

CHM 101: GENERAL CHEMISTRY I

COURSE UNIT: 2

COURSE SYNOPSIS

- ELEMENTARY THERMOCHEMISTRY
- RATES OF REACTION

Course Lecturer: Dr A. J. Anifowose



What is Thermochemistry?

Thermochemistry is an aspect of chemistry that deals with the amount of heat exchange (i.e., absorbed or released) during a chemical reaction

A **thermochemical equation** is a chemical equation with the ΔH for the reaction included

Rules of Thermochemistry

1. The magnitude of ΔH is directly proportional to the amount of reactant or product:
 - (i) If a reaction is divided by 2, so is ΔH
 - (ii) If a reaction is multiplied by 6, so is ΔH
2. ΔH for the reaction is equal in magnitude but opposite in sign for ΔH for the reverse of the reaction
3. The value of ΔH is the same whether the reaction occurs in one step or as a series of steps. This rule is a direct consequence of the fact that ΔH is a state variable. This rule is a statement of **Hess's Law**.

Reaction Energy:

- a. The study of energy in chemical reactions is called **thermodynamics**, which literally means "changes in heat."
- b. The standard conditions for thermodynamics are
 - i. Standard temperature = $25\text{ }^{\circ}\text{C} = 298\text{ K}$
 - ii. Standard Pressure = 1 atm
 - iii. Notice that these are different than STP for gases (where $ST=273\text{ K}$ and $SP = 1\text{ atm}$).
- c. All chemical reactions either release or require (absorb) energy when they occur. Another way for saying this is that reactions either "give off" or "take in" energy.
- d. Heat energy is referred to in this course as enthalpy (H).
 - i. Enthalpy is the heat absorbed or released by a system at constant pressure.
 - ii. It is impossible to measure enthalpy directly. Only changes in enthalpy are used in this course. We only use " ΔH " in this course. $\Delta H = H_{final} - H_{initial}$
 - iii. Units of heat energy. We will use joules (J) or kilojoules (kJ).

iv. System (the chemical reaction under study), surroundings (every place in the universe except the system), and universe (the system and the surroundings)

v. **Exothermic reactions:** An exothermic reaction is a reaction in which heat is released by the system to the surroundings. From the perspective of the system, "heat is given off." For an exothermic reaction, the sign of ΔH is negative. When a reaction is exothermic (ΔH is negative), that is a **favourable** condition. Enthalpy is just one of the variables involved when predicting whether or not a reaction will occur, but reactions which release heat are more likely to occur than ones in which heat is required, all things being equal.

Example: As water freezes, it must get rid of (release, give off) heat. Therefore, if the water is considered the system, then the freezing of water is exothermic

vi. **Endothermic reactions:** An endothermic reaction is a reaction in which heat is absorbed by the system from the surroundings. From the perspective of the system, "heat is taken in." For an endothermic reaction, the sign of ΔH is positive. When a reaction is endothermic (ΔH is positive), that is an **unfavourable** condition. Enthalpy is just one of the variables involved when predicting whether or not a reaction will occur, but reactions which absorb heat are less likely to occur than ones in which heat is released, all things being equal.

Example: As ice melts, it has to absorb heat. Therefore, if ice is defined as the system, then the melting of ice is endothermic.

Conventions for Thermochemical Equations

1. The sign of ΔH indicates whether the reaction is endothermic or exothermic; ΔH is directly proportional to the amount of reactant or product
2. The coefficients of the thermochemical equation represent the number of moles of reactant and product.
3. The phases of all reactant and product species must be stated
4. The value of ΔH applies when products and reactants are at the same temperature, usually 25 °C

For calculations:

- If a reaction is divided by 2, so is ΔH ; if a reaction is multiplied by 6, so is ΔH
- ΔH changes sign when the reaction is reversed
- ΔH has the same value regardless of the number of steps

Types of Heat (Enthalpy) of Reaction

Heat of formation is defined as the change in enthalpy that takes place when one mole of the compound is formed from its element. It is denoted by change in heat of formation ΔH_f . The enthalpy of formation of an element in its standard state at 25 °C is "0" for its ΔH_f^\ominus .

Question: Find the standard change in enthalpy for the evaporation of water, and state whether the reaction is exothermic or endothermic.

(Water vapour, $H_f^\ominus = -241.82$ kJ/mol; liquid water, $H_f^\ominus = -285.82$ kJ/mol).

Answer: $\text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{O}_{(g)}$

$$\Delta H_{\text{rxn}}^\ominus = \Delta H_{f(\text{products})}^\ominus - \Delta H_{f(\text{reactants})}^\ominus$$

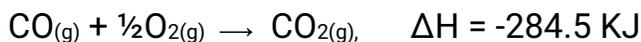
$$\Delta H_{\text{rxn}}^\ominus = -241.82 - (-285.82)$$

$$\Delta H_{\text{rxn}}^\ominus = 44 \text{ kJ/Kmol. Thus, the reaction is endothermic}$$

Question: Find the standard change in enthalpy for the condensation of water vapour, and state whether the reaction is exothermic or endothermic

Standard Heat of Formation: The standard heat of formation of a compound is defined as the change in enthalpy that takes place when one mole of the compound is formed from its element, all substances being in their standard state (298k and 1atm pressure).

Heat of reaction or Enthalpy of reaction: Heat of reaction may be defined as the amount of heat absorbed or evolved in a reaction when the number of moles of reactants, as represented by the balanced chemical equations, changed completely into the product.



The heat exchange accompanying a reaction taking place at 298k and one atmospheric pressure is called the **Standard Heat change or Standard Enthalpy change**. It's denoted by change in ΔH^\ominus

Standard Heat of Reaction (ΔH^\ominus) from standard heat of formation (ΔH_f^\ominus)

The standard heat of reaction is equal to the standard heat of formation of product—the standard heat of formation of reactant

$$\Delta H^\ominus = \Delta H_{f(\text{products})}^\ominus - \Delta H_{f(\text{reactants})}^\ominus$$

Let us consider the general reaction



$$\Delta H^\theta = \Delta H^\theta_{f(\text{products})} \rightarrow \Delta H^\theta_{f(\text{reactants})}$$

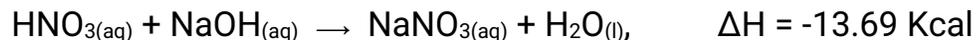
$$= [c \cdot \Delta H^\theta_f(C) + d \cdot \Delta H^\theta_f(D)] \rightarrow [a \cdot \Delta H^\theta_f(A) + b \cdot \Delta H^\theta_f(B)]$$

Heat of Combustion: The heat of combustion of a substance is defined as the change in enthalpy of a system when one mole of the substance is completely burnt in excess of air or oxygen. It is denoted by change in H_c



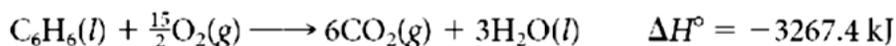
Heat of combustion is always -ve

Heat of Neutralization: Heat of neutralization is defined as the change in heat content (enthalpy) of the system when one form equivalent of an acid is neutralized by one form equivalent of a base or vice versa in dilute solution



Question:

Benzene, C_6H_6 , used in the manufacture of plastics, is a carcinogen affecting the bone marrow. Long-term exposure has been shown to cause leukemia and other blood disorders. The combustion of benzene is given by the following equation:

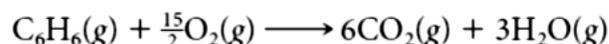


* (a) Calculate the heat of formation of benzene.

** (b) Calculate ΔH° for the reaction



*** (c) Calculate ΔH° for the reaction



given that ΔH_{vap} for benzene at 25°C is 33.6 kJ/mol .

SOLUTION

(a) Equation 8.4 takes the form

$$\Delta H^\circ = 6\Delta H_f^\circ CO_2(g) + 3\Delta H_f^\circ H_2O(l) - \Delta H_f^\circ C_6H_6(l)$$

Substituting values for all the variables except $\Delta H_f^\circ C_6H_6(l)$, we have

$$-3267.4 \text{ kJ} = 6 \text{ mol} \times \left(\frac{-393.5 \text{ kJ}}{1 \text{ mol}} \right) + 3 \text{ mol} \times \left(\frac{-285.8 \text{ kJ}}{1 \text{ mol}} \right) - \Delta H_f^\circ C_6H_6(l)$$

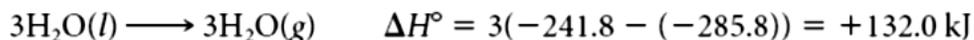
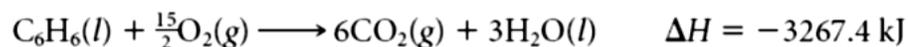
Solving,

$$\Delta H_f^\circ C_6H_6(l) = +49.0 \text{ kJ/mol}$$

(b) Notice that the reaction is the reverse of the combustion reaction. Not only that, all coefficients have been doubled. Thus,

$$\Delta H^\circ = -(-3267.4) \times 2 = +6534.8 \text{ kJ}$$

(c) The reaction is similar to the combustion reaction. The difference is the physical states of both benzene and water. Remember that heat of vaporization is the amount of heat needed to change liquid to gas. We apply Hess's law:



Adding the three chemical equations and the three ΔH° values, we get

$$\Delta H^\circ = -3267.4 \text{ kJ} + 132.0 \text{ kJ} - 33.6 \text{ kJ} = -3169.0 \text{ kJ}$$

ENTROPY

The randomness or disorder of a system is the entropy (S) of that system. The change in entropy denotes " ΔS ".

Highlights:

- ❖ When a reaction has a positive ΔS , that is a **favourable** condition. Entropy is just one of the variables involved when predicting whether or not a reaction will occur, but reactions which increase entropy are more likely to occur than ones in which the entropy decreases, all things being equal.
- ❖ When a reaction has a negative ΔS , that is an **unfavourable** condition. Entropy is just one of the variables involved when predicting whether or not a reaction will occur, but reactions which decrease entropy are less likely to occur than ones in which the entropy increases, all things being equal.
- ❖ Units of ΔS is **J/(K.mol)**

GIBBS FREE ENERGY AND REACTION SPONTANEITY

The spontaneity of a chemical reaction is the possibility of the reaction occurring or not without the aid of outside energy.

Highlights:

- ❖ If a reaction occurs without a net input of energy, it is called "spontaneous." This type of reaction actually releases ("gives off") useful energy.
- ❖ If a reaction requires energy in order to occur, it is called "nonspontaneous." This type of reaction "takes in" energy when it occurs.
- ❖ Gibbs free energy is the energy that is "free" to do work.
- ❖ Units of Gibbs free energy: most often kJ/mol.
- ❖ Important formula: $\Delta G = \Delta H - T\Delta S$, where ΔG is the change in Gibbs free energy.

Table summarizing favorability and spontaneity

End Result	Sign of ΔH	Sign of ΔS	Overall Sign of ΔG
Spontaneous	-ve (favourable)	+ve (favourable)	-
Depends on T	-ve (favourable)	-ve (unfavourable)	?
Depends on T	+ve (unfavourable)	+ve (favourable)	?
Nonspontaneous	+ve (unfavourable)	-ve (unfavourable)	+

LATTICE ENERGY

The positive and negative ion in an ionic crystal are held together by electrostatic forces. The bond energy is expressed in terms of the lattice energy which may be defined as the energy required (enthalpy change) to convert one mole of an ionic solid into gaseous ionic constituents.

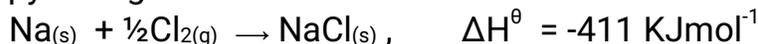


A Born-Haber cycle for the formation of NaCl crystal from its element

Hess Law Application in the Determination of Lattice Energy

Hess Law: Hess law state that if a chemical change can be made to take place in two or more different ways whether in one step or two or more steps, the amount of total heat changes is same, no matter by which method the change is brought about.

The lattice energy of an ionic crystal can be found by applying Hess law. Consider an enthalpy change for the direct formation of NaCl



Step 1: conversion of sodium metal to gaseous atom



Step 2: Dissociation of chlorine molecules to chlorine atoms



Step 3: Enthalpy of ionization; conversion of gaseous sodium to sodium ion by loss of an electron



Step 4: Chlorine atom gains an electron to form chlorine ion. The energy of electron affinity of chlorine



Step 5: Sodium and chloride ions get together and form the crystal lattice



$$\Delta H_f^\ominus = \Delta H_1^\ominus + \Delta H_2^\ominus + \Delta H_3^\ominus + \Delta H_4^\ominus + \Delta H_5^\ominus$$

$$-411 \text{ kJ} = 108 + 121 + 495 - 348 + (-\text{L.E.})$$

$$\text{Lattice energy} = +787 \text{ KJmol}^{-1}.$$

CHEMICAL KINETICS: RATES OF REACTION

This is the study of the rate of reaction in chemistry. A typical reaction rate unit is **M/s**, the change in concentration of a species per unit time. Increasing reaction rates is the goal of many industrial (and biological) processes.

Chemical kinetics covers the following.

1. The rate of reactions and rate laws;
2. The factors as temperature, pressure, concentration and catalyst that influences the rate of reaction;
3. The mechanism or the sequence of steps by which a reaction occurs.

The rate of chemical reaction depends on the nature of reactant, temperature, concentration or pressure of the reactant, surface area of the reactants and the presence of catalyst

1. Nature of the reactants: The complexity of the reactant will affect their ability to collide rightly.

2. Effect of temperature: A chemical reaction is affected by temperature because the velocity of the reacting molecules is altered by change in temperature. Increase in temperature increase the rate of reacting molecule. According to Maxwell-Boltzman's molecular velocity distribution, higher temperature activates more molecules to attain high velocity which is required for effective collision

3. Effect of pressure/concentration: With the exception of zero order reaction, the rate of chemical reaction is directly proportional to the concentration of the reacting specie or to the pressure of the reacting species (if the reactants are gaseous).

4. Effect of Surface Area: This is important only if the system is heterogenous. The larger the surface area for contact, the more molecules that are exposed to each other and the more the number of possible collisions.

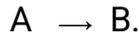
5. Effect of catalyst: The presence of catalyst can increase or decrease the speed of a reaction. For instance, hydrogen and oxygen do not combine but in the presence of platinum catalyst. Similarly, a small amount of glycerin slows down the decomposition of hydrogen peroxide.

In chemical kinetics, reaction can be categorized into two:

1. **Homogenous reaction:** It takes places entirely in one phase.
2. **Heterogeneous:** It takes place in two or more phases. For example, gaseous reaction taking place on the surface of a solid catalyst.

RATE OF REACTION

The rate of a reaction tells us the speed of reaction. Consider a simple reaction:



The concentration of reactant A decreases and that of B increases as time passes.

The rate of reaction is defined as the change in concentration of reactant or product per unit time. For the given reaction. The rate of reaction may be equal to the rate of disappearance of A which is equal to the rate of appearance of B . Therefore,

$$\text{rate} = -d[A]/dt = +d[B]/dt.$$

Where square bracket represents concentration of A and B . The negative sign shows the concentration of A decreases in the course of the reaction. Whereas the positive sign indicates increase in the concentration of B as the reaction proceeds.

THE RATE LAW

At a fixed temperature, the rate of a given reaction depends on concentration of reactant. The exact relationship between concentration and rate is determined by measuring the reaction rate with different initial reactant concentration. It is shown that the rate of reaction is directly proportional to the reaction concentration, each concentration being raised to some powers.

Thus, for a substance A undergoing reaction: rate, $r \propto [A]^n$, $r = k[A]^n$

For a reaction: $2A + B \rightarrow \text{product}$,

the reaction rate with respect to A or B is determined by varying the concentration of one reactant, keeping that of the other. Thus, the rate of reaction can be expressed as

$$\text{rate} = k[A]^m[B]^n$$

An expression which shows how the rate of reaction is related to concentration of reactant is called the **rate law** or **rate equation**.

The power (exponent) of concentration n or m in the rate law is usually small whole number integers 1,2,3 or fractional. The proportionality constant, k , is called the rate constant for the reaction

ORDER OF REACTION

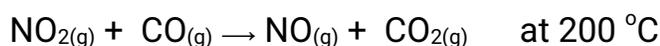
It is defined as the sum of the powers of the concentration in the rate law. Reactant orders are typically 0, 1, 2, 3, or sometimes 0.5. A zero order reactant means that the rate of the reaction is not influenced by the concentration of that particular reactant.

Consider the example of a reaction which has the rate law: $\text{rate} = k[A]^m[B]^n$.

The order of such a reaction is $m + n$.

The order of a reaction can also be defined with respect to a single reactant. Thus, the reaction order with respect to A is m , and n with respect to reactant B. the overall order of the reaction ($m + n$) may range from 1 to 3 and can be fractional. Examples of order of reaction.

The reaction will be classified as first order ($m + n = 1$); second order ($m + n = 2$); third order, if $m + n = 3$. A **zero order reaction** is the reaction which does not depend on the concentration of the reactant. A reactant whose concentration does not affect the reaction rate is not included in a rate law.



$$\text{rate} = k[\text{NO}_2]^2$$

Here, the rate does not depend on the concentration of CO, so it (CO) is not included in the rate law and the power of CO is understood to be zero. Therefore, the reaction is zero order with respect to CO, but second order with respect to NO₂. The overall reaction order is $2+0 = 2$.

MOLECULARITY OF A REACTION

Molecularity of an elementary reaction is defined as the number of reactant molecules involved in a reaction.

Differences between order and molecularity of a reaction

S/N	Order or a reaction	Molecularity of a reaction
1	It is the sum of powers of the concentration terms in the rate law expression	It is no of reacting species undergoing simultaneously collision in the elementary or simple reaction
2	It is an experimentally determined value	It is a theoretical concept
3	It can have fractional value	It is always a whole number
4	It can assume zero value	It cannot have zero value
5	Order of a reaction can change with the reaction condition such as pressure, temperature concentration	It is invariant of reaction condition for a given chemical equation

METHODS FOR THE DETERMINATION OF THE ORDER OF REACTION AND ITS RATE CONSTANT

(a) The Inspection method

Examples:

(i) For a reaction represented by the equation



Experiment	[A] (M)	[B] (M)	rate (Ms ⁻¹)
1	1.0	1.0	2.0
2	1.0	2.0	4.0
3	2.0	1.0	4.0

The data show that three experiments were carried out such that the concentrations of A and B are kept constant in two of the experiments. Looking at the data when [A] was maintained constant and [B] was doubled (experiment 1 and 2), the rate of reaction doubled. This implies that the rate is directly proportional to [B]. Hence, the order with respect to B is 1. Similarly, when [B] was kept constant and [A] was doubled (experiments 1 and 3), the rate of reaction doubled. Hence, rate was also first order in [A]. Therefore, the overall order of the reaction was 2. The rate constant, k , can be calculated by substituting a pair of values in the rate equation: $\text{rate} = k[A][B]$.

NOTE: If you double a reactant concentration for a second-order, the rate should increase four-fold and for a third-order, the rate should increase eight-fold.

(ii) For a reaction: $2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$

the initial rates of the reaction were determined for different concentrations of $N_2O_{5(g)}$

[N ₂ O ₅] (mol/L)	Rate (mol/L/h)
0.1	0.016
0.2	0.032
0.4	0.064

The data indicate that the rate is doubled as the concentration is doubled. Thus, $\text{rate} \propto [N_2O_5]^1$.

The reaction is therefore first-order and the rate equation is $\text{rate} = k[\text{N}_2\text{O}_5]^1$. The rate constant for the reaction is obtained by substitution of any pair of values from the table into the rate reaction:

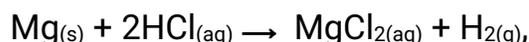
$$k = \text{rate}/[\text{N}_2\text{O}_5]$$

$$k = 0.016/0.1, k = 0.16 \text{ h}^{-1}.$$

(b) The rate curve method

The rate at a given concentration is the slope of the tangent to the concentration-time curve at that concentration. By assuming an order of reaction, a plot of the rate against concentration raised to the power which is equal to the assumed order is carried out. If the assumed order tallies with the actual order of the reaction then a linear plot will be obtained.

For a reaction:



The rate curve is obtained by plotting $[\text{HCl}]$ (mol/L) against time. The reaction rate obtained from rate curve is then plotted against $[\text{HCl}]^n$, where n stands for the assumed order. If a linear plot is obtained, then n represents the actual order of the reaction.

Experimentally, the value of n was found to be 2. The rate constant for the reaction can be obtained by substituting a pair of values into the rate equation:

$$\text{Rate} = k[\text{HCl}]^2.$$

(c) Integrated rates method (for your further read)

RATE OF REACTION

Introduction: The rate of a reaction is the rate at which products are formed or the rate at which reactants are used up in the reaction. Rate of reaction is the change in the concentration of a reactant or product with time. By definition, it is necessary to monitor the concentration of the reactant (or the product) as a function of time. Consider a reaction of molecular bromine and formic acid:



$$\text{Average rate} = \Delta[\text{Br}_2]/\Delta T$$

$$= -([\text{Br}_2]_{\text{final}} - [\text{Br}_2]_{\text{initial}})/(T_{\text{final}} - T_{\text{initial}})$$

Molecular Bromine is reddish brown in color. All other species in the reaction are colourless. As the reaction progresses, the concentration of Bromine steadily

decreases and its colour fades. This loss of colour and, hence, concentration can be monitored easily with a spectrometer, which registers the amount of visible light absorbed by bromine. Measuring the change (decreases) in bromine concentration at some initial time and then at some final time enables us to determine the average rate of the reaction during that interval.

The rate of any reaction depends on a number of factors, among which are concentration or pressure of reactants, temperature, presence of catalyst and nature of reactants. For instance, rate of reaction increases as the surface of the reactant is increased and this is why solid reactant reacts with less rate than powdered reactant.

Question

Using the data provided below

- Calculate the average rate over the first 50secs.
- Calculate the average rate over the first 100secs.

Time (s)	[Br ₂] (M)	Rate(M/s)	$k = \text{rate}(\text{s}^{-1})/[\text{Br}_2]$
0	0.012	4.2×10^{-5}	3.50×10^{-3}
50	0.0101	3.52×10^{-5}	3.49×10^{-3}
100	0.00846	2.96×10^{-5}	3.50×10^{-3}
150	0.00710	2.49×10^{-5}	3.51×10^{-3}
250	0.00500	1.75×10^{-5}	3.50×10^{-3}

- average rate over the first 50sec:
rate = $-(0.0101 - 0.012)/(50 - 0)$
rate = $1.9 \times 10^{-3}/50 = 3.8 \times 10^{-5}$ M/s
- calculate on your own following worked example in (i) above

Let us consider the effect the bromine concentration has on the rate of reaction. Looking at the data, the concentration at $t = 50$ s is double the concentration at $t = 250$ s and the rate of reaction at $t = 50$ sec is double the rate at $t = 250$ sec. Thus, as the concentration of bromine is doubled the rate of the reaction also doubles therefore, the rate of reaction is directly proportional to the bromine concentration

$$\text{rate} \propto [\text{Br}_2], \text{ thus } r = k [\text{Br}_2]$$

Where k is known as the rate constant

Because the rate of reaction has the unit of M/s and bromine concentration is in M, the unit of k is " s^{-1} ". It is important to note that k is not affected by bromine

concentration. To be sure, the rate is greater at a higher concentration and smaller at lower concentration of bromine, but the ratio of rate/[Br₂] remains the same provided the temperature does not change.

Reaction rate and Stoichiometry

We have seen that for stoichiometrically simple reactions of type A → B, the rate can either be expressed in terms of decrease in the reactant concentration or increase in product concentration. For more complex reactions, we must be careful in writing the rate expression.

Consider for example, 2A → B:

$$\text{Rate} = \frac{-1}{2} \frac{d[A]}{dt} = \frac{d[B]}{dt}$$

$$r = \frac{-1}{2} \times \frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$$

In general, for the reaction aA + bB → cC + dD . The rate is given by:

$$\text{rate} = \frac{-1}{a} \frac{\Delta[A]}{\Delta t} = \frac{-1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

Question

Find the rate expression for the following reaction in terms of disappearance and appearance of the product.

- 4NH₃(g) + 5O₂(g) → 4NO(g) + 6H₂O(g)
- CH₄(g) + ½ Br₂ (g) → CH₃Br(g) + HBr(g)

Answer:

$$\text{i. rate} = \frac{-1}{4} \frac{\Delta[\text{NH}_3]}{\Delta t} = \frac{-1}{5} \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{4} \frac{\Delta[\text{NO}]}{\Delta t} = \frac{1}{6} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

- calculate on your own, following the solved question in (i) above

Question: Consider the reaction: 4NO_{2(g)} + O_{2(g)} → 2N₂O_{5(g)}

Suppose that at a particular moment during the reaction molecular oxygen is reacting as the rate of 0.0024 Ms⁻¹

- At what rate is N₂O₅ being formed?
- At what rate is NO₂ reacting?

Answer:

a. $r = \frac{1}{2} \Delta [N_2O_5] / \Delta t$
 $0.0024 = \frac{1}{2} \Delta [N_2O_5] / \Delta t$
 $\Delta [N_2O_5] / \Delta t = 0.0024 \times 2$
 $\Delta [N_2O_5] / \Delta t = 0.0048 \text{ M/s}$

b. $r = -1/4 \Delta [NO_2] / \Delta t$
 $0.0024 = -1/4 \Delta [NO_2] / \Delta t$
 $\Delta [NO_2] / \Delta t = 4 \times 0.0024$
 $\Delta [NO_2] / \Delta t = -9.6 \times 10^{-3} \text{ M/s}$

RATE LAW OF FIRST ORDER REACTION

The rate of a first-reaction depends only on the concentration of one reactant, A.

A → products

By definition, rate = $-\Delta[A] / \Delta t$; **rate = $k[A]$**

Therefore, **$-\Delta[A] / \Delta t = k[A]$**

$d[A] / dt = -kt$ (Instantaneous rate of change described by calculus.)

$\ln([A] / [A_0]) = -kt$ (Calculus solution to the equation by integration)

$\ln[A] - \ln[A_0] = -kt$ or

$\ln[A_t] = -kt + \ln[A_0]$

$y = mx + c$

ALTERNATIVELY:

A → Product

Suppose at the beginning of a reaction time ($t = 0$), the concentration of A = a mol/L. If after time t , x mol of A has changed, the concentration of A is $a - x$.

We know that for a first order reaction, the rate of reaction (dx/dt) is directly proportional to the concentration of the reactant. Thus,

$$dx / dt = k(a-x)$$

$$dx / (a-x) = k dt \dots \dots \dots (1)$$

Integration of equation (1) gives $\int_0^x \frac{dx}{(a-x)} = \int_0^t k dt$

$$-\ln(a-x) + \ln a = kt \dots \dots \dots (ii)$$

$$k = 2.303/t \log (a/a-x)$$

$$k = 1/t \ln (a/a-x)$$

In terms of volume,

$$k = 2.303/t \log (V_0/V_0 - V_t)$$

Half-life of first order reaction

The half-life of a reaction is a useful parameter. The half-life of a first-order reaction is characteristic of the reaction and is **independent of the starting concentration of A** as proven in the equation below:

$$t = (1/k) \times \ln [A_0]/[A]$$

$$t_{1/2} = 1/k \times \ln (1/0.5)$$

$$t_{1/2} = (1/k) \times \ln 2 = (1/k) \times 0.693 = 0.693/k$$

$$t_{1/2} = 0.693/k$$

RATE LAW OF SECOND ORDER REACTION

Second order reactions in A can be easily described mathematically. (Note: Second order involving [A] and [B] reactants and third order reactions will not be covered here.

For second order reactions in A:

A → products

rate = $-\Delta[A]/\Delta t$, but now **rate = $k[A]^2$**

The graphable equation becomes: $1/[A] = 1/[A_0] + kt$

The half-life equation can be obtained by substituting $1/2[A_0] = [A]$

The half-life, $t_{1/2}$ then becomes, $t_{1/2} = (k[A_0])^{-1}$

This makes sense because a large rate constant leads to a faster reaction and short half-life. **In second order reactions, half-life does depend on the initial concentration of A** because a higher $[A_0]$ means more frequent collisions between A molecules

Calculations involving Rate law and order of reaction

Q1: For a reaction with $k = 5.50 \times 10^{-3} \text{ s}^{-1}$ at $45.0 \text{ }^\circ\text{C}$, what will be the concentration of A remaining after 12.0 min if the initial concentration of A is 0.200 M?

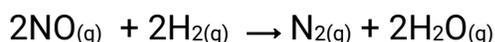
Answer: Since the unit of k (the reaction rate constant) is s^{-1} in the question, it shows that the reaction is a **first order**. The unit of k for a **second order** reaction is $M^{-1} s^{-1}$ (k is invariant when temperature is constant).

$$\ln[A] = -kt + \ln[A_0] = -5.50 \times 10^{-3} s^{-1} (12.0 \text{ min} \times 60 \text{ s}/1 \text{ min}) + \ln(0.200)$$

$$\ln[A] = -3.96 + (-1.61) = -5.57$$

$$[A] = 3.81 \times 10^{-3} \text{ M.}$$

Q2: The reaction of nitric oxide (NO) with hydrogen at 1280°C



From the following data collected at this temperature, determine (i) the rate law (ii) the rate constant (iii) the rate of the reaction when the concentration of NO = $12 \times 10^{-3} \text{ M}$ and concentration of H₂ = $6 \times 10^{-3} \text{ M}$

Experiment	[NO] (M)	[H ₂] (M)	Initial rate (M/s)
1	5×10^{-3}	2×10^{-3}	1.3×10^{-5}
2	10×10^{-3}	2×10^{-3}	5×10^{-5}
3	10×10^{-3}	4×10^{-3}	10×10^{-5}

Answer:

Generally, the rate law for the reaction is written as: $r = k[\text{NO}]^x[\text{H}_2]^y$

In Exp 1, $r = 1.3 \times 10^{-5}$, then

$$1.3 \times 10^{-5} = k(5 \times 10^{-3})^x (2 \times 10^{-3})^y \dots\dots(1)$$

In Exp 2, $r = 5 \times 10^{-5}$

$$5 \times 10^{-5} = k(10 \times 10^{-3})^x (2 \times 10^{-3})^y \dots\dots(2)$$

In Exp 3, $r = 10 \times 10^{-5}$

$$10 \times 10^{-5} = k(10 \times 10^{-3})^x (4 \times 10^{-3})^y \dots\dots(2)$$

Equation 2÷1 results:

$$\frac{5 \times 10^{-5}}{1.3 \times 10^{-5}} = \frac{k \times (10 \times 10^{-3})^x \times (2 \times 10^{-3})^y}{k \times (5 \times 10^{-3})^x \times (2 \times 10^{-3})^y}$$

$$3.85 = \frac{10^x}{5^x}$$

$$2^2 = 2^x$$

$$x = 2$$

Equation 3÷2 results:

$$\frac{10 \times 10^{-5}}{5 \times 10^{-5}} = \frac{k \times (10 \times 10^{-3})^x \times (4 \times 10^{-3})^y}{k \times (10 \times 10^{-3})^x \times (2 \times 10^{-3})^y}$$

$$2 = 2^y$$

$$y = 1$$

Hence, the rate law for the reaction is, $r = k[\text{NO}]^2[\text{H}_2]$

(ii) from equation 1,

$$1.3 \times 10^{-5} = k(5 \times 10^{-3})^2(2 \times 10^{-3})$$

$$k = \frac{1.3 \times 10^{-5}}{(5 \times 10^{-3})^2 \times (2 \times 10^{-3})}$$

$$k = 260 \text{ M}^{-2} \text{ s}^{-1}.$$

(iii) from the rate law, $r = k[\text{NO}]^2[\text{H}_2]$,

$$\text{When } [\text{NO}] = 12 \times 10^{-3} \text{ M and } [\text{H}_2] = 6 \times 10^{-3} \text{ M}$$

Then,

$$r = 260 (12 \times 10^{-3})^2(6 \times 10^{-3})$$

$$r = 2.25 \times 10^{-4} \text{ M s}^{-1}.$$

Q3: The reaction of $\text{S}_2\text{O}_8^{2-}$ with iodide is $\text{S}_2\text{O}_8^{2-}(\text{aq}) + 3\text{I}^-(\text{aq}) \rightarrow 2\text{SO}_4^{2-}(\text{aq}) + \text{I}_3(\text{aq})$

From the following data collected at a certain temperature determine the rate law

- the rate constant
- the order of reaction
- the rate of reaction when the initial concentration of $\text{S}_2\text{O}_8^{2-}$ and I are halved and doubled respectively
- Compare the rate of reaction I question (4) obtained in experiment (1)

Experiment	$[\text{S}_2\text{O}_8^{2-}] \text{ (M)}$	$[\text{I}^-] \text{ (M)}$	Initial rate (M/s)
1	0.08	0.034	2.2×10^{-4}
2	0.08	0.017	1.1×10^{-4}
3	0.16	0.017	2.2×10^{-4}

Summary of Kinetics of Zero order, first order and second order reactions

Order	Rate law	Conc.-time equation	Half-life ($t_{1/2}$)
0	rate = k	$[A]_t = -kt + [A]_o$	$t_{1/2} = [A]_o/2k$
1	rate = $k[A]$	$\ln[A]_t = -kt + \ln[A]_o$; OR $\ln([A]_t/[A]_o) = -kt$	$t_{1/2} = 0.693/k$
2	rate = $k[A]^2$	$1/[A]_t = kt + 1/[A]_o$	$t_{1/2} = (k[A]_o)^{-1}$

Q4: The conversion of cyclopropane to propene in the gas phase is a first order reaction with a rate constant of $6.7 \times 10^{-4} \text{ s}^{-1}$ at 500°C

- If the initial concentration of cyclopropane was 0.25 M, what is the concentration after 8.8 min?
- How long (in minutes) will it take the concentration of cyclopropane to decrease from 0.25 to 0.15 M
- How long (in mins) will it take to convert 74% of the starting material

Answer:

(a) Since the reaction is a first order and concentration-time dependent, the equation $\ln([A]_t/[A]_o) = -kt$ applies to solve the problem

$$[A]_t = ?$$

$$[A]_o = 0.25$$

$$k = 6.7 \times 10^{-4} \text{ s}^{-1}$$

$$t = 8.8 \text{ min} (= 528 \text{ s})$$

$$\ln(x/0.25) = -(6.7 \times 10^{-4} \times 528)$$

$$(x/0.25) = e^{-0.3538}$$

$$x = 0.176 \text{ M}$$

(b) $\ln([A]_t/[A]_o) = -kt$ which is the same as $\ln[A]_t - \ln[A]_o = -kt$

$$\ln 0.15 - \ln 0.25 = -(6.7 \times 10^{-4})t$$

$$-0.5108 = -(6.7 \times 10^{-4})t$$

$$t = 762.4 \text{ s (or 12.7 min)}$$

(c) If at time t , 74% of the starting material is converted, then what remains as $[A]_t$ is 26% of 0.25 M

$$\text{Hence, } [A]_t = 0.065 \text{ M}$$

$$\ln[A]_t - \ln[A]_0 = -kt$$

$$\ln 0.065 - \ln 0.25 = -(6.7 \times 10^{-4})t$$

$$-1.347 = -(6.7 \times 10^{-4})t$$

$$t = 33.5 \text{ min.}$$

ACTIVATION ENERGY AND TEMPERATURE DEPENDENCE OF RATE CONSTANTS

The Collision Theory of Chemical Kinetics

A reaction between two particles can occur only if they collide (usually in a gas or liquid phase). Therefore, a reaction rate is proportional to the rate of collision or the number of collisions per second.

The percentage of successful collisions in chemical systems varies greatly. In some systems, almost every collision results in chemical change; i.e., **instantaneous reaction**. In other systems, collisions rarely produce chemical change; i.e., a **slow reaction**. Therefore, the reaction rate is not the same as the collision rate but is often directly proportional to it. ***Chemical reactions occur when the energy of collision is enough to break reactant bands and form product bonds.*** If there is not enough kinetic energy in colliding species, reactant bonds will not break and new, product bonds will not form.

It stands to reason that higher temperatures (which increase the frequency of collisions and increase the energy of collisions) will increase all or most reaction rates.

The kinetic energy of the colliding particles must equal or exceed a certain minimum value in order for a reaction to proceed. ***This minimum energy is called the Activation Energy, E_a .*** If a collision has enough energy to break some reactant bonds, an ***Activated Complex*** may form. This is an intermediate state, higher in energy than the reactants that may lead to products or may lead back to the original reactants. The products that form may be lower in energy than the reactants (***exergonic or exothermic reaction***) or may be higher in energy than the reactants (***endergonic or endothermic reaction***)

The Arrhenius Equation

The Arrhenius Equation relates the rate constant k to the E_a (activation energy, J/mol or kJ/mol), R (the gas law constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T (the absolute temperature,

K):

$k = Ae^{-E_a/RT}$, **A** is not the reactant species, but a dimensionless constant (Arrhenius constant) called the collision frequency or frequency factor.

The rate of reaction doubles for every 10K rise in temperature. The relationship between temperature and rate constant is given by Arrhenius equation which is expressed as:

To adapt the equation to graphing, take the natural log of both sides. The equation becomes:

$$\ln k = \ln A - E_a/RT$$

or

$$\ln k = (-E_a/R)(1/T) + \ln A$$

The equation corresponds to $y = mx + c$. Thus, a graph of $\ln k$ against $1/T$ is linear; where m (the slope, -ve) = E_a/R and $\ln A$ = intercept of the graph.

Calculations involving use of Arrhenius Equation

For using the Arrhenius Equation algebraically to compare rate constant value at different temperatures, write two equations for different temperatures and therefore different k values.

$$\ln k_1 = \ln A - E_a/RT_1 \text{ and } \ln k_2 = \ln A - E_a/RT_2$$

$$\ln k_1 - \ln k_2 = -E_a/RT_1 + E_a/RT_2$$

$$\ln(k_1/k_2) = E_a/R(1/T_2 - 1/T_1) \text{ useful for solving for } T_1 \text{ or } T_2$$

Question: The rate constant for a first-order reaction is $4.5 \times 10^{-4} \text{ s}^{-1}$ at 25°C . What is its rate constant at 50°C if the activation energy is 35.6 kJ/mol ?

Answer: Note that the collision frequency **A**, being the same, has cancelled out of the equation.

$$T_1 = (25 + 273.2) \text{ K} = 298.2 \text{ K}, \text{ and } T_2 = (50 + 273.2) \text{ K} = 323.2 \text{ K}.$$

$$E_a = 35.6 \text{ kJ/mol which after conversion is } 35600 \text{ J mol}^{-1}, \text{ since } R \text{ is } 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\text{Using } \ln k_1 - \ln k_2 = -E_a/RT_1 + E_a/RT_2$$

$$\ln k_1 + E_a/RT_1 - E_a/RT_2 = \ln k_2; \quad \ln k_2 = \ln k_1 + E_a/R\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln k_2 = -7.71 \text{ s}^{-1} + 4281.93 \text{ K} (2.597 \times 10^{-4} \text{ K}^{-1})$$

$$\ln k_2 = -6.60, k_2 = 1.36 \times 10^{-3} \text{ s}^{-1}.$$

Further Reading

- Carey F. A. and Giuliano R. M. (2014) Organic Chemistry, 9th edn. McGraw-Hill Education, New York.
- Bahl A, Bahl B.S and Tull G.D (2012). Essentials of Physical Chemistry, S. Chand & Company LTD, 2012 Edition, New- Delhi.