3. Temperature-e.m.f. measurements show the transition temperature to be 146.6°.

4. The heat absorbed during transition of one mole of AgI_α to one mole of AgI_β, calculated from the slopes of the e.m.f.-temperature curves, is 1270 cal.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

DECOMPOSITION OF DIACETONE ALCOHOL BY WEAKER BASES

BY GÖSTA ÅKERLÖF

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Introduction

In two preceding papers[1] have been given the results of the measurements of the decomposition velocity of diacetone alcohol in alkali hydroxide-alkali salt solutions. In this paper will be presented some measurements with weaker bases, such as ammonia, used as catalysts. Similar measurements for hydrogen ion catalysis with weaker acids present have been carried out by Harned and Hawkins[1c] for the hydrolysis of ethyl formate and ethyl acetate.

Previously it has been shown by Arrhenius,[2] Brönsted,[3] Harned[1] and others,[4] that when a neutral salt, which in itself is a strong electrolyte, is added to a solution of a weak electrolyte, the dissociation of this increases. For water as a weak electrolyte this increase has been measured by Harned[4a,b] Harned and Swindells,[5] Åkerlöf,[6] and Harned and James[7] for a number of different salt solutions. At low salt concentrations the curves obtained for the decomposition velocity of diacetone alcohol in neutral salt solutions of the weaker bases seemed to be of the same type as the curves obtained for the concentration of water as an electrolyte in the same salt solutions. In other words, the concentration of the weak bases as electrolytes was changed by the addition of neutral salts in the same manner as for water.

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[1] (a) Åkerlöf, THIS JOURNAL, **48**, 3046 (1926); (b) **49**, 2955 (1927); (c) Harned and Hawkins, *ibid.*, **50**, 85 (1928). They give references relating to older literature on this subject.

[2] Arrhenius, *Z. physik. Chem.*, **31**, 197 (1899).

[3] Brönsted, *J. Chem. Soc.*, **119**, 574 (1921).

[4] (a) Harned, THIS JOURNAL, **47**, 930 (1925); (b) *Z. physik. Chem.*, **117**, 1 (1925); compare further (c) Schreiner, *Z. anorg. Chem.*, **135**, 333 (1924); (d) Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

[5] Harned and Swindells, THIS JOURNAL, **48**, 126 (1926).

[6] Åkerlöf, *ibid.*, **48**, 1160 (1926).

[7] Harned and James, *J. Phys. Chem.*, **30**, 1060 (1926).

The method proposed by Harned and Hawkins was used to calculate the concentration of the catalyzing ion and then from the mass action law the activity coefficients of the weak bases as electrolytes in their salt solutions. In agreement with the fundamental assumption made it was found that the curves for the activity coefficients came quite near each other. In many cases they seemed to superimpose well within the experimental uncertainties.

Experimental Methods and Materials

The weaker bases except ammonia were all obtained from the Eastman Kodak Company. Ammonia was redistilled from an alkali hydroxide solution with the usual precautions, but all the others were used without any attempt at further purification, due to well-known difficulties with small scale operations. An inquiry relative to the purity of the aliphatic amines used seemed to indicate that their purity was quite high. To judge from the methods used for their synthesis the amount of free ammonia present must in all cases have been very small. The bases were tested for the presence of carbonic acid and non-volatile matter. In a few cases slight traces were indicated but were considered as negligible. The method of measurement was the same as described in the preceding papers. In Table I are given some measurements for 0.2 *N* ammonia in sodium sulfate solutions.

TABLE I

SOME MEASUREMENTS WITH 0.2 *N* AMMONIA IN SODIUM SULFATE SOLUTIONS

Time, min.	1 *N* Na_2SO_4		2 *N* Na_2SO_4		3 *N* Na_2SO_4		4 *N* Na_2SO_4		5 *N* Na_2SO_4	
	Cath.	$K \cdot 10^6$	Cath.	$K \cdot 10^6$	Cath.	$K \cdot 10^6$	Cath.	$K \cdot 10^6$	Cath.	$K \cdot 10^6$
0	2.9	...	4.0	...	3.3	...	3.9	...	4.2	...
60	9.6	421	10.3	526	11.4	615	11.9	678	14.1	737
120	15.7	428	16.0	531	18.5	618	18.8	681	22.4	735
180	21.1	428	20.9	528	24.7	620	24.6	678	29.6	731
240	25.9	425	25.3	528	30.0	619	29.5	674	35.4	735
300	30.2	422	29.2	528	34.5	616	33.7	670	40.3	732
360	34.1	420	32.6	527	38.4	615	37.3	670	44.4	728
480	40.9	418	38.3	526	44.9	614	43.1	670	51.0	728
600	46.5	420	42.9	528	49.7	612	47.4	671	55.7	727
	73.5	...	59.3	...	64.7	...	59.2	...	67.6	...

It might be thought that the high volatility of the pure amines would cause errors due to their evaporation during the filling of the reaction tubes. The partial vapor pressure in 0.2 *N* pure aqueous solutions of some of the amines used may be estimated from a few measurements of Doyer[8] at 60° and those of Perman[9] for aqueous ammonia at varying temperature. Assuming proportionality in all cases, the following values

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[8] Doyer, *Z. physik. Chem.*, **6**, 486 (1890).

[9] Perman, *J. Chem. Soc.*, [2] **83**, 1168 (1903); Landolt-Börnstein, "Tabellen," **4th ed., p. 429.**

in mm. of mercury are obtained: ammonia, 2.2; methylamine, 1.6; dimethylamine, 1.6; ethylamine, 2.6; diethylamine, 9.2. At least the order of magnitude is certain. When a salt is added the vapor pressure of water decreases and therefore that of the amine may increase. Let us assume that the partial vapor pressure of the latter has increased to 30 mm. of mercury and that the back pressure from the vacuum pump is 5 mm. The time used for filling the reaction tubes was about five minutes. The diameter of the capillary was around 0.08 cm. and the total length 90 cm. Applying the formula of Poiseuille for the flow of liquids through a capillary, we find that even under ideal conditions an almost negligible quantity (approximately 3%) of the amine as gas may pass through the capillary. However, the partial vapor pressure of the amine must rapidly decrease during the filling of the reaction tube because the evaporating surface decreases at about the same rate as the gas bubbles disappear. Therefore the amount of the amine actually lost must be far less than calculated for continuous equilibrium conditions. Differentiation of the mass action formula shows that a small error for the stoichiometrical concentration gives a very much smaller error for the hydroxyl ion concentration. In agreement herewith the velocity measurements appeared always to be very consistent.

TABLE II

SUMMARY OF THE MEASUREMENTS OF THE VELOCITY OF DECOMPOSITION FOR DIACETONE ALCOHOL IN 0.2 N SOLUTIONS OF WEAKER BASES

	Methylamine				Dimethylamine				Trimethylamine			
	NaCl		Na_2SO_4		NaCl		Na_2SO_4		NaCl		Na_2SO_4	
m_s	K^a	K/K_0	K^a	K/K_0	K^a	K/K_0	K^a	K/K_0	K^a	K/K_0	K^a	K/K_0
0.00	458	1.00	458	1.00	240	1.00	240	1.00	62.5	1.00	62.5	1.00
.25	535	1.17	560	1.22	290	1.21	330	1.38	78.3	1.26	85.0	1.36
.50	559	1.22	609	1.33	312	1.30	375	1.56	86.7	1.39	100.2	1.61
.75	580	1.27	664	1.45	324	1.35	412	1.72	90.5	1.45	112	1.79
1.00	593	1.30	724	1.58	330	1.38	441	1.84	92.7	1.48	120	1.92
1.50	...	...	787	1.72	...	...	493	2.05	...	...	132	2.11
2.00	630	1.38	849	1.85	327	1.36	534	2.22	97.0	1.55	142	2.27
3.00	668	1.46	985	2.15	321	1.34	607	2.53	99.2	1.59	159	2.55
4.00	709	1.55	...	...	316	1.32	...	...	100.3	1.61	...	...
	Ethylamine[b]				Diethylamine				Triethylamine			
0.00	283	1.00	283	1.00	278	1.00	278	1.00	194	1.00	194	1.00
.25	325	1.15	354	1.25	330	1.19	358	1.29	241	1.24	258	1.33
.50	337	1.19	391	1.38	349	1.26	402	1.45	258	1.33	282	1.46
.75	351	1.24	421	1.49	355	1.28	431	1.55	269	1.39	297	1.53
1.00	360	1.27	456	1.61	359	1.29	456	1.64	280	1.44	313	1.61
1.50	...	...	499	1.76	...	...	492	1.77	...	...	325[c]	1.68
2.00	374	1.32	543	1.92	353	1.27	519	1.87	293[c]	1.51	...	...
3.00	388	1.37	625	2.21	347	1.25	560	2.02	...	...	...	...
4.00	396	1.40	...	...	341	1.23	583	2.10	...	...	...	...

TABLE II (*Concluded*)

	Ammonia				Tetramethylammonium hydroxide[d]		
	NaCl		Na_2SO_4		NaCl		
m_s	K^a	K/K_0	K^a	K/K_0	K^a	K/K_0	K/K_0^e
0.00	33.2	1.00	33.2	1.00	842	1.00	1.00
.25	38.5	1.16	49.5	1.49	...	...	...
.50	41.3	1.24	57.7	1.74	699	0.83	0.82
.75	42.5	1.28	64.0	1.93	...	...	...
1.00	43.0	1.30	70.5	2.13	626	0.74	0.71
1.50	...	...	79.0	2.38	...	...	...
2.00	40.7	1.23	88.0	2.65	530	0.63	0.58
3.00	36.6	1.10	103.0	3.10	445	0.53	0.48
4.00	33.5	1.01	112	3.37	396	0.47	0.44

[a] All K-values are to be multiplied by 10^{-5}.

[b] Due to unknown impurities in the ethylamine used, the velocity values found are probably all a little too small.

[c] The amine is partially salted out at higher salt concentrations.

[d] Tetramethylammonium hydroxide was used in 0.05 N solution.

[e] The values for K/K_0 with 0.1 N NaOH in NaCl solutions.

Experimental Results

The velocity measurements were carried out at 25° with the amines in sodium chloride or sulfate solutions. A summary of the results obtained is given in Table II. A few measurements with 0.05 N tetramethyl-

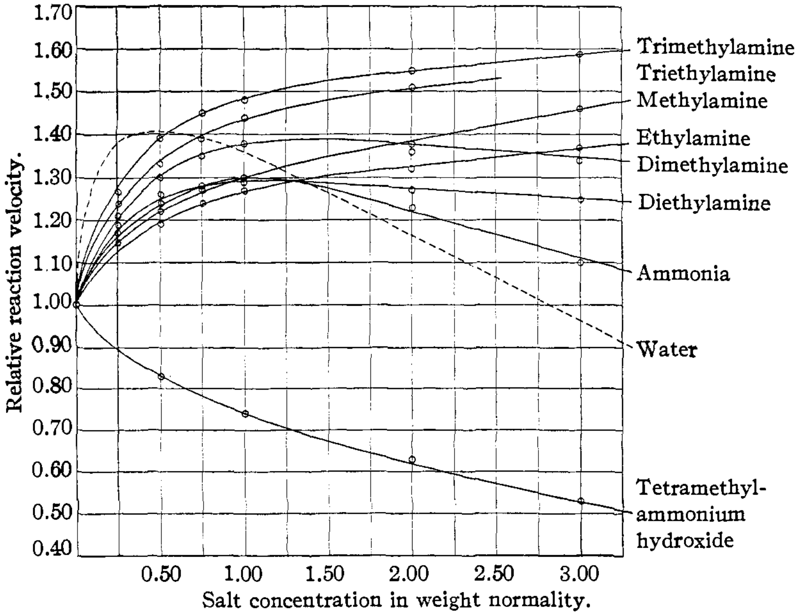

Fig. 1.—Curves for the relative decomposition velocity of diacetone alcohol in sodium chloride solutions of 0.2 N weaker bases.

ammonium hydroxide are also included. All salt concentrations m_s are given in weight normality. The amount of diacetone alcohol used was about 2% of the total volume of the solution. The velocity constants are given with the minute as unit of time. A graphical representation of the results is given in Fig. 1 for the amines in sodium chloride, in Fig. 2 in sodium sulfate solutions.

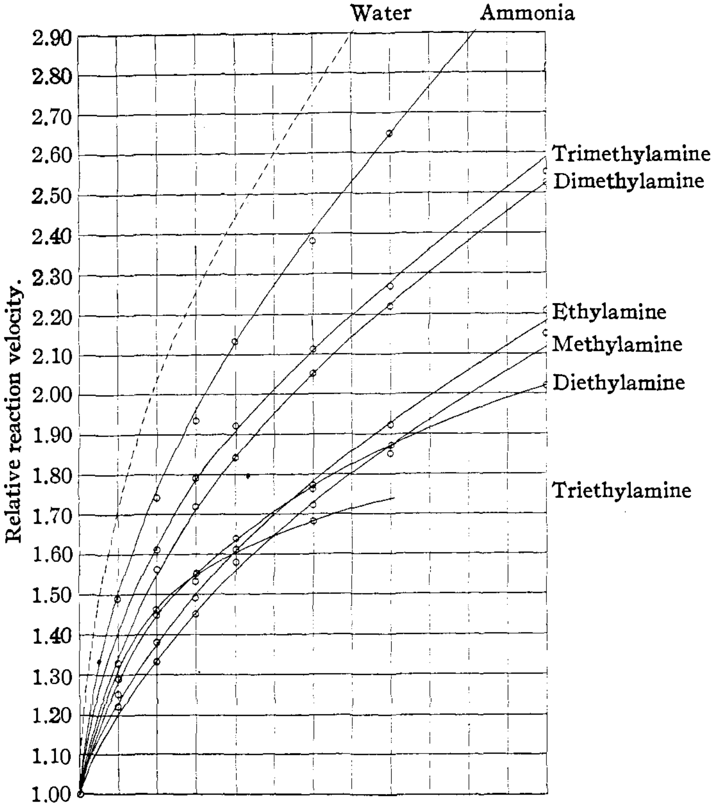

Fig. 2.—Curves for the relative decomposition velocity of diacetone alcohol in sodium sulfate solutions of 0.2 N weaker bases.

The Equilibrium Constants of the Weak Bases Used

The equilibrium constant k for the weak bases may be given by the following equation

$$k_{\mathrm{BOH}} = \frac{a_{\mathrm{B}} \cdot a_{\mathrm{OH}}}{a_{\mathrm{BOH}}} = \frac{\gamma_{\mathrm{B}} \cdot c_{\mathrm{B}} \cdot \gamma_{\mathrm{OH}} \cdot c_{\mathrm{OH}}}{\varphi_{\mathrm{BOH}} \cdot c_{\mathrm{BOH}}} = \frac{\gamma_{\mathrm{BOH}} \cdot c_{\mathrm{OH}}}{c_{\mathrm{BOH}}} \qquad (1)$$

where a denotes activities, γ ionic activity coefficients, c concentration and φ_{BOH} the activity coefficient of the non-electrolyte. The changes of φ_{BOH} may be relatively small. Therefore it may be assumed always to equal unity in pure aqueous solutions of the weaker bases. The equilibrium constants given in the literature are calculated without any reference to the changes of γ_{BOH}. At constant stoichiometrical concentration c we then obtain for the ratios between the equilibrium constants

$$k_1/k_2/k_3 \ldots = c_{OH(1)}/c_{OH(2)}/c_{OH(3)} \ldots \qquad (2)$$

The correction of c for c_{OH} is neglected because it is always comparatively small and the values of the equilibrium constants themselves seem many times to have appreciable errors. With the assumption of proportionality between hydroxyl ion concentration and reaction velocity, the following equation is obtained

$$\sqrt{k_1}/\sqrt{k_2}/\sqrt{k_3} \ldots = K_1/K_2/K_3 \ldots \qquad (3)$$

For ammonia the equilibrium constant seems to be known more accurately than for any other weak base. All the measurements were carried out by a conductivity method.[10] The curve for the changes of this constant for ammonia with varying temperature is shown in Fig. 3. Interpolation gives for 25° the value $k = 1.85 \times 10^{-5}$. Table III summarizes

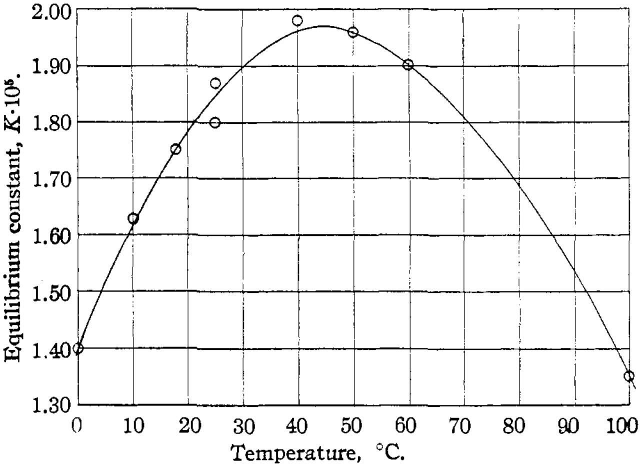

Fig. 3.—The equilibrium constant for ammonia at varying temperatures as obtained from conductivity measurements.

TABLE III

EQUILIBRIUM CONSTANT FOR AMMONIA AS CALCULATED FROM VELOCITY MEASUREMENTS

Base	k	$K \times 10^6$	k for ammonia
Dimethylamine	7.4×10^{-4}	240	1.42×10^{-5}
Trimethylamine	7.4×10^{-5}	62.5	2.09×10^{-5}
Diethylamine	1.3×10^{-3}	278	1.85×10^{-5}
Triethylamine	6.4×10^{-4}	194	1.88×10^{-5}
Ammonia	......	33.2	Mean 1.81×10^{-5}

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[10] (a) Lunden, *J. chim. phys.*, **5**, 574 (1907); (b) Kanolt, THIS JOURNAL, **29**, 1408 (1907); (c) Noyes, Kato and Sosman, *Z. physik. Chem.*, **73**, 1 (1910); (d) Landolt-Börnstein, "Tabellen," 4th ed., p. 1133.

the calculations of the value of this constant as obtained from the velocity measurements. The equilibrium constants used were measured by Bredig.[11] The mean value is only a little lower than the one obtained from the conductivity measurements but the agreement may seem to be rather accidental. It might seem to be possible to test the value for the equilibrium constant in another way. Assume that the proportionality factor between reaction velocity and mean activity of the base used is the same for a weak one as for a strong one. For 0.1 N sodium hydroxide the activity coefficient is $\gamma_{NaOH} = 0.767$ and the reaction velocity for the decomposition of diacetone alcohol $K = 0.0208$. With the equilibrium constant for ammonia $k = 1.85 \times 10^{-5}$ and the activity of the hydroxyl ion corrected according to the limiting function of Debye and Hückel, the calculation gives for 0.2 N solution $K = 49.2 \times 10^{-5}$ as against the measured value $K = 33.2 \times 10^{-5}$. At least the order of magnitude is the same for both values. The discrepancy seemed, however, to be too large and therefore the velocity value for the pure ammonia solution was remeasured with the greatest care. A slightly higher value was found but the difference from the previous value was so small that a correction was considered unnecessary.

For 0.2 N ammonia we may therefore accept the equilibrium constant $k = 1.85 \times 10^{-5}$ and the reaction velocity for the decomposition of diacetone alcohol $K = 33.2 \times 10^{-5}$. A summary of the calculations of the equilibrium constants for the other weak bases used from the velocity measurements with these reference values is given in Table IV.

TABLE IV

EQUILIBRIUM CONSTANTS CALCULATED FROM THE VELOCITY MEASUREMENTS

Base	$K \times 10^5$	k	k (Bredig)
Methylamine	458	3.5×10^{-3}	5.0×10^{-4}
Dimethylamine	240	9.7×10^{-4}	7.4×10^{-4}
Trimethylamine	62.5	6.5×10^{-5}	7.4×10^{-5}
Ethylamine	283	1.3×10^{-3}	5.6×10^{-4}
Diethylamine	278	1.3×10^{-3}	1.3×10^{-3}
Triethylamine	194	6.3×10^{-4}	6.4×10^{-4}
Ammonia	33.2[a]	1.85×10^{-5}[a]	......

[a] Reference values.

The k-values obtained for the weakest bases agree fairly well with the values measured by Bredig. The strongest bases are gases at ordinary temperatures and far more difficult to purify than the weaker ones. Since any impurity like free ammonia apparently must lower their k-values, it is believed, that our values are nearer the true ones than those previously given in the literature. The reaction velocity and k-value for ethylamine are probably a little too small.

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[11] Bredig, *Z. physik. Chem.*, 13, 289 (1894).

Activity Coefficients of the Weak Bases as Electrolytes in Sodium Chloride and Sulfate Solutions

In the preceding paper it was shown that the decomposition velocity for diacetone alcohol in pure aqueous solutions of the alkali hydroxides was proportional to their mean activity

$$K_{\mathrm{MeOH}} = R \cdot \gamma_{\mathrm{MeOH}} \cdot m_{\mathrm{MeOH}} \tag{4}$$

where R is the proportionality factor. For alkali hydroxide-salt solutions this simple formula cannot be applied but the reaction velocity may be expressed by the following equation

$$K_{\mathrm{MeOH(S)}} = R \cdot m_{\mathrm{MeOH}} \cdot F(x) \tag{5}$$

where (S) indicates an hydroxide-salt solution and $F(x)$ is a complex unknown factor. If we exchange the alkali hydroxide in the salt solutions against a weak base, the activity coefficient of the hydroxyl ion must remain nearly constant, because it is given by the nature of the environment, which remains nearly constant. The reaction velocity in the weak base-salt solution may then be expressed by a formula similar to (5)

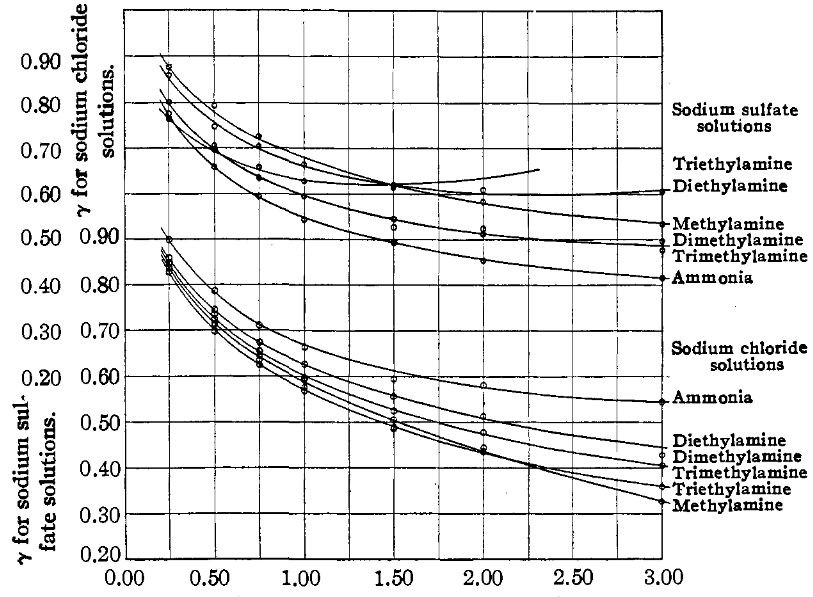

Fig. 4.—Curves for the mean activity coefficients of the weaker bases as electrolytes in sodium chloride and sulfate solutions calculated with the velocity measurements for 0.1 N sodium hydroxide in the same salt solutions.

$$K_{\mathrm{BOH(S)}} = R \cdot m_{\mathrm{OH(BOH)}} \cdot F(x) \tag{6}$$

Assuming complete dissociation of the hydroxide, division of (5) by (6) gives

$$K_{\mathrm{MeOH(S)}}/K_{\mathrm{BOH(S)}} = m_{\mathrm{MeOH}}/m_{\mathrm{OH(BOH)}} \tag{7}$$

From this equation we may calculate $m_{\mathrm{OH(BOH)}}$, when all other variables are known. Harned and Hawkins used the same method for calculating the hydrogen-ion concentration in weak acid-salt solutions. With the knowledge of $m_{OH(BOH)}$ we may use the mass action law to obtain γ_{BOH} on the assumption that φ_{BOH} (Equation 1) always equals unity. The magnitude of φ_{BOH} is connected with the salting out effect on the amines. At present we will disregard the influence of this factor in order to see whether we get reasonable values for the ionic activity coefficients of the weak bases without it. In Table V is given a summary of the calculated mean activity coefficients of the weak bases as electrolytes in sodium chloride and sulfate solutions. The curves for the mean activity coefficients are given in Fig. 4.

TABLE V

MEAN ACTIVITY COEFFICIENTS OF THE WEAKER BASES AS ELECTROLYTES IN SODIUM CHLORIDE AND SULFATE SOLUTIONS

		A. Methyl		B. Dimethyl		C. Trimethyl		D. Diethyl	
m_c	K_{NaOH}	K_{BOH}	γ_{BOH}	K_{BOH}	γ_{BOH}	K_{BOH}	γ_{BOH}	K_{BOH}	γ_{BOH}
0.25	184	53.5	0.84	29.0	0.85	7.83	0.84	33.0	0.86
.50	170	55.9	.74	31.2	.72	8.67	.70	34.9	.74
.75	158	58.0	.65	32.4	.64	9.05	.62	35.5	.68
1.00	149	59.3	.59	33.0	.59	9.27	.57	35.9	.63
1.50	133	61.0	.51	33.1	.52	9.57	.48	35.8	.56
2.00	121	63.0	.44	32.7	.48	9.70	.44	35.3	.51
3.00	101	66.8	.33	32.1	.40	9.92	.36	34.7	.43
4.00	91.8	70.9	.27	31.6	.37	10.03	.32	34.1	.39
		G. Methyl		H. Dimethyl		E. Triethyl		F. Ammonia	
0.25	200	56.0	0.88	33.0	0.80	24.1	0.83	3.92	0.90
.50	199	60.9	.80	37.5	.70	25.8	.71	4.13	.79
.75	199	66.4	.72	41.2	.64	26.9	.63	4.25	.71
1.00	200	72.4	.66	44.1	.59	28.0	.57	4.30	.66
1.50	204	78.7	.62	49.3	.53	29.0	.49	4.27	.59
2.00	210	84.9	.58	53.4	.51	29.3	.44	4.07	.58
3.00	224	98.5	.53	60.7	.48	...	...	3.66	.55
4.00	...	...	...	....	...	...	...	3.35	.54
		I. Trimethyl		K. Diethyl		L. Triethyl		M. Ammonia	
0.25	200	8.50	0.84	35.8	0.86	25.8	0.76	4.95	0.77
.50	199	10.02	.71	40.2	.75	28.2	.69	5.77	.66
.75	199	11.2	.63	43.1	.70	29.7	.66	6.40	.59
1.00	200	12.0	.59	45.6	.67	31.3	.63	7.05	.54
1.50	204	13.2	.55	49.2	.63	32.5	.61	7.90	.49
2.00	210	14.2	.52	51.9	.61	...	...	8.80	.45
3.00	224	15.9	.50	56.0	.60	...	...	10.30	.41

A–F, values for sodium chloride; G–M, values for sodium sulfate solutions. All reaction velocities to be multiplied by 10^{-4}.

Discussion of the Results

The values for the mean activity coefficients of the weaker bases as electrolytes given in Table V were calculated without any consideration that the values used for the reaction velocities did not refer to solutions of the same total ionic strength. Due to the approximate nature of the calculations, a correction seems to be unnecessary. It would cause only very slight changes for the values of the mean activity coefficients.

The curves for these activity coefficients in Fig. 4 show that for a given salt concentration values of the same magnitude were obtained for all the weaker bases used. Several curves superimpose on other curves in their entire length. For some of them where this is not the case, it seems as if they were superimposable within the experimental errors. In accordance with the assumption made for the method of calculation used this could be expected.

So far the results seem to be reasonable. However, at small salt concentrations the slope of the curves seems to be too small. In other words, the values obtained may be too high. There are no other electrolytes found with such high values for the mean activity coefficients in dilute solutions. On the contrary, we would expect these amines to have quite small activity coefficients in salt solutions on account of the complexity of their ions. In this case the addition of a small amount of salt would have caused a very sharp decrease for their activity coefficients.

It seems to be out of the question that the measurements themselves could have such large errors that they gave a distorted view of the calculations. The assumption of incomplete dissociation of the alkali hydroxide in hydroxide-salt solutions would give an increase for the activity coefficients and therefore cannot be considered. The salting out effect on the amines increases the value of φ_{BOH} and as we calculated the hydroxyl ion concentration without any assumption regarding this effect we have instead multiplied the activity coefficients with the increase in this factor. The increase must, however, be small even in fairly concentrated salt solutions, as might be concluded from the measurements with triethylamine.

It was shown above that the value for the decomposition velocity of diacetone alcohol in 0.2 *N* ammonia as calculated from the equilibrium constant and the velocity in 0.1 *N* sodium hydroxide ($49.2 \cdot 10^{-5}$) did not agree with the measured one ($33.2 \cdot 10^{-5}$). The proportionality factor for reaction velocity and ionic activity must have changed from the strong base to the weak one in the ratio of these two values. Harned and Hawkins found that the same proportionality factor could be used for strong as well as weak acids. A reason for the difference might be found in the difference in behavior the reactions used show towards the properties of the catalysts. Harned and Pfanstiel[12] have found it probable that the velocity of hydrolysis of ethyl acetate in solutions of hydrochloric acid is proportional to the activity of the hydrogen ion. For the decom-

[12] Harned and Pfanstiel, THIS JOURNAL, **44**, 2193 (1922).

position of diacetone alcohol in alkali hydroxide solutions the measurements seem to indicate that the velocity is proportional to the mean activity of the hydroxides. If then the cation present is exchanged against another one of different character it might be reasonable to expect a change also for the proportionality factor.

In Table VI are given some values for the mean activity coefficients of the weaker bases corrected for the change in proportionality factor from the alkali hydroxides to the weaker bases. There is also given a comparison between these corrected values and those derived from the measurements with tetramethylammonium hydroxide in sodium chloride solutions. The cation of this base must stand far nearer the cations of the weak bases than the alkali metal ions. In Fig. 5 are shown curves for the corrected and uncorrected values, a curve for values calculated from the measurements with tetramethylammonium hydroxide and the corresponding curves obtained by Harned and Hawkins for weak acids in sodium chloride solutions. Tetramethylammonium hydroxide apparently belongs to the strong bases, but it is considerably weaker than any one of the alkali hydroxides. The mean activity coefficients of the weaker bases obtained with the measurements for solutions of this hydroxide come between the corrected and uncorrected values given in Table VI.

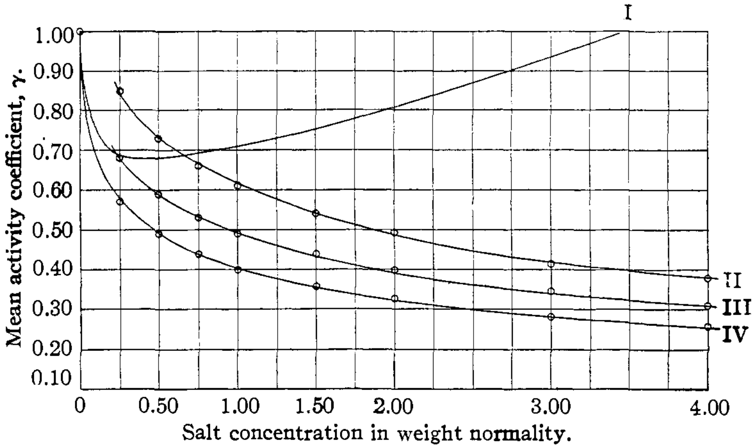

Fig. 5.—Comparison of the curves for the mean activity coefficients of the weaker bases as electrolytes in sodium chloride and sulfate solutions calculated:

I, with velocity measurements for 0.1 N sodium hydroxide (Curve II for dimethyl- or diethylamine in NaCl solutions); II, with velocity measurements for 0.05 N tetramethylammonium hydroxide (Curve III for dimethyl- and diethylamine in NaCl solutions); III, with corrected proportionality factor (Curve IV for dimethyl- and diethylamine in NaCl solutions); Curve I gives the activity coefficient for mono- or dichloro-acetic acid in sodium chloride solutions.

The corrected values seem to be of a reasonable magnitude with regard to the measurements of Harned and Hawkins. As was expected, quite small mean activity coefficients are obtained at high salt concentrations.

TABLE VI

CORRECTED MEAN ACTIVITY COEFFICIENTS FOR THE WEAKER BASES AS ELECTROLYTES IN SODIUM CHLORIDE AND SULFATE SOLUTIONS

	Methylamine			Dimethylamine			Trimethylamine		
m_s	I[a]	II[b]	III[c]	I[a]	II[b]	III[c]	I[a]	II[b]	III[c]
0.25	0.84	0.67	0.56	0.85	0.68	0.57	0.84	0.66	0.57
.50	.74	.59	.49	.72	.59	.49	.70	.58	.47
.75	.65	.52	.44	.64	.53	.43	.62	.51	.42
1.00	.59	.49	.40	.59	.49	.40	.57	.48	.38
1.50	.51	.42	.34	.52	.44	.35	.48	.42	.32
2.00	.44	.37	.29	.48	.40	.32	.44	.38	.30
3.00	.33	.28	.22	.40	.35	.27	.36	.31	.24
4.00	.27	.22	.18	.37	.31	.25	.32	.28	.22
	D[d]	E	F	G	H	I	K	L	M
0.25	0.58	0.56	0.60	0.59	0.54	0.56	0.58	0.51	0.52
.50	.50	.48	.53	.54	.47	.47	.50	.47	.44
.75	.45	.42	.48	.49	.43	.42	.47	.44	.40
1.00	.42	.38	.44	.45	.40	.40	.45	.42	.36
1.50	.37	.33	.40	.41	.36	.37	.42	.41	.33
2.00	.34	.29	.39	.39	.34	.35	.41	...	.30
3.00	.29	...	.37	.36	.32	.33	.40	...	.28

[a] Uncorrected values given in Table V for sodium chloride solutions.

[b] Values calculated from measurements with 0.05 *N* tetramethylammonium hydroxide in sodium chloride solutions.

[c] Values calculated with corrected proportionality factor.

[d] The letters D, E, F, etc., refer to those for the amines in Table V. All values are corrected.

Summary

Measurements of the decomposition velocity of diacetone alcohol in sodium chloride and sulfate solutions of weak bases are presented. A discussion of the equilibrium constants of the weak bases used has been given. The values found for the strongest bases are probably more accurate than values previously given in the literature.

The activity coefficients of the weaker bases as electrolytes in salt solutions cannot be calculated on the assumption that a weak base has the same proportionality factor between activity of the base and reaction velocity as a strong one. A correction factor for the activity coefficients was calculated from the reaction velocities measured in pure aqueous solutions of 0.1 *N* sodium hydroxide and one of the amines.

The corrected mean activity coefficients seem to have reasonable values. The decrease in dilute salt solutions is of the same magnitude as found by Harned and Hawkins for weak acids in the same salt solutions.

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