[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

Kinetics of the Reaction between Copper and Aqueous Ammonia[1]

BY R. W. LANE AND H. J. McDONALD

Introduction

While considerable research had been conducted on the general investigation of the reaction between copper and aqueous ammonia, the kinetics of this reaction was found to be only partially investigated. Yamasaki[2] investigated the rate of dissolution of metallic copper in ammonium hydroxide by rotating copper specimens at constant velocity and by supplying a steady current of purified air. His work indicated that electrolytic dissolution of copper and auto-catalysis by the cuprammonium compound in solution were the two independent chemical reactions responsible for the dissolution of copper. Zaretskii and Akimov[3] investigated the mechanism of corrosion of copper in aqueous solutions of ammonium compounds and attributed the corrosion to three processes, the first being the electrochemical solution of copper with formation of cuprous ammonia complex, the second, oxidation of the complex to form cupric ammonia complex and the third, electrochemical reduction of the cupric ammonia complex to cuprous ammonia complex.

In this investigation the order of the reaction, the rate-determining step, the energy of activation, the effect of ionic strength, viscosity, and surface area of the metal specimens on the reaction have been determined. Additional information has been obtained on (1) the effect of variation of linear velocity on the reaction and (2) the effect of variation in concentration of ammonium hydroxide on the reaction.

Experimental

Particular attention was given to the design of the apparatus in respect to exclusion of all metals from the reaction flask, and to maintenance of uniform linear velocity over all of the surface of the metal specimens. The apparatus consisted of a reaction flask into which oxygen was introduced and in which a cylinder of copper was revolved on a glass stirrer. The four prongs of the stirrer held the specimen (11.75 × 1.27 cm.) in position by adjustment through five equally spaced holes in the specimen. The fifth hole served as a lock to prevent the specimen from coming off the stirrer at high velocities. The oxygen was passed through three gas washing bottles, one containing sodium hydroxide solution and two containing measured amounts of ammonium hydroxide solution of the same molarity as that contained in the reaction flask and then was admitted to the reaction flask. The sodium hydroxide solution was used to eliminate carbon dioxide from the oxygen supply. The ammonium hydroxide solutions provided replacement of ammonia in the reaction flask, which had been lost by aeration. These solutions were immersed in the constant temperature bath along with the reaction flask. In this way, approximately the same partial pressure of ammonia was provided in the influent and effluent oxygen to the reaction flask.

The quality and description of the chemicals used in these experiments were: ammonium hydroxide, Reagent grade, General Chemical Co., copper metal, 0.008 in. thick, electrolytic sheet, J. T. Baker Chemical Co., average grain size (0.25 mm.); oxygen, 99.5% pure.

Ammonium hydroxide solutions were standardized to the desired molarity by titration with hydrochloric acid to the methyl red end-point. Copper metal specimens were annealed at 600° for thirty minutes in an electric furnace and cooled slowly. Just before an experiment was started, the specimen was immersed in 6 *N* nitric acid at 50° for one minute, then rinsed with distilled water, ethyl alcohol and anhydrous ethyl ether.

A Lumetron photoelectric colorimeter, model 400, with red filter (650) was used for determining the amount of dissolved copper formed during the progress of the reaction. The photelometric method of analysis used was based on the work of Yoe and Barton[4] and Mehlig.[5] Standard curves were prepared for the determination of copper content at each level of concentration of ammonium hydroxide and in this way direct reading of all samples could be made. Samples were therefore able to be returned to the reaction flask and a constant volume was held throughout the experiment. Several runs were made in which the weight losses of the specimen were checked against the colorimetric results throughout the experiment. Colorimetric results were found to be always within ±2% of the true concentration.

Results

While similar heterogeneous reactions reported in the literature have been found to be first order, zero order was found to fit the data best in this investigation. Accordingly, all reaction velocity constants have been calculated from the zero order equation.

Complete data, obtained in a series of experiments in which the molarity of ammonium hy-

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[1] Abstracted from the thesis submitted by R. W. Lane to Illinois Institute of Technology in partial fulfillment of the requirements for the degree of Master of Science in Chemistry, June, 1945.

[2] Yamasaki, *Science Repts. Tohoku Imp. Univ.*, 1st series, **9**, 169 (1920); *Proc. 7th Int. Congr. Applied Chem., London*, Sect. x, 174 (1909).

[3] Zaretskii and Akimov, *J. Applied Chem. U. S. S. R.*, **11**, 1161 (1938).

[4] Yoe and Barton, *Ind. Eng. Chem. Anal. Ed.*, **12**, 456 (1940).

[5] Mehlig, *ibid.*, **13**, 533 (1941).

Table I

M./l. of $Cu(NH_3)_4^{++}$/sq. cm. × 10^4

M./l. NH_4OH	0.2300	0.2300	0.3440	0.3440	0.3440	0.6890	0.6890	0.6890
Run no.	6	27	3	15	29	13	16	30
Time, min.								
2.25	0.085	....	....	....	....	....	....	....
5	....	....	....	....	0.294	....	....	....
10	.394	0.321	0.540	0.515	.530	0.680	0.546	0.739
15	....	....	....	....	.749	....	....	....
20	.614	.555	1.02	0.938	.934	1.48	1.44	1.55
30	.779	.687	1.34	1.21	1.24	2.36	2.40	2.42
40	.923	.816	1.53	1.46	1.48	3.19	3.19	3.21
50	1.06	.945	1.71	1.67	1.69	3.83	3.85	3.79
60	1.19	1.07	1.89	1.85	1.85	4.38	....	4.32
70	1.28	1.20	2.05	2.02	2.03	4.81	....	4.83
80	1.36	1.33	2.20	2.18	2.21	5.20	....	5.27
90	1.45	1.42	2.41	2.37	2.39	5.66	....	5.68
100	1.53	1.51	....	....	2.56	6.07	....	6.02
110	1.63	1.56	....	....	2.74	6.45	....	6.34
120	1.73	1.67	....	....	....	6.85	....	6.70
130	....	....	....	....	....	7.32	....	....

droxide was the only variable, are included in Table I.

Application of the accepted equation for autocatalytic reactions was made to these data but the inconsistent k values so obtained indicated this equation did not apply. Therefore the evidence in Fig. 1 and the results obtained with the autocatalytic equation seem to disprove Yamasaki's conclusions that the velocity of reaction is independent of the free ammonia concentration and that autocatalysis plays a major role in the reaction.

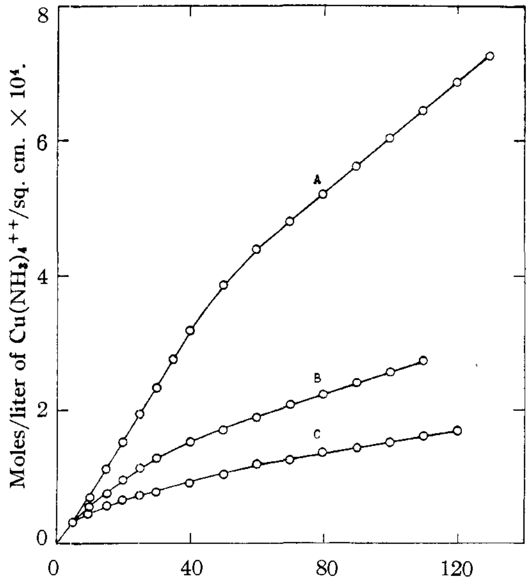

Fig. 1.—Effect of concentration of ammonium hydroxide on the rate of dissolution of copper at 29.6° and at a linear velocity of 13,300 cm./min.: curve A, 0.6890 M NH_4OH; curve B, 0.3440 M NH_4OH; curve C, 0.2300 M NH_4OH.

In Fig. 2, the influence of the temperature on the reaction is illustrated. By plotting log k_1 and log k_2 against $1/T$ (T = temperature in degrees Kelvin), the energy of activation for k_1 values was found to be 7100 calories and for k_2, 1670 calories. According to Bowen, Moelwyn-Hughes and Hinshelwood[6] the true energy of activation is obtained by a plot of log k/η against $1/T$ whenever the solvent has considerable influence on the reaction and the viscosity (η) effect is considerable. Application of this method to the data shows that the solvent does have considerable influence on the reaction for the energy of activation is increased to 12,850 calories for the

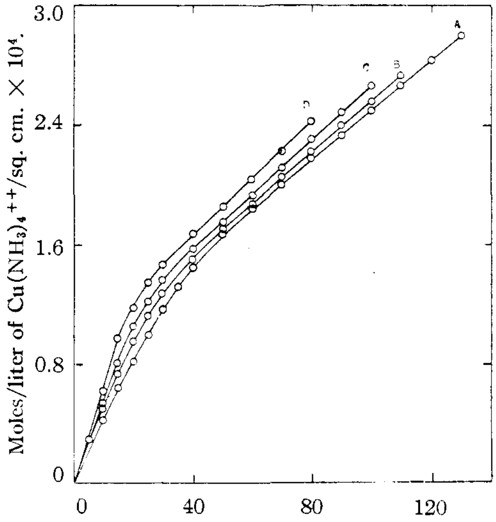

Fig. 2.—Effect of temperature on the rate of dissolution of copper in 0.3440 M ammonium hydroxide: curve A, 25.0°; curve B, 29.6°; curve C, 34.9°; curve D, 40.0°.

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[6] Bowen, Moelwyn-Hughes and Hinshelwood, *Proc. Roy. Soc.* (London), **A134**, 211 (1931).

initial part of the reaction and to 7050 calories for the latter part of the reaction.

Experimental work in variation of surface area of metal specimens was found to confirm Kilpatrick and Rushton's[7] work that variation in surface area had no influence on the reaction rate per unit area. These data serve to demonstrate the reproducibility of the results and may be used for verification of the authors' conclusions in their kinetic analysis of the results. Figure 1 shows the results listed in Table I in graphical form. Increase in the concentration of ammonium hydroxide is shown to definitely increase the reaction rate between copper and ammonia.

Two straight line portions were obtained for each curve and have been designated k_1 for the initial part of the reaction when the dissolution of copper is occurring at a rapid rate unhampered by the formation of insoluble corrosion products and k_2 for the latter part of the reaction when the rate is much slower and is somewhat hampered by the presence of insoluble corrosion products on the surface of the specimens. The following equations have been derived to show the relationship between reaction velocity constants and the initial ammonium hydroxide concentration at 29.6° and a linear velocity of 13,300 cm./min.

$$k_1 = (1.85 \times 10^{-6})\ 10000^{0.192\ \text{m./l.}\ NH_4OH}$$
$$k_2 = (5.26 \times 10^{-6})\ \text{m./l.}\ NH_4OH - (0.54 \times 10^{-6})$$

A complex reaction may often be simplified by adding a large excess of all the reactants except one and variation of this one permits direct determination of the exponent to which the concentration of the reactant is raised in the rate equation. As the exponents of the concentration terms in the rate equation indicate the order of the reaction, this method was applied to this research and the results indicated that the reaction is first order with respect to ammonium hydroxide. Therefore, despite the fact that zero order has been shown to fit the over-all reaction best, the chemical reaction involved may probably best be described as a first order reaction.

In Fig. 3, increase in linear velocity is shown to definitely increase the reaction rate. Choi, McDonald and Teeter's[8] work confirms this conclusion. Equations in the form of $k = aR^s$ were derived to show the relationship between the reaction rate constants (k) and the linear velocity (R). Numerous investigators[9] have found values of $^2/_3$ to 1 for s in this equation, while in this research, a value of 0.83 was obtained for the initial part of the reaction, indicating good agreement.

In Table II, increase in ionic strength by addition of potassium chloride is shown to increase the values of the reaction velocity constants or that is, increase the rate of the reaction.

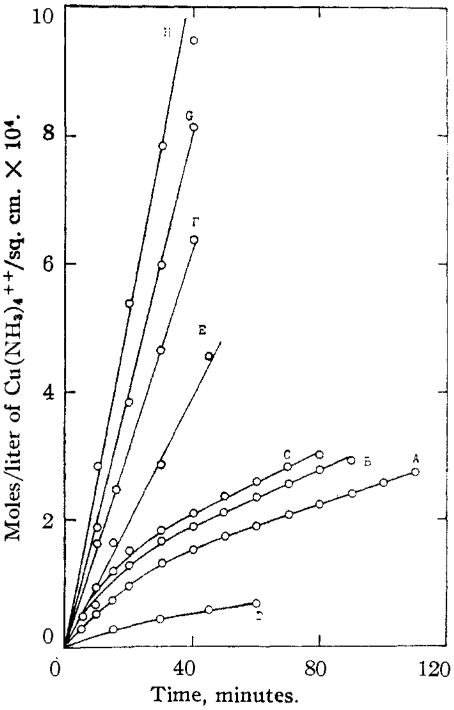

Fig. 3.—Effect of linear velocity on the rate of dissolution of copper in 0.3440 *M* ammonium hydroxide at 29.6°: curve A, 13,300 cm./min.; curve B, 21,920 cm./min.; curve C, 31,470 cm./min.; [Choi, McDonald, Teeter data (see footnote 8), NH_4OH = 0.7118 *M*, *T* = 25°] curve D, 0 cm./min.; curve E, 14,820 cm./min.; curve F, 26,240 cm./min.; curve G, 42,820 cm./min.; curve H, 51,380 cm./min.

TABLE II

Ionic strength, μ	$k_1 \times 10^6$	$k_2 \times 10^6$
0.0025	3.28	1.29
.0125	3.54	1.43
.0425	4.40	1.50
.1025	4.94	1.76

In Fig. 4, plots of the logarithms of the reaction velocity constants obtained from Table II against the square root of the ionic strength yield straight lines whose slopes are 0.82 and 0.49, respectively. The significance of these results in determining the mechanism of the reaction will be taken up in the discussion.

The influence of viscosity on the reaction was studied by adding sucrose to increase the viscosity and determining the reaction rate. It was found that increased viscosity decreased the reaction rate slightly.

Discussion

When a chemical reaction takes place in a heterogeneous system, the boundary of the phases is the important location where a number of factors may be instrumental in influencing the

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(7) Kilpatrick and Rushton, *J. Phys. Chem.*, **38**, 269 (1934).

(8) Choi, McDonald and Teeter, unpub. invest., Illinois Inst. Tech., 1945.

(9) (a) Wildermann, *Z. physik. Chem.*, **66**, 445 (1909); (b) Brunner, *ibid.*, **47**, 56 (1904); (c) Yamasaki, *Sci. Repts. Tohoku Imp. Univ.*, 1st series, **9**, 169 (1920); (d) Van Name and Edgar, *Am. J. Sci.*, **29**, 237 (1910).

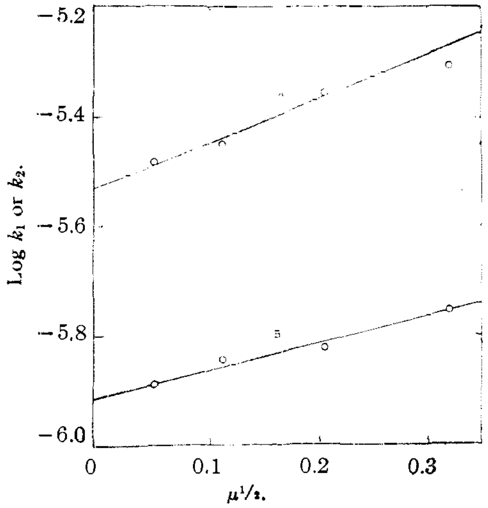

Fig. 4.—Variation of reaction velocity constants (from Fig. 4) with the square root of the ionic strength: curve A, k_1 values; curve B, k_2 values.

rate of reaction. This reaction must be bimolecular, for the solute must react with the solid for chemical change to occur. Three distinct processes occur in reactions of this kind; (1) solute molecules approach and collide with the solid surface, where (2) chemical reaction takes place, followed by (3) the recession of the products away from the interface into the bulk of the solution. While each of these processes may influence the over-all rate of reaction, the slowest process is considered the rate-determining step.

The temperature coefficient for a 10° rise in temperature for the initial part of the reaction is 1.56 and for the latter part of the reaction, 1.09. Hedges[10] lists temperature coefficients of 1.2 for a diffusion-controlled process and 2.0 for a chemically controlled process. Energy of activation values of 7100 calories for the initial part of the reaction and 1670 calories for the latter part of the reaction are close to the values of 3000 to 5000 calories stipulated for diffusion-controlled processes.[11] Increase in linear velocity did produce an increment in reaction velocity and this is a definite indication of a diffusion-controlled process, according to Hedges,[10] and King and Wiedenhammer.[12] Another indication that the reaction is diffusion-controlled in borne out in King and Wiedenhammer's[12] work on a similar diffusion-controlled reaction in which an increase in viscosity produced a decrease in reaction rate.

It therefore appears that the initial part of the reaction is partially diffusion and chemically controlled, while the latter part of the reaction is definitely diffusion-controlled. The rate controlling step from the standpoint of diffusion is either the diffusion of ammonium hydroxide to the metal surface or the removal of cupric tetrammino hydroxide from the surface. With the large excess of solute available at the start of the reaction this diffusion to the surface cannot be expected to be a slow process because of the continuous availability of the solute. The removal of the reaction product from the surface would therefore be expected to be the rate-controlling step. In the latter part of the reaction, accumulation of insoluble reaction product on the surface makes the diffusion more difficult and definitely rate-controlling. While the effect of increased linear velocity was not as great in this part of the reaction, this can be explained by the fact that the solution is now rich in reaction product and as a result, the concentration gradient is lower.

As the results indicate that a chemical reaction in the initial part of the reaction may be partially rate-determining, a thermodynamic investigation of the possible reactions should aid in determining the rate-controlling step. Consideration is therefore given to all possible combinations of cells to determine which reaction is most likely to occur. The reaction that yields the highest positive E^0 value and at the same time has no characteristics that prevent the reaction from going to completion will be considered the reaction most probable to occur.

In Table III, it will be noted that combination of equations (A) and (B) yields the resultant equation of the oxidation of copper by oxygen and that the combination of equations (D) and (E) yields the reaction between cupric oxide and ammonia. The equation (G) for the over-all reaction was obtained from the original four equations and is the generally accepted equation for this reaction. It is of interest to note at this time that equation (B) will later be shown to be the rate-determining step.

By employing Eyring's theory of absolute reaction rates, the Debye–Hückel theory and Brönsted's theory of the electrolyte effect, an equation can be derived that shows a definite relationship between the square root of the ionic strength and the reaction velocity constant. By application of this equation, calculation of the valence numbers of the ions involved in the rate-controlling step may be made. In the derivation of the equation, Eyring's[11] theory for absolute reaction rates provides for the formation of an activated complex (X), which is formed from the reactants and later decomposes into the products at a definite rate. It is understood that the initial reactants are always in equilibrium with the activated complexes. The reacting ions represented by the following equation were considered the most likely reactants in the rate controlling step.

$$OH + OH + Cu^0 = X^{=}$$

Plotting of the logarithms of the reaction velocity constants against the square roots of the ionic strengths, yields a slope equal to $-\alpha\Delta(z^2)$,

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[10] Hedges, "Protective Films on Metals," 1st ed., D. Van Nostrand Co., New York, N. Y., 1932.

[11] Glasstone, Laidler and Eyring, "Theory of Rate Processes," 1st ed., McGraw-Hill Book Company, Inc., New York, N. Y., 1941.

[12] King and Wiedenhammer, THIS JOURNAL, 58, 602 (1936).

where z = valence number of an ion taking part in the rate-determining step, and $\alpha = -0.509$. In this particular problem, we have $\Delta(z^2) = (-2)^2-((-1)^2 + (-1)^2 + (0)^2) = 2$. Then $2 \cdot -(-0.509) = 1.0$ for the slope. It is known that the slope obtained for the k_1 portion of the reaction is approximately 1.0; so it would appear that the reaction of hydroxide ions on the surface of the copper is the rate determining step. However, all possible combinations should be considered to be sure that this is the actual combination. In Table IV, the possible combinations of reactants are considered and calculation of the $\Delta(z^2)$ is made. It is observed that equations (b) and (g) also yield a $\Delta(z^2)$ of 2; so these reactions can also be considered possible mechanisms. In the case of (b), there might be some question as to the source of the hydrogen. In the case of (g), the complex formed is composed of NH_3 molecules and not NH_4^+ ions; so it seems questionable whether such a compound might be formed. So it appears that the rate-controlling step is the reaction between hydroxide ions and metallic copper. It should be pointed out at this time that it is possible that the chloride ion may have some specific effect on the reaction rate and therefore lead to an erroneous conclusion in regard to the mechanism. However, as conclusions on previous investigations of mechanisms of reactions have been based on variation of ionic strength by variation of chloride ion, it is felt that the mechanism proposed here is likewise justified. Future work employing other anions would nevertheless provide a worthy addition to the knowledge concerning this reaction.

TABLE III

THERMODYNAMIC INVESTIGATION OF THE MECHANISM OF THE REACTION BETWEEN COPPER AND AMMONIUM HYDROXIDE

(A)	$O_2 + 2H_2O + 4e^- = 4OH^-$	$E^0 = 0.0401$ v.
(B)	$4OH^- + 2Cu = 2CuO + 2H_2O + 4e^-$	$E^0 = 0.258$ v.
(C)	$2Cu + O_2 = 2CuO$	$E^0 = 0.659$ v.
(D)	$4NH_3 + Cu = Cu(NH_3)_4^{++} + 2e^-$	$E^0 = 0.05$ v.
(E)	$CuO + H_2O + 2e^- = 2OH^- + Cu$	$E^0 = -0.258$ v.
(F)	$4NH_3 + CuO + H_2O = Cu(NH_3)_4 + 2OH^-$	$E^0 = -0.208$ v.
(F)	$8NH_3 + 2CuO + 2H_2O = 2Cu(NH_3)_4^{++} + 4OH^-$	$E^0 = -0.208$ v.
(C)	$2Cu + O_2 = 2CuO$	$E^0 = 0.659$ v.
(G)	$2Cu + 8NH_3 + O_2 + 2H_2O = 2Cu(NH_3)_4^{++} + 4OH^-$	$E^0 = 0.45$ v.

TABLE IV

POSSIBLE COMBINATIONS OF REACTANTS AND CALCULATION OF $\Delta(z^2)$

	Reactions	Calculation of $\Delta(z^2)$
(a)	$2OH^- + Cu^0 = X^{=}$	2
(b)	$2OH^- + H_2 = X^{=}$	2
(c)	$Cu(NH_3)_2^+ + OH^- = X^0$	−2
(d)	$Cu(NH_3)_2^+ + 2NH_4^+ = X$	6
(e)	$Cu^{++} + 2OH^- = X^0$	−6
(f)	$Cu^+ + OH^- = X^0$	−2
(g)	$Cu^0 + 2NH_4^+ = X$	2
(h)	$Cu(NH_3)_4^{++} + 2OH^- = X^0$	−6

LaMer[13] has demonstrated this application of Brönsted's theory of the electrolyte effect in several reactions in which he has been able to ascertain the rate-controlling step.

Yamasaki[2] found that sodium hydroxide in small quantities increased the reaction rate, but that in large quantities, it decreased the rate. This is what would be expected as the additional OH^- ions provided by small quantities of sodium hydroxide would be expected to speed up the reaction but large quantities would slow the reaction by the formation of the insoluble product $Cu(OH)_2$, rather than the soluble cupric ammonia complex. Ammonium hydroxide plays its part by preventing the formation of a protective film in the initial part of the reaction. Later in the reaction, there is insufficient ammonium hydroxide to maintain all the copper and OH^- ions in solution, so the rate decreases because of an accumulation of reaction product on the surface.

Acknowledgments.—This project was aided by a research grant from the American Society for Metals. The authors wish to thank Revere Copper and Brass, Incorporated, and Mr. S. P. Snyder of their Technical Advisory Service, Dallas Division, for samples of copper and for their interest in the progress of the investigation. Acknowledgment is also made to Mr. John W. Cook of the Armour Research Foundation, who determined the grain size of the copper metal.

Summary

1. The over-all reaction of copper and oxygen saturated ammonium hydroxide is best presented as a zero order reaction and is largely controlled by diffusion.

2. The reaction appears to be first order with respect to ammonium hydroxide.

3. Equations have been formulated to show the relationship between the reaction velocity constants and the initial ammonium hydroxide concentration.

4. Variation in surface area of metal specimen does not influence the reaction rate per unit area.

5. Energies of activation for the reaction of 0.3440 *M* ammonium hydroxide on copper are k_1, 7100 calories; k_2, 1670 calories. Correction for the viscosity effect of the solvent raised these values to 12,850 calories and 7050 calories.

6. Equations have been formulated for the effect of linear velocity on the reaction rate.

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(13) LaMer, *J. Franklin Inst.*, **225**, 708 (1938); *Chem. Rev.*, **10**, 179 (1932).

7. The reaction rate was retarded by increased viscosity.

8. The reaction is composed of two separate zero order reactions, the initial reaction being partially chemically and diffusion controlled, and the later reaction being definitely diffusion controlled.

9. Thermodynamic considerations and influence of ionic strength, varied by chloride ion addition, indicate that the rate controlling step for the initial part of the reaction is $OH^- + OH^- + Cu^0 \rightleftharpoons X^=$.

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[CONTRIBUTION FROM THE BUREAU OF MINES, PETROLEUM EXPERIMENTAL STATION]

Low-Temperature Thermal Data on the Five Isomeric Hexanes[1]

BY DONALD R. DOUSLIN[2] AND HUGH M. HUFFMAN[3]

The Bureau of Mines is carrying on a research program to obtain precise and accurate values of the thermodynamic constants of petroleum hydrocarbons and related compounds. In this paper are presented the results of low-temperature thermal studies on the five isomeric hexanes. All of these compounds have been studied by other workers. Parks, Huffman and Thomas[4] and Parks, Huffman and Barmore[5] studied *n*-hexane over the temperature range 90 to 300° K. Stull[6] has also made a superficial investigation of all of the hexanes over the temperature range 90 to 320° K. More recently Pitzer and Kilpatrick[7] have made a careful study of 2,2-dimethylbutane over the temperature range 15 to 280° K. This duplication again affords an opportunity to compare results from (different) laboratories which claim high accuracy for their measurements.

Experimental

The Materials.—The hydrocarbons used in this investigation were A. P. I.–N. B. S. "Best" samples purified by the A. P. I. Research Project 6 at the National Bureau of Standards[8] and certified by them in regard to their purity.

In the course of the measurements the melting points of these compounds have been studied under equilibrium conditions in the usual manner.[9] Unfortunately it was impossible to crystallize 3-methylpentane, so its purity could not be checked by the freezing-point method. The experimental and certain derived data for four of these compounds are summarized in Table I.

TABLE I

MELTING POINT SUMMARY

0°C. = 273.16° K.

% Melted	T, °K. Obs.	T, °K. Calcd.	Melted	T, °K. Obs.	T, °K. Calcd.
n-Hexane, $N_x = 0.0498\ \Delta T$			2-Methylpentane $N_x = 0.0527\ \Delta T$		
9.3	177.8202	177.8202	11.4	119.507$_5$	119.504
26.1	.8307	.8307	24.2	.530$_0$	.529
54.2	.8336	.8336	48.2	.540$_5$	.541
77.4	.8346	.8345	72.2	.544$_5$	.544
88.6	.8346	.8347	89.6	.546$_5$	.546
100.0	...	.8349	100.0	...	.546
Pure	...	.8364	Pure	...	.552
Triple pt. 177.84 ± 0.05°K.			Triple pt. 119.55 ± 0.05°K.		
Impurity 0.0075 mole%			Impurity 0.029 mole%		
2,3-Dimethylbutane $N_x\ 0.00458\ \Delta T$			2,2-Dimethylbutane $N_x\ 0.00229\ \Delta T$		
22	145.058	145.038	27.3	174.095	174.035
47	.118	.117	51.8	.159	.150
58	.129	.130	77.4	.193	.193
90	.150	.150	91.1	.206	.206
100	...	.154	100.0	...	.212
Pure	...	.186	Pure	...	.279
Triple pt. 145.19 ± 0.05°K.			Triple pt. 174.28 ± 0.05°K.		
Impurity 0.015 mole%			Impurity 0.015 mole%		

A study of these data indicates that 2,3-dimethylbutane and 2,2-dimethylbutane do not obey Raoult's law over the entire range of composition (liquid–solid) studied. The differences between T(obs) and T(calcd) are much greater than the probable uncertainty in the temperature measurements. Both compounds have extremely low heats of fusion and consequently suffer large depressions in the melting point for small amounts of impurity, thus making the measurements more sensitive to deviations from ideal behavior. It is also possible that these measurements may indicate that solid solutions are formed. The calculated triple point temperatures and impurity are

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[1] Published by permission of the Director of the Bureau of Mines, U. S. Department of the Interior. Not copyrighted.

[2] Associate Physical Chemist, Bureau of Mines, Petroleum Experiment Station, Bartlesville, Okla.

[3] Principal Physical Chemist, Bureau of Mines, Petroleum Experiment Station, Bartlesville, Okla.

[4] Parks, Huffman and Thomas, THIS JOURNAL, **52**, 1032 (1930).

[5] Parks, Huffman and Barmore, *ibid.*, **53**, 3876 (1931).

[6] Stull, *ibid.*, **59**, 2726 (1937).

[7] Kilpatrick and Pitzer, *ibid.*, **68**, 1066 (1946).

[8] These samples of A.P.I.–N.B.S. hydrocarbons have been made available by the American Petroleum Institute and the National Bureau of Standards through the A. P. I. Research Project 44 on the "Collection, analysis, and calculation of data on the properties of hydrocarbons." The samples were purified at the National Bureau of Standards by the A. P. I. Research Project 6 on the "Analysis, purification and properties of hydrocarbons," under the supervision of Frederick D. Rossini, from material supplied by the following laboratories: *n*-hexane, 2-methylpentane, 3-methylpentane, and 2,2-dimethylbutane, by the A. P. I. Research Project 6 on the "Analysis, purification and properties of hydrocarbons," at the National Bureau of Standards; 2,3-dimethylbutane, by the Standard Oil Company (Indiana), Whiting, Indiana, and M. W. Kellogg Company, New York, N. Y.

[9] Douslin and Huffman, *ibid.*, **68**, 173 (1946).