

by two Swedish scientists, Guldberg and Waage. Their generalization, variously known as the *mass law*, *law of mass action*, and *law of concentration effect*, may be stated thus: *The rate of a chemical reaction is directly proportional to the mass of each reactant (raised to an exponent equal to the number of molecules of the reactant).*

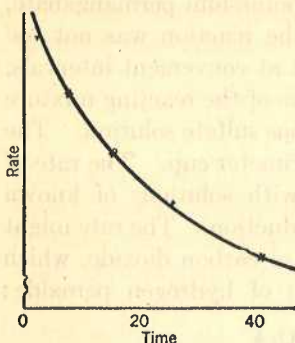


Fig. 33. Change of Reaction Rate with Time (Diminishing Concentration).

In consequence of this effect the rate of a reaction usually diminishes progressively as the reaction goes on and the mass, or concentration, of each reactant becomes less. This is not true, however, if a catalyst is formed during the course of the reaction. In this case the reaction is said to be *autocatalytic*, and its velocity increases. Thus, the reduction of permanganates by oxalic acid is catalyzed by the resulting manganous salt. Also, the rusting of iron is catalyzed by the iron rust formed in the process. The general effect of

changing concentration is illustrated by the decomposition of hydrogen peroxide in the presence of a catalyst for which data are shown in Table 42 and plotted in Figure 33. The concentration of hydrogen peroxide is expressed in terms of the number of ml. of a standard potassium permanganate solution with which a given volume of the hydrogen peroxide solution will react.

The effect of varying concentration upon reaction rate may be demonstrated clearly by the following experiments: If to several

TABLE 42

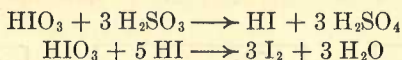
CHANGE OF RATE OF REACTION WITH CONCENTRATION¹

| TIME (MINUTES) | H ₂ O ₂ REMAINING (ML. KMnO ₄) | H ₂ O ₂ CHANGED (ML. KMnO ₄) | RATE OF CHANGE (ML. KMnO ₄ /MIN.) |
|-------------------|---|---|---|
| 0 | 46.1 | 0.0 | |
| 5 | 37.1 | 9.0 | 1.80 |
| 10 | 29.8 | 16.3 | 1.46 |
| 20 | 19.6 | 26.5 | 1.02 |
| 30 | 12.3 | 33.8 | 0.73 |
| 50 | 5.0 | 41.1 | 0.37 |

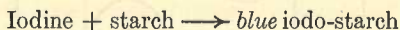
¹ Data from Bell and Gross, *Elements of Physical Chemistry*, New York, Longmans, Green & Co., 1929, p. 254.

solutions of equal total volumes but containing various measured volumes of a solution of sodium thiosulfate be added equal volumes of a solution of dilute hydrochloric acid, the time elapsing before the precipitate of sulfur becomes visible will be shorter the greater the concentration of the thiosulfate solution.

Another experiment giving particularly spectacular results is based upon the reaction between sulfurous acid and iodic acid.¹ Two consecutive reactions take place :



And if starch also is added to the reacting mixture :



Apparently the second reaction does not take place to an appreciable extent until the first reaction has gone to completion, *i.e.*, until all of the sulfurous acid has been oxidized by the iodic acid. The moment this change has been completed and iodine has begun to form by the second reaction, the color of the iodo-starch makes its appearance and the solution instantly turns blue. This can happen only if the iodic acid is in excess over the amount equivalent to the sulfurous acid present. The time elapsing, then, between the mixing of the two reacting solutions and the appearance of the blue color is a measure of the rate of the first reaction, the oxidation of the sulfurous acid by the iodic acid. By using equal amounts of prepared solutions of the two acids and varying the quantity of water added, *i.e.*, the concentration of each reagent, striking results may be obtained.

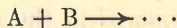
The law of concentration effect may readily be put into mathematical form. In a reaction of the type :



in which from this point of view we are not concerned with the products, the rate of the reaction is proportional to the concentrations of A, *i.e.*,

$$\text{rate} = k_1 [\text{A}]$$

For a reaction of the type :



¹ Detailed directions are given on p. 48 of H. S. Van Klooster, *Lecture Experiments in Physical Chemistry*, New York, The Chemical Publishing Co., 1919.

since $\text{rate} = k_1[A]$ when $[B]$ is constant
 and $\text{rate} = k_2[B]$ when $[A]$ is constant
 it follows that : $\text{rate} = k[A][B]$

when both $[A]$ and $[B]$ may vary.

We may visualize the process from the following considerations :
 Suppose we choose a small volume of the reacting mixture which contains 1 molecule each of A and B (the concentrations are here assumed equal).

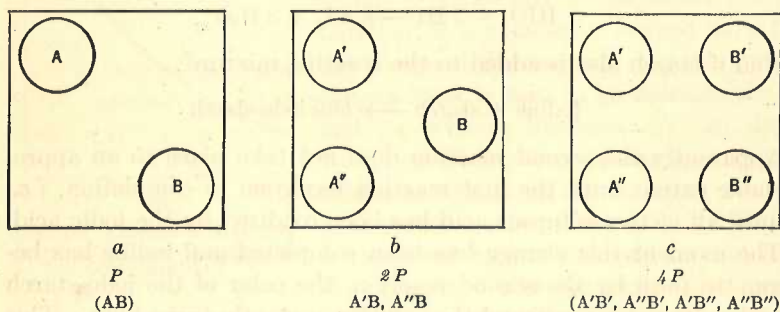
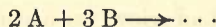


Fig. 34. A Kinetic Interpretation of Reaction Velocity.

In this case (Figure 34 *a*) there will be a certain probability (P) of the two molecules colliding and reacting. If now we double the concentration of A while keeping that of B constant (Figure 34 *b*), we shall have *two* A and *one* B in our small volume. The probability of collision will now be doubled ($2P$), for *either* A' or A'', combining with B, may form the product AB.¹ If we double the concentration of B also (Figure 34 *c*), we shall *quadruple* the probability of collision ($4P$), for either A' or A'' can combine with B' or B'' (forming A'B', A''B', A'B'', A''B''). For a reaction of a more complex type, such as :



the rate at any given time is given by the equation :

$$R = k[A]^2[B]^3$$

If there are *two* molecules of a substance indicated by the equation, its concentration is *squared* in the reaction rate expression ;

¹ A' and A'' are both molecules of reactant A, B' and B'' molecules of reactant B. Different individual molecules are designated, not different substances.

if *three*, the concentration is *cubed*. In general, if there are n molecules of a reactant involved, its concentration is raised to the n th power.

The constant that appears in any such expression for the rate of a reaction is called the *velocity constant*, for which we use the symbol K_v . The value of this constant depends upon the particular *reaction* and the particular *temperature* at which it is studied.¹

The real physical significance of the velocity constant is easily seen from an inspection of the rate equation for any particular reaction, e.g.:

$$R = K_v[A]$$

If $[A] = 1$, $R = K_v$. That is, K_v is the rate of the reaction in gram molecules per unit time when 1 gram molecule is reacting. This same significance attaches to the velocity constant, K_v , regardless of the complexity of the reaction.

(2) *Influence of temperature change.* If the same substances at the same concentrations are allowed to react at different temperatures, the rates are found to be quite different. The change of temperature therefore has a marked influence upon the specific rate constant, K_v . This may be shown experimentally in the case of the reaction between sodium thiosulfate and hydrochloric acid and the reduction of potassium permanganate by oxalic acid in the presence of sulfuric acid. In both these cases, a higher temperature causes the reaction to take place more rapidly. This is true for practically all reactions; in nearly every case the reaction is greatly accelerated by rise in temperature.

Different reactions are affected to a different degree by an increase in temperature. Thus, methyl acetate is hydrolyzed by sodium hydroxide 1.82 times as rapidly at 35° C. as at 25° C., while cane sugar (sucrose) is hydrolyzed by hydrochloric acid 4.13 times as rapidly at 35° C. as at 25° C. These figures are given by Rice and Urey,² who conclude: "These two examples represent the normal limits of the variation, and it is only very rarely that a homogeneous thermal reaction has a temperature coefficient greater than that obtaining in the hydrolysis of cane sugar or less than that in the corresponding reaction with methyl acetate."

As an *average* value it is convenient to remember that a *rise of*

¹ We shall see in the next section how K_v changes with temperature.

² Taylor, *A Treatise on Physical Chemistry*, II, 970. Second edition. New York, D. Van Nostrand Co., 1931.