[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Temperature Dependence of the Energy of Activation in the Dealdolization of Diacetone Alcohol

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Introduction

For many reactions the temperature dependence of the velocity constant can be satisfactorily described by the Arrhenius equation

$$d \ln k/dT = E_{\mathrm{act}}/RT^2 \qquad (1)$$

by considering the energy of activation E_{act} to be a constant independent of temperature. Under this assumption equation (1) becomes, on integration

$$\ln k = (-E_{\mathrm{act}}/RT) + 2.3B \qquad (2)$$

$2.3B$ is the constant of integration, which likewise should be independent of temperature. If we accept, however, the statistical interpretation of E_{act} as exemplified in Tolman's treatment,[2] namely, that E_{act} is the difference between the average energy of those molecules *which react* and the average energy of all the molecules, then as La Mer[3] has pointed out, E_{act} and B must necessarily be functions of the temperature,[4] and for consistency with thermodynamics B must involve a quantity which he called the entropy of activation. The slope of the $E_{\mathrm{act}} - T$ curve will give

$$dE_{\mathrm{act}}/dT = (\bar{c}_{j,\,\mathrm{act}} - \bar{c}_i) \qquad (3)$$

where $\bar{c}_i$ is the partial molal heat capacity of all the molecules and $\bar{c}_j$ is the partial molal heat capacity of all the molecules *which react.* $\bar{c}_j$ includes the k_j factors or specific reactivity rates for different reacting levels involved in the process of statistical averaging. Whether the temperature dependence will be of significant magnitude is a question which must be decided for each reaction by experiments covering as wide a temperature range as possible. This was the primary purpose of the research. The prevailing view as epitomized in the statement of Moelwyn-Hughes[5] "*As a general rule examples which appear to contradict the Arrhenius law may also be omitted for experience has shown that such seeming deviations can usually be attributed to the presence of impurities or inadequate control of temperature,*" is primarily a result of the difficulties inherent in precise temperature coefficient measurement and an unwarranted faith in the constancy of E_{act}. Since the temperature variation of E_{act} is frequently within the limits of experimental error, it is usually detectable only in those cases where the analytical method can be considerably refined as in the case of solution reactions, or where the temperature interval can be made comparatively large. Furthermore, it is recognized that relatively small errors in the temperature scale can produce a trend in E_{act}, which is without significance.

Although the literature contains a number of carefully investigated reactions,[3,6] which yield values for E_{act} which certainly are not independent of temperature, yet in most instances the authors have either ignored the effect or have drawn unduly conservative conclusions.[7] An important exception is to be noted in the recent papers of Semerano,[8] of Liebhafsky and Mohammed, and of Harned and Seltz.[9]

On recalculating the data of G. M. Murphy[10] on the dealdolization of diacetone alcohol $(CH_3)_2COHCH_2COCH_3 + OH^- = 2CH_3COCH_3 + OH^-$, carried out at 20, 25, 30 and 35°, one of us

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[1] This paper is abstracted from a dissertation submitted by Mary L. Miller in July, 1934, to the Faculty of Pure Science, Columbia University, in partial fulfilment of the requirements of the degree of Doctor of Philosophy.

[2] R. C. Tolman, "Statistical Mechanics with Applications to Physics and Chemistry," Chemical Catalog Co., New York City, 1927.

[3] V. K. La Mer, (a) *J. Chem. Phys.*, **1,** 289 (1933); (b) THIS JOURNAL, **55,** 1739 (1933).

[4] The necessity of some temperature dependence of E_{act} was first pointed out by Trautz, whose treatment recognized the role of specific heats but became rather involved. See also Kassel, and Scheffer and Brandsma. M. Trautz, (a) *Z. physik. Chem.*, **66,** 496 (1909); (b) *Z. Electrochem.*, **15,** 692 (1909); (c) *Z. anorg. allgem. Chem.*, **102,** 81 (1918); L. S. Kassel, *Proc. Nat. Acad. Sci.*, **16,** 358 (1930); Scheffer and Brandsma, *Rec. Trav. Chim.*, **45,** 522 (1926), and earlier papers.

[5] E. A. Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford University Press, London, 1933, p. 80.

[6] E. R. Schierz and H. T. Ward, THIS JOURNAL, **50,** 3240 (1928); E. L. Whitford, *ibid.*, **47,** 953 (1925); J. C. Crocker and F. H. Lowe, *Trans. Chem. Soc.*, **91,** 953 (1907); H. Olsson, *Z. physik. Chem.*, **133,** 233 (1928); A. Skrabal, *Monatsh.*, **63,** 23 (1933); M. Kilpatrick, THIS JOURNAL, **48,** 2091 (1926); F. O. Rice and M. Kilpatrick, *ibid.*, **45,** 1401 (1923); H. Essex and O. Gelormini, *ibid.*, **48,** 882 (1926).

[7] For example, for the formic acid decomposition, the statement ". . . there is a general tendency (for E_{act}) to increase but slightly with increase in temperature," is hardly a fitting description of the data when E_{act} increases by about 1800 cal. quite consistently in four solvents, 94.4, 92.78, 91.49 and 89.53% H_2SO_4, for the range 20 to 40° corresponding to $C_{\mathrm{act}} > 90$ cal. [Schierz and Ward (*loc. cit.*)].

[8] G. Semerano, *Gazz. chim. ital.*, **61,** 921 (1931).

[9] H. A. Liebhafsky and A. Mohammed, THIS JOURNAL, **55,** 3977 (1933); Harned and Seltz, *ibid.*, **44,** 1475 (1922).

[10] G. M. Murphy, *ibid.*, **53,** 977 (1931). See Ref. 3 (a) for calculations.

noted that they required a value for $C_{\mathrm{act}} \cong 200$ cal. mol^{-1} deg.$^{-1}$. Since a heat capacity of activation of this magnitude is astonishingly large, and could arise from an error in measurement at a single temperature, we have reinvestigated the kinetics of this reaction at 5-degree intervals from 0 to 50°.

The dealdolization reaction has been investigated extensively by Koelichen, Åkerlöf, French, John Miller and Kilpatrick at 25°. It is free from complicating side reactions and is pseudo unimolecular for constant concentrations of bases. The absolute velocity can be varied over wide limits by varying the concentration of the base used as catalyst; hence the reaction is well suited for investigation over a wide range of temperature.

II. Experimental Method

The velocity was measured by the dilatometric method. A solution prepared by diluting an appropriate volume of 0.25 *N* sodium hydroxide to about 250 cc. was evacuated and kept in a thermostat regulated to 0.01° (at 0.0 and 5 to 0.02°) for at least two and one-half hours. The reaction was initiated by adding 2%[11] by volume of diacetone alcohol. After boiling under vacuum, the mixture was transferred by pressure to the dilatometer. Vacuum was reapplied until no bubbles were visible. Pressure was again applied momentarily, about 8 cm. of mercury was introduced into the capillary, and after a predetermined time readings were begun. The equilibrium value was taken at a time appropriate to the given velocity and about an hour thereafter. The capillary was water-jacketed and kept within one or two degrees of the surrounding bath.

An important innovation in the present work was the determination of the concentration of alkali after completion of the reaction by titration of an aliquot with standard acid. The customary procedure is open to the objection that the concentrations calculated from the weight of water, alkali and substrate used in preparing the mixture, may be altered during the degassing process. After the equilibrium value had been obtained the solution was brought to room temperature in the dilatometer. The first aliquot was removed for density determination and a second withdrawn in an atmosphere of carbon dioxide-free air directly into the weight buret. For the slower reactions measurements were taken at equal time intervals. Thus it was not always necessary to obtain an equilibrium value since the Guggenheim method for calculating the constant[12] could then be used. Our procedure differs from that of Åkerlöf principally in the determination of the concentrations and in the filling of the dilatometer. Åkerlöf filled his dilatometer by suction, a method which involves considerable foaming. We minimized foaming by transferring the mixture using pressure as did John Miller and Kilpatrick.[13] Since these measurements are to be interpreted from the point of view of the collision theory, concentrations are expressed in terms of normality of the final solution rather than molality of the initial solution. Time is in minutes.

The results of some preliminary experiments involving distinct variations in the experimental procedure are given in Table I. Although of lower precision than the subsequent data, they serve to indicate that the factors investigated are relatively unimportant.

TABLE I

PRELIMINARY RUNS TO INVESTIGATE THE EFFECT OF MISCELLANEOUS FACTORS AT 25.00°

Factor investigated	Concn. NaOH	$k/c \times 10^3$
Darkened reaction tube	0.02993	226
Darkened reaction tube	.03971	221
Darkened reaction tube and light	.03381	228
protection during distn.	.04382	222
Previous sun exposure (9 hrs.)		
of diacetone alcohol	.02909	240
Sun exposure as above (94 hrs.)	.03033	225
In the presence of 0.0002 *M* Ba^{++}	.02474	228
In the presence of 0.002 *M* Ba^{++}	.03145	222
With excess acetone (2% by vol.)	.07724	225
Measurements using cathetometer	.05720	223
Three months later	.05622	223
Foaming method	.03666	219
Foaming method	.03321	219

The velocity constants *k* were calculated by the well-known equation for first order reactions, or at low temperatures, 0 and 5°, by the Guggenheim method; in many cases by both. Typical experiments illustrating the character of the results at 50° for high and low concentrations of sodium hydroxide are to be found in the Dissertation.

Preparation and Purity of Materials

Sodium Hydroxide.—An approximately 0.25 *N* stock solution was prepared with Kahlbaum "sodium hydroxide from sodium." This was freed from carbonate with barium hydroxide[14] and stored in a paraffin lined bottle.

Water.—The water was redistilled and freed from carbon dioxide by boiling.

Hydrochloric Acid.—0.05 *N* HCl was made up by weight from constant boiling acid[15] and standardized gravimetrically as chloride.

Methyl Alcohol.—An analyzed product from Eimer and Amend was distilled from sodium hydroxide and iodine[16] and fractionated with a 38-cm. Hempel column; sp. gr.$^{25}_{0}$ 0.800. The alcohol was not dried.

Diacetone Alcohol.—Diacetone alcohol, Eastman No. 1084, was distilled under about 20 mm. pressure (b. p.

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[11] Up to 5% was used in some of the faster reactions at 50°.

[12] E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

[13] J. Miller and M. Kilpatrick, THIS JOURNAL, **53**, 3217 (1931).

[14] J. E. S. Han and T. Y. Chao, *J. Ind. Eng. Chem., Anal. Ed.*, **4**, 229 (1932).

[15] G. A. Hulett and W. D. Bonner, THIS JOURNAL, **31**, 390 (1909).

[16] A. V. Rakovskiĭ and A. V. Frost, *Trav. Inst. Pure Chem. Reagents* (Moscow), **9**, 95 (1930), courtesy of *Chemical Abstracts*.

164°, uncorr.) and kept in resistance-glass bottles for not over a week. Table II gives the results of several runs at 0.0° using samples of diacetone alcohol which had been subjected to further purification processes. The preparation yielded a solution neutral to litmus.

Table II

Velocity Constants at 0.00° Using Diacetone Alcohol Purified by Different Methods

Method of purification	Concn. NaOH	k/c × 10^4
A commercial product		
Two distillations	0.1026	177.6
Two distillations	.1050	177.2
Three distillations	.1045	176.6
Two distillations, one crystn.	.1047	177.0
Eastman Kodak Co. product		
One distillation	.06740	176.5
One distillation, one crystn.	.07895	176.0
One distillation and one crystn.	.08328	176.0

Precision

Temperature.—A 24-junction copper–constantan thermocouple[17] which had previously been calibrated by Dr. Eichelberger in terms of the platinum resistance thermometer at Rockefeller Institute for Medical Research, was used for the temperature standard. During the course of these experiments it was recalibrated against the freezing point of benzene[18] 5.83°, the transition point of sodium sulfate[19] 32.384°, and against Baudin Thermometer No. 18537 at 25.00 and 40.15°. Temperatures so obtained are believed to be accurate to 0.01°.

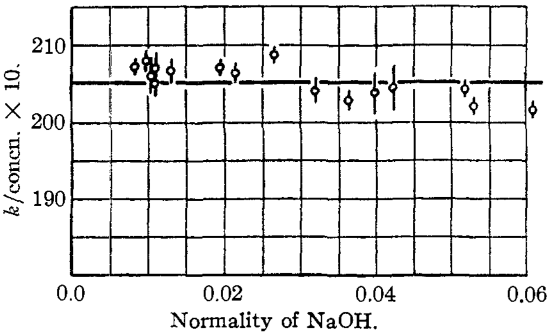

Fig. 1.—Concentration dependence of k/c values at 49.97°.

Concentration.—A precision of 0.1% was easily obtained in the titration of the sodium hydroxide content of the final solution, using weight burets and brom cresol purple as indicator.

Velocity.—The dilatometers[20] differed from those of Åkerlöf only in being equipped with a smaller water-jacket, graduated in millimeters. The reaction tube contained about 90 cc. and the capillary was usually 70 cm. long and 0.7 mm. in diameter. The height of the mercury was read to 0.1 mm. All dilatometers were calibrated to correct for irregularities in scale and bore. The readings were precise to 0.1% when at least 10 cm. from the initial and final values, which is the optimum precision to be expected in the k values.

Concentration Dependence.—From his measurements at 25° French[21] concludes that the ratio of velocity constant to molality is independent of sodium hydroxide concentration from 0.01 to 0.10 M, a conclusion which Murphy states that he has confirmed. From the point of view of temperature coefficient measurements it is important to ascertain whether this concentration independence of k/c obtains at the extremes of temperature to be examined. At 0.0° the relationship holds for the concentrations in Table II. Although runs at lower concentrations are undoubtedly possible, they were not made since the range already investigated covers a region readily measurable at 25°.

Table III

Dependence of k/c on NaOH Concentration at 49.97°

Concn. of NaOH	k/c × 10^2	Concn. of NaOH	k/c × 10^2
0.008275	207.3 ± 1.0	0.02647	208.6 ± 0.8
.009849	208.0 ± 1.5	.03230	203.8 ± 1.4
.01052	205.8 ± 2.7	.03662	202.7 ± 1.1
.01073	205.1 ± 2.0	.03976	203.9 ± 2.8
.01091	207.1 ± 3.2	.04228	204.5 ± 3.3
.01354	206.9 ± 1.5	.05190	204.2 ± 0.6
.01963	207.1 ± 0.8	.05323	202.0 ± 1.0
.02153	206.6 ± 1.3	.06087	201.4 ± 1.0

The data of Table III for k/c at 49.97° (see Fig. 1) reveal a decrease with rising concentration which is barely outside the experimental error.

Above 0.06 N sodium hydroxide the method of measurement becomes inapplicable, the constants being no longer reproducible and the solutions becoming slightly yellow. Åkerlöf,[22] while studying the effect of higher concentrations of sodium hydroxide, over 2 m, at 25°, found that at a velocity constant about equal to 0.1 (at 50° k = 0.1 when c = 0.05 N) the simple method broke down. He attributes this behavior to failure to maintain temperature equilibrium during the course of the reaction. Therefore for higher velocities he used a dilatometer containing a spiral through which the bath water was circulated.

In Fig. 2 we plot our data (Table IV) for k/c at 25° (circles) as a function of the concentration of sodium hydroxide, along with Koelichen's values[23]

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[17] W. C. Eichelberger, This Journal, **54**, 3105 (1932).

[18] T. W. Richards and J. W. Shipley, *ibid.*, **36**, 1825 (1914).

[19] H. C. Dickinson and Mueller, *Bull. Bur. Standards*, **3**, 656 (1907).

[20] Some of these dilatometers were kindly loaned by Prof. H. S. Harned and Dr. Åkerlöf, to whom we extend our thanks.

[21] C. C. French, This Journal, **51**, 3215 (1929).

[22] G. Åkerlöf, (a) *ibid.*, **48**, 3046 (1926); (b) *ibid.*, **49**, 2955 (1927); (c) *ibid.*, **50**, 733 (1928).

[23] K. Koelichen, *Z. physik. Chem.*, **33**, 129 (1900).

TABLE IV

DEPENDENCE OF k/c ON NaOH CONCENTRATION AT 25.00°

Concn. NaOH	$k/c \times 10^3$
0.02052	221.9 ± 0.3
.02920	223.3 ± 1.2
.05180	224.3 ± 0.6
.06160	221.8 ± 0.2
.07099	222.2 ± 0.8
.08637	219.4 ± 0.1
.1045	221.0 ± 0.8
	221.9 ± 1.0

(crosses) for k/c obtained by averaging his closely agreeing values for sodium hydroxide and barium hydroxide at 25.2° and reducing by 2% for comparison at 25°. Both sets of data are in excellent agreement and amply verify the linear dependence of k upon the concentration of sodium hydroxide.

On the other hand, the k/m values of French,[24] of Murphy,[25] and of Åkerlöf,[22] although agreeing fairly well among themselves are distinctly lower (6% at 0.1 N and 10% at 0.01 N) than ours, and furthermore exhibit a concentration dependence. The discrepancy persists even after we correct our k/c values to the k/m concentration scale as indicated by the dashed line in Fig. 2.

Incomplete removal of bubbles or leakage at the stopcock is not the explanation although in individual cases these factors may contribute to the scattering of the k/c values. We suspect that the discrepancy arises in the determination of the concentration of alkali. Our method of direct determination by titration at the conclusion of the reaction eliminates any possibility of reporting incorrect values for the concentration due to absorption of carbon dioxide during the process of filling the dilatometer and to the presence of acid impurities in the diacetone alcohol.

None of the previous investigators, except Koelichen, gives the method of preparation or the characteristics of the diacetone alcohol used. We find that 20 g. of the Eastman product contains 1.2×10^{-4} mole of acid, whereas the preparation Diacetone (Commercial Solvents) contains 2×10^{-3} mole of acid. The presence of acid impurities would lead to a decrease in k/m values with decreasing molality of sodium hydroxide, and is consistent with the hypothesis that these errors enter in the data of French, Murphy and Åkerlöf.

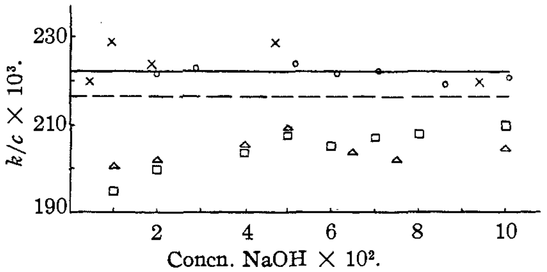

Fig. 2.—Concentration dependence of k/c at 25.00°: ○, this investigation, Table IV; ×, Koelichen k/c; △, French k/m; □, Murphy k/m; ——, mean of Table IV; ----, Table IV corrected to k/m scale.

Methyl Alcohol Effect

Since the recalculation of Murphy's data indicated a change in C_{act} with addition of methyl alcohol to the solvent, it seemed desirable to obtain a few points on the energy of activation–temperature curve for a water–methyl alcohol mixture, with a view, not only of affording a check on the general character of the water curve but possibly of shedding light on the mechanism of the reaction.

Tests showed that the final titration was unaffected by the quantity of alcohol used. Since the procedure of boiling by vacuum would remove slightly different amounts of alcohol at different temperatures, it was necessary to measure the methyl alcohol concentration in the final solution. This was accomplished by constructing density–alcohol concentration curves at each temperature, using a fixed quantity of diacetone alcohol in the mixture and allowing the sodium hydroxide concentration to vary only over narrow limits.

Experimental Results

A summary of the velocity constants obtained at eleven different temperatures is given in Table V.

TABLE V

VELOCITY CONSTANTS WITH AQUEOUS SODIUM HYDROXIDE

T., °C.	No. of expts. in average	Average k for 0.1 N NaOH
0.00	7	$(176.7 \pm 0.5) \times 10^{-5}$
5.86	2	$(322.1 \pm 2.2) \times 10^{-5}$
9.79	2	$(484.9 \pm 2.3) \times 10^{-5}$
14.98	2	$(825.7 \pm 3.7) \times 10^{-5}$
19.92	2	$(134.7 \pm 0.8) \times 10^{-4}$
25.00	7	$(221.9 \pm 1.0) \times 10^{-4}$
29.90	3	$(357 \pm 2) \times 10^{-4}$
34.97	2	$(568.8 \pm 1.0) \times 10^{-4}$
40.01	2	$(896.8 \pm 2.8) \times 10^{-4}$
45.11	4	$(140.2 \pm 1.1) \times 10^{-3}$
49.97	16	$(205.2 \pm 1.9) \times 10^{-3}$

The velocity constants, corrected to 18.5%

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[24] C. C. French, THIS JOURNAL, 51, 3215 (1929).

[25] G. M. Murphy, *ibid.*, 53, 977 (1931).

by volume of methyl alcohol in the final solution, are given in Table VI.

TABLE VI

VELOCITY CONSTANTS USING 18.5% OF METHYL ALCOHOL

T., °C.	No. of expt. in average	Average k for 0.1 N NaOH
0.00	2	$(93.14 \pm 0.64) \times 10^{-5}$
11.22	2	$(339.7 \pm 0.9) \times 10^{-5}$
14.84	2	$(507.7 \pm 2.8) \times 10^{-5}$
25.04	2	$(152.6 \pm 1.0) \times 10^{-4}$
29.98	1	256.1×10^{-4}
34.99	1	428.0×10^{-4}
49.95	2	$(183.2 \pm 0.1) \times 10^{-3}$

For comparison with the collision theory, the values of E_{act} and the integration constant B are given in Tables VII and VIII. The nature of the temperature dependence is strikingly exhibited by plotting these E_{act} and B values against temperature as in Figs. 3 and 4. From these curves the following points are observed. (1) E_{act} increases by nearly 1400 calories from 5 to 32.5° and then decreases by 500 calories (over five times the probable error) to 45°. (2) In the presence of 18.5% methyl alcohol E_{act} follows a similar course to 32.5°. (3) E_{act} increases by 1500 calories at 20° on the addition of 18.5% methyl alcohol. (4) Addition of 18.5% methyl alcohol produces an increase of one logarithmic unit in B. (5) The B values parallel the E_{act} values very closely.

TABLE VII

E AND B VALUES FROM THE ARRHENIUS EQUATION AT DIFFERENT TEMPERATURES

(′ for 15° interval, ″ for 20°, others for 10°)

Mid-point of temp. interval, °C.	E_{act}, cal.	B moles liter/min.
4.89	15850	10.92
7.49	16100′	11.13′
9.96	16230″	11.22″
10.42	16500	11.42
12.89	16550′	11.46′
14.85	16620	11.52
15.43	16680″	11.56″
17.39	16770′	11.63
19.84	16920″	11.75″
19.99	16850	11.69
22.44	17040′	11.83′
24.91	17250	11.97
24.97	17040″	11.84″
27.44	17180′	11.93
29.96	17220″	11.96″
29.98	17240	11.98
32.50	17270′	12.00′
34.95	17190	11.94
35.05	17290″	12.02″
37.50	17250′	11.98′
39.93	16960″	11.78″
40.04	17350	12.05
42.47	16930′	11.76′
44.99	16720	11.61

TABLE VIII

E AND B VALUES FROM THE ARRHENIUS EQUATION FOR DIFFERENT TEMPERATURE INTERVALS IN THE PRESENCE OF 18.5 VOLUME PER CENT. OF METHYL ALCOHOL

Interval, °C.	Mid-point of temp. interval	E_{act}[a] cal.	B moles liter-min.
0–11.22	5.61	17810	12.21
0–14.84	7.42	17870	12.27
0–25.04	12.52	18090	12.43
11.22–14.84	13.03	(18070)	(12.41)
11.22–25.04	18.13	18330	12.61
14.84–25.04	19.94	18420	12.68
25.04–29.98	27.51	(18840)	(12.98)
25.04–34.99	30.01	18930	13.05
29.98–34.99	32.48	(19040)	13.12
25.04–49.95	37.49	19110	13.18
29.98–49.95	39.96	19190	13.23
34.99–49.95	42.47	19240	13.27

[a] The precision of E is estimated at 90 cal. and that of B at 0.07 unit in B, the estimate being obtained as follows. The "average error" of the mean is averaged for all temperatures and used to obtain the ∂k_1. The $\partial E)_{k_1k_2T\Delta T} \cong 0$ and $\Delta T = 10°$ $\partial(\Delta T) = 0.02°$. Numerical values are taken at 25°.

$$\partial E)_{k_1k_2T_1T_2} = \frac{-RT_1T_2 \ ln k_1/k_2 \ \partial(\Delta T)}{(\Delta T)^2} = 34 \text{ cal.}$$

$$\partial B)_{kT} = \frac{\partial E}{2.3RT} = 0.067$$

$$\partial E)_{k_2(\Delta T)T_1T_2} = \frac{-RT_1T_2 \ \partial k_1}{\Delta T k_1} = 60 \text{ cal.}$$

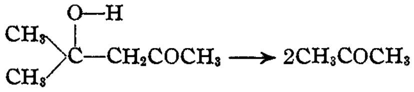
$$\partial B)_{ET} = 2.3\partial k/k = 0.008$$

$$\partial B)_{Ek} \cong 0$$

$$\partial E)_{k_1(\Delta T)T_1T_2} = 60 \text{ cal.}$$

$$\Delta E = 90 \text{ cal.} \qquad \Delta B = 0.07 \text{ unit of } B$$

A survey of the literatures shows that reactions which have so far demonstrated a marked temperature dependence of E_{act} fall roughly into two classes; namely, those involving a halogen compound and those which are either a hydrolysis or a proton change.[26] The present reaction is of the latter type being the reversal of an aldol process.



$$(CH_3)_2C(OH)—CH_2COCH_3 \longrightarrow 2CH_3COCH_3$$

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(26) A. (1) Decomposition of acetone dicarboxylic acid, E. Wiig, *J. Phys. Chem.*, **32**, 961 (1928); (2) Dehydration of citric,[a] formic,[b] and malic acids,[c] (a) E. J. Wiig, THIS JOURNAL, **52**, 4729 (1930); (b) E. R. Schierz and H. T. Ward, *ibid.*, **50**, 3240 (1928); (c) E. L. Whitford, *ibid.*, **47**, 953 (1925); (3) Alkaline hydrolysis of amides, J. C. Crocker and F. H. Lowe, *Trans. Chem. Soc.*, **91**, 953 (1907); (4) Alkaline hydrolysis of esters, H. Olsson, *Z. physik. Chem.*, **133**, 233 (1928); (5) Hydrolysis of ethers, A. Skrabal, *Monatsh.*, **63**, 23 (1933); (6) Decomposition of nitrosotriacetonamine (possibly), M. Kilpatrick, THIS JOURNAL, **48**, 2091 (1926); (7) Inversion of cane sugar, E. A. Moelwyn-Hughes, *Z. physik. Chem.*, **B26**, 281 (1934); B. (1) Sodium phenolates plus alkyl iodides, D. Segaller, *J. Chem. Soc.*, **105**, 106 (1914); (2) Bromoacetates plus thiosulfates (very slight), V. K. La Mer, THIS JOURNAL, **55**, 1739 (1933); La Mer and Kamner, *ibid.*, **57**, 2662 (1935); (3) Acetone plus iodine (very slight), F. O. Rice and M. Kilpatrick, *ibid.*, **45**, 1401 (1923).

It was pointed out in the previous theoretical paper[27] that when E_{act} is strictly independent of temperature B reduces to log Z^0, where Z^0 is the gas kinetic collision number, since in the expression

$$B = \log Z^0 + \frac{1}{2.3R}\int_0^T \left(\frac{\partial E_{act}}{\partial T}\right)\frac{dT}{T} \qquad (4)$$

the last term to the right involving the change in energy of activation with temperature vanishes. It should be remarked that although B for this reaction is not far from the order of magnitude predicted for a pure collision number,[28] however, its behavior with temperature is not at all the $T^{1/2}$ effect which would be demanded and the constant increment on the addition of methyl alcohol indicates its complex nature. Obviously the increase of one logarithmic unit in B can hardly be interpreted as arising solely from a ten-fold increase in the number of collisions.

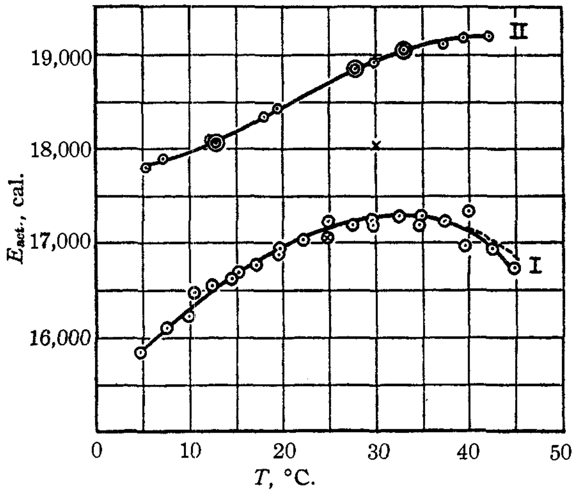

Fig. 3.—Temperature dependence of the Arrhenius E: I, water solution; II, 18.5% methyl alcohol; ×, Murphy's data; ◉, very small temperature interval.

The presence of such difficulties is recognized even by the proponents of the extreme form of the collision theory. Since the linear extrapolation of the log k − $1/T$ curve to infinite temperature, by which the collision number, Z, is obtained, cannot be made unless E_{act} is independent of temperature, some authors have attempted to correct E_{act} and others to correct B to justify this procedure. Moelwyn-Hughes' theory[29] would obtain the "true" E_{act} for reactions of this type (*i. e.*, involving a neutral molecule and an ion), which exhibit a marked discrepancy between the calculated and observed collision frequency by using for the calculation, not k, but k divided by the viscosity coefficient. Such a procedure implies that if the corrected E_{act} is to be independent of temperature the measured E_{act} was not. It may be recalled that the reactions which required this interpretation include the acid hydrolysis of esters and amides, the decomposition of nitrosotriacetoneamine, hydrolysis of sugars and the hydrolysis of γ stearolactone. A like treatment, applied to the present reaction,[30] gives E^*_{act} = 21,300 cal. and B^* = 13.9, a good correlation. However, in methyl alcohol solution E^*_{act} = 23,800 cal. and B^* = 14.9, making the former agreement seem purely fortuitous.

The parallel behavior of E_{act} and B previously pointed out is not surprising in the special case where T is the independent variable, but is a consequence of equation (4) relating B to the entropy of activation.

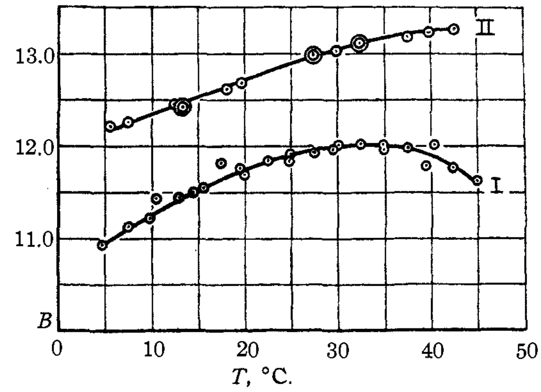

Fig. 4.—Diacetone alcohol: I, solvent water; II, solvent 18.5% methyl alcohol.

Thus, by differentiating the expressions for E_{act} and 2.3 B in respect to temperature and forming the ratio, we get

$$2.3\,\frac{dB}{dE} = 2.3\,\frac{dB}{dT}\Big/\frac{dE_{act}}{dT} = \frac{1}{RT}$$

The above considerations apply solely to the dB/dE resulting from a change in temperature and are not to be confused with the rough parallelisms between E_{act} and B[31] observed when either the solvent or one of the reactants is changed.

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[27] V. K. La Mer, (a) *J. Chem. Phys.*, **1**, 289 (1933); (b) THIS JOURNAL, **55**, 1739 (1933).

[28] The fortuitous nature of such agreement has been emphasized by Polissar, and by D. T. Lewis and Hudleston: M. J. Polissar, *ibid.*, **54**, 3105 (1932); D. T. Lewis and L. J. Hudleston, *Trans. Chem. Soc.*, 1398 (1932).

[29] E. A. Moelwyn-Hughes, *Phil. Mag.*, **14**, 112 (1932).

[30] Since the following approximations were made in order to use the viscosity data ("I. C. T."), a constancy of E^*_{act} of better than ±300 cal. can hardly be expected: (1) graphical interpolation for concentration and temperature; (2) additivity of η for acetone and methyl alcohol solutions; (3) negligible change in η due to the small amount of sodium hydroxide present.

[31] W. A. Holzschmidt, *Z. anorg. allgem. Chem.*, **200**, 82 (1931); S. Roginsky and L. Rosenkewitsch, *Z. physik. Chem.*, **10B**, 47 (1930); J. K. Syrkin, *Z. anorg. allgem. Chem.*, **199**, 28 (1931).

Summary

1. The velocity constant for the diacetone alcohol decomposition in the presence of dilute sodium hydroxide has been measured at 5° intervals from 0 to 50°.

2. The constancy of ratio of velocity constant to sodium hydroxide concentration has been confirmed over a limited concentration range at 25°.

3. The energy of activation, calculated from the Arrhenius equation for a series of temperature intervals, has been shown to be a function of temperature well outside the limits of error. E_{act} increases consistently from a value of 15,850 cal. at 5° to 17,250 at 32.5 and then decreases by about 400 cal. at 45°.

4. On the addition of 18.5% of methyl alcohol E_{act} increases by over 1700 cal. but the general character of the E_{act}–T curve remains little changed to 30°.

5. The corresponding B values from the integrated Arrhenius equation, $\ln k = 2.3\,B - (E_{act}/RT)$, both in water and the methyl alcohol solution parallel these E_{act} values and furnish experimental evidence for abandoning the unfortunate term "temperature independent constant" for this quantity.

6. The data show that the collision theory is inadequate and that the entropy of activation is an important quantity in considering solution reactions.

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The Structure and Entropy of Ice and of Other Crystals with Some Randomness of Atomic Arrangement

BY LINUS PAULING

Investigations of the entropy of substances at low temperatures have produced very important information regarding the structure of crystals, the work of Giauque and his collaborators being particularly noteworthy. For example, the observed entropy of crystalline hydrogen shows that even at very low temperatures the molecules of orthohydrogen in the crystal are rotating about as freely as in the gas;[1] subsequent to this discovery the phenomenon of rotation of molecules in crystals was found to be not uncommon. Also the entropy values of carbon monoxide[2] and nitrous oxide[3] show that in crystals of these substances the molecules are not uniquely oriented, but have instead a choice between two orientations, presumably the opposed orientations CO and OC or NNO and ONN along fixed axes. It is pointed out in this note that the observed entropy of ice at low temperatures provides strong support for a particular structure of ice, and thus gives an answer to a question which has been extensively discussed during the past few years.

It has been generally recognized since the discovery of the hydrogen bond[4] that the unusual properties of water and ice (high melting and boiling points, low density, association, high dielectric constants, etc.) owe their existence to hydrogen bonds between water molecules. The arrangement of oxygen atoms (but not of hydrogen atoms) in crystals of ice is known from x-ray studies;[5] it is not a close-packed arrangement (as of sulfur atoms in the high-temperature form of hydrogen sulfide), but a very open one, like that of the silicon atoms in high-tridymite. Each oxygen atom in ice is tetrahedrally surrounded by four other oxygen atoms at the distance 2.76 Å., and it has been assumed that it is bonded to these atoms by hydrogen bonds, the number of hydrogen atoms being just that required to place one hydrogen atom between each pair of oxygen atoms. (Similarly in high-tridymite there is an oxygen atom between each pair of silicon atoms; we might say that each silicon atom is attached to four others by oxygen bonds.)

The question now arises as to whether a given hydrogen atom is midway between the two oxygen

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[1] W. F. Giauque and H. L. Johnston, THIS JOURNAL, **50**, 3221 (1928); L. Pauling, *Phys. Rev.*, **36**, 430 (1930).

[2] J. O. Clayton and W. F. Giauque, THIS JOURNAL, **54**, 2610 (1932).

[3] R. W. Blue and W. F. Giauque, *ibid.*, **57**, 991 (1935); K. Clusius, *Z. Elektrochem.*, **40**, 99 (1934).

[4] W. M. Latimer and W. H. Rodebush, THIS JOURNAL, **42**, 1419 (1920).

[5] D. M. Dennison, *Phys. Rev.*, **17**, 20 (1921); W. H. Bragg, *Proc. Phys. Soc.* (London), **34**, 98 (1922); W. H. Barnes, *Proc. Roy. Soc.* (London), **A125**, 670 (1929).