

RATE OF REACTION IN TERMS OF EXTENT (ξ) OR ADVANCEMENT OF THE REACTION

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ABSTRACT

The aim of this work was to illustrate the rate of a chemical reaction in terms of advancement or extent of reaction, denoted as ξ . We applied theoretical mathematical treatments to hypothetical chemical reaction via decay of reactants. A more consistent and succinct definition of the rate of a given reaction has been observed to be given in terms of advancement or extent ξ of the reaction. This method of simplification of the kinetics of reaction rates is hereby presented for enhancement of the study of chemical kinetics.

INTRODUCTION

The subject of chemical kinetics is involved with the problem of how, and what rate, a system not initially in equilibrium may change so as to attain equilibrium. Chemical kinetics is intimately connected with the three variables: time, concentration, and temperature.

Experimentally, when we study the rate of conversion of one substance into another, we often find that this rate depends on the concentration of the reactants. Different reactions show different concentration dependence, and this allows us to learn about the mechanism of a reaction. The term “mechanism” therefore connotes the statement of all the elementary steps which constitute the statement of the mechanism of the reaction. It answers the question of how a reaction occurs [1-5].

Measurement of Reaction Rate

The rate of a reaction can be broadly defined as the rate of change of the concentration of any of the species in the reaction mixture. Thus, it is the rate of formation of the products or the rate of disappearance of the reactants. Kinetic studies of reactions are generally carried out at constant temperatures. A reaction mixture of known composition is prepared and thermostated (kept at constant temperature); and the decrease in the concentration of the reacting substance or the appearance of the reaction products, is measured as a function of time by some suitable means. From such concentration – time data the kinetic behavior of the process can be deduced with the aid of certain principles which will be discussed in the latter publications.

Also, the dependence of the rate on temperature is obtained by repeating this procedure at a number of suitable different temperatures. The

simplest and obvious way of following concentration changes occurring in a reaction is to remove samples (aliquots) from the system at various time intervals, stop (quench) the samples to determine the concentration of either a reactant or a product [1-5].

At times, if at all possible, chemists prefer to follow the concentration changes in a reacting system by employing some physical property which changes with time, and from which the requisite concentration can be deduced. In gaseous reaction involving volume changes, the property most commonly observed is the variation in pressure at constant volume, or the changes in volume at constant pressure. This latter method can also be used in liquid system and is called dilatometry. Other physical methods which have been used under suitable conditions include: Conductivity; Colorimetry (absorbance); reflective index variation; polarography; mass spectrometry; gas evolution; magnetic susceptibility and polarimetry (optically active species).

The Rate of Reaction (R)

The rate of reaction is best expressed in collaboration with mathematical illustrations.

The rate of reaction (R) is the velocity or speed by which a reaction proceeds. It is the rate of disappearance of a reactant or appearance of a product of a given reaction. The rate of reaction can therefore be expressed as the rate of change of the concentration of any of the species in a given reaction system.

Consider a hypothetical reaction of interest in the form:



The concentrations of A, B and P are represented by [A], [B] and [P] respectively. The rate of formation of product P is $\frac{d[P]}{dt}$ and the rate of disappearance of A is $-\frac{d[A]}{dt}$. And in this case, the rate of reaction can be expressed as

$$\text{Rate} = \frac{d[P]}{dt} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} \quad (2)$$

This is so, because B molecules must be consumed for every A molecule consumed, and in the process a P molecule is formed. These can be depicted diagrammatically as shown in Fig. 1.

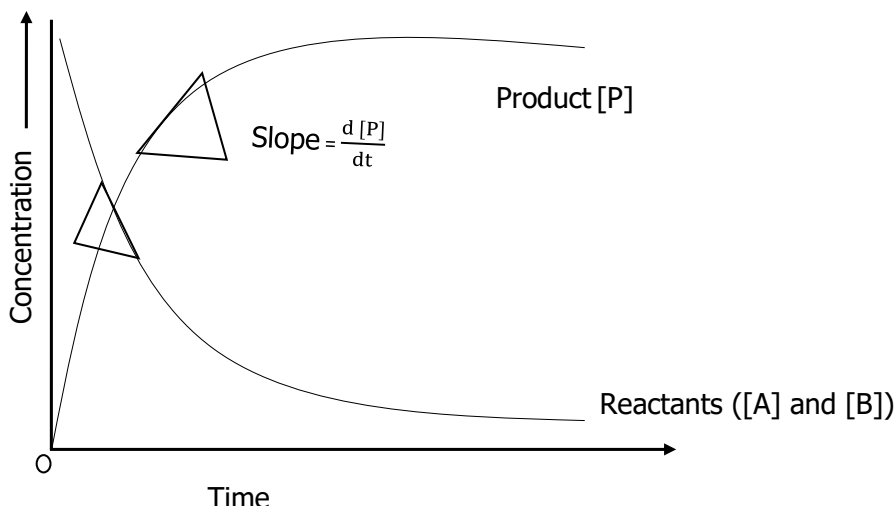


Figure 1: Rate of concentration with time

This simple situation is complicated when the coefficients of the reactants or products are not unity. For instance, a reaction in which



the situation is less clear cut.

In this case, the concentration of B changes at twice the rate of change of the concentration of A, while the concentration of C increases at three times the rate of decrease of A.

The rate expression would be

$$\frac{d[D]}{dt} = \frac{1}{3} \frac{d[C]}{dt} = -\frac{1}{2} \frac{d[B]}{dt} = -\frac{d[A]}{dt} \quad (4)$$

Therefore, to avoid any ambiguity, it is advisable to state the rate of any reaction in conjunction with the concentration of any species in the reaction. A more consistent and succinct definition of the rate of a given reaction can be given in terms of the advancement ξ , of the reaction. That is,

$$-\delta[A] = -\delta\xi; \quad -\delta[B] = -2\delta\xi; \quad -\delta[C] = 3\delta\xi \quad \text{and} \quad -\delta[D] = \delta\xi$$

$$\text{Rate} = \frac{d\xi}{dt} = \frac{\text{change in advancement of reaction}}{\text{change in time}}$$

The rate of change in advancement is known as true rate and it is denoted by

$$\frac{d\xi}{dt} = \text{True Rate}$$

Rate of Reaction in Terms of Advancement, ξ

Consider the reaction:



Let the given reaction proceed by change in advancement, $\delta\xi$. By inspection, the concentration of B decreases twice the concentration of the appearance of D and the concentration of C increases three times that of the decrease in concentration of A.

The various changes in the concentration of the species can be expressed as follows:

A precise interpretation of the rate in terms of advancement requires the above reaction to be written in the form of a simple equation as follows:



Subtracting A and 2B from both sides we obtain:

$$0 = -A - 2B + 3C + D \quad (7)$$

Generally,

$$0 = v_A A + v_B B + v_C C + v_D D + \dots (8)$$

where the coefficients v_X in equation (8) are positive for products and negative for reactants. For instance, in equation (6), $v_A = -1$, $v_B = -2$, $v_C = 3$ and $v_D = 1$ for the reaction. The change in concentration of A in (6) is $v_A \delta\xi$ and is denoted by

$$-\delta[A] = v_A \delta\xi = -\delta\xi$$

where v_A is -1 .

The rate of change of concentration of A is $\frac{-d[A]}{dt}$ and it is denoted by

$$\frac{-d[A]}{dt} = v_A \frac{d\xi}{dt} = v_A \times (\text{True Rate}) = \frac{-d\xi}{dt}$$

Similarly,

$$\frac{-d[B]}{dt} = v_B \frac{d\xi}{dt} = -2 \frac{d\xi}{dt}$$

$$\frac{d[C]}{dt} = v_C \frac{d\xi}{dt} = 3 \frac{d\xi}{dt}$$

$$\frac{d[D]}{dt} = v_D \frac{d\xi}{dt} = \frac{d\xi}{dt}$$

Worked Example

For a certain reaction, the advancement data presented in Table 1 below were obtained. Determine the rate of reaction following advancement for A, B, C, and D.



Table 1: Advancement data for a certain reaction

ξ (mold m ⁻³)	12.1	10.3	8.0	6.2	4.1	2.0	0
t (seconds)	0	5	10	15	20	25	30

Interpretation

Observe that the given kinetic data is for a reaction since the concentration or advancement decreases gradually.



$$0 = -2A - 4B + C + 3D$$

$$v_A = -2, v_B = -4, v_C = 1 \text{ and } v_D = 3$$

True Rate:

$$\frac{d\xi}{dt} = \frac{\xi_2 - \xi_1}{t_2 - t_1} = \frac{0 - 12.1}{30 - 0} = -\frac{12.1}{30}$$

$$= -0.4 \text{ mol dm}^{-3} \text{ s}^{-1} \text{ for reactants}$$

$$= +0.4 \text{ mol dm}^{-3} \text{ s}^{-1} \text{ for products.}$$

$$\frac{-d[A]}{dt} = v_A \frac{d\xi}{dt} =$$

$$-2 \times (-0.4) = 0.8 \text{ mol dm}^{-3} \text{ sec}^{-1}$$

$$\frac{-d[B]}{dt} = v_B \frac{d\xi}{dt} =$$

$$-4 \times (-0.4) = 1.6 \text{ mol dm}^{-3} \text{ sec}^{-1}$$

$$\frac{d[C]}{dt} = v_C \frac{d\xi}{dt} = 1 \times 0.4 = 0.4 \text{ mol dm}^{-3} \text{ sec}^{-1}$$

$$\frac{d[D]}{dt} = v_D \frac{d\xi}{dt} = 3 \times 0.4 = 1.2 \text{ mol dm}^{-3} \text{ sec}^{-1}$$

Following equation (3) and (4), it can be shown that the rate for equation (9) is given by

$$\text{Rate} = -\frac{1}{2} \frac{d[A]}{dt} = -\frac{1}{4} \frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{1}{3} \frac{d[D]}{dt}$$

Dividing the rate of advancement by their appropriate stoichiometric coefficients, we have

$$-\frac{1}{2} \frac{d[A]}{dt} = \frac{0.8}{2} = 0.4 \text{ mol dm}^{-3} \text{ sec}^{-1},$$

$$-\frac{1}{4} \frac{d[B]}{dt} = \frac{1.6}{4} = 0.4 \text{ mol dm}^{-3} \text{ sec}^{-1};$$

$$\frac{d[C]}{dt} = \frac{0.4}{1} = 0.4 \text{ mol dm}^{-3} \text{ sec}^{-1},$$

$$\text{and } -\frac{1}{3} \frac{d[D]}{dt} = \frac{1.2}{3} = 0.4 \text{ mol dm}^{-3} \text{ sec}^{-1}.$$

Note that the true rate can be obtained from the slope of a plot of advancement of the reaction versus time t , since slope = $\frac{d\xi}{dt}$.

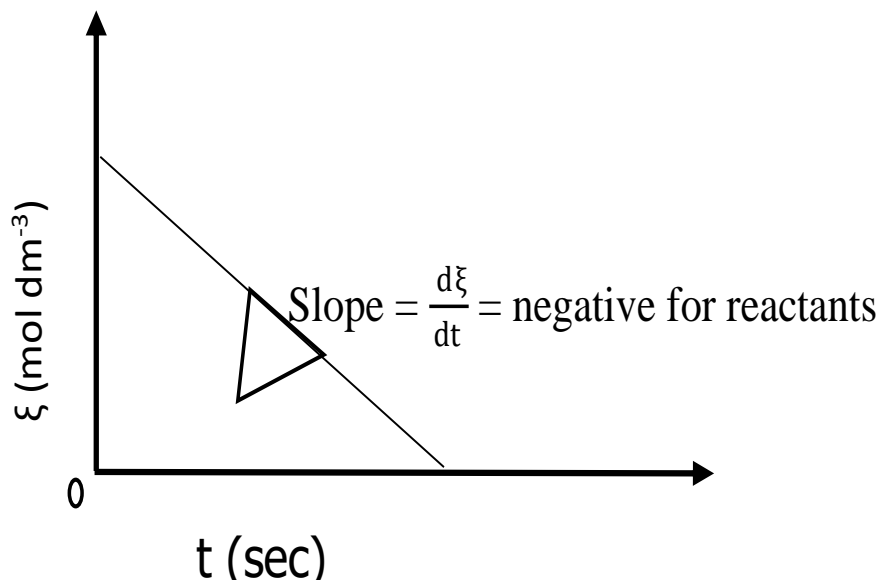


Figure 2: True rate as slope of advancement against time

CONCLUSION

The aim of this research was to illustrate the rate of a chemical reaction in terms of advancement or extent of reaction, ξ , which is very rare to be obtained in most physical chemistry literatures. The illustration shows clearly why reactants are decreasing and as a result, products are increasing. The work also explains the equality of the rate equation in terms of the stoichiometry of the reaction.

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REFERENCES

1. Ekop, A. S. (2005) Basic Principles in Chemical Kinetics. Lisjohnson Resource Publishers, Lagos, Nigeria.
2. Roselaar, L. C. (1975) Systematic Physical Chemistry. John Murray Publishing Company, London.
3. Moore, W. J. (1972) Physical Chemistry. Group Limited, London.
4. Moron, S.H; and Lando, J. E. (1974). *Fundamentals of Physical Chemistry*. Macmillan Publishing Company Inc., USA.
5. Mortimer, R. G. (2008) Physical Chemistry. Elsevier Academic Press, Burlington MA, USA.