benzene and a trace of toluene. The conversions of the butyl- and amylbenzenes were to rather complex mixtures, with the reactions following no clear-cut course and being affected by the configuration of the alkyl group. A summary of their results is given in Table II. The data are not strictly comparable owing to the fact that in the thermal study it was necessary to go to a considerably higher temperature to obtain appreciable conversion than in the catalytic study.

TABLE II

THERMAL CRACKING OF ALKYLBENZENES BY DOBRYANSKII, KANEP AND KATSMAN

Compound Cracked	% C_6H_6	% Toluene	% Styrene	% Gas
Ethylbenzene	14.0	1.4	17.0	18.5
n-Propylbenzene	0.3	36.5	2.4	7.3
i-Propylbenzene	6	0.5	44	9.1
t-Butylbenzene	2.4–8	2.0–1.4	6.0	6.0–19.7
Butylbenzene	0.8	8.4	14.5	32
Amylbenzene	0.5	11.0	10.2	34.1
i-Amylbenzene	0	16.5	3.6	25

It is evident that the thermal and catalytic reactions are different, for the reaction products are different. Further, the catalytic reaction is much more selective.

Summary

During the cracking of ethylbenzene, cumene, *n*-butylbenzene and technical amylbenzene in the presence of synthetic catalysts of the silica–alumina type at 400–500° and atmospheric pressure, benzene and the corresponding alkene are formed with ease and great selectivity when the side chain contained three or more carbon atoms, the yield of benzene being at least 90% in each case. The order of decreasing susceptibility to cracking is cumene, the technical amylbenzene, *n*-butylbenzene, and, in a lower order of magnitude, ethylbenzene. No toluene, styrene, etc., was found in any product in this study.

The alkenes formed apparently undergo subsequent reactions to some extent for some hexenes are formed in the cumene tests, presumably by polymerization of the initially formed propylene. The olefinic products from butylbenzene undergo the hydrogen transfer reaction; some butanes are formed.

CHICAGO, ILLINOIS RECEIVED APRIL 7, 1944

[CONTRIBUTION FROM GIBBS CHEMICAL LABORATORY, HARVARD UNIVERSITY]

The Kinetic Analysis of Consecutive Irreversible First Order Reactions

BY C. GARDNER SWAIN

The rate constants of one-step irreversible first or second order reactions are so readily obtained that an attempt is generally made in chemical kinetics to find limiting conditions of reactant concentrations, *p*H, solvent, *etc.*, under which the rate will obey one of these simple laws. Perhaps the most frequently encountered mechanism of higher complexity not in practice reducible to a simple one-step process is one involving two consecutive irreversible first order reactions

$$\mathrm{A} \xrightarrow[x_1]{k_1} \mathrm{B} \xrightarrow[x_2]{k_2} \mathrm{C} \qquad (a)$$

Here A, B, and C represent starting material, intermediate product, and final product; k_1 and k_2 represent the rate constants of the two steps; x_1 and x_2 the extents of reaction (moles per unit volume) along them at any time, *t;* and *a* the initial concentration of A.

The concentrations of A, B, and C can be readily calculated if the rate constants are known. The expressions were first obtained by Esson.[1]

$$[\mathrm{A}] = ae^{-k_1t} \qquad (1)$$

$$[\mathrm{B}] = \frac{ak_1}{k_1 - k_2}\left(-e^{-k_1t} + e^{-k_2t}\right) \qquad (2)$$

$$[\mathrm{C}] = a\left[1 + \frac{1}{k_1 - k_2}\left(k_2e^{-k_1t} - k_1e^{-k_2t}\right)\right] \qquad (3)$$

However, the converse problem of obtaining the rate constants rapidly and accurately from a set of experimental data has not received an adequate solution.· This is the practical problem with which we are concerned below.

Let us first define *F* as a function equal to the sum of x_1 and x_2. It is then a function of time and equal to [B] + [C]. Using equations (2) and (3)

$$F = a\left[2 - \left(\frac{k_1 - 2k_2}{k_1 - k_2}\right)e^{-k_1t} - \left(\frac{k_1}{k_1 - k_2}\right)e^{-k_2t}\right] \qquad (4)$$

Now it very frequently happens that the only analytical method available to follow two consecutive reactions measures the function *F* directly, this therefore constituting the entire data from which the rate constants k_1 and k_2 must be obtained. This is true, for example, when one measures a common by-product or effect produced *in each step, e. g.*, hydrogen or halide ion from the hydrolysis of a dihalide, an α-particle produced by radioactive decay, a one-electron oxidation change, or a heat or volume change associated with each step. The function *F* is then equal to the concentration of this by-product, or the fraction of the total magnitude of this effect multiplied by 2*a*. Experimental data on the decline in concentration of a reagent consumed in each step and present in large excess (or in small excess but not entering into the rate

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[1] W. Esson, *Phil. Trans. Roy. Soc.* (London), **156**, 220 (1866); *cf.* A. Rakowski, *Z. physik. Chem.*, **57**, 321 (1907).

determining parts of the steps) are an equally direct measure of F, which then equals the concentration of this common reagent which has reacted at any time. In general, even when no common substance is involved, the experimental data are either already in the form of F *vs.* t or else by a suitable combination of two analyses readily capable of giving F *vs.* t. The problem is now one of determining k_1 and k_2 from the data on F *vs.* t.

From equation (4) it would seem that it ought to be possible to estimate k_1 and k_2 from the initial and final slopes of $(2a - F)$ on a simple logarithmic plot.

$$-\frac{\mathrm{d}\ln(2a - F)}{\mathrm{d}t} = \frac{k_1\left(\frac{k_1 - 2k_2}{k_1 - k_2}\right)e^{-k_1t} + k_2\left(\frac{k_1}{k_1 - k_2}\right)e^{-k_2t}}{\left(\frac{k_1 - 2k_2}{k_1 - k_2}\right)e^{-k_1t} + \left(\frac{k_1}{k_1 - k_2}\right)e^{-k_2t}} \quad (5)$$

At zero time the slope is $k_1/2$, and at infinite time it is k_2 if $k_2 < k_1$.

However, such an estimate is usually far from correct if any sizable fraction of the curve is used to define the slope. For example, if the second rate constant is one-tenth of the first and if the initial rate is approximated by using a 10% point and the origin, the estimated k_1 will be 5% too low. The value of k_2 estimated from the slope at 70% reaction, instead of at 100%, is 16% too high. If the second rate constant is twice the first, k_1 estimated from a 10% point and the origin will be 12% too high. In this case k_2 cannot be estimated at all from the final slope since the latter approaches k_1, not k_2, when $k_2 > k_1$.

The problem can, of course, be solved by calculating whole curves from equation (4) for various assumed values of k_1 while holding k_2 constant, then picking the best k_1 and varying k_2 systematically, then readjusting k_1 with the best k_2, *etc.*, until an acceptable fit is obtained. However, since the initial estimates of k_1 and k_2 from the initial and final slopes are so poor, such a procedure is tedious and time-consuming in the extreme. A somewhat more direct procedure is to take the time and percentage reaction values for two well-spaced points and substitute them in equation (4). An equation is then obtained from each point relating k_1 and k_2. If k_1 is plotted *versus* k_2 for each equation on the same graph, the intersection of the two curves gives the desired values. However, this is also a very tedious process. This is largely due to the fact that the equations are transcendental. Even when k_2 is assumed for the purpose of obtaining a point on one of the curves, the corresponding k_1 can only be calculated by a process of successive approximations. The best way to do this is to plot the difference of the two sides of the equation against k_1, guessing values of k_1 that give both positive and negative differences. Then the value which gives a zero difference can be read off the plot. Thus each point on the two curves for k_1 *vs.* k_2 has to be obtained by a separate plot, and each of these separate plots in turn is composed of many points calculated from the complex general equation. If several curves are to be fitted, the data and experience gained from the fitting of one curve prove to be of little or no assistance in subsequent calculations. Each calculation requires many hours.

We have developed and used with considerable success in this Laboratory a generalized solution of equation (4). This solution makes it possible to obtain k_1 and k_2 in a few minutes to better than 1% accuracy for any new case reduced to the mechanism set forth above. This generalized solution is in the form of a table of k_2/k_1 *versus* k_1t values for different percentage reactions (see Table I). If the data for two different percentage reactions are plotted on two semi-transparent sheets of logarithmic graph paper (see Fig. 1), and if one is then laid over the other, displacing the abscissas by an amount equal to the ratio of the times for the two percentage reactions, k_2 and k_1 are obtained directly from the k_2/k_1 and k_1t values of the intersection. Solutions are simply read off the same pair of graphs for any new case that may arise.

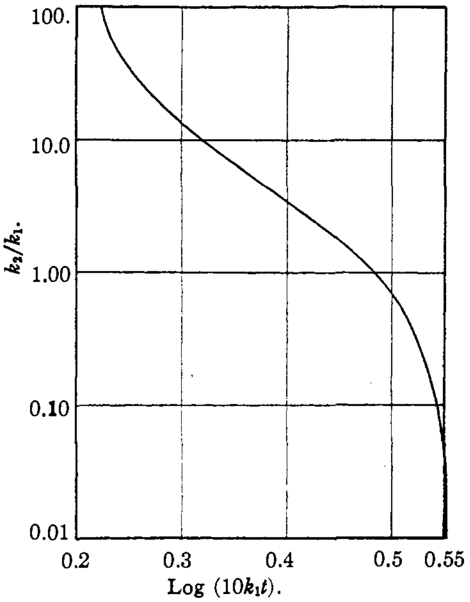


Fig. 1.—Plot of k_2/k_1 *vs.* log $(10\ k_1t)$ for 15% reaction.

This solution is most useful when the experimental data are obtained in the form of F *vs.* t directly. In other cases where two analyses must be made to enable F to be calculated, the relative advantage of this solution is less, because in such cases [A] *vs.* t, and hence k_1 by equation (1) can ordinarily be obtained directly from the data, and k_2 can then be obtained by solving only a single transcendental equation. However, this solution affords the most rapid method of obtaining the rate constants to 1% accuracy even in such cases.

TABLE I[2]

k_2/k_1	k_1t (and log 10 k_1t) for		
	15%	35%	70%
100	0.168 (0.224)	0.436 (0.639)	1.21 (1.082)
50	.172 (0.237)	.441 (0.644)	1.21 (1.084)
20	.188 (0.275)	.457 (0.660)	1.23 (1.090)
10	.209 (0.319)	.484 (0.685)	1.26 (1.100)
5	.236 (0.373)	.536 (0.729)	1.32 (1.121)
2	.277 (0.442)	.664 (0.809)	1.54 (1.187)
1.5	.289 (0.460)	.686 (0.836)	1.65 (1.217)
1.1	.300 (0.477)	.734 (0.865)	1.80 (1.256)
0.9	.308 (0.489)	.766 (0.884)	1.93 (1.285)
.7	.315 (0.498)	.806 (0.907)	2.11 (1.324)
.5	.324 (0.511)	.863 (0.936)	2.41 (1.382)
.2	.342 (0.534)	.999 (0.999)	3.81 (1.581)
.1	.349 (0.543)	1.078 (1.033)	6.19 (1.792)
.05	.353 (0.548)	1.132 (1.054)	11.10 (2.045)
.02	.355 (0.550)	1.173 (1.069)	26.55 (2.424)
.01	.356 (0.551)	1.188 (1.075)	52.09 (2.717)

The calculations that led to Table I are as follows. On making the substitutions

$$\phi = \frac{F}{a} - 2;\ \theta = k_1t;\ \rho = k_2/k_1$$

equation (4) is reduced to

$$\phi(\rho - 1) = e^{-\rho\theta} - (2\rho - 1)e^{-\theta} \qquad (6)$$

This is a transcendental equation not readily solved for θ. However, if one guesses θ_0 as the value of θ, the error, ϵ, can be closely approximated.

$$\theta = \theta_0 + \epsilon$$

$$\epsilon \cong \frac{\phi(\rho - 1) + (2\rho - 1)e^{-\theta_0} - e^{-\rho\theta_0}}{(2\rho - 1)e^{-\theta_0} - \rho e^{-\rho\theta_0}} \qquad (7)$$

Usually four approximations with a given value of ρ gave a value of θ constant to four decimal places.

In making the graphs from Table I, it is necessary to plot log θ, or else θ on a log scale, and it is convenient to use also a log scale for ρ to obtain a large range and constant percentage accuracy vertically. The curves then all have the general sigmoid shape of the 15% curve shown in Fig. 1. For most purposes two cycles covering the range 0.10 to 10.0 are adequate. An ideal graph paper for plotting would be two- or four-cycle logarithmic on the short side, one-cycle logarithmic on the long side. Since this is not generally obtainable, one must either plot log θ values as in Fig. 1 or else both plot and read off values of θ with a long log scale, *e. g.*, an edge cut from the long side of a sheet of one-cycle semilog paper. The same abscissa scale must be used on all three plots, though different portions of it are used.

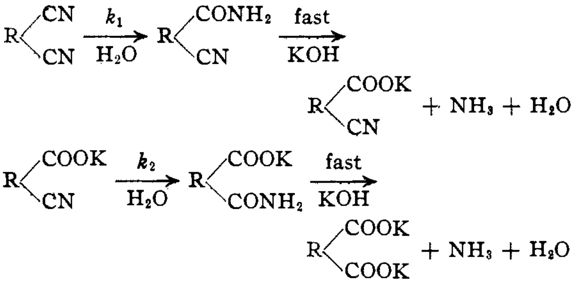
The procedure outlined above gives the desired rate constants for the following reason. The plot of k_2/k_1 *vs.* k_1t (ρ *vs.* θ) for a given percentage reaction may be considered as a plot of k_2/k_1 *vs.* k_1 since t is a known constant in any particular case. Two such plots for two different percentage reactions represent two simultaneous equations for k_2/k_1 in terms of k_1, and their intersection with scales properly superposed must give the unique pair of values of the two rate constants consistent with the data for both percentage reactions. The ordinate scales are drawn the same in the different plots and are therefore readily superposed. However, the abscissa scales are k_1t, not k_1, and to bring corresponding k_1 values together the abscissa scales must be plotted logarithmically and displaced one relative to the other by the ratio of the times for the two percentage reactions. This is obvious because with logarithmic scales the displacement, which can be written as

$$\log\,[\theta]_{m\%} - \log\,[\theta]_{n\%} = \log\,[k_1]_{m\%}t_{m\%} - \log\,[k_1]_{n\%}t_{n\%}$$

must equal log $(t_{m\%}/t_{n\%})$ if $[k_1]_{m\%}$ is to equal $[k_1]_{n\%}$. The graphs are easily read by holding them against a window pane, or a plate of glass illuminated from below.

In practice it is often found that of the three pairs possible using the 15, 35 and 70% graphs, two give sharp intersections and the third tangency over a short range. The unsatisfactory pair varies with the problem at hand. If this mechanism is inconsistent with the experimental curve, disagreeing values of k_1 and k_2 will be obtained from the various pairs. It is then best to plot a theoretical curve using equation (4) and the average rate constants from the three pairs to decide if the divergence is within the experimental error.

Example.—The hydrolysis of 2,7-dicyanonaphthalene, studied by Kaufler,[3] is an example of two consecutive first order reactions.



$$\mathrm{R}\begin{matrix}\mathrm{CN}\\ \mathrm{CN}\end{matrix} \xrightarrow[\mathrm{H_2O}]{k_1} \mathrm{R}\begin{matrix}\mathrm{CONH_2}\\ \mathrm{CN}\end{matrix} \xrightarrow[\mathrm{KOH}]{\text{fast}} \mathrm{R}\begin{matrix}\mathrm{COOK}\\ \mathrm{CN}\end{matrix} + \mathrm{NH_3} + \mathrm{H_2O}$$

$$\mathrm{R}\begin{matrix}\mathrm{COOK}\\ \mathrm{CN}\end{matrix} \xrightarrow[\mathrm{H_2O}]{k_2} \mathrm{R}\begin{matrix}\mathrm{COOK}\\ \mathrm{CONH_2}\end{matrix} \xrightarrow[\mathrm{KOH}]{\text{fast}} \mathrm{R}\begin{matrix}\mathrm{COOK}\\ \mathrm{COOK}\end{matrix} + \mathrm{NH_3} + \mathrm{H_2O}$$

The reaction was carried out in amyl alcohol at 126° with a large excess of both water and potassium hydroxide present. The reaction was followed by sweeping out the ammonia formed by a stream of air, absorbing it in standard acid, and titrating the absorbent at intervals. The data obtained by Kaufler for a typical run are given in Fig. 2. The early titers are undoubtedly too low because of the time lag for quantitatively sweeping over the ammonia formed in the reaction vessel.

Kaufler fitted these data to equation (4), using the two- and six-hour points and the tedious

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(2) The assistance of Mrs. Mary K. Frye in calculating Table I is gratefully acknowledged.

(3) F. Kaufler, *Z. physik. Chem.*, **55**, 502 (1906).

method of plotting k_1 *vs.* k_2 curves for each equation

$$0.581 = 0.5613\left[2 - \left(\frac{k_1 - 2k_2}{k_1 - k_2}\right)e^{-2t} - \left(\frac{k_1}{k_1 - k_2}\right)e^{-2t}\right]$$

$$0.8675 = 0.5613\left[2 - \left(\frac{k_1 - 2k_2}{k_1 - k_2}\right)e^{-61} - \left(\frac{k_1}{k_1 - k_2}\right)e^{-6t}\right]$$

He obtained the values $k_1 = 1.007$ hr.$^{-1}$ and $k_2 = 0.161$ hr.$^{-1}$.

We can find little fault with the closeness of fit of these final values. However, they were obtained only after an amount of work nearly as great as that involved in the entire calculation of Table I. The calculations performed by Kaufler in solving this problem are of no further use. Table I, however, directly gives the solution for any problem of this type. Using the graphs drawn from Table I the rate constants are obtained in a few minutes as follows

% reaction	Time, hrs.	Log t
15	22′ = 0.367	−0.436
35	64′ = 1.067	+0.028
70	4:12′ = 4.200	+0.623

Pair of graphs	Displacement	k_2/k_1	log $(10k_1t)$	k_1	k_2
15%,35%	(−0.436) − (0.028) = −0.464 Place 0.536 of 15% graph on 1.000 of 35% graph	0.200	0.534	0.933	0.186
35%.70%	(+0.028) − (0.623) = −0.595 Place 1.000 on 1.595	0.189	1.002	0.943	0.178
15%.70%	(−0.436) − (0.623) = −1.059 Place 0.400 on 1.459	0.189	0.535	0.935	0.177
			Average =	0.937	0.180

The times used were taken from the best curve visually drawn through the points on a simple logarithmic plot. It is impossible to draw a curve through the first point without having reverse curvature at the start. This experimental point appears to be about 5% low. The curve was drawn through or very close to all the other points. The agreement between the k_1 and k_2 values obtained with different pairs of graphs is satisfactory and typical of that obtained with kinetic data following this mechanism and having 1–2% accuracy for most of the points. The average k_1 and k_2 values for the three pairs are 0.937 and 0.180 hr.$^{-1}$. Our values are based on a visually fitted curve running through the experimental points, and weight the early portion of the reaction more heavily than Kaufler's values, which were based on two actual experimental points rather late in the reaction (51.8 and 77.3%). It is hard to say which are the more accurate values. Figure 2 gives the calculated curves for the two sets. The average deviation of the calculated from the experimental points for our values is 1.4%, compared to 1.8% for Kaufler's. His values are 7.5% higher for k_1 and 11% lower for k_2 than ours, and give a k_1/k_2 ratio of 6.25, whereas we obtain 5.21.

In view of this uncertainty in the final values of k_1 and k_2 it might seem that the calculation methods are not very accurate. This is not the case. It is important to distinguish uncertainties in the final values of k_1 and k_2 arising from inaccuracy of the experimental data from uncertainties due to the calculation method itself, such as errors in plotting, superposing, and reading graphs. The total uncertainty due to inaccuracies in the calculation of k_1 and k_2 once the times corresponding to two percentage reactions are chosen is not over ±0.2% for k_1 and ±1.0% for k_2. To demonstrate this we have taken the times for 15, 35, and 70% reaction from the solid curve in Fig. 2, which was calculated for $k_1 = 0.937$ and $k_2 = 0.180$ hr.$^{-1}$, treated them as experimental data, and repeated the process of calculating rate constants. Then exactly the same values, 0.937 ± 0.002 and 0.180 ± 0.001 hr.$^{-1}$ were obtained from all three pairs of graphs. On the other hand, although these data were selected as typical good kinetic data, better than most reported in the literature, the rate constants cannot be expected to be obtained more accurately than ±5–10% with errors of ±1–2% in the individual points. Thus the uncertainty in the rate constants is here due to uncertainty in deciding what times correspond to given percentage reactions and in no way to inaccuracies in fitting once the times have been chosen. Errors due to the latter are very slight and would be comparable with the experimental error only for very exceptional sets of kinetic data having average deviations less than one-tenth of those in the present case, or under 0.2% of the total reaction for individual experimental points.

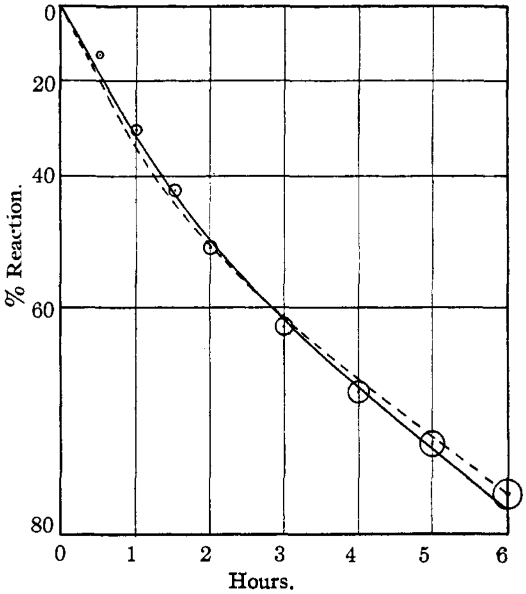

Fig. 2.—Hydrolysis of 2,7-dicyanonaphthalene. Experimental points are drawn with 1% error circles. Dashed curve is calculated for $k_1 = 1.007$, $k_2 = 0.161$ hr.$^{-1}$; solid curve for $k_1 = 0.937$, $k_2 = 0.180$ hr.$^{-1}$.

In addition to providing evidence for the mechanism such curve fitting may be useful in other ways. The carboxylate ion in the intermediate product is seen to cause the nitrile grouping in the opposite ring of the napthalene nucleus to hydrolyze at only 38% of the rate which it would if the first nitrile had not been hydrolyzed. This is a quantitative measure of the ease of electromeric relay of the negative charge of the carboxylate ion across this ring system. The rate constants make possible the calculation of the time when the concentration of monosubstitution product is at a maximum, a useful fact if an isolation of the intermediate product is to be attempted.

$$t = \frac{\ln k_1 - \ln k_2}{k_1 - k_2} = 2.18 \text{ hr.}$$

The maximum concentration of this cyanonaphthoic acid is calculated from equation (2) to be 67.6% of *a*.

Acknowledgment.—The author wishes to express his indebtedness to Professor E. B. Wilson, Jr., who suggested to him the possibility of throwing equation (4) into the form of equation (6) on which the generality of the method depends. He also wishes to thank Professor Paul D. Bartlett for many helpful suggestions in writing the manuscript.

Summary

Given a set of rate constants for consecutive irreversible first order reactions, the changes of concentration of starting material and intermediates can be calculated relatively easily by well known methods. The converse problem of obtaining the rate constants from a set of experimental data requires a tedious calculation involving successive approximations. The initial and final slopes on a simple logarithmic plot are not in practice found to be accurate measures of the two rate constants in a two step process. A generalized graphical solution has been developed for the rate constants of two successive first order reactions

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

which is especially useful in cases where the rate is followed by measuring the formation or consumption of any substance which is produced or consumed in equal amount in each step. This at once gives the rate constants to better than 1% accuracy from the values of the time for two different percentage reactions. The same graphs are used for all cases, and the data for drawing them are presented in tabular form.

CAMBRIDGE, MASS. RECEIVED JULY 13, 1944

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

The Conductivity of Sulfuric Acid in Methanol at 20, 30 and 35°[1]

BY E. W. KANNING,[2] J. B. BYRNE[3] AND E. G. BOBALEK[2]

Recent measurements[4] of the conductance of sulfuric acid in methanol at 25° indicate that the primary dissociation of sulfuric acid is very nearly complete at high dilution, and in even the most dilute solutions secondary dissociation can be considered as negligible. Thus, sulfuric acid may be regarded essentially as a univalent electrolyte when dissolved in methanol. From such a consideration, values were reported for the limiting equivalent conductance and thermodynamic dissociation constant of sulfuric acid in methanol at 25°.

In order to confirm the conclusions indicated by the measurements at 25° and to obtain data useful in the interpretation of electromotive force studies being made in this Laboratory, measurements were made of the conductivity of sulfuric acid in methanol at 20, 30 and 35°. It was the original intention of the authors to cover a wider range of temperature but because of experimental difficulties at higher temperatures the work was discontinued above 35°. Results are reported for the limiting equivalent conductances and thermodynamic dissociation constants of sulfuric acid in methanol at 20, 30 and 35°.

Experimental

The apparatus and technique, including the preparation of reagents, for this investigation were the same as described in the previous publication.[4] The entire series of measurements was made using two of the three cells described therein. The constants of these cells, determined at 25°, were 0.63741 and 0.30995. The constants at other temperatures were computed from the constant at 25° by the equation,

$$C_t = C_{25}(1 - \alpha \Delta t)$$

C_t represents the cell constant at $t°$, Δt the difference in temperature, $t° - 25°$ and α the linear coefficient of expansion of Pyrex glass. The value of α[5] taken was 0.37×10^{-5}.

Solutions were prepared by direct weighing of solute and solvent for concentrations greater

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[1] This paper is constructed from a dissertation presented by Joseph B. Byrne to the Faculty of the Graduate School of Indiana University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Present address: The Dow Chemical Company, Midland, Michigan.

[3] Present address: The Dow Chemical Company, Great Western Division, Pittsburg, California.

[4] Kanning, Bobalek and Byrne, THIS JOURNAL, 65, 1111 (1943).

[5] G. W. Morey, "Properties of Glass," Reinhold Pub. Corp., New York, N. Y., 1938, p. 289.