volume change; optical methods such as polarimetry, refractometry, colorimetry, and spectrophotometry; electrical methods such as conductivity, potentiometry, polarography, and mass spectrometry. Theoretically any property which changes sufficiently could be used to follow the course of a reaction. Thermal conductivities, solidification temperatures, viscosities (for polymerization reactions), coagulating power towards colloids, and heats of reaction are among the more unusual properties which have been utilized.

In general, a physical method of analysis has the advantage of being rapid so that more experimental points are available in a given time. Measurements can frequently be made in the reaction vessel so that sampling with its attendant errors is eliminated. The system is usually not destroyed by the method nor even perceptibly disturbed. Often it becomes possible to make automatic and continuous recordings of the changes in property. Physical methods, however, have the limitation of not giving absolute values of concentration directly. Furthermore, errors due to side reactions may be enormously magnified. For example, in spectrophotometric studies, small amounts of highly colored impurities or by-products will obscure the desired quantities. For a complete study of any given reaction, more than one method of analysis should be used. It is especially desirable that the stoichiometry of the reaction be verified to be sure that the reaction being studied is one in which the products are known with certainty.

Correlation of Physical Properties with Concentrations

One requirement of any physical measurement as a criterion of extent of reaction is that the property being measured differs appreciably from reactants to products. Another requirement is that the property varies in some simple manner with the concentrations of reactants and products. The most common and useful relationship is that the physical property be a linear function of the concentration. Such a relationship exists, for example, between concentration and electrical conductance, optical density, rotation of polarized light, and pressure of gases. In dilute solutions, many physical properties such as the specific volume, refractive index, vapor pressure, and fluidity become linear functions of the concentration. In practice, of course, many of these linear relationships will break down if applied over too wide a range of concentration, the reasons being not only deviations from ideal behavior but also nonlinearities in the mathematical forms of the ideal laws relating the properties to concentration.

A general equation can be derived for relating a measured physical quantity with concentration if a linear relationship exists. Suppose we have the reaction which goes to completion

$$nA + mB + pC = rZ \tag{1}$$

where Z includes all products. Let λ be the value of the physical property at any time t.

$$\lambda = \lambda_M + \lambda_A + \lambda_B + \lambda_C + \lambda_Z \tag{2}$$

where the first term is the contribution of the medium and the others vary with concentration as, for example,

$$\lambda_A = k_A[A]$$

k_A being a proportionality constant. Letting the initial concentrations of reactants be a, b, and c, respectively, and the reaction variable x be the equivalents reacting in time t, then

$$\lambda = \lambda_M + k_A(a - nx) + k_B(b - mx) + k_C(c - px) + k_Z rx \tag{3}$$

and

$$\lambda_0 = \lambda_M + k_A a + k_B b + k_C c \tag{4}$$

$$\lambda_\infty = \lambda_M + k_B(b - ma/n) + k_C(c - pa/n) + k_Z ra/n \tag{5}$$

where λ_0 and λ_∞ are the initial and final values of λ, and in equation 5 it is assumed that A is the reactant present in limiting amount. Subtracting (4) from (5) gives us

$$\lambda_\infty - \lambda_0 = k_Z \frac{ra}{n} - k_A a - k_B \frac{ma}{n} - k_C \frac{pa}{n} \tag{6}$$

and (4) from (3)

$$\lambda - \lambda_0 = k_Z rx + k_A nx - k_B mx - k_C px \tag{7}$$

so that we may write

$$\lambda - \lambda_0 = x\,\Delta k \qquad \lambda_\infty - \lambda_0 = (a/n)\,\Delta k$$

and

$$\lambda_\infty - \lambda = (a/n - x)\,\Delta k$$

where

$$\Delta k = k_Z r - k_A n - k_B m - k_C p$$

From these we may get the kinetically useful relationships

$$\frac{nx}{a} = \frac{\lambda - \lambda_0}{\lambda_\infty - \lambda_0} \tag{8}$$

$$\frac{a}{a - nx} = \frac{\lambda_\infty - \lambda_0}{\lambda_\infty - \lambda} \tag{9}$$

It is also possible to express $(b - mx)$ and $(c - px)$ in terms of the measured variable. The result is of the form

$$\frac{b}{b - mx} = \frac{(b/a)(\lambda_\infty - \lambda_0)}{(b/a)(\lambda_\infty - \lambda_0) - (m/n)(\lambda - \lambda_0)} \tag{10}$$

Considerable simplification can be obtained by using equivalent concentrations of reactants, so that $b/a = m/n$, etc.

Reactions which do not go to completion can be handled also if the equilibrium constant is known independently. We shall illustrate the use of equations 8 and 9 with several examples taken from the literature for reactions both in solution and in the gas phase.

Reactions in the Gas Phase

Lack of space will not permit an extended discussion of apparatus and experimental methods. Fortunately a number of excellent references are available to the reader in various treatises.[1–8]

The most useful methods for following gaseous reactions are manometric. This may be a direct measurement of pressure in systems where there is a change in the number of moles such as the decomposition of phosgene

$$COCl_2 = CO + Cl_2 \tag{11}$$

or where a reaction product is removed continuously by absorption or condensation. For example, in the reaction

$$H_2 + Cl_2 = 2HCl \tag{12}$$

the acid may be removed by absorption in water. Or the pressure may be read intermittently after removing a product, so that in reaction 12 chlorine and hydrogen chloride may be condensed by liquid air and the residual pressure of the hydrogen measured.

Table I gives some results obtained in the decomposition of di-*t*-butyl peroxide by Raley, Rust, and Vaughan.[9] This substance decomposes in a first-order reaction to give essentially acetone and ethane

$$(CH_3)_3COOC(CH_3)_3 = 2(CH_3)_2CO + C_2H_6 \tag{13}$$

so that the pressure should increase to three times its original value as the reaction proceeds. Actually, it is found that there is only a 2.88-fold increase in pressure since a small amount of the peroxide gives other products.

The total pressure listed in Table I also includes a small partial pressure due to nitrogen which was used to force the peroxide into the reaction vessel. Nevertheless, we set

$$x/a = (P - P_0)/(P_\infty - P_0) \qquad (a - x)/a = (P_\infty - P)/(P_\infty - P_0)$$

For a first-order reaction $t = (1/k) \ln [a/a - x)]$, which can be expressed also as $t = (1/k) \ln (P_\infty - P_0) - (1/k) \ln (P_\infty - P)$. Figure 1 shows the logarithm of $(P_\infty - P)$ plotted against the time, the linearity confirming the first-order kinetics. Table I also shows the first-order rate constants calculated for successive 3-minute intervals from the equation

$$k = \frac{1}{t - t'} \ln \frac{(P_\infty - P')}{(P_\infty - P)}$$

The average of these agrees with the specific rate constant obtained by multiplying the slope of Fig. 1 by 2.303. One of the characteristics of a first-order reaction is that the initial concentration need not be known; the value of P_0 does not necessarily enter into the calculations. Actually in this experiment P_0 was not measured but obtained from an extrapolation

Table I

DECOMPOSITION OF DI-*t*-BUTYL PEROXIDE AT 154.6°
(Raley, Rust, and Vaughan[9])

Time, min	Total Pressure, mm	$P_\infty - P$	$k \times 10^4$ [a] sec^{-1}
0	173.5	318.3	
2	187.3	304.5	
3	193.4	298.3	3.58
5	205.3	286.5	3.39
6	211.3	280.5	3.42
8	222.9	268.9	3.50
9	228.6	263.2	3.45
11	239.8	251.9	3.61
12	244.4	247.4	3.44
14	254.5	237.3	3.32
15	259.2	232.5	3.43
17	268.7	223.1	3.43
18	273.9	217.9	3.60
20	282.0	209.7	3.45
21	286.8	204.9	3.42
∞	491.8		
			Av. 3.46 ± 0.07

[a] Rate constants evaluated for successive 3-min intervals.