Kinetics of the Dissolution of Sodium in Liquid Ammonia*

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Introduction

Solutions of alkali metals in liquid ammonia were first investigated by Weyl[1] in 1864. However, it was not until 1938 that chemical kinetics was rigorously applied by Burgess and Kahler[2] to these unusual solutions of the most electropositive metals.

There are two distinct, consecutive reactions of metallic sodium with liquid ammonia. The first is that of the solution of the metal in liquid ammonia with the subsequent formation of a deep blue colored solution. This dissolution process is not accompanied by the evolution of any gases. The second reaction is that of the dissolved sodium combining with the ammonia, forming sodamide and liberating hydrogen.

This research centers about the chemical kinetic approach to the first reaction, that is, the rate

Fig. 1.—Over-all diagram of the apparatus. The bevel gears allow the sample assembly to be moved vertically.

of dissolution of sodium in liquid ammonia. A literature survey revealed that no previous work done on this particular aspect of the problem had been published. The specific rate constant was evaluated, the apparent energy of activation was determined, and the functional relationship between the specific rate constant and the linear velocity was obtained. Within the range of variables encountered in the experimental work, it has been shown that the dissolution process is under diffusion control. In addition, the effect of making the sodium anodic and cathodic was observed.

Experimental

All of the experimental work was carried out at atmospheric pressure, so of necessity the tests had to be run at temperatures below the normal boiling point of the liquid ammonia. As with other kinetic studies of this type, it was deemed advisable to use cylindrical samples rotated about their own axes.

Apparatus and Procedure.—The low temperature for the experimental work was maintained with a Dry Ice–acetone bath. Figure 1 is an over-all diagram of the apparatus. The double-walled container was made of metal, while the actual reaction vessel was a 600-ml. beaker. The cover of the latter was made of Transite, which previous tests showed to be unattacked by the sodium–liquid ammonia solution.

The motor was a variable speed fractional horse power electric motor, which had a built-in governor and reduction gears. The Dry Ice–acetone bath was also equipped with a stirrer to ensure against excessive temperature gradients within the depth of the bath.

The samples of sodium were hollow cylinders, of about 4 cm. outside diameter, 3 cm. inside diameter and 1.5 cm. high. These cylinders were cut with dies in a mechanical pellet press, all cutting operations being done under dry petroleum ether. The cylinders of sodium were forced onto a glass sample holder which was made from a Gooch crucible holder. The arrangement of bevel gears whereby the mounted metal specimen could be lowered into the liquid ammonia in a minimum amount of time, is clearly shown in Fig. 1. The sodium was Baker and Adamson analytical grade metallic sodium.

The ammonia was that produced by the Armour Ammonia Works. This ammonia is a by-product of the packing house industry and as such is superior in quality to that obtained from by-product coke ovens. A steel surge tank was constructed so that liquid ammonia at one atmosphere pressure could be withdrawn from the cylinder of ammonia.

The method chosen to follow the dissolution of the meta was to extract small samples of the solution at definite time intervals. Due to the high vapor pressure of liquid ammonia at temperatures in the range of −40 to −50°, it was found almost impossible to pipet samples with conventional pipets. The method used was to insert a glass tube, 6 mm. in diameter and 15 cm. long, vertically into the solution of liquid ammonia and let the liquid level rise in the tube until it was approximately equal to that of the liquid level in the reaction chamber. Then the tube was withdrawn.

The pipets were calibrated with water at several different depths and calibration charts were drawn. By using the depth of solution in conjunction with these charts, it was possible to determine the size, in ml., of each sample. In general, the values were between 0.8 and 1.0 ml. Correc-
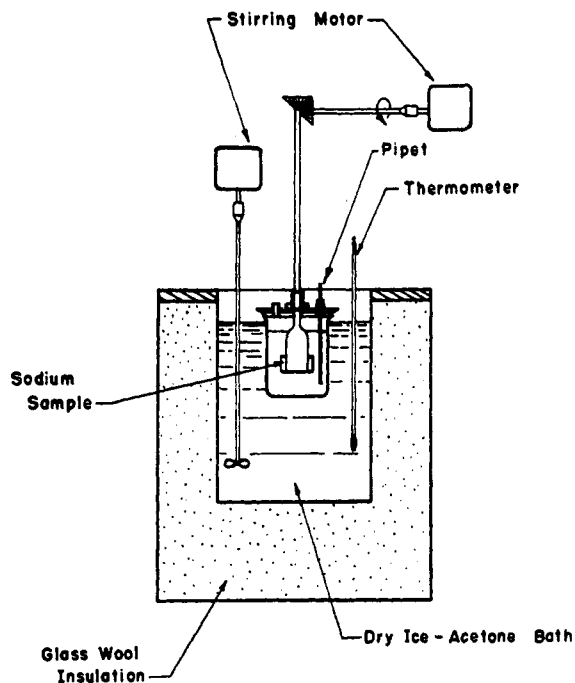
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(1) W. Weyl, "About the Metal Ammonium Compound," Ann. Physik., 121, 601 (1864).

(2) Wayland M. Burgess and Harry L. Kahler, Jr., THIS JOURNAL, 60, 189 (1938).

tions were made for the volume of the sample, stirrer and pipets, because when these were immersed the depth of the solution rose.

In a similar manner the volume of the solution was obtained by a calibration chart for the vessel in which the reaction took place. This chart had "volume of solution contained" plotted as a function of the "depth of solution."

When samples were to be extracted, the pipet and its contents were withdrawn and transferred to a previously chilled test-tube, each pipet being placed in a separate test-tube. These test-tubes were allowed to warm up gradually to room temperature, thus boiling off the liquid ammonia and leaving a white deposit. On one run this residue was analyzed and found to have a mole ratio of sodium carbonate to sodium hydroxide of approximately 4 to 7. Although this could be considered to be a typical composition, the exact ratio would depend upon the condition of the air in the immediate vicinity of the test-tubes.

The residue in the test-tubes was dissolved in about 100 ml. of water. This aqueous solution was then boiled down to about half its volume in order to rid the solution of any ammonia which might have been entrapped in the residue. After this boiling operation the vapor of the boiling solution would not turn moist red litmus paper blue, nor could the odor of ammonia be detected. These solutions were then titrated with standardized hydrochloric acid to the modified methyl orange indicator end-point in the conventional manner.

It was found that all the samples of the solution had to be extracted within about one minute, due to the fact that after this time the pitting on the metal surface became excessive. Thus the exposed area of the sodium became larger and the rate appeared to increase. There also appeared to be an induction period immediately following the immersion of the sodium into the liquid ammonia. This, too, is typical of heterogeneous reactions.

The Reaction Rate.—As with other heterogeneous systems, when a chemical reaction is taking place, there is superimposed upon the specific chemical processes certain interfacial factors which operate at the boundary of the two phases and influence—and sometimes dominate—the velocity of the specific reaction. There are three distinct processes occurring in this reaction: (a) solvent molecules approach and collide with the metallic surface, (b) these solvent molecules chemically react with the metal, and (c) the products of this chemical reaction recede from the interface into the bulk of the solution.

Several experimental determinations were made and it was found that when log $(a_s - x)$ was plotted vs. t—where a_s is concentration of the saturated solution in moles per liter, x is concentration in the same units at time t, in minutes—then a straight line was obtained. Figure 2 shows runs F and H plotted in this manner, and Table I contains the experimental data.

The fact that the value of the saturated solution enters into the linear plot immediately gives a possible clue as to the type of reaction which is being measured, i. e., a diffusion process. This would eliminate reaction (b) as mentioned above. Furthermore, experience has shown that reaction (a) is invariably a faster reaction than (c). This leaves the diffusion of the products away from the surface as the probable rate determining process of this reaction.
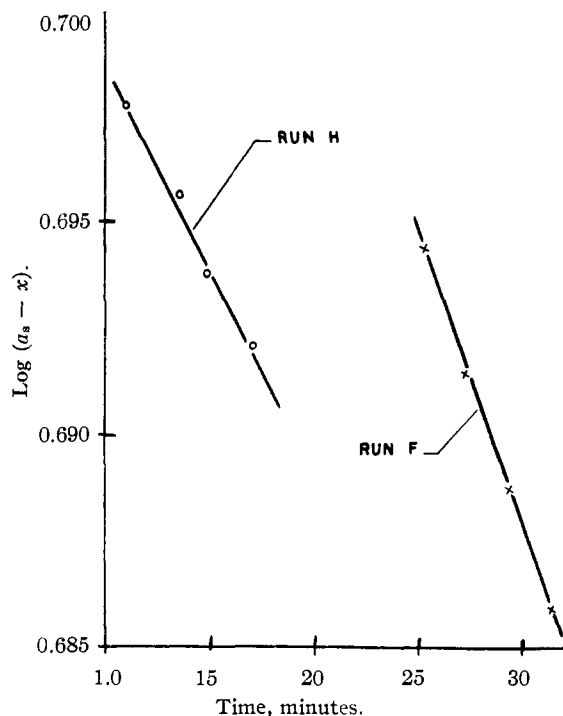

Fig. 2.—Log $(a_s - x)$ as a function of time for runs F and H. Equation 2 shows the correlation between the slope of these lines and the specific rate constant.

TABLE I

SUMMARY OF EXPERIMENTAL DATA

Run	Temp., °C.	Vol. of soln., ml.	R. p. m.	D,[a] cm.	h,[a] cm.	$k \times 10^3$	P,[a] cm.	v, cm./ min.
A	−38.0	306	834	3.80	1.26	1.43	1.80	9432
B	−40.0	291	832	3.79	1.69	1.12	1.82	9514
C	−51.2	292	805	3.80	1.27	0.74	1.80	9116
D	−48.2	295	804	3.81	1.40	.88	1.81	9453
E	−40.5	278	116	3.80	0.97	.22	1.79	1305
F	−40.8	306	302	3.75	1.09	.44	1.77	3305
G	−40.5	304	296	3.83	1.29	.68	1.81	3366
H	−40.2	282	293	3.86	1.53	.22	1.82	3342

Concentration, N, in moles/liter at time, t, in min.

Run	Sample 1 x	t	Sample 2 x	t	Sample 3 x	t	Sample 4 x	t	Satd. soln. a_s
A	0.086	0.31	0.246	0.61	0.345	0.76	0.502	0.91	4.985
B	.007	0.44	.059	0.59	.116	0.74	.227	0.89	4.992
C	.019	0.27	.069	0.42	.117	0.57			5.040
D	.022	0.32	.045	0.47	.099	0.62	.211	0.92	5.027
E	.015	2.03	.022	2.23	.033	2.43	.054	2.63	4.995
F	.048	2.53	.082	2.73	.113	2.93	.144	3.13	4.996
G	.075	1.06	.106	1.26	.151	1.46	.249	1.66	4.995
H	.015	1.09	.038	1.34	.060	1.49	.079	1.69	5.001

[a] D is outside diameter, h is height and $\bar{P}$ the centroid of the metal sample. In all cases, the inside diameter was 2.81 cm. In all runs, $x = 0.000$ at $t = 0$.

It can be shown[3] that under these conditions the differential equation

$$\frac{dx}{dt} = k \frac{A}{V}(a_s - x) \tag{1}$$

(3) Arthur A. Noyes and Willis R. Whitney, Z. physik. Chem., **23**, 689 (1897).

is applicable. Here k is the specific rate constant, A is the area of the metal surface in square centimeters, V is the total volume of solution in liters, t_i is the induction period in minutes, and the other symbols have the notation as mentioned previously. Integration yields

$$\log (a_s - x) = \frac{-kA}{2.303 V} (t - t_i) + \log a_s \qquad (2)$$

which represents, essentially, a first order reaction and is similar to the one used by King[4] to describe the reactions of metals dissolving in acids under certain conditions.

The values for the concentration of the saturated solutions over the range from −40 to −50° were computed from the determinations of Ruff and Zender,[5] and Ruff and Geisel.[6] It is unfortunate that these values are given in mole ratio of ammonia to sodium. Obviously, if R is this ratio, then the normality is

$$N = \frac{1000 \, D'}{22.997 + 17.032R} \qquad (3)$$

where D' is the density of the solution. The value used for D' (0.5782 g./ml.) was that found by Kraus, Carney and Johnson,[7] and Johnson and Meyer[8] for the saturated solution at −33.8°. In lieu of sufficient density data, this value was considered to be constant over the range from −40 to −50°. This is undoubtedly a fairly good assumption.

If the left side of equation 2 is expanded by use of Taylor's formula into a polynomial in x, and if only the first two terms are used (this appears to be valid due to the small values of x, and the fact that the errors incurred would be less than the
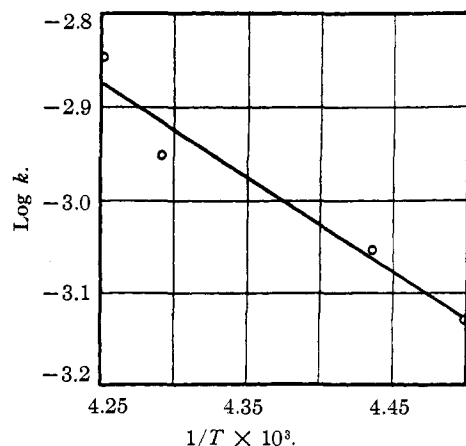

Fig. 3.—Log k as a function of $1/T$ for runs A, B, C and D. The slope of the line is $E/2.303 \, R$, where E is the apparent energy of activation.

(4) Cecil V. King, THIS JOURNAL, **57**, 828 (1935).

(5) Otto Ruff and Julian Zender, Ber., **41**, 1948 (1908).

(6) Otto Ruff and Emil Geisel, ibid., **39**, 828 (1906).

(7) Charles A. Kraus, E. Seaton Carney and Warren C. Johnson, THIS JOURNAL, **49**, 2206 (1927).

(8) Warren C. Johnson and Albert W. Meyer, ibid., **54**, 3621 (1932).

experimental error), then equation 2 has the form

$$x = \frac{ka_s A}{V}(t - t_i)$$

In the range of temperatures which were encountered, a_s varies only about 1% of the average value so it may be considered as constant and incorporated in k. Thus

$$x = k' \frac{A}{V} (t - t_i) \qquad (4)$$

It is immediately apparent that this equation represents a zero order reaction in which the rate of change in the amount of the dissolved solute is a function only of the exposed area of the solid.

When x is plotted as a function of t it is seen that the zero order equation fits the data during the limited time range to the same degree as does the first order diffusion equation. It should be noted that the term t_i, which is the induction period, enters into both the zero order and the first order equations. On the graph, if the curve were extrapolated to zero concentration, then the corresponding time coördinate would be the induction period. As stated previously, the phenomenon of such an induction period is frequently encountered in heterogeneous reactions.

The fact that the data appear to fit the zero order equation can be explained in two ways. First, the reaction itself may be zero order. Second, the reaction may be diffusion controlled, following the first order diffusion equation, but due to the relatively small values of x, appear to follow the zero order equation by virtue of the fact that the zero order equation represents the limiting case of the diffusion equation. Which of these two possible explanations presents the more nearly correct view of the dissolution process will be seen when the change in the specific rate constant with temperature and surface velocity is considered.

The Apparent Energy of Activation.—The apparent energy of activation was obtained graphically from a plot of log k as a function of $1/T$, where T is the absolute temperature. Figure 3 shows runs through A through D plotted in this manner. It can be shown easily that the slope of this line is $E/2.303 \, R$; where E is the apparent energy of activation and R the gas constant.

The data used in Fig. 3 appear in Table II.

TABLE II

Run	Temp., °C.	$k \times 10^3$
A	−38.0 ± 1.0	1.43 ± 0.23
B	−40.0 ± 1.0	1.12 ± .18
C	−51.2 ± 1.0	0.74 ± .12
D	−48.2 ± 1.0	0.88 ± .14

These runs were made at essentially the same linear velocity of the metal surface. The value of 4.2 kcal. was obtained by the method of least squares and thus represents the most probable value.

It was found that the change in viscosity of the solutions of sodium in liquid ammonia, in the same range of temperature and concentration as encountered in the experiments, was negligible. Hence, no corrections for viscosity had to be made.

The values of k used in the evaluation of the critical energy increment were those for the first order diffusion equation. The plot of log k vs. $1/T$ also serves the purpose of obtaining the apparent energy of activation from the values of k' which are those for the zero order reaction. This is immediately apparent from the functional relationship which exists between k and k'.

Low values of the critical energy increment are in general associated with diffusion controlled processes. It is a necessary but not sufficient condition for this type of process. This low value of the apparent energy of activation shows that it is possible that the first order diffusion equation describes the reaction, but it does not eliminate the possibility that the dissolution process is of zero order. Further evidence, such as the change in k with linear velocity of the metal specimen is therefore necessary before the nature of the rate process can be stated.

The Relationship of k and Linear Velocity.— The linear velocity of a cylindrical surface revolving about its own axis is of course equal to its circumference times the revolutions per unit time. However, with the form of the sample used, this would lead to an erroneous value. Consequently, the centroid of the hollow cylinder was used in computing the linear velocity of the metal surface. Figure 4 shows k as a function of v, the linear velocity in cm./minute. The data appear in Table III.

TABLE III

Run	Temp., °C.	v, cm./min.	$k \times 10^3$
A-B	−40.5 ± 1.0	9470 ± 280[a]	1.14 ± 0.18[b]
E	−40.5 ± 1.0	1305 ± 39	0.22 ± .04
F	−40.8 ± 1.0	3358 ± 99	0.44 ± .07

[a] Average values of runs A and B. [b] Value at −40.5° on Fig. 3.

Clearly, a linear relationship exists between k and v. The analytical form of this at −40° is

$$k = (1.13 \times 10^{-7}) v + 7.0 \times 10^{-5} \qquad (5)$$

The units of k are liters/sq. cm./minute, or specifically the moles dissolved per minute with an area of 1 sq. cm. and a concentration gradient of 1 mole/liter.

This relationship between the specific rate constant and the surface velocity of the metal specimen can be interpreted to mean that the rate determining step is diffusion controlled, at least within the linear speeds from zero to 10,000 cm./minute. Due to the construction of the apparatus, it was considered judicious not to exceed 10×10^3 cm./minute for the surface velocity of the sodium sample.
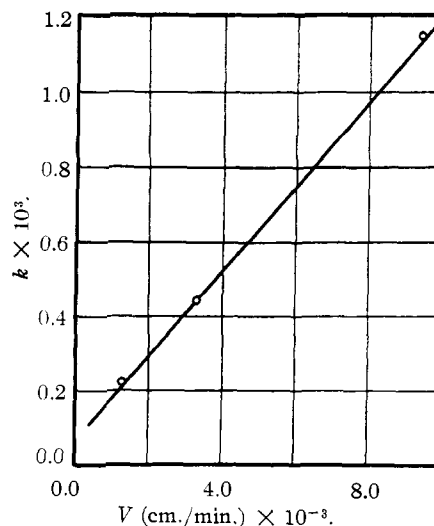

Fig. 4.—Relationship of k and linear velocity at −40°.
$$k = (1.13 \times 10^{-7})_v + 7.0 + 10^{-5}.$$

The Effect of Anodic and Cathodic Charges.— Due to the nature of the solution, it was thought that it would be of interest to ascertain the effect of making the sodium anodic or cathodic. Accordingly, the ring of metal had aluminum wires embedded in the inside surface adjacent to the glass and a carbon rod extending into the solution approximately 2 cm. from the cylindrical surface of the sodium was installed. Two runs were made, one with the sodium charged anodically and the other with the sodium charged cathodically. The voltage was about four volts and the current about two amperes in both cases. The results are summarized in Table IV, which also includes the value of k for the uncharged sodium. All these runs were made at essentially the same temperature and linear velocity.

TABLE IV

Run	Sodium	$k \times 10^3$
F	Uncharged	0.44 ± 0.07
G	Cathodic	.68 ± .11
H	Anodic	.22 ± .04

Discussion

The path followed in the pursuit of a solution to the problem may be summarized as follows. The experimental data appeared to fit a zero order equation and a first order diffusion equation about equally well. The apparent energy of activation determined from the values of k at different temperatures showed that the process could be diffusion controlled but did not eliminate the possibility of other processes. When the specific rate constant was found to be a function of the surface velocity of the metal specimen it was interpreted as being the result of a diffusion process. Thus the experimental data fitting a zero order equation was no doubt due to the fact that for small values of x—concentration of the

dissolved substance in moles/liter at time t— the first order diffusion equation has the same form as a zero order rate equation.

The fact that making the sodium anodic slows up the dissolution process and causing the sodium to be cathodic accelerates this reaction shows that the dissolution process is of an electrochemical nature. With the dissolution of most metals in an aqueous solution, if the metal is made cathodic, then the anodic reaction—that of the oxidation of the metal to form ions—is inhibited. Evidently, in the case of sodium dissolving in liquid ammonia the slowest step of the dissolution process is the cathodic reaction, which, according to the so-called solvated electron theory[9,10,11] would be the association of varying amounts of ammonia with the liberated electrons. However, the solvated electron theory in conjunction with the experimental facts of anodic and cathodic charges help only in the speculations as to the nature of the process and offer no definite proof as to the mechanism of the dissolution process.

(9) Charles A. Kraus, This Journal, **36**, 871 (1914).

(10) Charles A. Kraus and Walter W. Lucasse, *ibid.*, **43**, 2529 (1921).

(11) W. Conard Fernelius and George W. Watt, *Chem. Rev.*, **20**, 195 (1937).

Conclusions

The conclusions which can be drawn from this investigation are: 1. The data appear to fit a zero order and a first order equation about equally well.

2. The apparent energy of activation of 4.2 kcal. is relatively low, showing that a diffusion process is possible.

3. An increase in the linear velocity of the metal specimen increases the reaction rate. At 40° the functional relationship is $k = (1.13 \times 10^{-7}) v + 7 \times 10^{-5}$ thus showing that a diffusion process is probable.

4. Charging the sodium alters the dissolution rate.

5. These points support the view that within the range of concentration, linear velocity, pressure and temperature which were encountered in the experimental work, the dissolution process is of an electrochemical nature which is under diffusion control and therefore first order.

[Contribution from The Institute of Paper Chemistry]

The Rate of Esterification of Primary and Secondary Hydroxyls of Cellulose with p-Toluenesulfonyl (Tosyl) Chloride[1]

By Emil Heuser,[2] Merle Heath and Wm. H. Shockley

Formation of the p-toluenesulfonyl or tosyl ester offers a possible means for measuring the relative rates of esterification of the primary and secondary alcoholic groups of cellulose. Since it has been shown that the tosyl ester in the primary position in glucose is replaceable by iodine on treatment with an excess of sodium iodide in a suitable medium,[3] a number of investigators have applied this method to cellulose derivatives[4-7] and cellulose,[7-8] also, in order to determine the distribution of tosyl groups between the primary and secondary positions. Evidence has recently been published,[8] however, which indicates that the distinction between primary and secondary hydroxyl groups by this method is not exact under all conditions; analyses of some of the products imply the introduction of slightly more than one iodine atom per glucose unit into tosylated cellulose.

(1) A portion of this work was carried out in connection with U. S. Army Quartermaster Corps Contract No. W44-109-qm-1209 (O. I. No. 2963).

(2) Present address: 339 Vista de la Playa, La Jolla, California.

(3) Oldham and Rutherford, This Journal, **54**, 366 (1932).

(4) Cramer and Purves, *ibid.*, **61**, 3458 (1939).

(5) Mahoney and Purves, *ibid.*, **64**, 9, 15 (1942).

(6) Gardner and Purves, *ibid.*, **64**, 1539 (1942).

(7) Honeyman, *J. Chem. Soc.*, 168 (1947).

(8) Malm, Tanghe and Laird, This Journal, **70**, 2740 (1948).

In the present work, a chemically reactive cellulose was prepared by regeneration of cotton linters from a solution of cellulose xanthate, replacing the water successively with methanol, ethyl ether and, finally, cyclohexane. This sequence of solvent replacements has previously been used by Staudinger and Mohr.[9] Samples swollen in pyridine were esterified with a solution of tosyl chloride (amounting to 10 moles per anhydroglucose unit) in pyridine for various periods of time at 25°. The tosyl derivatives were then treated with sodium iodide in acetonylacetone at 115–120°,[5-6] after which they were analyzed for combined iodine and combined tosyl (sulfur).

Because the degree of substitution of the sample with the longest esterification time (ten hours) was still less than one group per anhydroglucose unit, another sample of reactive cellulose was prepared by the same method and a second series of tosylations and iodine replacements was made, this time including esterification periods up to fifty hours. Data from the two series were fairly consistent and indicated that the rate of reaction of both primary and secondary hydroxyls was proportional to the concentration of free hydroxyls of

(9) Staudinger and Mohr, *Ber.*, **70**, 2299 (1937).