400 and 57 mm., nevertheless, the decrease in the energy is in the correct direction. As for the frequency factors, we can only conclude that they are reasonable, since a rather limited temperature range was used in their evaluation.

The constant k_1k_6/k_2 is found to be independent of the total pressure within the precision of our measurements. This result is in complete agreement with the proposed mechanism. From this value one could estimate the equilibrium constant for the dissociation of N_2O_5 into NO_2 and NO_3 if one knew the value for k_6, or *vice versa*.

It is interesting to note that the temperature coefficient for k_2/k_6 is small and negative. This of course means that the activation energy E_2 associated with k_2 is slightly less than E_6 associated with k_6. Our accuracy is such that we can with confidence say only that $(E_2 - E_6)$ is small, and that if we regard E_2 as probably small because the reaction is merely a recombination, then E_6 must also be small. It is however interesting to note that the trend of activation energies with pressure, like that found for k_1 by Johnston, *et al.*,[4] is consistent with the prediction of unimolecular rate theory[8] that the activation energy of a unimolecular decomposition should fall off at low pressures, and that a bimolecular association with no activation energy at high pressures will have a negative "activation energy" at low pressures. Thus if we assume that the high pressure limit of E_2 is zero, we may interpret the data to mean that the high pressure limit of E_1, 21.0 kcal./mole, represents the dissociation energy of N_2O_5; that E_6 is also nearly zero; and that the negative quantity $(E_2 - E_6)$ essentially measures the predicted "negative activation energy" of the association of NO_2 and NO_3 at low pressures.

Conclusion.—We have investigated the unimolecular decomposition reaction of N_2O_5 in the presence of NO with our fast-scanning infrared spectrometer. The results obtained from this method were found to be consistent with those obtained from other methods. In addition, we have been able to obtain for the first time a quantitative estimate of the inhibition constant k_2/k_6. Finally, we can reasonably conclude that this spectroscopic method can be applied equally well to other relatively fast gas-phase reactions.

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[8] L. S. Kassel, "Kinetics of Homogeneous Gas Reactions," New York, N. Y., 1932, pp. 95–100; A. F. Trotman-Dickenson, "Gas Kinetics," New York, N. Y., 1953, pp. 62–64.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KENTUCKY]

Solvents Having High Dielectric Constants. VI. Diffusion in N-Methylacetamide[1,2]

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The self-diffusion coefficients of N-methylacetamide over the temperature range 35 to 60°, and the sodium ion in sodium chloride solutions in N-methylacetamide at 40°, have been determined. Concentrations of the salt varied from 2.5×10^{-3} to 0.25 molar. The capillary method was employed with stirring accomplished by rotating the capillary holder. For the pure solvent the diffusion coefficient increases from 4.11×10^{-6} to 7.33×10^{-6} cm.²/sec. as the temperature is raised. The value for the sodium ion decreases from 2.58×10^{-6} to 1.97×10^{-6} cm.²/sec. as the salt concentration is increased one hundred fold. The activation energy for self-diffusion in the amide is equal to that for viscous flow. Also it is equal to the activation energy for the self-diffusion of water.

Interest in N-methylacetamide as a solvent to be used in diffusion studies arises from its unusual properties. It dissolves readily both organic and inorganic solutes. At 40° its dielectric constant is 165.5 and its viscosity is 0.03019 poise.[3] Sodium chloride was chosen as the solute for this study because the literature contains diffusion data for this salt in water[4] and its conductance and transference numbers in N-methylacetamide have been calculated from measurements in this Laboratory.[5]

Wang[6] has discussed the theory and described the procedure for measuring diffusion coefficients by the capillary method. Mills and Kennedy[7] and Mills and Adamson[8] reported studies of probable experimental errors in this method and have described some improvements in techniques. These procedures together with a technique modified for viscous media have been used in the present work.

Experimental

Materials.—Reagent grade sodium chloride was recrystallized and fused.

Sodium-22 chloride was obtained from the Isotopes Division, U.S.A.E.C., Oak Ridge, Tennessee.

N-Methylacetamide was prepared by the method described in an earlier paper from this Laboratory.[3] The solvent which was used froze above 29° and had a specific conductance of 2×10^{-6} ohm^{-1} cm.$^{-1}$ at 40°.

Active N-methylacetamide was prepared from C^{14}-enriched $BaCO_3$, obtained from Oak Ridge, by first synthesizing acetic acid-1-C^{14}. This synthesis was accom-

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[1] Abstracted from a dissertation submitted by William D. Williams as a part of the requirements for the Ph.D. degree at the University of Kentucky.

[2] This work was supported in part by a contract with the Office of Ordnance Research.

[3] L. R. Dawson, P. G. Sears and R. H. Graves, THIS JOURNAL, **77**, 1986 (1955).

[4] J. H. Wang and S. Miller, *ibid.*, **74**, 1611 (1952).

[5] E. D. Wilhoit, Dissertation, University of Kentucky, 1956.

[6] J. H. Wang, THIS JOURNAL, **74**, 1182 (1952).

[7] R. Mills and J. W. Kennedy, *ibid.*, **75**, 5696 (1953).

[8] R. Mills and A. W. Adamson, *ibid.*, **77**, 3454 (1955).

plished by the method of Sakami, Evans and Gurin[9] except that the product was extracted with ethyl ether.

Capillary tubes were constructed from precision bore tubing having an internal diameter of 0.05 cm. One end was sealed with a flat plate and the other end was ground smooth and square. The lengths were measured with a carefully calibrated micrometer microscope. The volume was determined by filling with mercury and weighing. The capillary cells were held in a four-pronged glass holder mounted on a shaft which passed through a mercury-seal into a one-liter flask. A large oil-filled bath surrounding the flask maintained its temperature constant to ±0.02°.

Solutions.—N-Methylacetamide solutions were prepared in a dry box under positive nitrogen pressure and handled so as to avoid prolonged contact with the atmosphere.

Procedure.—Preliminary experiments using a paddle stirrer while the capillaries were held stationary in N-methylacetamide yielded Δl values (as described by Wang[6]) indicating insufficient stirring at speeds up to 150 r.p.m. The calculated Δl effect became zero, however, when the capillary holder was rotated in the bath solution at 75 r.p.m. This technique seems to be applicable to the more viscous solvents.

Wang's procedure for determining total activity of radioactive sodium in a capillary cell by evaporation of the contents and washings on a sample plate did not yield precise results in the present work. Because of the inconsistencies which appeared it became desirable to use a known amount of inert sodium chloride as a carrier and determine the specific activity. After a diffusion run, which required from three to five days, the contents of each cell was washed with alcohol, followed by thorough rinsing, into a centrifuge tube using a syringe and needle. A carefully measured constant amount of sodium chloride solution was added and the tube allowed to stand for several hours with intermittent shaking. Then concentrated hydrochloric acid was added and the precipitate was plated from an acetone slurry by a centrifugal plating device similar to that described by Ames and Willard.[10] The activity in the capillary cell before diffusion was calculated from the volume of the capillary and the specific activity of a measured volume of active solution which was carried through the same procedure as that used for the capillary contents after the diffusion run.

Evaluation of the activity of pure N-methylacetamide, both before and after diffusion, was accomplished by wet combustion followed by precipitating the evolved CO_2 as $BaCO_3$ and measuring the specific activity. The apparatus consisted of a combustion flask, a scrubber and an absorption vessel. The sample was oxidized by heating with a Van Slyke–Folch solution and the CO_2 was absorbed in a $BaCl_2$–$Ba(OH)_2$ solution. Caution was exercised to exclude contamination from the atmosphere and to ensure complete oxidation of the sample and effective recovery of all products. The precipitated $BaCO_3$ was plated from an acetone slurry in the same manner as the sodium chloride samples.

A calibrated, thin-window, methane flow proportional counter was used for assaying. Self-absorption corrections were made on all samples. From the results the ratio C_0/C_{av} was calculated, where C_0 is the activity in the capillary before diffusion and C_{av} is the activity in the capillary after diffusion.

Results

With capillaries varying in length only from 1.444 to 1.755 cm. in the experiments on the self-diffusion of sodium ion, the Δl effect appeared to be zero at 75 r.p.m. and no unusual inconsistencies were noted. However in studying the self-diffusion of N-methylacetamide with capillaries from 1.5 to 3.5 cm. long the results showed some dependence upon the length of the capillary regardless of the rate of stirring, but appeared to approach a limit as the length of the capillary increased. By plotting log D *versus* $1/l$ an extrapolated limiting value was obtained. This plot was used as a correction curve to determine the ratio of the limiting diffusion coefficient to that at any capillary length. It was used also as a correction curve for the sodium chloride diffusion data assuming that similar conditions existed in the sodium chloride solutions. The corrections amounted to from 3.5 to 6.9%.

The properties of N-methylacetamide and the self-diffusion coefficients at temperatures within the range 30 to 60° are shown in Table I.

TABLE I

PHYSICAL PROPERTIES AND SELF-DIFFUSION COEFFICIENTS OF N-METHYLACETAMIDE

Temp. °C.	Density (g./ml.)	Viscosity (poise × 10^2)	Dielectric constant	$D \times 10^6$ (cm.^{2}/sec. cor.)	$D\eta/T$ (× 10^{10})
30	0.9503	3.888	178.9		
35		3.440		4.11	4.58
40	.9420	3.021	165.5	4.58	4.42
45		2.704		5.10	4.34
50	.9335	2.413	151.8	5.93	4.43
60		1.966		7.33	4.33

Table II contains corrected values for the self-diffusion coefficients of sodium ion determined by using tracer amounts of radioactive sodium at several concentrations of sodium chloride. These values were calculated from the measured ratios of C_0/C_{av} by the equation[6]

$$\frac{Dt}{l^2} = \frac{4}{\pi^2} \ln \left(\frac{8}{\pi^2} \times \frac{C_0}{C_{av}} \right)$$

TABLE II

SELF-DIFFUSION COEFFICIENTS OF Na^+ IN SODIUM CHLORIDE SOLUTIONS IN N-METHYLACETAMIDE AT 40°

Concn. of NaCl (mole/l.)	$D \times 10^6$ (cm.^{2}/sec.; cor.)	Concn. of NaCl (mole/l.)	$D \times 10^6$ (cm.^{2}/sec.; cor.)
0.0025	2.58	0.1000	2.17
.010	2.48	.1500	2.15
.0256	2.40	.2000	2.04
.0500	2.29	.2500	1.97
.0750	2.23		

Each coefficient reported represents the mean of from four to eight measurements with standard derivations ranging from 0.5 to 2%.

Although the results reported in Tables I and II cannot be considered to be very accurate, it is believed that the over-all error is not greater than 5%.

Discussion

As a test of the accuracy of our experimental methods the self-diffusion of sodium ion in 0.30 *M* aqueous sodium chloride was determined using the procedure (including stirring by rotating the cell holder) which has been described above. The mean value from six of our determinations was $(1.359 \pm 0.031) \times 10^{-5}$ cm.^{2} sec.$^{-1}$, which is in excellent agreement with the value $(1.35 \pm 0.038) \times 10^{-5}$ cm.^{2} sec.$^{-1}$ obtained by Wang and Miller,[4] using capillaries in a bath agitated rapidly by a mechanical stirrer.

Using conductance data reported in an earlier paper from this Laboratory[3] and transference numbers determined here recently (based upon the conductance of trimethyloctadecylammonium octa-

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[9] W. Sakami, W. E. Evans and S. Gurin, THIS JOURNAL, **69**, 1110 (1947).

[10] D. P. Ames and J. E. Willard, *ibid.*, **73**, 164 (1951).

decylsulfate in N-methylacetamide) in conjunction with the Nernst equation, the modified Onsager[11,4]

$$D = \frac{RT\lambda^\circ}{ZF^2} - \frac{\lambda^\circ ZF}{3N\epsilon}(2.694 \times 10^{16})\sqrt{\frac{4\pi}{\epsilon RT}}\left[1 - \sqrt{\mathrm{d}(\omega)}\right]\sqrt{\Sigma CZ^2}$$

limiting diffusion equation for the sodium chloride solution becomes

$$D_{\mathrm{NA}^+} \times 10^6 = 2.3 - 0.142\sqrt{C}$$

Experimental values were not determined at low enough concentration to permit reliable extrapolation of a plot of D *versus* $\sqrt{C}$; however the slope of such a plot is much greater in the experimental range than the theoretical limiting value. If the theoretical value of the slope is approached at infinite dilution, our values at the lower concentrations indicate that it is approached from above and that there is a maximum in the curve, similar to the maximum found with aqueous sodium chloride solutions.

The self-diffusion coefficient of the solvent is nearly twice that of the sodium ion in the salt solutions. A similar relationship has been found in water.[4] Constancy of the $D\eta/T$ values suggests that the diffusing unit remains unchanged as the temperature is varied from 30 to 60°. If the diffusing unit in the solvent is the single molecule and if as a first approximation the rates of diffusion of two species may be considered to be inversely proportional to the square roots of their molecular weights, the sodium ion must be solvated with three or four molecules of N-methylacetamide. Since it is difficult to believe that the sodium ion holds firmly attached so many molecules of solvent as it moves through a highly polymerized liquid, the data may be interpreted as inferring that distortion in the solvent about the ion produces interference to its motion equivalent to the displacement of three or more solvent molecules. This distortion in the solvent about the sodium ion may be the "solvation" effect which causes its mobility to be approximately equal to the mobility of the tetra-*n*-butylammonium ion in N-methylacetamide as reported earlier from this Laboratory.[12] The calculated value of the Arrhenius activation energy for the self-diffusion of N-methylacetamide is 4.64 kcal./mole. This is in good agreement with an activation energy for viscous flow of 4.6 kcal./mole obtained from data reported earlier.[3] Obviously the rate-controlling step is the same in the two processes.

It is of interest to note that this value is the same as the activation energy for the self-diffusion of water between 10 and 50° (4.58 kcal./mole) reported by Wang.[13] Probably in each case the breaking of a hydrogen bond is involved. This fact lends credence to the "liquid polymer" concept of the structure of N-methylacetamide.

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[11] L. Onsager, *Ann. N. Y. Acad. Sci.*, **46**, 241 (1945).

[12] L. R. Dawson, E. D. Wilhoit and P. G. Sears, THIS JOURNAL, **78**, 1569 (1956).

[13] J. H. Wang, *ibid.*, **73**, 510 (1951).