

to 0.0015 g. with a 40-g. sample of iodine pentoxide. This deficiency is far greater than the apparent experimental error.

The atomic weight of iodine calculated from the corrected experimental ratio of silver to iodine pentoxide, 0.646231, found by Baxter and Tilley, is 126.937, on the basis of the atomic weight 107.880 for silver. The coincidence is striking that the discrepancy in the composition of iodine pentoxide, though a little more than half as large, is in the same direction as that indicated by our experiments.

By combining the experimental ratios of silver and iodine to iodine pentoxide the ratio of iodine to silver is found to be 1.176579 and the atomic weight of iodine 126.929 on the basis of $\text{Ag} = 107.880$. This value for iodine differs very little from that found by direct comparison with silver, 126.932.

The percentage of iodine in iodine pentoxide is apparently too small, the percentage of oxygen too large. If the extra oxygen is wholly or in part in the form of a higher oxide, the oxidizing power of the iodine pentoxide should be too large. In a subsequent paper will be described a comparison of arsenic trichloride with iodine pentoxide in which it appears that this is the case. If the apparent excess of oxygen indicated by our work, 0.005%, is wholly in the form of the heptoxide, the proportion of the latter would be ten times as large.

We cannot avoid the conclusion, therefore, that iodine pentoxide of normal composition is difficult if not impossible to prepare and that conclusions based upon its actual composition are not sufficiently reliable for work of high precision.

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SALT AND MEDIUM EFFECTS ON THE TEMPERATURE COEFFICIENT OF VELOCITY OF DECOMPOSITION OF DIACETONE ALCOHOL¹

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The hydroxide-ion catalysis of diacetone alcohol has recently been investigated by Åkerlöf,² who determined the influences of different hydroxides at various concentrations and both weak and strong hydroxides in salt solutions upon the reaction rate. Further, results were obtained by him which showed the effects on this reaction rate of addition of some alcohols and other organic solvents to the aqueous hydroxide solutions. Results contained in this investigation demonstrate the influences of the

¹ The present study constitutes a part of a thesis presented to the Graduate School of Yale University as partial fulfilment of the requirements of the degree of Doctor of Philosophy, 1930.

² Åkerlöf, *THIS JOURNAL*, **48**, 3046 (1926); **49**, 2955 (1927); **50**, 733 (1928).

addition of sodium chloride and methyl alcohol upon the temperature coefficient of reaction rate of the decomposition of diacetone alcohol catalyzed by suitable concentrations of sodium hydroxide. Measurements of the reaction rate at 20, 25, 30 and 35° in the presence of various strengths of sodium hydroxide between 0.01 and 0.1 molal have also been obtained.

Experimental Results

Since the measurements were made by means of a dilatometer and by a method similar to that described by Åkerlöf, little further need be added here. The temperature was controlled to within $\pm 0.005^\circ$ during a given measurement. Considerable care was exercised in the preparation of the solutions and the purification of the chemicals. The velocity constant was computed by the equation

$$K = \frac{1}{t} \log \frac{l_\infty}{l_\infty - l_t} = 0.434k \quad (1)$$

where l_∞ is the length read on the dilatometer which corresponded to complete reaction, and l_t that which corresponded to the quantity changed in time, t . The over-all accuracy of this measurement is estimated to be approximately $\pm 1\%$. Table I contains the results. The column headings are self-explanatory.

TABLE I
VELOCITY CONSTANTS AND TEMPERATURE COEFFICIENTS OF THE DECOMPOSITION OF
DIACETONE ALCOHOL

| $K \times 10^4 = 0.434k \times 10^4$ | | | | | | | |
|------------------------------------------------|----------|----------|----------|----------|-----------------|-----------------|--|
| (1) Sodium Hydroxide Solutions | | | | | | | |
| m (NaOH) | K_{20} | K_{25} | K_{30} | K_{35} | K_{30}/K_{20} | K_{35}/K_{25} | |
| 0.01 | 12.5 | 19.6 | 32.5 | 53.0 | 2.60 | 2.68 | |
| .02 | 26.0 | 40.0 | 67.0 | 106.0 | 2.58 | 2.65 | |
| .04 | 52.2 | 81.5 | 134.9 | 220.6 | 2.59 | 2.70 | |
| .05 | 65.5 | 104.1 | 167.5 | 279.4 | 2.56 | 2.68 | |
| .06 | 78.7 | 123.0 | 202.0 | 330.2 | 2.56 | 2.68 | |
| .07 | 91.5 | 144.8 | 234.9 | 385.6 | 2.57 | 2.66 | |
| .08 | 103.2 | 166.5 | 264.0 | 440.8 | 2.56 | 2.64 | |
| .10 | 133.5 | 210.0 | 350.2 | 565.6 | 2.62 | 2.69 | |
| | | | | | 2.57 | 2.67 | |
| (2) Sodium Hydroxide-Sodium Chloride Solutions | | | | | | | |
| NaOH (0.05) + NaCl (m) | | | | | | | |
| m | K_{20} | K_{25} | K_{30} | K_{35} | K_{30}/K_{20} | K_{35}/K_{25} | |
| 0.00 | 65.5 | 104.1 | 167.5 | 279.4 | 2.56 | 2.68 | |
| .1 | 64.5 | 100.2 | 163.6 | 270.0 | 2.54 | 2.70 | |
| .2 | 63.6 | 98.5 | 162.6 | 265.4 | 2.56 | 2.69 | |
| .4 | 60.0 | 92.5 | 154.0 | 250.4 | 2.57 | 2.72 | |
| .5 | 58.0 | 89.0 | 149.0 | 242.6 | 2.57 | 2.73 | |
| .6 | 56.1 | 85.8 | 144.2 | 232.0 | 2.58 | 2.70 | |
| .8 | 53.2 | 81.0 | 137.5 | 219.5 | 2.60 | 2.71 | |
| 1.0 | 50.8 | 77.8 | 132.0 | 208.5 | 2.60 | 2.72 | |
| | | | | | 2.57 | 2.70 | |

TABLE I (Concluded)
 (3) Water-Methyl Alcohol Mixtures
 NaOH (0.1) + CH₃OH (C, %)

| C, % | K ₂₀ | K ₂₅ | K ₃₀ | K ₃₅ | K ₂₀ /K ₂₅ | K ₂₅ /K ₂₀ |
|------|-----------------|-----------------|-----------------|-----------------|----------------------------------|----------------------------------|
| 0 | 133.5 | 210.0 | 350.2 | 565.6 | 2.62 | 2.69 |
| 10 | 98.8 | 156.0 | 268.1 | 433.5 | 2.71 | 2.78 |
| 20 | 71.2 | 116.0 | 200.7 | 337.0 | 2.82 | 2.90 |
| 30 | 51.8 | 88.8 | 147.8 | 261.0 | 2.86 | 2.94 |
| 40 | 38.5 | 67.1 | 111.9 | 198.6 | 2.91 | 2.96 |
| 50 | 28.2 | 51.6 | 84.3 | 154.9 | 2.98 | 3.00 |
| 60 | 20.8 | 38.9 | 63.7 | 120.0 | 3.02 | 3.08 |

Discussion of Results

(1) **Hydroxide Catalyst.**—For the purpose of the present discussion, we shall supplement Brønsted's³ theory of homogeneous reaction velocity by the inclusion of the term containing the energy of activation of the diacetone alcohol per mole, Q_{12} , and obtain

$$V = km_A m_{OH} \frac{\gamma_A \gamma_{OH}}{\gamma_i} e^{-Q_{12}/RT} \quad (2)$$

m_A and m_{OH} are the concentrations, γ_A and γ_{OH} the activity coefficients of the diacetone alcohol and hydroxide ion, respectively, and γ_i the activity coefficient of the intermediate. At constant temperature, this reduces to Brønsted's equation,

$$V = k' m_A m_{OH} \frac{\gamma_A \gamma_{OH}}{\gamma_i} \quad (3)$$

In dilute solutions the kinetic factor $\gamma_A \gamma_{OH} / \gamma_i$ approaches unity and Equation 3 becomes

$$V = k' m_A m_{OH} \quad (4)$$

That the velocity constant k' is proportional to the hydroxide concentration in the region of concentration from 0.01 to 0.1 molal has been shown by French,⁴ and confirmed at all concentrations by the data in the first part of Table I. Since this is the case, the temperature coefficient is independent of the hydroxide concentration, as shown by the velocity constant ratios in the sixth and seventh columns of the table.

At hydroxide concentrations from 0.2 to 6 *M*, Åkerlöf found that the reaction velocity conformed with that predicted by the equation

$$v = km_A m_{OH} \sqrt{\gamma_M \gamma_{OH}} \quad (5)$$

Since the variation of the activity coefficient with the temperature is small, and probably uniform, we would also expect the temperature coefficient of the reaction velocity to be independent of the hydroxide concentration in the more concentrated solutions.

(2) **Hydroxide-Chloride Catalysts.**—From the ratios of the velocity

³ Brønsted, *Chem. Rev.*, **5**, 286 (1928).

⁴ French, *THIS JOURNAL*, **51**, 3215 (1929); see also Harned and Åkerlöf, *Trans. Faraday Soc.*, **24**, 676 (1928).

constants at different temperatures contained in the last two columns of the second part of Table I, it is clear that the temperature coefficient of the velocity constant is independent of the concentration of the added salt. Further, the mean values of the temperature coefficients are the same as those in the case of the pure hydroxide solutions within the error of the present experimental method.

From these results the value of Q_{12} may be readily computed. Thus, from Equation 2, we find that

$$k = Ae^{-Q_{12}/RT} \quad (6)$$

whence, the equation of Arrhenius

$$\frac{d \ln k}{dT} = \frac{Q_{12}}{RT^2} \quad (7)$$

may be obtained by differentiation. Integrating between the limits k_{35} and T_1 and k_{25} and T_2 , we obtain

$$\ln \frac{k_{35}}{k_{25}} = \frac{Q_{12}}{R} \frac{(T_1 - T_2)}{T_1 T_2} \quad (8)$$

Substituting 308.1° for T_1 and 298.1° for T_2 and converting to common logarithms, we find that

$$Q_{12} = 42,011 \log \frac{k_{35}}{k_{25}} \quad (9)$$

If we substitute the average values, 2.67 and 2.70, from the last columns of parts (1) and (2) of Table I for k_{35}/k_{25} in this equation, we obtain $Q_{12} = 17,918$ cal. and $Q_{12} = 18,122$ cal., respectively. Thus the value of Q_{12} may be taken to be 18,000 cal.

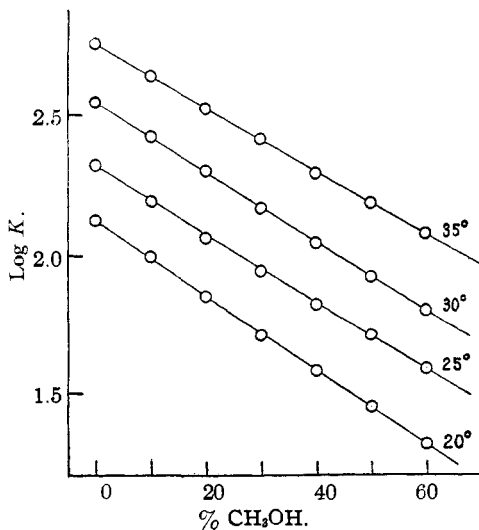


Fig. 1.

(3) **Hydroxide Catalyst in Water-Methyl Alcohol Mixtures.**—The addition of methyl alcohol to the aqueous solution of sodium hydroxide decreases the velocity of decomposition of diacetone alcohol. This was previously shown at 25° by Åkerlöf, who studied the effects of six organic solvent-water mixtures containing sodium hydroxide upon this reaction rate. In Fig. 1 the logarithm of the velocity constants at 20, 25, 30 and 35° contained in the third

part of Table I are plotted against the weight percentages of methyl alcohol. The plots appear as straight lines up to a concentration of 60% alcohol.

It is important to observe, however, that the temperature coefficient is not independent of the methyl alcohol concentration, but that the ratios of the velocity constants at 30 and 20°, and at 35 and 25°, increase with increasing methyl alcohol content, as shown by the sixth and seventh columns of the third part of Table I.

The writer takes this opportunity to thank Professor Herbert S. Harned for help and suggestions obtained from him during the course of this work.

Summary

1. The reaction velocity constant of decomposition of diacetone alcohol catalyzed by hydroxides has been measured at 20, 25, 30 and 35° in aqueous solutions of sodium hydroxide of different concentrations, in aqueous hydroxide-salt solutions, and in water-methyl alcohol mixtures containing sodium hydroxide.

2. The temperature coefficient of reaction velocity is independent of the strength of hydroxide. It is also independent of the sodium chloride concentration in the hydroxide-salt mixtures.

3. The temperature coefficient, however, is not independent of the concentration of methyl alcohol in the alcohol-water mixtures containing 0.1 *M* sodium hydroxide.

4. The energy of activation has been computed and is found to be 18,000 cal. The error in this observation is approximately $\pm 0.7\%$.

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

A THEORY OF THE ARRANGEMENT OF PROTONS AND ELECTRONS IN THE ATOMIC NUCLEUS

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From a study of the number of protons and electrons in those atomic species whose atomic weights are approximately integral multiples of four, together with data on their abundance, I have been led to a geometrical representation of the atomic nuclei in which the protons and electrons are arranged in a definite space lattice. It appears certain that the nucleus must be held together by the coupling of the proton spins, and the model may be interpreted as the pattern determined by the directions of the spin vectors. In the proposed model the angle between any two proton vectors is that formed by lines from two corners of a tetrahedron to its center, and this in the new quantum mechanics is the angle at which two elementary spin vectors add to give a resultant of two units.

It seems reasonable to expect that existing relations would appear more clearly defined in the case of the atomic species with atomic weights