes are to SUPPLIMENT the Text, They do NOT Replace reading the Text Material. Additional material that is in the Text will be on your tests!

To get the most information, READ THE CHAPTER prior to the Lecture, bring in these lecture notes and make comments on these notes. These notes alone are NOT enough to pass any test!

Demo: Reaction of Barium Hydroxide octahydrate [$Ba(OH)_2$ ° 8 H_2O] and Ammonium Nitrate [NH_4NO_3]. First forms a slush, then a liquid, then freezes outside of container.

Thermochemistry is the science of relationships between heat and other forms of energy.
It is concerned with the study of the quantity of heat absorbed or evolved by chemical reactions.

Energy is the Potential or Capacity [Energy of Motion is **Kinetic Energy**] to move matter.
Different forms of energy can be interconverted: Coal → Steam → Electricity → Refigerator

Kinetic Energy

Kinetic Energy = $E_k = ½ m v^2$ **m** = mass, **v** = velocity **E_k = kg m^2/s^2 = joule (J)**

1 joule per second = 1 watt. A house might use 1000 kilowatt hours per month = 3.6 billion J

SI Unit of Energy is the joule

1 calorie (cal – non SI Unit of Energy) = 4.184 J – or the amount of energy required to raise 1g H_2O 1° C.

PROBLEM: E_k of a 50.0 kg [@ 130 lbs] person moving at 26.8 m/s [@ 60 mph]
E_k = ½ * 59.0 kg * (26.8 m/s)^2 = 21,188 = **2.12 x 10^4 kg m^2/s^2 = 2.12 x 10^4 joule = 22.2 kJ**

PROBLEM: 130 lb person moving at 60 mph has the Kinetic Energy of 2.12 kJ * 1 cal / 4.184 J = **5.07 kcal**

Example 6.1: A baseball traveling at 75 mph [33.5 m/s], weights 143 g, what is it's E_k?
E_k = ½ * 0.143 kg * (33.5 m/s)^2 = **80.2 J** 80.2 J * 1 cal / 4.184 J = **19.2 cal**

Exercise 6.1: An electron traveling at 5.0 x 10^6 m/s [how fast is this in mph?], weighs 9.11 x 10-^{31} kg. What is it's E_k in J and cal?
E_k = ½ * 9.11 x 10^{-31} kg (5.0 x 10^6 m/s)^2 = **1.13 x 10^{-17} J**
1.13 x 10^{-17} J * 1 cal / 4.184 J = **2.7 x 10^{-18} cal**

Potential Energy

Potential Energy is the energy an object has due to it's position in a field of force.
E_p = m g h m = mass, g = acceleration of gravity, h = height
The height is usually compared to the surface of the earth.
Water going over a water fall has Potential Energy which is converted to Kinetic Energy

Internal Energy is the sum of objects Potential and Kinetic Energy

Law of Conservation of Energy: Energy may be converted from one form to another, but the total quantity of energy remains constant.

Concept Check 6.1: A solar powered water pump has photovoltaic cells to generate electricity which runs the motor to pump water up to a storage tank. What energy conversions are involved?

Heat of Reaction

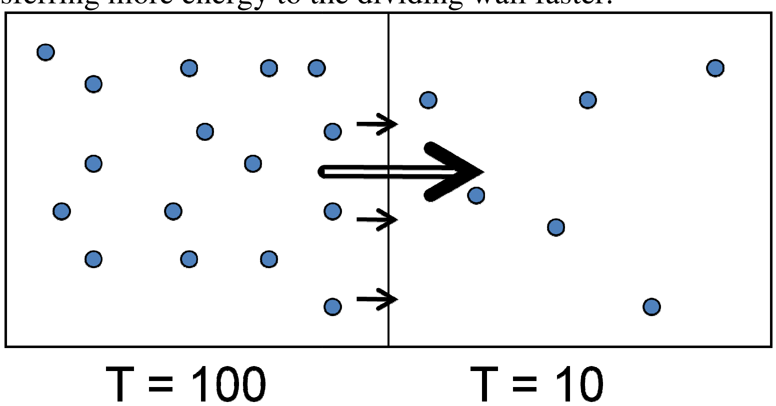
Thermodynamic System is the substance or mixture of substances under study in which a change occurs
Surroundings are everything in the vicinity of the Thermodynamic System.

Heat is the energy that flows into or out of a system because of a difference in temperature between the Thermodynamic System and it's Surroundings.

Energy flows between them to establish a temperature equality or thermal equilibrium. **Heat flows** from a region of higher temperature to one of lower temperature.

Heat is defined by q. q is positive if heat is absorbed, negative if heat is evolved.

Example: Two vessels in contact, each with oxygen gas, one is hotter than the other. The hotter one has the average molecular speed greater than the cooler one. Molecules in the hotter one hit the wall more than the cooler one transferring more energy to the dividing wall faster.



Heat of Reaction [at a given T] is the value of q required to return a system to the given temperature at the completion of a reaction.
Exothermic Process is a chemical reaction or physical change in which heat is evolved [q = -].
Endothermic Process is a chemical reaction or physical change in which heat is absorbed [q = +].

EXAMPLE: 1 mole of Methane burns in xcs oxygen to generate 890 kJ of heat.

$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$ $\quad q = -\,890$ kJ

$Ba(OH)_2 \bullet 8\,H_2O + 2\,NH_4NO_3 \rightarrow 3\,NH_3\uparrow + 10\,H_2O + Ba(NO_3)_2$ $\quad q = +\,170.8$ kJ

Exercise 6.2: Ammonia burns with a Pt Cat to from nitric oxide

$4\,NH_3 + 5\,O_2 \rightarrow Pt \rightarrow 4\,NO + 6\,H_2O$ $\quad$ evolves 1170 kJ of heat

Is the reaction exo or endo thermic? What is the value for ΔH which = q = ?

Enthalpy

Enthalpy (H) is an extensive property of a substance that can be used to obtain the heat of absorbed or evolved in a chemical reaction.

SEE FIGURE 6.7 Climbing the mountain

Extensive Property depends only on the amount of the substance.

State Function is a property of a system that depends only on it's present state

Changes in Enthalpy doe not depend on how a change was made, only it's initial and final state

Enthalpy of Reaction is the change in enthalpy for a reaction at a give T and P = ΔH

Change in Enthalpy = $\Delta H = H_{(products)} - H_{(reactants)} = q_p$

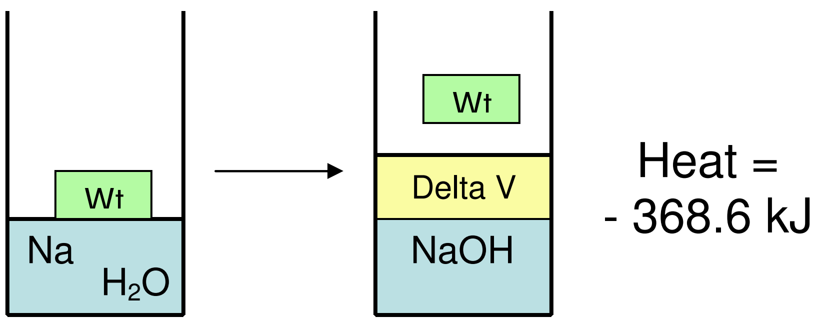
Enthalpy of a reaction, ΔH, EQUALS the heat of the reaction, q, at constant P.

EXAMPLE: $2\ Na + 2\ H_2O \rightarrow 2\ NaOH + H_2\uparrow$ $\Delta H = -368.6$ kJ [heat is evolved]

Enthalpy and Internal Energy

Enthalpy = Internal Energy (U) + Pressure (P) * Volume (V)

Consider a reaction at constant P, where we put heat into the system.



Reaction run at constant Pressure. $\Delta H = H_f - H_i = (U_f + PV_f) - (U_i + PV_i)$

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

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

$-P\Delta V$ is the energy required to change the volume at constant pressure = **pressure-volume work**

Bla bla bla

Thermochemical Equations

Thermochemical Equation is the chemical equation for a reaction in which the equation is given a molar interpretation and the enthalpy of reaction for these molar amounts is written directly after the equation.

$2\ Na_s + 2\ H_2O_l \rightarrow 2\ NaOH_{aq} + H_2\uparrow$ $\Delta H = -368.6$ kJ [heat is evolved]

Note: Phase labels [s = solid, l = liquid, aq = water solution] must be included.

$2\ H_{2\,g} + O_{2\,g} \rightarrow 2\ H_2O_g$ $\Delta H = -483.7$ kJ Product is vapour

$2\ H_{2\,g} + O_{2\,g} \rightarrow 2\ H_2O\,l$ $\Delta H = -571.7$ kJ Product is liquid

Example 6.2: Sodium Hydrogen Carbonate in water reacts with Hydrochloric Acid. The reaction absorbs 12.7 kJ of heat at Pk for each mole of SHC. Write the thermochemical equation?

Rules for Thermochemical Equations

1. When a thermochemical equation is multiplied by any factor, the value of ΔH for the new equation is obtained by multiplying the value of ΔH in the original equation by that same factor.

2. When a chemical equation is reversed, the value of ΔH is reversed in sign.

$N_{2\,g} + 3\,H_{2\,g} \rightarrow 2\,NH_{3\,g}$ $\quad \Delta H = -\,91.8$ kJ

$2\,N_{2\,g} + 6\,H_{2\,g} \rightarrow 4\,NH_{3\,g}$ $\quad \Delta H = -\,2 * 91.8$ kJ $= 184$ kJ

$2\,NH_{3\,g} \rightarrow N_{2\,g} + 3\,H_{2\,g}$ $\quad \Delta H = +\,91.8$ kJ

Example 6.2: Two moles of Hydrogen reacts with One mole of Oxygen to give liquid water and 572 kJ of heat. Write the forward and reverse reactions for One Mole of Water!

$2\,H_{2\,g} + O_{2\,g} \rightarrow 2\,H_2O_{\,L}$ $\quad \Delta H = -\,572$ kJ

$2\,H_2O_{\,L} \rightarrow 2\,H_{2\,g} + O_{2\,g}$ $\quad \Delta H = +\,572$ kJ

Stoichiometry & Heats of Reaction

Methane burns in Oxygen to give products and 890.3 kJ.

$CH_{4\,g} + 2\,O_{2\,g} \rightarrow CO_{2\,g} + 2\,H_2O_{\,L}$ $\quad \Delta H = -\,556$ kJ

Grams of Methane → Moles of Methane → kJ of heat

Example 6.4: How much heat is evolved with 9.07×10^5 g of ammonia is produced by:

$N_{2\,g} + 3\,H_{2\,g} \rightarrow 2\,NH_{3\,g}$ $\quad \Delta H = -\,91.8$ kJ

$$9.07 \times 10^5 \text{ g } NH_3 * \frac{1 \text{ mole } NH_3}{17.0 \text{ g } NH_3} * \frac{-91.8 \text{ kJ}}{2 \text{ mol } NH_3} = -\,2.45 \times 10^6 \text{ kJ}$$

Example 6.4: How much heat is evolved when 10.0 g of hydrazine:

$2\,N_2H_{4\,L} + N_2O_{4\,L} \rightarrow 3\,N_{2\,g} + 4\,H_2O_{\,g}$ $\quad \Delta H = -\,1049$ kJ

$$10.0 \text{ g } N_2H_4 * \frac{1 \text{ mol } N_2H_4}{32.02 \text{ g}} * \frac{1 \text{ mol } N_2O_4}{2 \text{ mol } N_2H_4} * \frac{-\,1049 \text{ kJ}}{1 \text{ mol } N_2H_4} = -\,163.80 = -\,164 \text{ kJ}$$

Heats of Reaction

Heat Capacity (C) of a sample of substance is the quantity of heat needed to raise the temperature of the sample 1^o C or 1^o K

$\mathbf{q = c\,\Delta t}$ $\quad \Delta t$ = change in temp.

Molar Heat Capacity is it's heat capacity for one mole of substance.

Specific Heat Capacity is the quantity of heat required to raise the temperature of ONE GRAM of a substance 1^o C.

Heat required to raise the temp of a sample = **$q = s * m * \Delta t$**

s = specific heat   m = mass in grams Δt = temp change

Example 6.5: 15.0 g of H_2O was heated from 20.0^o C to 50.0^o C at P_k. How much heat was absorbed, s = 4.18 J / gC

$q = s * m * \Delta t = 4.18 \text{ J / g}^oC * 15.0g \ (50.0^o C – 20.0^o C) = 1.88 \times 10^3$ J = **1.88 kJ**.

Example 6.6: Iron has a specific heat of 0.449 J / g^oC. How much heat is needed for 5.00 g going from 20.0^o C to 100.0^o C?

$q = s * m * \Delta t = 0.449 \text{ J / g}^oC * 5.00g * (100.0^o C - 20.0^o C) = 179.6 =$ **180 J**

Calorimeter is a device used to measure the heat absorbed or evolved during a physical or chemical change.

The **Coffee Cup Calorimeter** [2 nested foam coffee cups] is a constant pressure calorimeter.

The Bomb Calorimeter is a closed vessel, the pressure does not remain constant but the volume does.

Example 6.6: 0.562g graphite is placed in a calorimeter with Xcs O_2 at 25.00^o C and 1atm. On reacting, the temp goes from 25.00^o C to 25.89^o C. The heat capacity of the calorimeter is 20.7 kJ/^oC. What is the heat of reaction?

Heat from the reaction = Heat absorbed by the calorimeter = $q_{reaction} = s * m * \Delta t =$

$- 20.7 \text{ kJ/}^oC * 0.562 \text{ g} * (25.89^o C - 25.00^o C) = - 18.4$ kJ   [negative = exothermic]

$C_{graphite} + O_{2\ gas} \rightarrow CO_{2\ gas}$

$$1 \text{ mole } C_{graphite} * \frac{12 \text{ g C}}{1 \text{ mole C}} * \frac{- 18.4 \text{ kJ}}{0.562 \text{ g }^oC} = - 3.9 \times 10^2 \text{ kJ} =$$

Exercise 6.7: 33 ml of 1.20 M HCl reacts with 42 ml of NaOH [in Xcs]. The temp goes from 25.0^oC to 31.8^oC. What is the Enthalpy Change ΔH?

Total mass = 33.00 ml + 42.00 ml = 75.00 ml. = Approx 75 g. [the density of water is 1.000 g / ml]

The Specific Heat of water is 4.184 J/g^oC

$q_{reaction} = s * m * \Delta t = 4.184 \text{ J/g}^oC * 75 \text{ g} * [31.8^oC - 25.0^oC] =$ **2133.8 J**

<u>Hess's Law of heat summation</u> states for a chemical reaction that can be written as the sum of two or more steps, the enthalpy change for the overall equation equals the sum of the enthalpy changes for the individual steps.

PROBLEM: It's hard to directly measure the ΔH for C to CO as it continues on to go to CO2. So

$C_{graphite} + O_{2\ gas}$	$\rightarrow CO_{2\ gas}$	FIRST	$\Delta H = - 393.5$ Kj
$2 C_{graphite} + 2 O_{2\ gas}$	$\rightarrow 2 CO_{2\ gas}$	TIMES 2	$\Delta H = - 393.5$ Kj * 2
$2 CO + O_{2\ gas}$	$\rightarrow 2 CO_{2\ gas}$	SECOND	$\Delta H = - 566.0$ kJ
-or- $2 CO_{2\ gas}$	$\rightarrow 2 CO + O_{2\ gas}$	FLIP IT	$\Delta H = + 566.0$ kJ

Then add Times 2 and FLIP IT:

$2 C_{graphite} + 2 O_{2\ gas}$	$\rightarrow 2 CO + O_{2\ gas}$	ADD EM	$\Delta H = - 393.5$ Kj* 2 + 566.0 Kj = **- 221.0 kJ**

PROBLEM: A. $S_{solid} + O_{2\,gas} \rightarrow SO_{2\,gas}$ $\Delta H = -297$ kJ
B. $2\,SO_{3\,gas} \rightarrow 2\,SO_{2\,gas} + O_{2\,gas}$ $\Delta H = 198$ kJ

Determine: C. $2\,S_{solid} + 3\,O_{2\,gas} \rightarrow 2\,SO_{3\,gas}$

From A.	$2\,S_{solid} + 2\,O_{2\,gas}$	$\rightarrow 2\,SO_{2\,gas}$	$\Delta H = -297$ kJ * 2
From B.	$2\,SO_{2\,gas} + O_{2\,gas}$	$\rightarrow 2\,SO_{3\,gas}$	$\Delta H = -198$ kJ
	$2\,S_{solid} + 3\,O_{2\,gas}$	$\rightarrow 2\,SO_{3\,gas}$	**ΔH =- 792 kJ**

PROBLEM: What is the enthalpy of reaction, ΔH for the formation of tungsten carbide.
$W_{solid} + C_{graphite} \rightarrow WC_{solid}$ But this reaction happens at 1400° C!

We Know: A.	$2\,W_{solid} + 3\,O_{2\,gas}$	$\rightarrow 2\,WO_{3\,solid}$	$\Delta H = -1685.8$ kJ
B.	$C_{graphite} + O_{2\,gas}$	$\rightarrow CO_{2\,gas}$	$\Delta H = -393.5$ kJ
C.	$2\,WC_{solid} + 5\,O_{2\,gas}$	$\rightarrow 2\,WO_{3\,solid} + 2\,CO_{2\,gas}$	$\Delta H = -2391.8$ kJ

A * ½

$W_{solid} + 3/2\,O_{2\,gas}$	$\rightarrow WO_{3\,solid}$	$\Delta H = -1685.8$ kJ / 2 = **- 842.9 kJ**
$C_{graphite} + O_{2\,gas}$	$\rightarrow CO_{2\,gas}$	ΔH = **- 393.5 kJ**

C reversed * 1/2

$WO_{3\,solid} + CO_{2\,gas}$	$\rightarrow WC_{solid} + 5/2\,O_{2\,gas}$	$\Delta H = 2391.8$ kJ / 2 = **1195.9 kJ**
$W_{solid} + C_{graphite}$	**$\rightarrow WC_{solid}$**	**ΔH = 40.5 kJ**

Standard Enthalpies of Formation

Standard State the standard thermodynamic condition chosen for substances when listing or comparing data: 1 atm and 25° C. Delta H Zero = **ΔH^o = the Standard Enthalpy of Reaction**

Must specify the exact form of the element – solid, liquid, or gas.

Allotrope is one or more distinct forms of an element in the same physical state. O_2 = Oxygen O_3 = Ozone
Reference Form is the stablest form (physical state and allotrope) of the element under standard thermodynamic conditions. At 25°C O_2 is Oxygen, Graphite is carbon.

Standard Enthalpy of Formation: ΔH^o_f is the enthalpy change for the formation of one mole of trhe substance in its standard state from it's elements on the reference form and in their standard states.

PROBLEM: ΔH^o_f of water. Stablest form of oxygen and hydrogen is O_2 gas and H_2 gas.
$O_{2\,gas} + ½\,H_{2\,gas} \rightarrow H_2O_{liq}$ ΔH^o_f = = 285.8 kJ

Methane reacts with Chlorine

$CH_{4\,g} + 4\,Cl_{2\,g} \rightarrow CCl_{4\,g} + 4\,HCl_{gas}$ ΔH = ?

A.	$C_{graphite} + 2\,H_{2\,gas}$	$\rightarrow CH_{4\,gas}$	$\Delta H = -79.4$ kJ
B.	$C_{graphite} + 2\,Cl_{2\,gas}$	$\rightarrow CCl_{4\,liq}$	$\Delta H = -135.4$ kJ
C.	$½\,H_{2\,gas} + ½\,Cl_{2\,gas}$	$\rightarrow HCl_{gas}$	$\Delta H = -92.3$ kJ

Reverse A	$CH_{4\,gas}$	$\rightarrow$ **$C_{graphite} + 2\,H_2$**	$\Delta H = 79.4$ kJ
B.	**$C_{graphite}$** $+ 2\,Cl_{2\,gas}$	$\rightarrow CCl_{4\,liq}$	$\Delta H = -135.4$ kJ
4 * C	**$2\,H_{2\,gas}$** $+ 2\,Cl_{2\,gas}$	$\rightarrow 4\,HCl_{gas}$	$\Delta H = -92.3$ kJ * 4
	$CH_{4\,g} + 4\,Cl_{2\,g}$	$\rightarrow CCl_{4\,g} + 4\,HCl_{gas}$	$\Delta H = -429.7$ kJ

Practice Questions:

Review Questions: All Example Problems in the chapter

Concept Questions: 6.28

Practice Problems: 6.35, 6.37, 6.43, 6.49, 6.51, 6.53, 6.57, 6,115

Concept Check 6.1 PROBLEM: A solar powered water pump has photovoltaic cells to generate electricity which runs the motor to pump water up to a storage tank. What energy conversions are involved?

1. Sun energy to electricity
2. Electric energy stored in a battery as chemical energy
3. Chemical Energy converted back to electricity to run the motor
4. Motor rotates as electricity is converted to Kinetic Energy
5. KE from motor rotation to motion of the water up against gravity.

Example 6.2 PROBLEM: Sodium Hydrogen Carbonate in water reacts with Hydrochloric Acid. The reaction absorbs 12.7 kJ of heat at Pk for each mole of SHC. Write the thermochemical equation?

$$NaHCO_{3\ aq} + HCl_{\ aq} \rightarrow NaCl_{\ aq} + H2O_{\ l} + CO_{2\ g} \qquad \Delta H = +\ 12.7\ kJ$$