

# Thermochemistry Notes

Study of energy changes related to chemical reactions.

## Work and Energy

Energy is defined as the capacity to do work  
Potential energy (such as  $mgh$ )  
Kinetic energy ( $\frac{1}{2}mv^2$ )

SI unit of energy is the joule (J)

Work is defined as applying a force  $F$  through a distance  $d$   $W = Fd$

A force of 1N applied through a distance of 1m does 1J of work (Units:  $\text{kg m}^2/\text{s}^2$  or Nm)

**Note:** Work and energy have the same units = joules

## Thermochemistry Definitions

**System:** The portion of the universe under study.

**Surroundings:** Everything else besides the system.

**Interaction:** Exchange of energy and or matter between the system and its surroundings.

### **Systems:**

**Open system:** Exchanges both matter and energy with its surroundings.

**Closed system:** Exchanges only energy with its surroundings.

**Isolated system:** Exchanges neither energy nor matter with its surroundings.

## Internal Energy (E) – Total energy of the system

Kinetic (thermal) energy:  
Translational  
Rotational  
Vibrational

Potential energy  
Nuclear forces  
Electrostatic attractions (Chemical energy)  
Intramolecular - Bonds between atoms  
Intermolecular - Attractions between molecules

Heat ( $q$ ) = energy *transfer* (kinetic energy)  
Caused by temperature differences  
System and surroundings reach thermal equilibrium

A system does not *contain* heat.

Energy (in the form of thermal kinetic energy) is transferred from the hotter region to the colder region until thermal equilibrium is established.

## Work (w)

Transfer of energy between a system and its surroundings.

Usually due to some physical change to the system.

A system does not *contain* work.

Focus is on pressure-volume (P-V) work: Work done when gases are expanded or compressed.

(See pressure-volume work diagram)

$$P = F/A \quad F = PA$$

$$\text{Work (w)} = \text{force (F)} \times \text{distance (h)} \\ = P \times A \times h$$

$$(A)(h) = \Delta V \quad \therefore \\ \text{Work (w)} = P\Delta V \quad (\Delta V = V_f - V_i)$$

A negative is added as a sign convention to show that when a system loses energy (i.e. is transferred from the system to the surroundings) the work is negative. Therefore

$$w = -P\Delta V$$

## 1<sup>st</sup> Law of Thermodynamics

Internal energy (E) is a **state function**.

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

A **state function** only depends on the current conditions of the system and not upon how that state was reached.

Cannot measure absolute internal energy

Internal energy is a *state function*

Depends on the present state of the system and not on its history

Heat (q) and work (w) are *not* state function (They are not contained in the system and exist as a consequence of a change in the system)

For a given change, different combinations of heat and work can lead to the same  $\Delta E$ .

*Functions of state are reversible.*

**Law of Conservation of Energy:** In a physical or chemical change, energy can be exchanged between a system and its surroundings, but no energy can be created or destroyed.

**First Law of Thermodynamics:**

$$\Delta E = q + w$$

Heat absorbed by the system	Increases energy of the system	$q > 0$
Work done on the system		$w > 0$
Heat given off by the system	Decreases energy of the system	$q < 0$
Work done by the system		$w < 0$

So “positive” is measured relative to the system.

**Sample Problems:**

- In a process in which 89J of work is done on a system, 567J of heat is given off. What is  $\Delta E$  of the system?

- In a particular process, the internal energy of a system increases by 41.4J and the quantity of work the system does on its surroundings is 81.2J. Is heat absorbed or given off by the system? What is the value of q?

- In an adiabatic process, a system that is thermally insulated from its surroundings so there is no exchange of heat ( $q=0$ ). If an ideal gas undergoes an adiabatic expansion against a constant pressure, a) does the gas do work? b) Does the internal energy of the gas increase, decrease, or remain unchanged? c) What happens to the temperature?

## Heats of Reaction and Enthalpy Change, $\Delta H$

	<b>Isolated System</b>	<b>Open/Closed System</b>
<b>Exothermic Reaction</b> Chemical energy $\rightarrow$ Thermal energy	System Temperature increases	Heat given off to surroundings ( $q < 0$ for system)
<b>Endothermic Reaction</b> Thermal energy $\rightarrow$ Chemical energy	System Temperature decreases	Heat absorbed from surroundings ( $q > 0$ for system)

**Heat of Reaction ( $q_{\text{rxn}}$ ):** The quantity of heat exchanged between the reaction system and its surroundings for a reaction *occurring at a fixed temperature*.

(Assume only pressure-volume type of work for the following examples)

For reactions that take place at **constant volume**:

$$w = -P\Delta V = 0 \text{ (no volume change)}$$

$$\Delta E = q + w = q_v$$

$$q_v = \Delta E$$

For reactions that take place at constant pressure:

$$\Delta E = q + w = q_p - P\Delta V$$

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

## Enthalpy

Most reactions are carried out at constant pressure in open vessels.

Enthalpy (H)  $\equiv$  E + PV

$q_p$  = enthalpy change for a reaction =  $\Delta H$

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

### Properties of Enthalpy

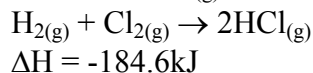
1. Enthalpy is an extensive property (depends upon the amount present)
2. Enthalpy is a state function (E, P and V are state functions)
3. Enthalpy changes have unique values ( $\Delta H = q_p$ )

An enthalpy diagram can be used to illustrate the enthalpy change of a reaction. The enthalpy, H, is plotted on the Y-axis and the progression of the reaction on the X-axis.  $\Delta H$  is the value that is determined.

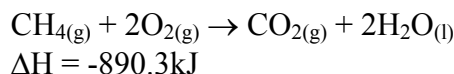
### Sample Problems:

1. Given the equation  $3 \text{O}_{2(g)} \rightarrow 2 \text{O}_{3(g)}$   $\Delta H = +285.4 \text{ kJ}$ , calculate  $\Delta H$  for the following reaction.  $3/2 \text{O}_{2(g)} \rightarrow \text{O}_{3(g)}$ .
2. Given the equation:  $2\text{Ag}_2\text{S}_{(s)} + 2\text{H}_2\text{O}_{(l)} \rightarrow 4\text{Ag}_{(s)} + 2\text{H}_2\text{S}_{(g)} + \text{O}_{2(g)}$   $\Delta H = +595.5 \text{ kJ}$ , calculate  $\Delta H$  for the following reaction.  
 $\text{Ag}_{(s)} + 1/2 \text{H}_2\text{S}_{(g)} + 1/4 \text{O}_{2(g)} \rightarrow 1/2 \text{Ag}_2\text{S}_{(s)} + 1/2 \text{H}_2\text{O}_{(l)}$
3. Express the following information as a chemical equation. At  $25^\circ\text{C}$  and at a constant pressure, dinitrogen trioxide gas decomposes to nitrogen monoxide and nitrogen dioxide gases with the absorption of  $0.533 \text{ kJ}$  of heat for every gram of dinitrogen trioxide that decomposes.

4. What is the enthalpy change when  $12.8 \text{ g H}_{2(g)}$  reacts with excess  $\text{Cl}_{2(g)}$  to form  $\text{HCl}_{(g)}$ ?



5. What volume of  $\text{CH}_{4(g)}$ , measured at  $25^\circ\text{C}$  and  $745 \text{ Torr}$ , must be burned in excess oxygen to release  $1.00 \times 10^6 \text{ kJ}$  of heat to the surroundings?



## Calorimetry

Measurement of heat energy transfer

**Heat Capacity (C)**  $\equiv$  Quantity of heat required to change the temperature of a system by 1°C (or 1K)

$$C = q/\Delta T$$

### Sample Problems:

1. Calculate the heat capacity of a sample of brake fluid if the sample must absorb 911J of heat for its temperature to rise from 15°C to 100°C.

2. A burner on an electric range has a heat capacity of 345J/K. What is the value of  $q$ , in kilojoules, as the burner cools from a temperature of 467°C to a room temperature of 23°C?

### **Molar Heat Capacity/Specific Heat**

Molar heat capacity =  $C/n$ , where  $C$  is the heat capacity and  $n$  is the moles.

Specific heat =  $C/m = q/(m\Delta T)$ , where  $m$  is the mass in grams and  $\Delta T = T_f - T_i$

1 calorie = 1 cal = amount of energy required to raise the temperature of 1g of water by 1°C (at 1 atm).

$$1 \text{ cal} = 4.184 \text{ J}$$

$$1 \text{ kilocalorie} = 1 \text{ Cal} = 1,000 \text{ cal}$$

The specific heat of water is 4.184J/g°C

### Sample Problems:

1. How much heat, in calories and kilocalories, does it take to raise the temperature of 814g of water from 18.0°C to 100°C?

2. What mass of water, in kilograms, can be heated from 5.5°C to 55.0°C by  $9.09 \times 10^{10}$  J of heat?

3. A 454g block of lead is at an initial temperature of 22.5°C. What will be the temperature of the lead after it absorbs 4.22kJ of heat from its surroundings?

4. How many grams of copper can be heated from 22.5°C to 35.0°C by the same quantity of heat that can raise the temperature of 145g of H<sub>2</sub>O from 22.5°C to 35.0°C?

### Enthalpy, Specific heats and Chemical reactions:

Using a Styrofoam cup calorimeter:

*All the heat lost by the hot solid is gained by the water in the cup.*

The Styrofoam acts as a good insulator and has a low specific heat.

If a reaction takes place inside a insulated calorimeter  $q_{\text{rxn}} = -q_{\text{calorimeter}}$  If this reaction takes place under constant pressure  $q_{\text{rxn}} = q_p$

### Sample Problems:

1. A 23.9g sample of iridium is heated to 89.7°C and then dropped into 20.0g of water in a calorimeter. The temperature of the water rises from 20.1°C to 22.6°C. Calculate the specific heat of iridium.

2. A 135g piece of iron (specific heat, 0.449J/g°C) is heated to 225°C in an oven. It is then dropped into a Styrofoam cup calorimeter containing 250.0mL of glycerol ( $d = 1.261 \text{ g/mL}$ ) at 23.5°C. The temperature of the glycerol rises to a maximum value of 44.7°C. Use this data to determine the specific heat of glycerol.

3. Without doing detailed calculations, determine the final temperature if 200.0mL of water at 80°C is added to 100.0mL of water at 20°C.

4. A 100.0mL portion of 0.500M HBr at 20.29°C is added to 100.0mL of 0.500M KOH, also at 20.29°C, in a foam cup calorimeter. After mixing, the temperature rises to 23.65°C. Calculate the heat of this reaction. (Assume system is isolated, insulated, volumes are additive and density and specific heat of solution is that of pure water.)

5. Express the result of question 4 for molar amounts of reactants and products. You will need a balanced chemical reaction equation.

6. A 125mL sample of 1.33M HCl and 225mL of 0.625M NaOH, both initially at 24.4°C, are allowed to react in a calorimeter. What is the final temperature that would be observed in the calorimeter? ( $\Delta H = -57.2\text{kJ/mol}$ )

### Bomb Calorimeter

For combustion reactions and other reactions involving gases.

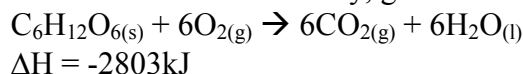
The chamber of the bomb calorimeter keeps the system at a constant volume.

$\Delta E = q_v = q_{\text{rxn}} = -q_{\text{calorim}}$  where  $q_{\text{calorim}} =$  heat capacity of calorimeter  $\times \Delta T$

Note that this is not necessarily the enthalpy  $\Delta H$ . Enthalpy is measured at constant pressure. (i.e.  $q_p = \Delta H = \Delta E + P\Delta V$ )

### **Sample Question:**

1. A 0.8082g sample of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) is burned in a bomb calorimeter assembly, and the temperature is noted to rise from 25.11°C to 27.21°C. Determine the heat capacity of the bomb calorimeter assembly, given:



### Hess's Law of Heat Summation

The heat of a reaction is constant, whether the reaction is carried out directly in one step or indirectly through a number of steps.

**Reversing** an equation:

Changes the sign of  $\Delta H$

**Multiplying** coefficients in an equation:

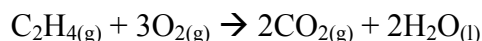
Multiplies the value of  $\Delta H$  by the same amount.

Multiplying factors may be fractional.

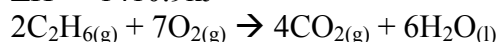
### **Sample Problem:**

1. Calculate the enthalpy change for the reaction  $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$   $\Delta H = ?$

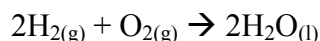
Given:



$$\Delta H = -1410.9\text{kJ}$$



$$\Delta H = -3119.4\text{kJ}$$



$$\Delta H = -571.6\text{kJ}$$

## Standard Enthalpy of Formation

Scale of relative enthalpies.

### **Standard state of solid or liquid:**

Pure element or compound at 1atm and the temperature of interest (often 25°C)

### **Standard state of gas:**

Pure gas substance acting ideal at 1atm and the temperature of interest.

**Standard enthalpy of reaction ( $\Delta H^\circ$ )** is the enthalpy change for standard state reactants yielding standard state products.

**Standard enthalpy of formation (heat of formation) ( $\Delta H^\circ_f$ )** = enthalpy change in creating 1 mole of a substance at standard state conditions from its elements at standard states and in its reference form.

*The standard enthalpy of formation of a pure element in its reference form is 0.* (ex. Carbon as graphite. Graphite is the reference form of carbon.)

To determine the standard enthalpy of a reaction from standard heats of formation:

$$\Delta H^\circ = \sum v_p \times \Delta H^\circ_f(\text{products}) - \sum v_r \times \Delta H^\circ_f(\text{reactants})$$

and  $v$  refers to the stoichiometric coefficients of the reactants and products.

### **Sample Problems:**

1. Use data from table 6.2 (p257) to calculate  $\Delta H^\circ$  for the combustion of butane gas,  $C_4H_{10}$ , to produce gaseous carbon dioxide and liquid water.

2. The combustion of thiophene,  $C_4H_4S_{(l)}$ , a compound used in the manufacture of pharmaceuticals, produces carbon dioxide and sulfur dioxide gases and liquid water. The enthalpy change in the combustion of one mole

of  $C_4H_4S_{(l)}$  is -2523kJ. Use this information and data from Table 6.2 to establish  $\Delta H^\circ_f$  for  $C_4H_4S_{(l)}$ .

### Ionic Reactions in Solutions:

Since cations and anions cannot be formed in isolation, you cannot directly extend enthalpy to the formation of single ions.

$H^+_{(aq)}$  is arbitrarily assigned an enthalpy of formation of zero. The formation of other ions are measured relative to this.

### **Sample Problem:**

Given that  $\Delta H^\circ_f[Mg(OH)_{2(s)}] = -924.5\text{kJ/mol}$ , what is the standard enthalpy change,  $\Delta H^\circ$ , for the reaction of aqueous solutions of magnesium chloride and potassium hydroxide?