[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 202]

REACTIONS WITH VERY LARGE APPARENT TEMPERATURE COEFFICIENTS

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RECEIVED NOVEMBER 27, 1928 PUBLISHED APRIL 5, 1929

During the last few months three reactions, of widely different types, have been reported to exhibit a dependence upon temperature considerably greater than is usual. R. P. Bell[2] studied the oxidation of benzoyltoluidine by potassium permanganate, the reaction taking place at a benzene–water interface; he reported a temperature coefficient of 13 for this reaction. The present author[3] has been unable to duplicate his results, and finds instead a value of about 2. Topley and Hume[4] investigated the dehydration of calcium carbonate hexahydrate crystals in the presence of liquid water; the reaction is apparently propagated throughout the separate crystals from active centers and the linear rate of propagation has a temperature coefficient of about 12. Patterson and McAlpine[5] have published measurements on the rate of decomposition of bornyl naphthalene-β-sulfonate, menthyl benzenesulfonate and menthyl naphthalene-β-sulfonate in toluene, nitrobenzene, ethylene dibromide, pyridine and methyl, ethyl, *n*-propyl, *n*-butyl and *sec.*-butyl alcohols. They did not investigate the effect of varying concentration or varying time of reaction (all their runs were for one hour), but only the dependence of percentage decomposition upon temperature. For the alcohols and pyridine they found a normal temperature coefficient, for toluene a very low one, while for ethylene dibromide and nitrobenzene the apparent temperature coefficient starts at a low value and increases rapidly; in a typical case, it increases from 1.5 to 150 in a 20° temperature range.

The purpose of the present paper is to discuss these latter measurements, to show how they may be accounted for by reactions with normal values for their separate temperature coefficients, and to make such other remarks upon the general nature of chemical reactions as the experiments suggest.

The Decomposition of Calcium Carbonate Hexahydrate.—Topley and Hume[4] have interpreted their experimental results to mean that the reaction is propagated throughout any given small crystal from reaction centers which arise on its surface; they have determined the approximate linear rate of propagation which this hypothesis requires and find

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[1] National Research Fellow in Chemistry.

[2] Bell, *J. Phys. Chem.*, **32**, 882 (1928).

[3] Kassel and Schaffer, THIS JOURNAL, **51**, 965 (1929).

[4] Topley and Hume, *Proc. Roy. Soc. London*, **120A**, 211 (1928).

[5] Patterson and McAlpine, *J. Chem. Soc.*, 2464 (1928).

that at 0° the reaction front advances 0.135 layer of molecules per second. If we attempt to find a mechanism which will give this rather rapid rate, and at the same time account for the high temperature coefficient, considerable difficulty is encountered. By assigning a reasonable value to the vibration frequency, Topley and Hume calculated the fraction of the vibrations, β, which resulted in decomposition; they found 2.7×10^{-14}. They then pointed out that if reaction followed upon activation at a single degree of freedom, the expected value of β would be 10^{-33}, and even if, in analogy to the theory of unimolecular gas reactions, it was supposed that every molecule which acquired sufficient energy in 11 degrees of freedom (22 energy terms) decomposed, they found a value of β of only 2×10^{-25}.

It is possible to extend these calculations somewhat, on the basis of the more satisfactory form of the unimolecular reaction theory which has been given by Rice and Ramsperger and the author.[6] First it is found that, if the classical form of the theory is to be used, the number of degrees of freedom is to be taken as not more than half of the theoretically possible number; now $CaCO_3 \cdot 6H_2O$ has 23 atoms and therefore 63 internal degrees of freedom. Hence in our calculations we will take 30 degrees of freedom instead of the 11 used by Topley and Hume. We may now distinguish two possible courses which the reaction could take. It might be that practically every activation resulted in decomposition, that is, that during the time of a single vibration an activated molecule was almost sure to decompose. In this case the rate of reaction is equal to the rate of activation, and the fraction β of all vibrations resulting in reaction is simply the fraction W_E of the molecules which contain energy in excess of the critical energy E at any instant. If we have 30 degrees of freedom, $E = 41{,}300 + 29RT$, approximately. This gives $E = 57{,}000$, and at 0° $W_E = 10^{-18}$. This is still less than β by a considerable factor, which could not be changed much by any reasonable increase in the number of degrees of freedom.

A second possibility is that only a few of the activated molecules decompose. Then if the specific reaction rate depends upon the total energy in the way that the author has given for gas reactions, the mathematical theory of these reactions may be used without change. In particular, the simple relation $d \ln K/dT = E/RT^2$ is approximately restored. We calculate that $W_E = 5 \times 10^{-10}$, which is actually large compared to β. Thus the theory is self-consistent. There is nevertheless a very serious objection to this interpretation. If we consider only the molecules in the reaction front, and write for their reaction rate $K = Ae^{-E/RT}$, we calculate that $A = 10^{32}$. This value should be comparable with that

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[6] Rice and Ramsperger, This Journal, **49**, 1617 (1927); **50**, 617 (1928); Rice, *Proc. Nat. Acad. Sci.*, **14**, 113, 118 (1928); Kassel, *J. Phys. Chem.*, **32**, 225, 1065 (1928).

of the same quantity in the unimolecular gas reactions. For the eight such reactions now well established, A ranges from 3×10^{11} to 9×10^{15}.[7] It seems rather unlikely, therefore, that a value as great as would be required here is acceptable. It is possible to say roughly what the physical meaning of A is; a large value of A means that the rate of transfer of energy within a molecule from one part to another is high; in terms of the quantum mechanics, this seems to mean that the interaction energy of the various oscillators is large. One would expect, from a general chemical standpoint, that the interaction energy would be less for a rather unstable coördination compound such as calcium carbonate hexahydrate than for a stable organic molecule. Azo-*iso*propane, with 22 atoms, is directly comparable with calcium carbonate hexahydrate, with 23; and azo-*iso*propane has $A = 4 \times 10^{14}$. On this basis it seems to the author necessary to reject the foregoing mechanism.

Thus it does not seem satisfactory to regard this dehydration as a single reaction with an energy of activation of approximately 40,000 calories. An alternative view is that the reaction occurs in steps. Now Topley and Hume have stated that there is no evidence for the existence of intermediate hydrates, but this only means that they do not occur in very large amount. We are dealing here with a surface reaction, and it would seem quite possible for an appreciable amount of the reaction front to consist of lower hydrates without any direct evidence of their existence being obtained. It remains to be seen whether a stepwise dehydration offers a satisfactory explanation of the temperature coefficient.

It is perhaps rather unlikely that the actual dehydration should require as many as six steps; partly for this reason, but more for the sake of simplicity, we shall consider the simpler case of a compound AB_3. We assume that the following reactions occur: (1) $AB_3 = AB_2 + B$; (2) $AB_2 = AB + B$; (3) $AB = A + B$; (4) $AB_2 + B = AB_3$; (5) $AB + B = AB_2$. B corresponds to the water, which is always present during the experiments, and we may take its concentration to be constant and absorb it into the reaction rate constants. The other substances are all solids. We shall suppose that the reaction starts at an active center, perhaps a fault in the crystal, and is propagated from it in the following way: the layer of molecules surrounding this center is at liberty to react according to the scheme given above. When the reaction in this layer has acquired a definite degree of completion, the next layer starts to react; and this process continues until the entire crystal has decomposed. We further suppose that the first three reactions above all have the rate constant p, and that the last two have the constant q, where $p \ll q$. It is possible to carry through the analysis using different constants for each reaction, but there does not seem to be any profit in such a complication.

[7] Kassel, This Journal, **50**, 1351 (1928).

Now for a layer just beginning to react we may write down the following equations

$$\frac{\mathrm{d}x}{\mathrm{d}t} = -px + qy \tag{1}$$

$$\frac{\mathrm{d}y}{\mathrm{d}t} = px - (q + p)y + qz \tag{2}$$

$$\frac{\mathrm{d}z}{\mathrm{d}t} = py - (q + p)z \tag{3}$$

$$\frac{\mathrm{d}D}{\mathrm{d}t} = pz \tag{4}$$

$$x(0) = a, \quad y(0) = z(0) = D(0) = 0 \tag{5}$$

where

$$x = [\mathrm{AB_3}], \quad y = [\mathrm{AB_2}], \quad z = [\mathrm{AB}], \quad D = [\mathrm{A}]$$

The symbol [ ] here means a *surface* concentration. To solve these equations for D it is most convenient to solve the first three of them for z. We differentiate (2) once, and (3) twice, and eliminate x and y and their derivatives from the six equations (1), (2), (2′), (3), (3′) and (3″). The resulting equation is

$$\frac{\mathrm{d}^3z}{\mathrm{d}t^3} + (2q + 3p)\frac{\mathrm{d}^2z}{\mathrm{d}t^2} + (q^2 + 2pq + 3p^2)\frac{\mathrm{d}z}{\mathrm{d}t} + p^3 = 0$$

It is well known that the general solution of (6) is

$$Z = Ae^{-m_1t} + Be^{-m_2t} + Ce^{-m_3t}$$

where m_1, m_2, and m_3 are the roots of

$$m^3 + (2q + 3p)m^2 + (q^2 + 2pq + 3p^2)m + p^3 = 0$$

The exact expressions for these roots are too unwieldy to use; it is more convenient to make use of the fact that $p \ll q$ and write down the approximate values.

$$m_1 = -p\left[\frac{p^2}{q^2 + 2pq + 3p^2} + \text{terms in } \left(\frac{p}{q}\right)^5\right]$$

$$m_2 = -q\left[1 + \frac{3}{2}\frac{p}{q} - \sqrt{\frac{p}{q} - \frac{3}{4}\left(\frac{p}{q}\right)^2} + \text{terms in } \left(\frac{p}{q}\right)^{5/2}\right]$$

$$m_3 = -q\left[1 + \frac{3}{2}\frac{p}{q} + \sqrt{\frac{p}{q} - \frac{3}{4}\left(\frac{p}{q}\right)^2} + \text{terms in } \left(\frac{p}{q}\right)^{5/2}\right]$$

If we adopt the notation

$$\frac{p^2}{q^2 + 2pq + 3p^2} = F \qquad 1 + \frac{3}{2}\frac{p}{q} = S \qquad \sqrt{\frac{p}{q} - \frac{3}{4}\left(\frac{p}{q}\right)^2} = R$$

these become, to the same approximation as before

$$m_1 = pF + \dots \qquad \begin{aligned} m_2 &= -q[S - R + \dots] \\ m_3 &= -q[S + R + \dots] \end{aligned}$$

It remains to evaluate the constants A, B and C. We know that at $t = 0$, $z = 0$, and it may also be shown that the initial conditions require $\mathrm{d}z/\mathrm{d}t = 0$. These conditions will be satisfied if

$$A + B + C = 0 \qquad -pFA - q(S - R)B - q(S + R)C = 0$$

Hence

$$C = \frac{S - R}{2R} A; \quad B = \frac{S + R}{2R} A$$

It is now easy to get D by integration; we find

$$\frac{D}{A} = \frac{1}{F} \{1 - e^{-pFt}\} - \frac{S + R}{S - R} \times \frac{p}{2qR} \{1 - e^{-q(S - R)t}\} + \frac{S - R}{S + R} \times \frac{p}{2qR} \{1 - e^{-q(S + R)t}\}$$

For small values of t all the terms must be considered, but when t is larger the first one becomes dominant; in fact, during almost the entire course of the reaction the other two terms are entirely negligible. The course of the reaction is shown in the following table for the special case $p = 0.01\ q$.

TABLE I

COURSE OF THE REACTION

qt	T_1	T_2	T_3	D/A
0.1	0.001	−0.00535	0.00438	0.00003
1.0	.01	− .03664	.02770	.00106
10.0	.10	− .06111	.04122	.08011
1000.0	10.00	− .06111	.04122	9.980
100000.0	952.9	− .06111	.04122	952.9
∞	10203	− .06111	.04122	10203

Here $$T_1 = \frac{1}{F} \{1 - e^{-pFt}\}$$

$$T_2 = -\frac{S + R}{S - R} \times \frac{p}{2qR} \{1 - e^{-q(S - R)t}\} \qquad T_3 = \frac{S - R}{S + R} \times \frac{p}{2qR} \{1 - e^{-q(S + R)t}\}$$

It is evident from this table that for all practical purposes, except when we are interested in the initial stage of the reaction, we need consider only the first term; but this term corresponds to a reaction with a rate constant given by

$$k = pF = p^3/(q^2 + 2pq + 3p^2)$$

We wish now to see whether this mechanism is in agreement with the experimental facts for the case of calcium carbonate hexahydrate. First we notice that it is possible to account for the temperature coefficient. If we put $p_1 = 0.01\ q_1$; $p_2 = 3p_1$; $q_2 = 1.5q_1$, where the subscripts 1 and 2 refer to temperatures 10° apart, we find $k_2 = 11.76\ k_1$. That is, if the dissociations have a temperature coefficient of 3, and the associations a temperature coefficient of 1.5, that of the overall reaction will be 11.76.

We must next show that it is possible for the dissociations to take place fast enough. The reaction front passes over 0.135 layer of molecules per second at 0°. If we suppose that the reaction begins in the next layer when the hydrate has been reduced to $1/e$ of its original concentration, and also that $p = 0.01\ q$, we can easily calculate that $p = 1350$. Then, writing $p = Ae^{-E/RT}$, and choosing E to make the temperature coefficient 3, we get $E = 16{,}200$ calories and $A = 10^{15}$. This value for A is reasonable and our experience in calculating the rates of unimolecular gas reactions convinces us that there will be no difficulty in producing activation fast enough.

It is also worth noticing that the reverse reactions can occur as fast as we have postulated. A temperature coefficient of 1.5 corresponds to an energy of activation of 6000 calories, and if we calculate the bimolecular rate in the manner used so successfully by Hinshelwood for gas reactions we find that 10^{-5} of the collisions could lead to combination. The actual bimolecular rate that we have assumed is 135,000; it seems reasonable to take the number of collisions per second equal to the vibration frequency, which Topley and Hume estimated as 5×10^{12}; if we do this we find that the fraction of successful collisions need only be 3×10^{-8}. It is, of course, not a source of difficulty that there are fewer successful collisions than would seem possible; if there had been an inequality in the other direction the scheme would have required modification.

It thus appears that the foregoing tentative explanation of the decomposition of calcium carbonate hexahydrate is perfectly consistent. There is no direct evidence supporting it, and it would seem very difficult to obtain any. Its chief merit is that it is one way, and the only way known at present, to account for the experimental results in this reaction; it shows that these results do not require any additions to the general reaction rate theory, as might at first sight be supposed.

The Decomposition of Menthyl and Bornyl Esters.—The work of Patterson and McAlpine was more from the organic than from the kinetic standpoint. They did not determine the order of the reactions and therefore did not calculate any reaction rate constants. In our analysis of their data we will first suppose that there is a homogeneous unimolecular decomposition, and calculate constants on that basis. For each ester–solvent combination we obtain a series of constants, one at each temperature. The results are of three types, illustrated by the following tables.

TABLE II

DECOMPOSITION OF MENTHYL BENZENESULFONATE IN TOLUENE

Temperature, °C.	85		90		95		100		105
% Decomp. = x	0.98		1.04		1.06		2.23		2.37
Log 100/(100−x)	0.00428		0.00454		0.00463		0.00979		0.01042
E_0		3100		1100		40900		3500	

TABLE III

DECOMPOSITION OF MENTHYL BENZENESULFONATE IN NITROBENZENE

Temperature °C.	85		90		95		100		105
% Decomp. = x	2.37		2.75		5.88		12.87		82.15
Log 100/(100−x)	0.01042		0.01211		0.02632		0.05983		0.74836
E_0		7870		40800		45600		140000	

TABLE IV

DECOMPOSITION OF MENTHYL BENZENESULFONATE IN BUTYL ALCOHOL

Temperature °C.	75	80	85	90	95	100	105
% Decomp. = x	4.10	6.77	10.85	17.27	28.15	45.14	60.23
Log 100/(100 − x)	0.01818	0.03044	0.04988	0.08234	0.14367	0.26074	0.40044
E_0		25200	24800	26000	29600	32600	24000

In these tables the first two lines are taken directly from the paper of Patterson and McAlpine; the numbers in the third line are proportional to the calculated unimolecular constants and those in the last are the values of the energy of activation calculated from the constants at two successive temperatures by the Arrhenius equation. Before proceeding further it may be well to point out that if constants were calculated for a bimolecular reaction, they would increase more rapidly at the higher temperatures where the reaction goes nearly to completion. Thus, if the data in Table III are calculated on the basis of a bimolecular reaction, the heat of activation for the first interval is unchanged, while that for the last is increased from 140,000 to 200,000, this latter value corresponding to a 31-fold increase in the rate for 5°. There are other cases in which the change is still more marked.

There does not seem to be any trend in the values of the heat of activation in Table IV. Similar results are found for each of the three esters whenever the solvent is an alcohol or pyridine. The average value of the energy of activation for each of the ester–solvent combinations of this type comes out 25,000 to 27,000 calories, which is to be considered as constant within the experimental error. It therefore seems altogether likely that the reaction is truly unimolecular in these solvents.

With nitrobenzene and ethylene dibromide as solvents, the results follow the type of Table III, in several cases with still more startling increases in the energy of activation. When an apparent increase in the energy of activation with increase in temperature is observed, it is usually to be ascribed to two reactions, either simultaneous or successive. Then in the normal case the energies of activation observed will be intermediate between the true energies of activation of the separate reactions; but since an energy of activation of 140,000 calories, corresponding as it does to a temperature coefficient of about 150, is utterly out of the question, it becomes necessary to seek some other explanation of the results. It occurred to the author that the reaction in these solvents might be autocatalytic. Investigation proved that it was actually possible to account for the type of result observed by a mechanism of this sort. If we write $dx/dt = a(A - x) + b(A - x)x$ and solve for x at $t = 1$, we find $x/A = (P - 1)/(P + R)$, where $R = bA/a$ and $P = e^{a(R+1)}$. Now if we assume appropriate values of a and R and let them vary with the temperature in the normal way, we can get x/A to have the type of temperature coefficient found experimentally. Two ways in which this may be done are shown in Table V.

TABLE V

CALCULATED RESULTS

(a)				(b)			
a	R	Ab	x/A	a	R	Ab	x/A
0.027	2.5	0.067	0.0275	0.027	10.24	0.276	0.0306
.036	5.0	.180	.0386	.036	17.92	.645	.0491
.048	10.0	.480	.0589	.048	31.36	1.51	.1033
.064	20.0	1.28	.1189	.064	54.88	3.51	.3834
.0853	40.0	3.41	.4385	.0853	96.04	8.19	.9739
.1137	80.0	9.10	.9920				

If it is supposed that the intervals in this table represent 5°, then the 10° temperature coefficient for the uncatalyzed reactions is $(4/3)^2$ or 1.78 in both cases; in (a) that for the catalyzed reaction is $(2 \times 4/3)^2$ or 7.11, while in (b) it is $(7/4 \times 4/3)^2$ or 5.44. It is not impossible that the catalyst should enter into the equation as a square, in which case somewhat smaller temperature coefficients for the catalyzed reaction would suffice; but there is no great objection to a value of 5 or so, and here again it must be urged that no importance attaches to the details of the calculation, only the general result being significant. It thus appears possible to account for the experimental results in nitrobenzene and ethylene dibromide by a combination of an uncatalyzed, probably unimolecular decomposition with a temperature coefficient in the neighborhood of 2, with a simultaneous decomposition, catalyzed by one of the reaction products, with a temperature coefficient that may be as great as 5 or 6, but may be somewhat lower.

It is hard to draw any definite conclusion about the decomposition in toluene; the sudden increase in rate between 95 and 100° shown in Table II is surely due to accumulated experimental error, and the table as a whole suggests a temperature coefficient of about 1.5; the other two esters have been studied over ranges of but 5 and 10°, respectively, and both show a temperature coefficient from 1.00 to 1.05. It is not at all certain whether the difference is real or not. A temperature coefficient of 1.2 or less would suggest heterogeneous catalysis, either by the walls or by dust particles, but there can be no certainty as to this without further data.

We have thus been able to account moderately well for all the experimental results by assuming three different types of decomposition: a heterogeneous catalyzed reaction, a homogeneous uncatalyzed one and a homogeneous catalysis by the reaction products. An explanation of this character cannot be considered satisfactory unless reasons can be produced for the changing importance of the various types as the solvent is changed. This is not hard to do; Patterson and McAlpine state that the products of the decomposition are a sulfonic acid and such substances as camphene and dibornylene as well as more complex hydrocarbon residues. Now hydrogen ion, and in particular unsolvated hydrogen ion, is the most notorious catalyst in all organic chemistry and it may well be the catalyst here. It is well known that pyridine and alcohol form complex ions with H^+ and the catalysis would thus be reduced in these solvents; the extent of the reduction is not easily predictable, but it is not surprising that the catalytic action is in fact practically stopped. Nitrobenzene and ethylene dibromide do not combine with H^+ to any appreciable extent, and thus in these solvents the catalysis is marked. We should expect it to be important in toluene also, but since in this solvent the decomposition obtained was always slight, it is impossible to tell whether this prediction is verified. The magnitude of the uncatalyzed reaction also varies in about the way we expect; it is greatest in the alcohols, which are the most polar solvents used, and greatest of all in methyl alcohol. In nitrobenzene, pyridine and ethylene dibromide the uncatalyzed rate is about the same, considerably less than in even butyl alcohol, while in toluene it is very much less than in any of the other solvents. The electric moment of the nitrobenzene molecule is known to be some 7 or 8 times that of toluene, so that the rate should be greater in nitrobenzene. Ethylene dibromide is symmetrical and should have a small or zero moment; there does not seem to be any available data as to this. If there is a wall reaction or a dust reaction it is probably independent of the solvent, but even though the entire reaction in toluene is due to this source, it would not be of importance in any of the other solvents. The qualitative variation of reaction rate with solvent for these decompositions is thus seen to be in agreement with theoretical predictions.

The remaining uncertainties as to the mechanism of these reactions could almost certainly be cleared up by a study from the kinetic standpoint. It does not appear to the author, however, of great importance that this should be done. The preceding analysis seems to leave little doubt that all the facts can be accounted for without introducing any new principles into reaction rate theory.

Summary

1. The possibility of regarding the decomposition of calcium carbonate hexahydrate crystals as a single reaction with a temperature coefficient of about 12 has been discussed; it appears that a reaction of this character is very improbable. It is then shown how the experimental results can be accounted for by assuming that the reaction occurs in steps, all but the last one being reversible.

2. The apparently strange behavior of the temperature coefficient of reaction rate in the decomposition of bornyl and menthyl sulfonates in certain solvents has been accounted for on the basis of autocatalysis by the resulting acid, and the general effect of the solvent upon these reactions has been shown to agree with predictions based on the character of the solvent.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA]

THE HEAT CAPACITIES OF ISOPROPYL ALCOHOL AND ACETONE FROM 16 TO 298°K. AND THE CORRESPONDING ENTROPIES AND FREE ENERGIES

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RECEIVED NOVEMBER 28, 1928 PUBLISHED APRIL 5, 1929

The heat capacities of *iso*propyl alcohol and acetone have been studied by Parks and the author[2] from 70 to 298°K. Equilibrium measurements at several temperatures were also made for the reaction $CH_3CHOHCH_3 = CH_3COCH_3 + H_2$ in the gaseous state[3] in order to show that the third law of thermodynamics held, at least for all practical purposes, for this organic reaction. An exact test was not possible since heat capacity data for gaseous *iso*propyl alcohol and acetone were not available for extrapolating the results of the equilibrium measurements and since considerable uncertainty was involved in extending the heat capacity curves for crystalline *iso*propyl alcohol and acetone below 70°K. The present work, carrying the specific heat measurements to 16°K., was undertaken to remedy this latter defect. The temperature range covered before has been reinvestigated with increased accuracy and measurements have been obtained in the large temperature gaps which were omitted in the previous work. Details of the apparatus and methods used were given in a previous paper.[4]

Materials

*Iso*propyl Alcohol.—The best grade of *iso*propyl alcohol (99 to 100%) of the Special Chemicals Company was used. It was refluxed over lime for eighteen hours and carefully fractionated three times. The middle portion taken for the measurements had a volume of about 200 cc. and a boiling-point range of 0.03°. The density was $d_4^{25} = 0.78095$, while Brunel[5] found $d_4^{25} = 0.78084$ for 100% *iso*propyl alcohol. The density determination corresponds to 99.95% of alcohol on the basis of purity adopted by Parks and Kelley.

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[1] National Research Fellow in Chemistry.

[2] Parks and Kelley, THIS JOURNAL, **47**, 2089 (1925).

[3] Parks and Kelley, *J. Phys. Chem.*, **32**, 734 (1928).

[4] Kelley, THIS JOURNAL, **51**, 180 (1929).

[5] Brunel, *ibid.*, **45**, 1336 (1923).