

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

ACTIVITY COEFFICIENT OF DIACETONE ALCOHOL IN AQUEOUS SALT SOLUTIONS

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RECEIVED AUGUST 7, 1928

PUBLISHED APRIL 5, 1929

Introduction

Our present theories for the velocity of catalyzed reactions in concentrated solutions of strong electrolytes are handicapped because little is known concerning a number of the variables which may have to be considered. For an ever-increasing number of reactions we know quite definitely that the velocity is either a function of or parallel to the thermodynamic activities of the electrolytes present. Thus far our knowledge of the influence of changes of the activity coefficients of the reacting substance is very incomplete. This investigation has been carried out in order to get an idea of the magnitude of the changes of the relative activity coefficient of diacetone alcohol in concentrated hydroxide-salt solutions. Experimental methods suitable for this study were limited both in number and accuracy. The changes in partition coefficient between the salt solutions and an insoluble organic liquid have been utilized.

Experimental Method

According to Gibbs the activity of a certain component is the same in all phases of a polyphase system in equilibrium at constant temperature. The activity is defined as the product of the activity coefficient γ and the concentration c

$$\gamma_1 c_1 = \gamma_2 c_2 = \gamma_3 c_3 = \dots$$

where the subscripts denote the different phases. Let us assume that the activity coefficient of diacetone alcohol in pure water has the value of unity. Dissolved in another solvent, as toluene, the activity coefficient may be considered as a constant and independent of the concentration, because the partition coefficient with pure water is a constant. We then obtain for the activity coefficient of diacetone alcohol in a salt solution

$$\gamma = k \times c_1/c_2$$

where k is the partition coefficient with pure water and c_1 and c_2 are the concentrations of the diacetone alcohol in the salt solution and toluene, respectively. These values are measured simultaneously.

To determine these concentration changes a Zeiss interferometer was employed. After some difficulties in obtaining clear spectra for solutions with solvents other than water had been overcome, the following procedure was adopted. First a series of salt solutions was made up in 500-cc. Erlenmeyer flasks. All salt concentrations were calculated as weight normality. The amount of water used was 400 g. at lower concentrations and 300 g. at higher ones. Usually a very carefully filtered, highly con-

centrated standard solution of the salt was used for making up the solutions. Most of the c. p. or analyzed chemicals used contained a large amount of dust.

After the salt solution had been given a careful mixing, about 50 cc. was poured over the edge of the flask, which was slowly rotated. Immediately after this, amounts of solution containing 100 g. of water were weighed off in two 250-cc. Erlenmeyer flasks with ground-glass stoppers. In order to avoid evaporation of water the weighing had to be done rapidly. The average accuracy of the weighing was about 0.1–0.2 g. Wetting of the ground surface inside the neck of the flasks by the solutions was avoided. To one of these weighed solutions was added 100 cc. of solvent containing about 1% of diacetone alcohol and to the other one also 100 cc. of solvent but with only 0.2% of the alcohol present. It was found that when the pure solvents used were shaken with an aqueous salt solution rather stable emulsions were formed. The addition of a small amount of diacetone alcohol seemed to prevent this and the solutions cleared rapidly. The difference in diacetone alcohol concentration of the two different samples of the solvent added to the salt solutions was measured very carefully.

After the solvent had been added the glass stoppers to the flasks were wetted with two or three drops of the solvent, rotated with a slight pressure until an optically clear joint had been obtained and finally pressed in hard. Then the flasks were shaken vigorously three or four times for three to five-minute periods at intervals of about one hour. Tests of the efficiency of the shaking seemed to show that after the second one the differences obtained probably were caused by other experimental errors. After the last shaking had been completed the solutions were left for twenty-four hours so that they became perfectly clear. If the measurements were started shortly after the last shaking the results seemed to be very erratic. The enormous sensitivity of the interferometer and the very small concentration differences that had to be used, required optically clear solutions.

For the measurement the two layers in each flask were first separated. The upper one was removed by pouring the greater part of the liquid slowly over the edge of the flask into a 150-cc. Erlenmeyer flask, which was immediately closed with a rubber stopper. A small separatory funnel was used to obtain the lower layer free from the upper one. The remaining solution was poured slowly into the funnel and then withdrawn ten to fifteen minutes later. It was found to be desirable to obtain the amount of diacetone alcohol in the salt solution indirectly. The solutions containing salt were therefore thrown away and only the solvent solutions were used for the measurement.

The difference between the apparent total amount of diacetone alcohol present and that retained by the organic solvent after shaking with the salt solution, gave the amount in the latter. This gives the following equation for the calculation of the activity coefficient of the diacetone alcohol

$$\gamma = \frac{R_0 - R_1}{R_1} \times \frac{R_2}{R_0 - R_2}$$

where R_0 is the reading for the original solvent solutions, R_1 after shaking with water and R_2 after shaking with the salt solution (all values corrected).

The solutions were now ready to be used. The two compartments of the all-glass cells belonging to the interferometer were washed out carefully three or four times with their respective solutions, then filled to overflowing and the glass covers put on in such a way that no air bubbles were inclosed. Finally the cell was wiped dry, the end-plates polished and the cell placed in the little kerosene bath of the interferometer. Water could not be used for the bath, because it was impossible to remove all of the solvent from the outside of the cell by wiping, due to the afterflow from the casing around the upper part of the cell. When placed in water the thin oil film on the surface of the end-plates became uneven, which completely distorted or entirely blotted out the spec-

tra. The correct reading of the interferometer was very difficult. The distance between two spectral bands was about 16 units on the scale. The greatest difficulty was to choose the right bands. At times four or five bands in the upper spectrum appeared to have nearly the same color and by pairs to coincide with the two middle bands of the lower spectrum. An error of three or four times 16 units, therefore, could easily be made. This necessitated high sensitivity to small variations in color and considerable experience in judging the appearance of the bands.

When the cells had been placed in the interferometer bath the liquid was stirred slowly at the rate of about twenty to forty turns a minute. The time required to get a reading varied between five and twenty minutes. Too rapid stirring caused splashing and usually gave very poor spectra. When the rate was too slow the time necessary to obtain a good reading lengthened considerably and sometimes also gave distorted spectra. Splashing of the bath liquid was rather difficult to avoid because the bath had to be kept nearly full and kerosene has a low viscosity. Exchange of kerosene for other liquids with higher viscosity (as ethyl phthalate) brought in other disadvantages which were considered as far from serious. Kerosene evaporating from the outside of the bath slowly attacked the Canada balsam with which the prisms of the interferometer were fastened. This caused continuous changes of the zero point of the instrument. In order to avoid these changes the commercial kerosene was fractionated and the fraction boiling around 350° was used. This decreased to a large extent the zero point changes. They amounted only to a few units a week.

A large number of solvents were tried out for these experiments. Solvents with low boiling point and high volatility, like toluene or benzene, could not be used. Bromobenzene and cymene were finally selected as most suitable. The former was first washed by inside spraying with water for four to five hours. The water velocity was about 2-3 liters a minute. At higher velocities emulsions were formed. Then the solvent was dried with fused calcium chloride and vacuum distilled in a large all-glass still. The commercial cymene was first distilled three times from concentrated potassium hydroxide solution. It was then washed in a continuous stream of water for four to five hours, dried and redistilled in high vacuum. When shaken with water this solvent separated rapidly and became perfectly clear. The diacetone alcohol was used as obtained from Eastman Kodak Co. It contained slight traces of water but attempts at further drying failed. Mesityl oxide and water were formed. The former is insoluble in the latter and therefore separated upon further addition of water. However, the amount of impurities present was too small to affect the results perceptibly.

Correction of the Interferometer Readings

The readings on the interferometer were not exactly proportional to the diacetone alcohol concentration. With increasing concentration the correction necessary to obtain proportionality with the true values increased. At the end of the scale the correction amounted to about 300 units. The correction curve seemed to be characteristic for the instrument and independent of the nature of the solvent employed. Table I gives a summary of the measurements for the determination of the correction curve.

For the calculation of the experimental results which will be presented below, the corrections were obtained graphically. The corrections necessary when the diacetone alcohol concentration in the salt solution phase also is measured directly might be indicated here. Diacetone

alcohol has a higher refractive index than water. The addition of salt to pure water gives a higher refractive index to the solution. A given

TABLE I
MEASUREMENTS FOR CORRECTION CURVE OF THE INTERFEROMETER

I. WATER SOLUTIONS						
W. D. A. ^a	Obs. value, A	Interp. value, B	Ratio 10^{-1} B/W. D. A.	Corr. value	Error of B	
0.00	0000	0000	270	0000	000	
.10	0273	0273	273	0270	003	
.20	0549	0552	276	0540	012	
.30	0837	0837	279	0810	027	
.40	1122	1128	282	1080	048	
.50	1427	1425	285	1350	075	
.60	1722	1728	288	1620	108	
.70	2034	2037	291	1890	147	
.80	2342	2352	294	2160	192	
.90	2677	2673	297	2430	243	
1.00	3004	3000	300	2700	300	
II. CYMENE SOLUTIONS						
C. D. A.	0.00	0000	0000	143 ^b	0000	000
1.00	0143	0143	143	0143	000	
2.00	0289	0288	144	0286	002	
3.00	0437	0435	145	0429	006	
4.00	0589	0584	146	0572	012	
5.00	0741	0735	147	0715	020	
6.00	0893	0888	148	0858	030	
7.00	1051	1043	149	1001	042	
8.00	1207	1200	150	1144	056	
9.00	1359	1359	151	1287	072	
10.00	1522	1520	152	1430	090	
III. BROMOBENZENE SOLUTIONS						
C. D. A.	0.00	0000	0000	272	0000	000
1.00	0277	0275	275	0272	003	
2.00	0561	0556	278	0544	012	
3.00	0837	0843	281	0816	027	
4.00	1126	1136	284	1088	048	
5.00	1428	1435	287	1360	075	
6.00	1719	1740	290	1632	108	
7.00	2034	2051	293	1904	147	
8.00	2370	2368	296	2176	192	
9.00	2692	2691	299	2448	243	
10.00	3017	3020	302	2720	300	

^a W. D. A. gives the amount of diacetone alcohol present in weight per cent. For cymene and bromobenzene, standard solutions containing 6.978 volume per cent. of diacetone alcohol were used. C. D. A. gives the number of cc. of these solutions diluted to a total of 100 cc.

^b This value instead of 142 was used because it gave better agreement with the measurements for water and bromobenzene solutions.

amount of diacetone alcohol must then cause a smaller deviation in the interferometer when dissolved in the salt solution as compared with the one for pure water. With the proper scale correction applied, a linear decrease is obtained with increasing salt concentration. After correcting for scale deviation, the reading obtained for the salt solution used in the partition experiment and multiplying with the corrected decrease ratio for the salt solution used, all measurements are comparable and give the correct activity coefficient. However, this method is quite complicated to carry out and should ordinarily be avoided.

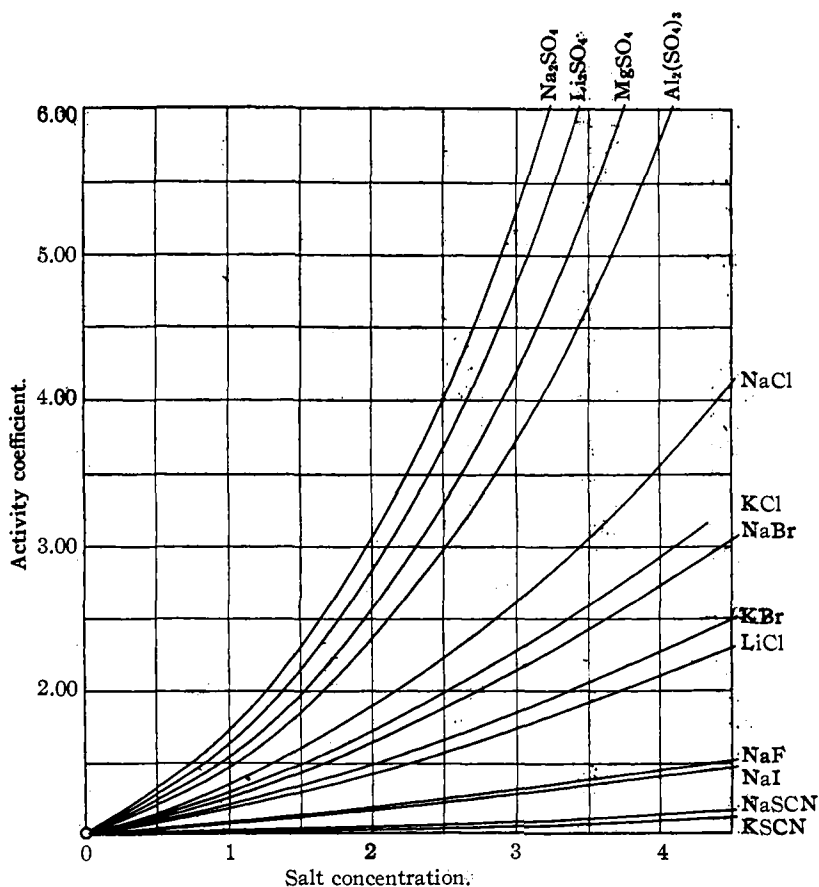


Fig. 1.—Curves for the relative activity coefficient of diacetone alcohol in various salt solutions.

Experimental Results

Table II gives a summary of the measurements. All interferometer readings are the uncorrected values. The temperature for the measure-

ments was on the average 24° with a maximum variation of about one degree. A suitable thermostat was not available but the temperature coefficients seem to be quite small or negligible. The general accuracy of the results is a little difficult to judge but most probably the relative errors in the distribution of the curves seldom exceed 5%. The results are also independent of the nature of the solvents used, that is, the same values were obtained either for bromobenzene or cymene (a mixture of ethyl phthalate and bromobenzene also gave the same result). Up to the limit of the concentration that could be used for diacetone alcohol,

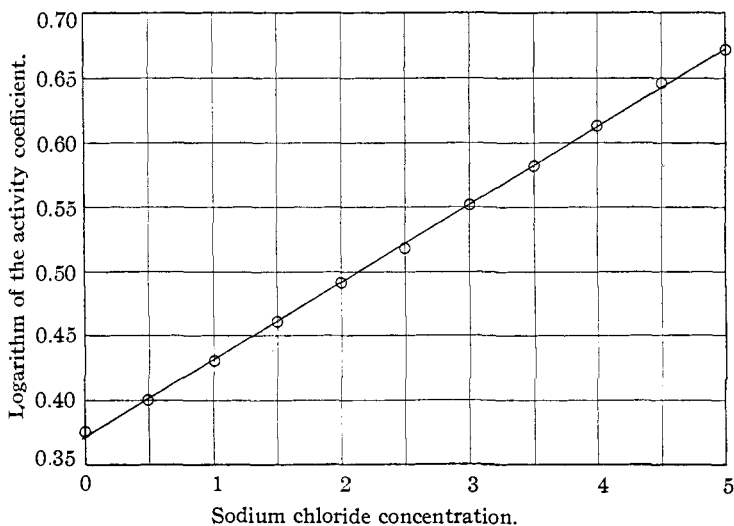


Fig. 2.—Curve for the logarithm of the relative activity coefficient of diacetone alcohol in sodium-lithium chloride solutions at constant total normality of 5 *N*.

the activity coefficients obtained seemed to be independent of the concentration either in the organic solvent phase or the salt solution used. All salt concentrations in Table II are expressed in weight normality per 1000 g. of water. Fig. 1 gives the curves for the measurements at increasing salt concentrations; Fig. 2 is the curve for the logarithm of the activity coefficients at constant total molarity in sodium-lithium chloride solutions. Fig. 3 shows the corresponding curves at varying constant total molarity. All curves in this last figure are drawn as straight, parallel lines because this seemed best to represent the results. It gives an analogy to the curves obtained by Åkerlöf¹ for the decomposition velocity of diacetone alcohol in alkali hydroxide-salt solutions at varying constant total molarity.

Table II also contains the values for $(\log \gamma)/N$. These values seem

¹ Åkerlöf, *THIS JOURNAL*, 49, 2955 (1927).

to be fairly constant. Randall and Failey² have recently shown that this probably is true for non-electrolytes in salt solutions. In Table III is given a comparison between the values for the activity coefficients of a few gases in 2 *N* sodium and potassium chloride and sodium sulfate solutions and those obtained for diacetone alcohol in the same salt solutions.

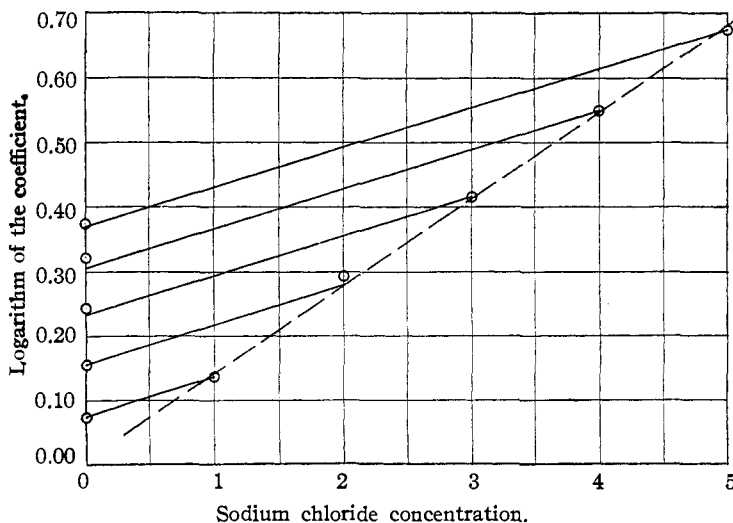


Fig. 3.—Curves for the logarithm of the relative activity coefficient of diacetone alcohol in sodium-lithium chloride solutions at varying constant total normality.

Considering the large probable errors of the solubility measurements used for the calculation of the activity coefficients of the gases, we might perhaps be justified in assuming them to be approximately independent of the nature of the gas employed or constant for a given salt solution.

TABLE II

RELATIVE ACTIVITY COEFFICIENT OF DIACETONE ALCOHOL IN SALT SOLUTIONS

<i>N</i>	NaCl Solutions		KCl Solutions		NaBr Solutions	
	<i>R</i>	$\gamma (\log \gamma)/N$	<i>R</i>	$\gamma (\log \gamma)/N$	<i>R</i>	$\gamma (\log \gamma)/N$
0.00	326	1.00 ...	326	1.00 ...	628	1.00 ...
1.00	432	1.37 0.136	416	1.31 0.118	756	1.28 0.107
1.50	507	1.66 .146	465	1.50 .118
2.00	582	1.97 .147	520	1.72 .117	920	1.68 .113
2.50	650	2.27 .141	593	2.02 .122
3.00	724	2.62 .139	648	2.26 .118	1057	2.09 .107
3.50	810	3.05 .138	706	2.53 .115	1180	2.50 .111
4.00	900	3.55 .137	793	2.97 .118	1248	2.76 .110
4.50	987	4.07 .135	1319	3.05 .108
5.00	1083	4.71 .135	1393	3.39 .106
		Mean .139		Mean .118		Mean .109

² Randall and Failey, *Chemical Reviews*, 4, 271, 285, 291 (1927).

TABLE II (Continued)

N	KBr Solutions			NaI Solutions			KI Solutions		
	R	γ	$(\log \gamma)/N$	R	γ	$(\log \gamma)/N$	R	γ	$(\log \gamma)/N$
0.00	628	1.00	...	628	1.00	...	628	1.00	...
1.00	735	1.23	0.0902	680	1.10	0.0449	665	1.08	0.0320
1.50	705	1.16	.0440	682	1.11	.0310
2.00	860	1.53	.0923	725	1.21	.0410	707	1.17	.0336
2.50	749	1.26	.0404	736	1.23	.0363
3.00	977	1.84	.0882	776	1.33	.0409	759	1.29	.0365
3.50	1043	2.04	.0887	795	1.37	.0394	775	1.32	.0347
4.00	1116	2.29	.0898	822	1.43	.0391	802	1.39	.0391
4.50	1177	2.49	.0900
5.00	1258	2.82	.0900
		Mean	.0900		Mean	.0414		Mean	.0342
	LiCl Solutions			NaSCN Solutions			KSCN Solutions		
0.00	628	1.00	...	628	1.00	...	628	1.00	...
1.00	715	1.18	0.0732	641	1.03	0.0115	636	1.02	0.0071
1.50
2.00	818	1.43	.0766	655	1.06	.0117	652	1.05	.0104
2.50
3.00	942	1.75	.0807	664	1.08	.0106	659	1.06	.0090
3.50	985	1.87	.0776	671	1.09	.0107	665	1.08	.0092
4.00	1062	2.10	.0806	680	1.10	.0112	673	1.09	.0098
4.50	1112	2.27	.0790	686	1.12	.0111	680	1.10	.0100
5.00	1141	2.37	.0765	691	1.13	.0108	685	1.12	.0098
		Mean	.0774		Mean	.0111		Mean	.0093
	Na ₂ SO ₄ Solutions			Li ₂ SO ₄ Solutions			MgSO ₄ Solutions		
0.00	326	1.00	...	326	1.00	...	326	1.00	...
1.00	520	1.71	0.233	514	1.69	0.227	488	1.59	0.200
1.50	639	2.22	.230
2.00	812	3.06	.242	768	2.84	.226	698	2.49	.198
2.50	976	4.00	.241
3.00	1167	5.33	.242	1069	5.04	.234	1004	4.18	.207
3.50	1337	6.81	.238	1172	5.37	.208
4.00	1496	8.33	.230	1390	7.33	.216
4.50	1548	9.17	.214	1537	10.4	.226
5.00	1823	13.5	(.265)	1755	12.4	.218
		Mean	.238		Mean	.228		Mean	.210
	MgCl ₂ Solutions			AlCl ₃ Solutions			Al ₂ (SO ₄) ₃ Solutions		
0.00	312	1.00	...	312	1.00	...	312	1.00	...
1.00	379	1.24	0.094	368	1.20	0.080	454	1.54	0.188
2.00	457	1.55	.095	445	1.50	.088	633	2.34	.184
3.00	547	1.95	.099	523	1.83	.087	882	3.70	.189
4.00	633	2.33	.092	628	2.31	.091	1186	5.99	.194
5.00	726	2.82	.090	707	2.71	.087	1492	9.52	.195

N is the salt concentration in weight normality. R is the interferometer reading for the bromobenzene or cymene phase. Pure water and bromobenzene gave R = 628 with a diacetone alcohol total of R = 2825, both in the bromobenzene phase. Pure water and cymene gave (1) R = 326 for a diacetone alcohol total of R = 2824 and (2) R = 312 for an alcohol total of R = 2682, all values for the cymene phase.

TABLE II (Concluded)

MEASUREMENTS WITH NaCl-LiCl SOLUTIONS AT CONSTANT TOTAL NORMALITY OF 5 N
Bromobenzene used as solvent for these measurements

NaCl	LiCl	R	γ	$\log \gamma$
0.00	5.00	1141	2.37	0.375
0.50	4.50	1182	2.51	.400
1.00	4.00	1230	2.69	.430
1.50	3.50	1280	2.89	.461
2.00	3.00	1330	3.10	.492
2.50	2.50	1375	3.30	.519
3.00	2.00	1430	3.57	.552
3.50	1.50	1478	3.82	.582
4.00	1.00	1530	4.12	.614
4.50	0.50	1583	4.44	.647
5.00	.00	1622	4.70	.672

TABLE III

ACTIVITY COEFFICIENTS FOR GASES IN 2 N NaCl, KCl AND Na₂SO₄ SOLUTIONS

	NaCl	KCl	Na ₂ SO ₄
Oxygen	1.83	1.70*	1.93 ^a
Hydrogen	1.55	1.45	...
Nitrous oxide	1.59	1.45	2.14
Acetylene	1.54	1.35	2.00
Hydrogen sulfide	1.32	1.28	3.47
Mean	1.56	1.45	2.39
Diacetone alcohol	1.90	1.72	3.00

^a Values obtained from data in Abegg-Auerbach, "Handbuch der anorg. Chemie," 6, 1 (1927). Other data from Randall and Failey.

If this is the case we apparently obtain the same or at least a very similar distribution of the curves for the activity coefficients of the gases in salt solutions as for those of diacetone alcohol.

Discussion of the Results

These measurements were undertaken in order to determine, if possible, whether or not the decomposition velocity of diacetone alcohol in alkali-hydroxide-salt solutions was influenced by changes in the activity coefficient of the reacting substance. In Fig. 4 are given some of the curves for the relative activity coefficients of ethyl acetate in various salt solutions as calculated from the solubility measurements of Glasstone and Pound.³ A comparison of these curves with those in Fig. 1 shows a very striking similarity. Their distribution is nearly the same in both cases. In Fig. 5 are the curves for the velocity of hydrolysis of ethyl acetate by 0.1 N hydrochloric acid in various salt solutions.⁴ Fig. 6 shows the corre-

³ Glasstone and Pound, *J. Chem. Soc.*, 127, 2660 (1925); cf. further Glasstone, Dimond and Jones, *ibid.*, 128, 2935 (1926).

⁴ Data for Fig. 5 obtained from Harned, *THIS JOURNAL*, 40, 1461 (1918); Bowe, *J. Phys. Chem.*, 31, 290 (1927).

sponding curves for the decomposition of diacetone alcohol in 0.1 *N* alkali hydroxide-salt solutions.⁵ In the case of ethyl acetate there is a great similarity between the distribution of the curves for velocity and activity coefficients. For diacetone alcohol the two sets of curves are also distributed in a similar manner, although their direction is widely different. For sodium chloride solutions the velocity decreases and

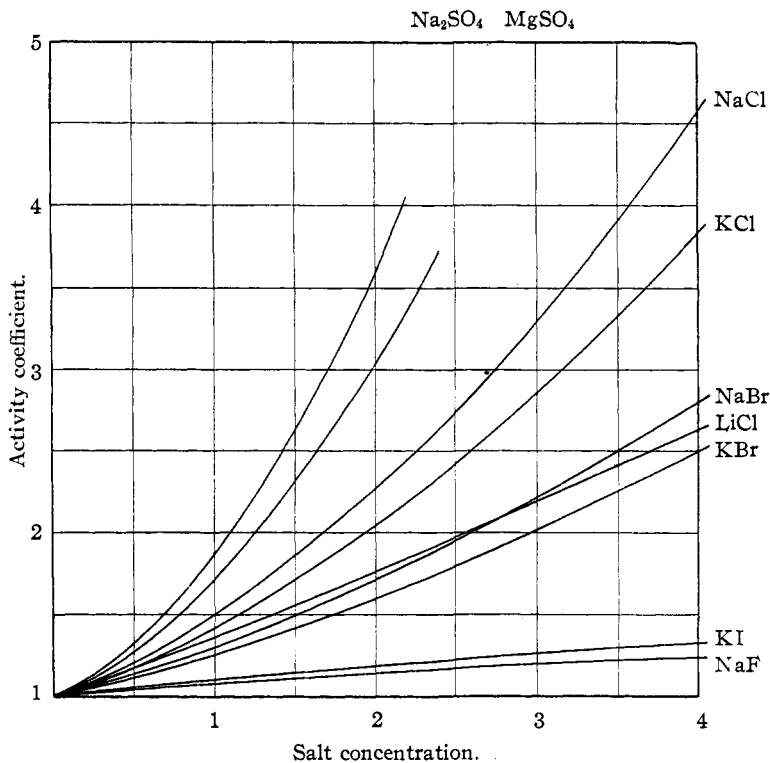


Fig. 4.—Curves for the relative activity coefficient of ethyl acetate in various salt solutions as calculated from solubility measurements of Glasstone and Pound, and Glasstone, Dimond and Jones.

activity coefficient increases rapidly. The curves for sodium sulfate, chloride, bromide, iodide and sulfocyanide solutions follow each other in the same order and at about the same distance in relation to each other. The position of the activity curves for potassium salt solutions below those for sodium salts are exceptions to identical distribution of activity and velocity curves.

In view of these facts we might feel inclined to believe that in the case of ethyl acetate velocity and activity of the reacting substance are

⁵ Data for Fig. 6 are obtained from Åkerlöf, *THIS JOURNAL*, 48, 3046 (1926).

intimately connected. The data at present available are not very accurate but it seems as if this could be the case.⁶ The use of a similar explanation for diacetone alcohol appears to offer great difficulties because direction and distribution of velocity and activity curves are not always the same. Decrease in velocity and increase of activity would give the velocity as an inverse function of the activity, while for sulfate

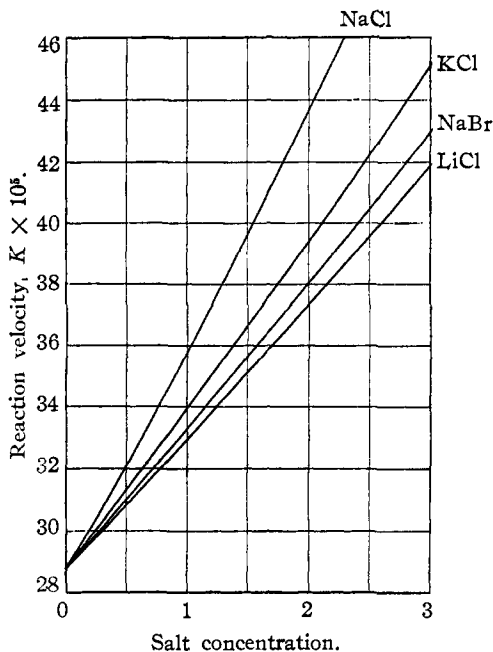


Fig. 5.—Curves for the velocity of hydrolysis of ethyl acetate by 0.1 *N* hydrochloric acid in various salt solutions.

same valence. Then the velocity is proportional to the concentration of the reacting ion and the activity coefficient of the substance B.

Previously it has been shown by Åkerlöf⁸ that the decomposition velocity of diacetone alcohol in pure aqueous solutions of the alkali hydroxides at higher concentrations is proportional to the activity coefficients of the hydroxides. Furthermore, the consideration of the velocity as a function of the activity of the reacting substance leads to different equations for different salts present. Adhering to the validity of the equation

⁶ Harned and Åkerlöf, *Trans. Faraday Soc.*, **24**, 666 (1918).

⁷ Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); *ibid.*, **115**, 337 (1925); cf. further Bjerrum, *ibid.*, **108**, 82 (1924); *ibid.*, **118**, 251 (1925); Christiansen, *ibid.*, **113**, 35 (1924).

⁸ Åkerlöf, *THIS JOURNAL*, **49**, 2955 (1927).

solutions where both velocity and activity increase with increasing salt concentration, the former apparently would be proportional to a function of the latter.

According to the theory of Brönsted,⁷ the velocity of a simple chemical reaction, which does not give definite intermediary products, is given by the equation

$$v = k(A)(B) \frac{\gamma_A \times \gamma_B}{\gamma_X}$$

where v is the velocity, k is a constant, (A) and (B) are the concentration of the two reacting substances A and B and γ_A , γ_B and γ_X are activity coefficients of A, B and X. The latter is a collision compound of momentary existence. If A is an ion, the intermediate is also an ion with the

of Brönsted, this may indicate that the activity coefficient of diacetone alcohol is canceled by γ_X . Then we must also assume that X is formed by the addition of both cation and anion of the hydroxide and has the character of a neutral molecule. This would give the velocity as being proportional to the concentration of the hydroxide and as a function of the activity coefficient of the same in qualitative agreement with the measurements.

If this explanation approaches the true conditions, we could expect to find the same or at least a very similar distribution of the curves for ve-

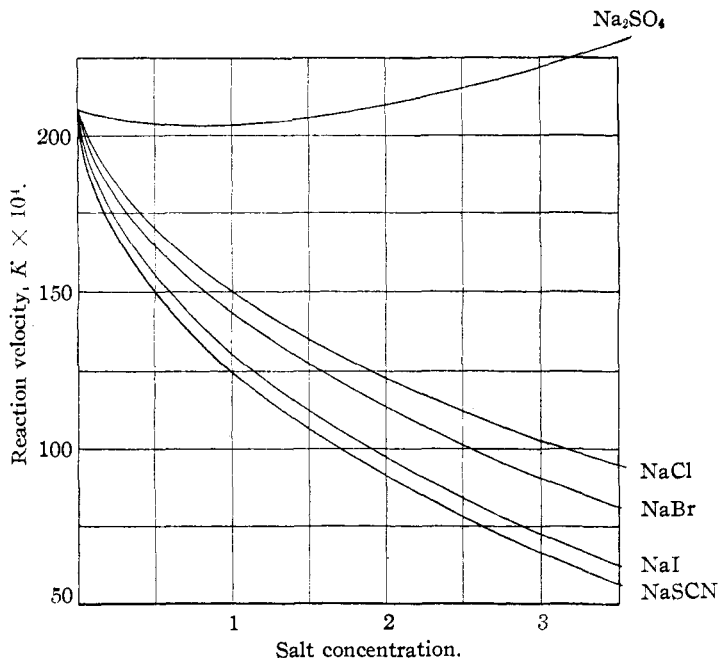


Fig. 6.—Curves for the decomposition velocity of diacetone alcohol in 0.1 N alkali hydroxide-salt solutions.

locity and activity coefficients of the hydroxides in hydroxide-salt solutions. When the salt present decreases the velocity this conclusion seems to be approximately valid, as shown in Fig. 7.⁹ The sulfate solutions might seem to be an exception and therefore make our explanation questionable. On the other hand, the sulfates increase the activity coefficients of the reacting substance very rapidly and this increase is relatively many times larger than the increase in reaction velocity at corresponding salt

⁹ Data for Fig. 7 are from measurements of Åkerlöf, *THIS JOURNAL*, **48**, 3046 (1926); *ibid.*, **48**, 1160 (1926); Harned, *ibid.*, **47**, 684, 689 (1925); Harned and James, *J. Phys. Chem.*, **30**, 1060 (1926); Douglas, "Thesis," University of Pennsylvania, 1926.

concentrations. Most probably this must tend to cause larger deviations from a function of the activity of the electrolytes present.

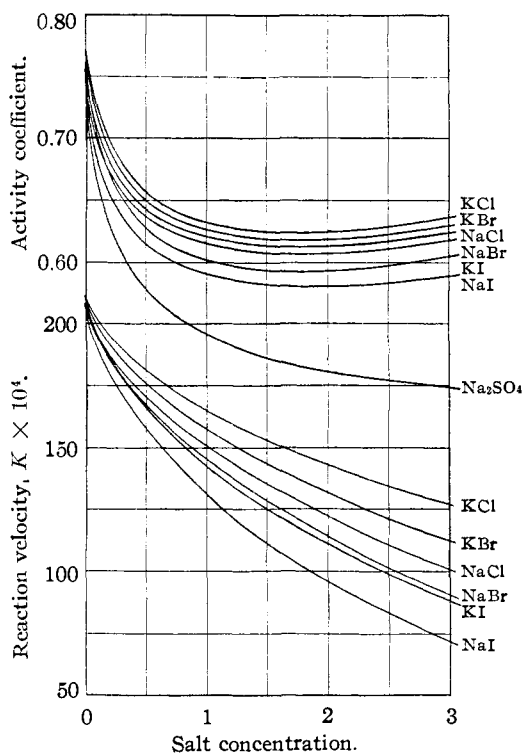


Fig. 7.—Curves for the decomposition velocity of diacetone alcohol in 0.1 *N* alkali hydroxide-salt solutions and the curves for the activity coefficient of the hydroxides in the same salt solutions.

Summary

The relative activity coefficient of diacetone alcohol in various salt solutions at $24 \pm 1^\circ$ has been measured, using an interferometric method to determine the partition coefficient of diacetone alcohol between the salt solutions and an insoluble organic liquid.

The results obtained agree closely in order of magnitude and distribution with the results of the calculation of the activity coefficient of ethyl acetate in the same salt solutions from solubility measurements of Glassstone and Pound. The relative activity coefficients for some permanent gases in these salt solutions are apparently also of the same order of magnitude and give most probably the same distribution as obtained for diacetone alcohol and ethyl acetate.

A short discussion has been given of the relation of these results to

the theory of Brönsted of velocity of reactions catalyzed by strong electrolytes. It seems to be very difficult to find a thoroughly satisfactory explanation of the changes of the decomposition velocity of diacetone alcohol in various solutions of strong electrolytes.

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THE SOLUBILITIES OF LEAD PHOSPHATES¹

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RECEIVED AUGUST 20, 1928

PUBLISHED APRIL 5, 1929

Although some measurements have been made of the solubilities of the secondary and tertiary phosphates of lead in water, no measurements have been made under conditions sufficiently well defined to allow of calculation of the solubility products of these salts, and hence to allow of calculation of the solubilities under various conditions.

The solubilities of these salts are of biological interest in connection with lead poisoning and the lead treatment of cancer. Some evidence has been obtained by Aub and others,² and by Brooks³ that inorganic lead compounds are transformed into lead phosphate in the body, lead phosphate being regarded as the least soluble salt of lead under body conditions.

The solubility of lead phosphates is thus probably the limiting factor with regard to lead-ion concentrations in the body, and the subject has been discussed from this point of view by W. C. M. Lewis.⁴ The work of Fairhall⁵ shows that the primary phosphate of lead, $\text{PbH}_4(\text{PO}_4)_2$, is much more soluble than the other phosphates except in very acid solutions and this salt is thus of no great biological importance.

We are not concerned here primarily with the biological aspects of the subject, the purpose of the present paper being to present measurements undertaken to determine the solubility products of the secondary and tertiary phosphates of lead. We shall, however, show reason to correct the statement² that whereas the tertiary phosphate is the stable salt under normal body conditions, a slight shift of equilibrium to the acid side converts this salt to the secondary phosphate.

¹ This investigation was undertaken on behalf of the Liverpool Medical Research Organization, Professor W. Blair Bell, Director, University of Liverpool.

² Aub, Fairhall, Minot and Reznikoff, "Monograph on Lead Poisoning," Williams and Wilkens Co., Baltimore, 1926.

³ Brooks, *Biochem. J.*, **21**, 766 (1927).

⁴ W. C. M. Lewis, *J. Cancer Research*, **11**, 16 (1927).

⁵ Fairhall, *THIS JOURNAL*, **46**, 1593 (1924).