

[CONTRIBUTION FROM THE COBB MEMORIAL LABORATORY, UNIVERSITY OF VIRGINIA,
No. 77]

THE KINETICS OF GAS REACTIONS AT CONSTANT PRESSURE

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RECEIVED JUNE 8, 1931

PUBLISHED AUGUST 5, 1931

The classical equations of reaction kinetics, relating the velocity of reaction to the concentrations of the reacting substances, were originally developed to describe the behavior of reactions occurring in liquid systems. In such systems the volume remains approximately constant. In the hands of van't Hoff, Bodenstein and others, the same equations were found to be applicable to gaseous reactions occurring at constant volume. In this period the kinetics of gas reactions were almost invariably studied by the so-called "static" method, in which the volume is maintained constant, and the progress of reaction is followed by noting the change in pressure.

In recent years there has been an increasing tendency to employ the flow method, which consists in streaming the gases through the reaction space, and determining the extent of reaction by analysis of the exit gases. This method differs essentially from the static method in that the reaction takes place at constant pressure. Nevertheless, it has been a common practice to apply to results obtained by this method the kinetic equations which hold for reactions at constant volume.

It is the object of the present paper to point out that kinetic equations for reactions at constant volume are not necessarily applicable to reactions at constant pressure, and to indicate how the latter are to be correctly treated.

Homogeneous, Unimolecular Gas Reactions.—Reactions of the first order are defined in two different ways, either (1) as those in which a constant fraction of the material reacts in unit time, or (2) as those in which the rate of change of concentration is proportional to the concentration of reacting substance. Accordingly, if n_A , n_B denote the number of moles of substances A and B , respectively, present in volume V , and c_A , c_B their respective concentrations, the rate of the reaction, $A \rightarrow \nu B$, could be expressed in either of the following ways

$$-\frac{dn_A}{dt} = k_1 n_A \quad (1)$$

$$-\frac{dc_A}{dt} = k_2 c_A = k_2 n_A / V \quad (2)$$

If the reaction is carried out at constant volume, $dc_A (= d(n_A/V)) = (1/V)dn_A$, and the two expressions are equivalent. For reactions conducted at constant pressure, however, the volume does not remain constant (except in the special case where $\nu = 1$). Under this condition, therefore, Equations 1 and 2 are not equivalent. The difference between them can best be seen in their integrated forms

$$k_1 t = \ln n'_A/n_A \quad (1a)$$

$$k_2 t = \ln c'_A/c_A = \ln \frac{n'_A}{n_A} \cdot \frac{V}{V'} \quad (2a)$$

where the primes represent the conditions at zero time. If the gas consists of pure *A* at the start, V/V' varies from unity at $t = 0$, to ν at $t = \infty$. From this it can readily be shown that $k_2 = \nu k_1$ at $t = 0$, while at $t = \infty$, $k_2 = k_1$. Hence if either k_1 or k_2 is actually constant, the other will vary by a factor of ν during the course of the reaction.

While it is clear that these equations can not both be correct, they have been employed indiscriminately in the literature. Thus, for example, of three recent papers by different authors dealing with the homogeneous, unimolecular decomposition of hydrocarbons at constant pressure, one employs rate constants calculated by means of Equation 1 and two by means of Equation 2.

The generally accepted theory of homogeneous, unimolecular reactions leaves no doubt that Equation 1 rather than Equation 2 is the correct form. Of the total number of molecules of reactant, n_A , a given fraction are in the necessary activated state, and of this fraction a further fraction suffers reaction in unit time independent of the concentration.¹

Homogeneous, Unimolecular Reactions in Flow Systems.—There are two methods by which reactions may be carried out at constant pressure, (1) the "flow" method, and (2) a method involving a closed system of variable volume. Equation 1a, obtained by direct integration of Equation 1, is obviously in suitable form for application to Method 2. On the other hand, its utility in the flow method is limited by the fact that the "time of contact" is not a directly measurable quantity. If the rate of flow of the entering gases is maintained constant, the time of contact t depends on the extent to which the volume changes during the progress of the reaction.

Let the volume of the reaction space be V_b , and let V' represent the volume of gas, at the temperature and pressure of the reaction space, entering per unit time. If there were no change in volume due to the reaction, the time of contact would be simply V_b/V' . However, in the reaction $A \rightarrow \nu B$, the volume changes from $V' = (RT/P)n'_A$ to $V = (RT/P)(n_A + n_B) = (RT/P)(\nu n'_A - [\nu - 1]n_A) = V'(\nu - [\nu - 1]n_A/n'_A)$, where n'_A is the number of moles of *A* entering the reaction space per second, and n_A is the number passing any given point per second. If, under these conditions, we treat V_b as a variable, we may write

$$\frac{dV_b}{dt} = V = V'(\nu - [\nu - 1]n_A/n'_A)$$

Substitution of dt from this equation in Equation 1 gives

¹ Equation 1 probably applies strictly only to an ideal gas. In real gases it would seem that the fraction of the molecules in an activated state cannot be independent of the concentration, and it is further possible that the fraction of the activated molecules which decompose in unit time may also depend to some extent on concentration.

$$-V' \left(\nu - [\nu - 1] \frac{n_A}{n_A'} \right) dn_A = k_1 n_A dV_b$$

On integration,

$$k_1 V_b / V' = \nu \ln \frac{n_A'}{n_A} - (\nu - 1) \left(1 - \frac{n_A}{n_A'} \right)$$

where V_b is the volume of the whole reaction space, out of which n_A moles of A issues per second. If F represents the fraction of A which reacts, then

$$k_1 V_b / V' = \nu \ln \frac{1}{1 - F} - (\nu - 1)F \quad (3)$$

In treating reactions in flow systems it has been the common practice hitherto to calculate the time of contact as the ratio of the volume of the reaction space to the average of the entering and exit rates of flow.² While this procedure gives a fair approximation when the fractional conversion is not too great, the simplicity and exactness of Equation 3 would seem to make approximations needless.

First Order, Catalyzed Reactions.—When we turn to first order gas reactions which are catalyzed by a solid surface, we find that when the volume varies neither Equation 1 nor Equation 2 is correct. This fact will be apparent from the following derivation.

We may assume that the reaction is of the first order either because (1) the velocity is determined by the rate of collision of (activated) molecules of reactant with the surface, or because (2) a small portion of the surface is occupied by adsorbed molecules, a given fraction of which are transformed in unit time. In Case (1) the rate of reaction, that is, the number of moles of reactant disappearing in unit time, is a given fraction of the number colliding with the surface, and this in turn is equal to $(v/4)Sc_A$, where S is the surface area, v is the average velocity of the molecules, and c_A is their concentration. Thus, at a given temperature

$$-\frac{dn_A}{dt} = k_3 \cdot \frac{v}{4} Sc_A = k_3 n_A / V \quad (4)$$

It may be noted that this equation is dimensionally correct, since k_3 is dimensionless and both sides reduce to number per unit time.

In Case (2) the rate is proportional to the amount of gas adsorbed, and the latter is also determined by S and the concentration in the gas phase. Thus for small adsorption the result is the same as for Case (1). The principle is, of course, the same whether the adsorption is small or large, but in the latter event the order of reaction will differ from the first, and we should have to write

$$-\frac{dn_A}{dt} = k'S \frac{c_A}{1 + ac_A}$$

where a is the constant of the Langmuir adsorption equation.*

² Pease [THIS JOURNAL, 51, 3470 (1929)] has, however, already elaborated the proper treatment of time of contact, and has applied it to the bimolecular polymerization of acetylene.

To integrate Equation 4 it is necessary to express V as a function of n_A . Let us assume that the reaction is $A \rightarrow \nu B$, and that the gas entering the reaction space per second occupies the volume V' , and is composed of n'_A moles of A and no B . Then, as before, $V = V'(\nu - [\nu - 1]n_A/n'_A)$ and $dt = (1/V)dV_b$, where V_b now represents the free space in the reaction tube not occupied by the catalyst. With these values of dt and V substituted in Equation 4, integration gives

$$\frac{kSY_b}{V'^2} = \nu^2 \ln \frac{n'_A}{n_A} - 2\nu(\nu - 1) \left(1 - \frac{n_A}{n'_A}\right) + \frac{(\nu - 1)^2}{2} \left(1 - \frac{n_A^2}{n'^2_A}\right)$$

Because of the somewhat complex nature of this exact expression, it is often preferable in practice to substitute an approximate equation previously suggested,³ which may be written in the form

$$-\frac{\Delta n_A}{\Delta t} = kS\bar{c}_A$$

where \bar{c}_A is the average concentration of A in the entering and exit gases, and Δt is V_b divided by the average rate of flow. This equation necessarily fails at high percentage conversions, but ordinarily involves only a negligible error for conversions up to at least 50%.

Bimolecular Reactions.—The treatment of homogeneous, bimolecular gas reactions at constant pressure is complicated to some extent because of the fact that the rate of collision in a gas whose volume is changing does not appear to have been studied. The correct form of velocity equation may readily be obtained, however, by considering a homogeneous, reversible reaction which is unimolecular in one direction and bimolecular in the other. Thus, in the reaction $A \rightleftharpoons 2B$, the rate to the right is

$$-\frac{dn_A}{dt} = k_1 n_A$$

If we assume that the rate to the left is given by the expression

$$\frac{dn_A}{dt} = k_2 V c_B^2 \quad (5)$$

then, at equilibrium where the two rates are equal

$$k_1 n_A = k_2 V c_B^2, \text{ or } c_B^2/c_A = k_1/k_2 = K$$

where K is the equilibrium constant. Since, as may readily be shown, the usual ways of writing the bimolecular velocity equation do not give this necessary result, it may be assumed that Equation 5 is correct.

In the case of a catalyzed, bimolecular reaction, it may be shown by reasoning exactly analogous to that used in the corresponding unimolecular case that Equation 5 has the proper form. The equation can readily be applied by expressing n_A , V and dt in terms of n_B , V_b and the initial conditions, followed by integration. In practice, however, if the percentage conversion is not too great, it will usually be sufficient to employ the approximation

³ Benton, *Ind. Eng. Chem.*, 19, 494 (1927).

$$\frac{\Delta n_A}{\Delta t} = k_2 \bar{V} \bar{c}_B^2$$

where \bar{V} and \bar{c}_B are the average volume and the average concentration of B , based on the entering and exit gases.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

ELECTRIC MOMENT AND MOLECULAR STRUCTURE. V. THE POLYMETHYLENE BROMIDES

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RECEIVED JUNE 10, 1931

PUBLISHED AUGUST 5, 1931

These measurements upon compounds containing two dipoles separated by a carbon chain of varying length were undertaken with the object of studying the effect of the carbon chain upon the positions of the dipoles relative to one another and thus of extending our knowledge of the shape and behavior of the chain. The bromide doublets were used as being simple dipoles obtainable in compounds with chains of different length. Subsequent measurements have been made upon the diethyl esters of dicarboxylic acids¹ and upon the glycols,² in both of which classes of compounds the dipoles are more complex.

Apparatus

The dielectric constants of the solutions of the substances under investigation have been measured with a capacity bridge, part of which was presented by the Bell Telephone Laboratories. This part consisted of two fixed resistance arms with small adjustable resistances and capacities for balancing small inequalities and shielded in-put and out-put transformers, the whole mounted in a case with the parts carefully shielded. The other two arms of the bridge consisted of two condensers with series resistances as used previously in this Laboratory.³ The source of current was a Western Electric Company variable oscillator, which was operated at a frequency of 50,000 cycles in these measurements. The balance of the bridge was obtained by passing the current through a six-tube amplifier with a detector and a multimeter, adjustable to read microamperes, as null instrument. The condenser in which the liquid was measured consisted of concentric gold-plated cylinders fitting closely into a small glass vessel similar to that used in earlier measurements.⁴ The densities of the liquids were determined with a pycnometer of the type previously employed⁵ and

¹ Smyth and Walls, *THIS JOURNAL*, **53**, 527 (1931).

² Smyth and Walls, *ibid.*, **53**, 2115 (1931).

³ Smyth, Morgan and Boyce, *ibid.*, **50**, 1536 (1928).

⁴ Smyth and Stoops, *ibid.*, **51**, 3312 (1929).

⁵ Smyth and Morgan, *ibid.*, **50**, 1547 (1928).