

CHM 101

THERMOCHEMISTRY

DEFINITIONS

ENERGY is the capacity to do work

Kinetic energy $E_k = 0.5 mv^2$ (i)

Potential energy is energy an object possess by virtue of its position

PE = mgh (ii)

Where h is the height of the object, g is the gravitational constant and m is the mass of the object.

WORK is the energy used to cause an object with mass to move (distance 'd') against force (F)

W = F d = mgd (iii)

Where m is the mass of the object and g is the force due to gravity

SYSTEM: an **open system** is one in which matter and energy can be exchanged with the surroundings.

An **isolated system** is one in which matter and energy cannot be exchanged with the surroundings

Closed system is one that exchange energy but not matter with its surroundings.

FIRST LAW OF THERMODYNAMICS

Energy cannot be created or destroyed it can only be transformed from one form to another i.e. energy is conserved.

The **internal energy U** of a system is the sum of all kinetic and potential energies of all its components.

The change in internal energy ΔU is the difference between U_{final} and U_{initial}

A positive value ΔU indicates the system as gained energy from its surrounding, a negative value of ΔU indicates that the system as lost energy to its surroundings.

$\Delta U = Q + W$, Q is the heat absorbed or evolved by the system.

U increases when work is done on a system or heat is added to a system.

Sign conventions for Q, W and ΔU

+Q = the system gains heat

—Q = the system losses heat

+w = work is done on the system

—w = work is done by the system

+ ΔU = net gain of energy by the system

— ΔU = net loss of energy by the system

An **endothermic** process is one in which the system absorbs heat while an **exothermic** process is one that losses heat

A **state function** is the property of a system that is determined by specifying the system's condition like temperature, pressure. The value of a state function depends only on the present state and not the path the system took to attain the state.

Enthalpy H accounts for heat flow in processes occurring at constant pressure. No form of work is performed other than expansion /compression i.e. pressure – volume work

$$W = - P \Delta V \quad (\text{iv})$$

Recall $W = FD = F \Delta D$

$$P = F/A \text{ (A is area)}$$

$$\Delta V = A \times \Delta D$$

$$H = U + PV \quad (\text{v})$$

$$\Delta H = \Delta U + P \Delta V = (Q + W) \quad - W = Q_p \quad (\text{vi})$$

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

A positive value of ΔH implies that the system has gained heat and a negative value of ΔH means the system has lost heat to the surrounding.

When a reaction is carried out in a constant volume container, ΔV is zero.

Enthalpies of Reactions

The enthalpy change that accompanies a reaction is called the enthalpy of reaction.

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

A negative ΔH value means the reaction is exothermic; a positive ΔH value means the reaction is endothermic.

Enthalpy is an extensive property. The magnitude of ΔH is directly proportional to the amount of reactant consumed in the process.

The enthalpy for a reaction is equal in magnitude, but opposite in sign, to ΔH for the reverse reaction.

The enthalpy change for a reaction depends on the state of the reactants and products.

Heat Capacity and Specific Heat

The heat capacity C of an object is the amount of required to raise its temperature by 1K.

The greater the heat capacity, the greater the heat required to produce a given increase in temperature.

The molar heat capacity C_m is the heat capacity of one mole of a substance. The heat capacity of one gram of a substance is known as the specific heat capacity C_s and it varies slightly with temperature.

$$C_s = \text{quantity of heat transferred/grams of substance} \times \text{change in temperature} = Q/m \Delta T \quad (\text{viii})$$

The heat absorbed by a solution is calculated from the equation

$$Q_{\text{soln}} = C_s \times m \times \Delta T \quad (\text{ix})$$

For dilute aqueous solution the specific heat of the solution is approximately the same as that of water, 4.18J/gK

Heat of combustion calculated from the measured temperature increase in a bomb calorimeter is

$$Q_{\text{rxn}} = - C_{\text{cal}} \times \Delta T \quad (\text{x})$$

$- C_{\text{cal}}$ is the heat capacity of the calorimeter.

HESS'S LAW OF HEAT SUMMATION

The law states that if a reaction is carried out in a series of steps, ΔH for the overall reaction will equal the sum of the enthalpy changes for the individual steps.

The overall enthalpy change for the process is independent of the paths between the final and initial states of the reaction.

Hess's law provides a useful means of calculating energy changes that are difficult to measure directly.

Worked Examples on Energy

Example 1.

A bowler lifts a 5.4- kg (12-lb) bowling ball from ground level to a height of 1.6m (5.2 feet) and then drops the ball back on the ground. (a) What happens to the potential energy of the bowling ball as it is raised from the ground? (b) What quantity of work, in J, is used to raise the ball? (c) After the ball is dropped, it gains kinetic energy. If assumed we that all of the work done in part (b) has been converted to kinetic energy by the time the ball strikes the ground, what is the speed of the ball at the instant just before it hits the ground? (Note: the force due to gravity is $F = m \times g$, where m is the mass of the object and g is the gravitational constant; $g = 9.8 \text{ m/s}^2$).

SOLUTION

- Because the bowling ball is raised to a greater height above the ground, its potential energy increases.
- The ball has a mass of 5.4kg, and it is lifted a distance of 1.6 m. To calculate the work performed to raise the ball, we use both Equation 5.3 and $F = m \times g$ for the force that is due to gravity:

$$w = F \times d = m \times g \times d = (5.4 \text{ kg})(9.8 \text{ m/s}^2)(1.6 \text{ m}) = 85 \text{ kg} \cdot \text{m}^2/\text{s}^2 = 85 \text{ J}$$

- When the ball is dropped, its potential is converted to kinetic energy. At the instant just before

the ball hits the ground, we assume that the kinetic energy is equal to the work done in part(b), 85J:

$$E_k = \frac{1}{2}mv^2 = 85 \text{ J} = 85 \text{ kg} \cdot \frac{\text{m}^2}{\text{s}^2}$$

We can now solve this equation for v :

$$v^2 = \left(\frac{2E_k}{m} \right) = \left(2 \left(85 \text{ kg} \cdot \frac{\text{m}^2}{\text{s}^2} \right) / 5.4 \text{ kg} \right) = 31.5 \text{ m}^2/\text{s}^2$$

$$v = \sqrt{\frac{31.5 \text{ m}^2}{\text{s}^2}} = \frac{5.6 \text{ m}}{\text{s}}$$

Practice exercise

What is the kinetic energy, in J, of a) an Ar atom moving with a speed of 650m/s, b) a mole of Ar atoms moving with a speed of 650m/s (hint: 1 amu = 1.66×10^{-27} kg)

Example 2:

How much heat is related when 4.50 g of methane gas is burned in a constant pressure system?

Solution

By adding the atomic weights of C and 4H, we have 1 mol CH₄ = 16.0 g CH₄. We can use the appropriate conversion factors to convert grams of CH₄ to moles of CH₄ to kilojoules:

$$\text{Heat} = (4.50 \text{ g CH}_4) \left(1 \frac{\text{mol CH}_4}{16.0 \text{ g CH}_4} \right) (-890 \frac{\text{kJ}}{1 \text{ mol CH}_4}) = -250 \text{ J}$$

The negative sign indicates that the system released 250kJ into the surroundings.

Practice exercise

Hydrogen peroxide can decompose to water and oxygen by the following reaction:



Calculate the value of q when 5.00 g of H₂O₂(l) decomposes at constant pressure

Example 3:

How much heat is required to warm 250g of water from 22°C to 98°C? The specific heat capacity of water is 4.18J/g-K. What is the molar heat capacity of water?

Solution:

$$\begin{aligned} \Delta T &= (98 - 22) = 76^\circ\text{C} = 76\text{K} \\ Q &= C_s m \Delta T \\ &= 4.18 \times 250 \times 76 = 79420 \text{ J} \\ 1 \text{ mol of water} &= 18.0 \text{ g} \\ C_m &= 4.18 \times 18.0 = 75.24 \text{ J/mol K} \end{aligned}$$

Calculate the enthalpy change for the reaction between 50mL of 1.0 M HCl and 50mL of 1.0 M NaOH when the temperature changes from 21°C to 27.5°C. (Specific heat of water is 4.18J/g-K, density of solution is 1.0g/mL)

$$\begin{aligned} \text{HCl(aq)} + \text{NaOH(aq)} &\rightarrow \text{H}_2\text{O(l)} + \text{NaCl(aq)} \\ \text{Total volume of solution} &= 100\text{mL} \\ \text{its mass} &= 100\text{g} \\ \Delta T &= (27.5 - 21)^\circ\text{C} = 6.5^\circ\text{C} = 6.5\text{K} \\ \Delta H = Q_{\text{rxn}} = C_s m \Delta T &= - 4.18 \times 100 \times 6.5 = - 2717 \text{ J} = 2.717 \text{ kJ} \\ 1.0 \text{ M} &= 1.0\text{M/L} \\ \text{i.e. no of moles of solution} &= 0.050\text{L} \times 1.0\text{mol/L} = 0.050 \text{ M} \\ \Delta H/\text{mol} &= - 2.717/0.05 = - 5.434\text{kJ/mol} \end{aligned}$$

Practice question;

Calculate the enthalpy change for the reaction between 50mL of 1.0 M HCl and 50mL of 1.0 M AgNO₃ when the temperature changes from 23°C to 26.5°C. (Specific heat of water is 4.18J/g-K, mass of solution is 100.0g)

Given the following enthalpies of combustion, calculate the enthalpy of combustion of carbon to carbon monoxide.

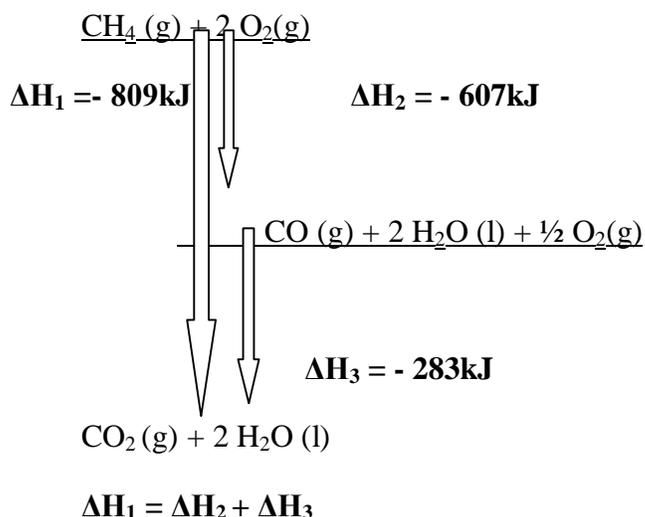


Solution ;



Equation (i) – equation (ii) = $\text{C(s)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO(g)} \quad \Delta H = -110.5\text{kJ}$

Enthalpy diagram illustrating Hess's law



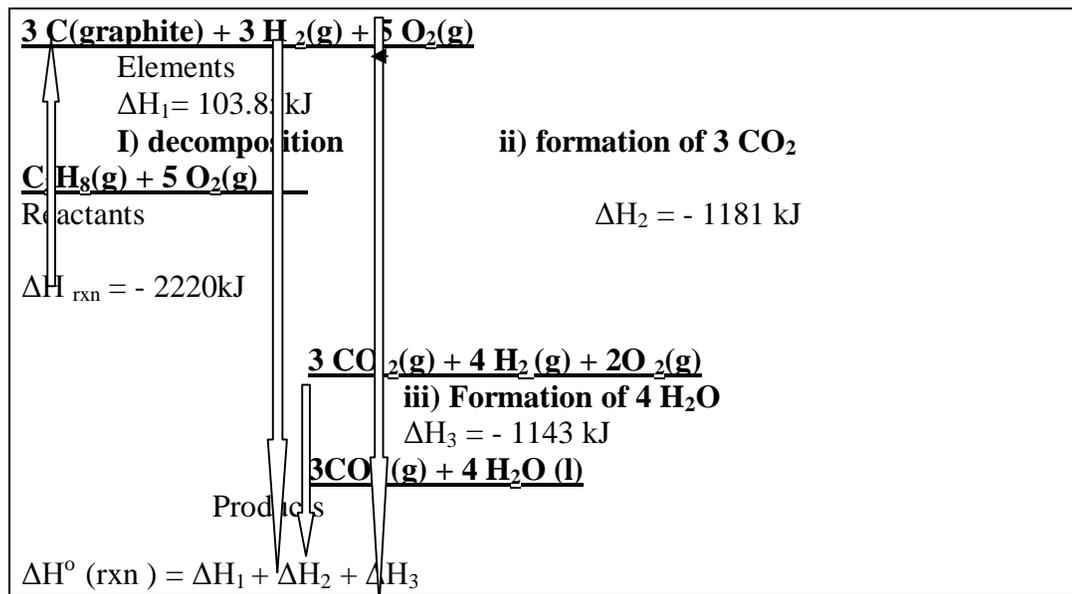
The enthalpy change associated with the formation of a compound from its constituent element is known as enthalpy of formation.

The standard enthalpy change of a reaction is defined as the enthalpy of change when all reactants and products are in their standard states.

The standard enthalpy of formation of a compound, ΔH_f° , is the change in enthalpy for the reaction that forms one mole of the compound from its elements. Both reactants and products must be in their standard states.

By definition the standard enthalpy of the most stable form of any element is zero because there is no formation reaction needed when the element is already in its standard state.

Enthalpy diagram relating the change for a reaction to enthalpies of formation.



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

RATES OF REACTION/ CHEMICAL KINETICS

The speed of a chemical reaction is the change in the concentration of reactants or products per unit time.

For a reaction $A \rightarrow B$

Rate of reaction after time t is given as rate of disappearance of A or rate of appearance of B

$$\frac{-\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t} \quad (i)$$

For the reaction, $a A + b B \rightarrow c C + d D$

Rate of reaction is given by,

$$\text{Rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t} \quad (ii)$$

Worked examples:

Given the concentration of A at 20 s is 0.54 M and at 40 s its concentration is 0.30 M .

Calculate the average rate at which A disappears over a time interval of 20 s to 40 s

$$\text{Average rate of } A = -\frac{\Delta[A]}{\Delta t} = \frac{-0.30 - 0.54}{40 - 20} = 1.2 \times 10^{-2} \text{ M/s}$$

Given the concentration of B decreases from 0.100 M to 0.600 M when the time changes from 0 s to 210 s , calculate the initial rate of reaction of B

$$\text{Rate} = -\frac{\Delta[B]}{\Delta t} = \frac{-0.600 - 0.100}{210 - 0} = 1.9 \times 10^{-4} \text{ M/s}$$

Reaction rates decreases as reaction proceeds, because the concentration of reactants decreases.

Factors That Affect Rates of Reactions

1. Physical state of the reactants: when reactants are in different phases for example when a solid reacts with a liquid the reaction is limited to the area of contact. Reactions involving solids will proceed faster if the surface area of the solid is increased.
2. Concentration of the reactants: as concentration increases the frequency with which the reactants collide increases and the rates of reaction increases.
3. Temperature: rates of chemical reactions increases as the temperature increases. Increasing temperature increases the kinetic energy of molecules, at higher energy more molecules collide more frequently.
4. Catalyst speed up rates of reaction without being used up.

Reaction rates depend on the frequency of collisions between molecules. The greater the frequency of collisions, the greater the rate of reactions.

The rate law

For the reaction, $a A + b B \rightarrow c C + d D$

The rate law is written in the form

$$\text{Rate} = k [A]^m [B]^n \quad (\text{iii})$$

Generally the rate law can be written as

$$\text{Rate} = [\text{reactant 1}]^m [\text{reactant 2}]^n \quad (\text{iv})$$

Where k is the rate constant, and it is temperature dependent. The exponents' m and n are whole numbers (0, 1, 2) are known as the reaction order. The overall order of the reaction is the sum of the m and n .

The unit of the rate = (units of rate constant) (units of concentration)² for the reaction above is

$$\text{Unit of rate constant} = \frac{\text{units of rate}}{(\text{units of concentration})^2} = \frac{M/s}{(M)(M)} = M^{-1} s^{-1} \quad (\text{v})$$

The rate of a first order reaction depends on the concentration of only one reactant raised to the first power.

$$\text{Rate} = \frac{-\Delta[A]}{\Delta t} = k [A] \quad (\text{vi})$$

The integrated rate law is written as $\ln [A]_t = -kt + \ln [A]_0$ (vii)

The rate of a second order reaction depends on the concentration of one reactant raised to the second power or on the concentrations of two different reactants.

$$\text{Rate} = \frac{-\Delta[A]}{\Delta t} = k [A]^2 \quad (\text{viii})$$

The integrated rate law is written as $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$ (ix)

A plot of $1/[A]$ against t will give a straight line with a slope equal to k and an intercept equal to $1/[A]_0$.

The half – life of a reaction $t_{1/2}$, is the time required for the concentration a reactant to reach one – half of its initial value, $[A]_{t_{1/2}} = \frac{1}{2}[A]_0$ (x)

The half – life of a first order reaction is derived as follows

$$\ln = \frac{1/2[A]_0}{[A]_0} = -k t_{1/2} \quad (\text{xi})$$

$$\ln 1/2 = k t_{1/2} \quad (\text{xii})$$

$$t_{1/2} = \frac{\ln 1/2}{k} = \frac{0.693}{k} \quad (\text{xiii})$$

The half – life of a second order reaction is given as

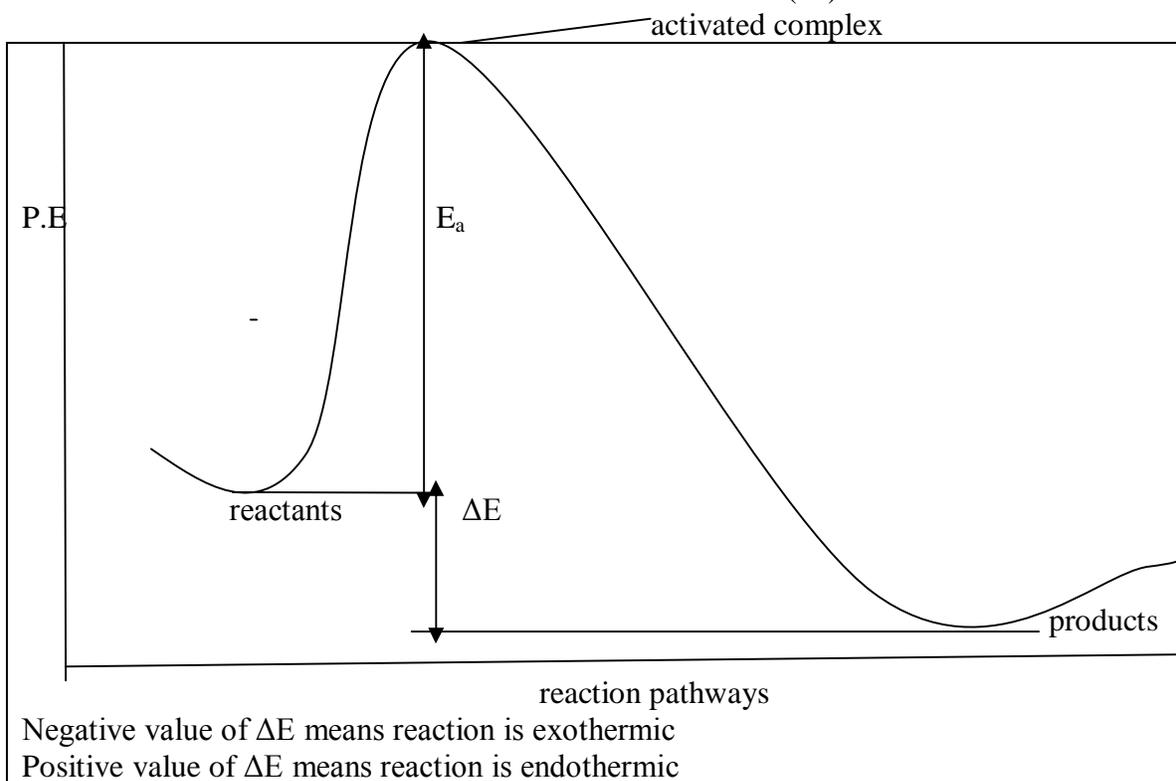
$$t_{1/2} = \frac{1}{k [A]_0} \quad (\text{xiv})$$

It depends on the initial concentration of the reactant. The lower the initial concentration, the greater the half – life.

Activation energy – E_a is the minimum energy required to initiate a chemical reaction.

Generally the lower the activation energy the faster the rate of reaction. As the temperature at which a reaction is carried out increases, a greater fraction of molecules has kinetic energy greater than the activation energy which causes more effective collisions and a greater rate of reaction. The fraction of molecules that has energy equal to or greater than E_a is given by the expression

$$F = e^{-E_a/RT} \quad (\text{xv})$$



The Arrhenius Equation is based on three factors

- The fraction of molecules that possess the an energy greater than E_a
- The number of collisions occurring per second
- The fraction of collisions that have the appropriate orientation.

The Arrhenius equation is written as

$$k = Ae^{-E_a/RT} \quad (\text{xvi})$$

$$\ln k = \ln A - \frac{E_a}{RT} \quad (\text{xvii})$$

A plot of $\ln k$ versus $1/T$ will give a straight line with slope equal to $-\frac{E_a}{RT}$ and intercept on y axis as $\ln A$.

At two different temperatures T_1 and T_2 , a reaction has rate constants k_1 and k_2

$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \quad (\text{xviii})$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2} \quad (\text{xix})$$

$$\ln \frac{k_1}{k_2} = \frac{E_a}{RT} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (\text{xx})$$

The frequency factor A is nearly constant as the temperature is varied. A is related to the probability the frequency of collisions and the probability that the collisions are favourably oriented for reaction.

Reference Texts

Advanced Chemistry By Philip Matthews

Chemistry the Central Science by Brown and Murphy

Introduction to Physical Chemistry by G. I. Brown