THE ACTIVITY COEFFICIENT OF GASES IN AQUEOUS SALT SOLUTIONS

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GENERAL INTRODUCTION

In this and the following papers, we shall review the data for the effect of electrolytes upon the thermodynamic properties of aqueous solutions of non-electrolytes and the undissociated portion of weak electrolytes. It will be shown that the undissociated part of a moderately strong electrolyte behaves in just the same way as do typical non-polar substances.

In the development of the theory of strong electrolytes, we have used the term "activity coefficient" to express the number by which the molality of a substance must be multiplied to give the measured activity or thermodynamic behavior of that substance. The deviation of the activity coefficient from unity measures the deviation of the behavior of the substance from the laws of the perfect solution. Because the deviations of the ions, into which the strong electrolytes were assumed to be dissociated, were large, this field has received a large amount of detailed study.

Even for aqueous solutions of single non-electrolytes the experimental determinations of the activity coefficients are meager and not always concordant. Lewis and Randall (1) reviewed some of the older freezing point and vapor pressure data, and came to the conclusion that the divergence functions[1] h and j were of such a nature that h/m or j/m assumed a constant value in dilute solutions. Previously it had been assumed that moderately concentrated aqueous solutions of most non-electrolytes

[1] $j = 1 - \frac{\theta}{\lambda m}$; $h = 1 + \frac{\ln a_1}{r} = 1 + \frac{55.51 \ln a_1}{m}$ where θ = freezing point depression; m = molality; $\lambda = 1.858$; a_1 = activity of water, and r = mol fraction solute/mol fraction water.

obey Henry's Law, but Lewis and Randall calculated the activity coefficients, $\gamma = a_2/m$, of several substances, and found in aqueous solutions of glycerine as dilute as 0.1 M, $\gamma = 1.006$, and in 5 M solutions, $\gamma = 1.348$.

Various authors have considered the effect of electrolytes in lowering the solubilities of non-electrolytes, and particularly the solubilities of gases, in water.

Setschenow (2) proposed the empirical formula $S = S^\circ e_{-}^{kc}$, which is equivalent to $kc = ln\ (S^\circ/S)$, where k is a constant for a given salt, c is the salt concentration in mols per liter, S° is the solubility of gas in pure water under standard conditions, and S is the solubility in the salt solutions.

Jahn from the measurements of Gordon (3) gave the formula, $(S^\circ - S)/c^{\frac{2}{3}} = k$, which is also empirical. Rothmund (4) gives a simplification of Setschenow's equation, namely $(S^\circ - S)/S^\circ = kc$; Euler (5) and Geffcken (6) relate the "salting out" to an increase of the internal pressure of the solution caused by electrolytes. Hildebrand (7) shows that as the compressibilities of aqueous solutions increase the "salting out" diminishes.

Finally, Debye and McAulay (8) have considered the activity coefficients of non-electrolytes in the presence of electrolytes. They showed that the deviations of a_2/N_2 from unity, due to the effect of the non-electrolyte in lowering the dielectric constant of water, are given as a first approximation by the equation:

$$\ln a_2/\mathrm{N}_2 = \alpha\, n' \frac{\Sigma\, \nu_i\, z_i^2\, e^2}{2\, D^\circ\, r\, k\, T}, \tag{1}$$

where a_2 is the activity of non-electrolyte, N_2 the mol fraction of non-electrolyte, n' the number of molecules of salt per cm³ of solution, ν_i the number of ions of the i^{th} kind in each salt molecule, z_i the valence of an ion of the i^{th} kind, e the charge of an electron, d° the dielectric constant of water, r the mean ionic radius, k the Boltzmann gas constant, and T the absolute temperature. The constant α is defined by the relation, $D = D^\circ\ (1 - \alpha n)$ where D is the dielectric constant of a solution of the non-electrolyte, and n is the number of molecules of non-electrolyte per cm³.

Preliminary to a study of the weak electrolytes we wish to examine the numerous data with reference to this relation.

It is not practical at the present time to treat the freezing point, vapor pressure, and osmotic pressure data, for these methods give the activity of the water and we are not in a position fully to separate the effect of the electrolyte and non-electrolyte upon its activity. Also the non-electrolyte will have an effect on the activity of the electrolyte.

ACTIVITY COEFFICIENT OF GASES

The determination of the solubility of a gas is difficult; for example, it has been shown by Cady, Elsey and Berger (9) that an error of 100 per cent may be made if the liquid is violently shaken, as is usually done.[2]

We have examined all of the apparently reliable data and have summarized in the following tables the results of our study.

If we consider, for example, the reaction, $O_2(g) = O_2(aq)$, then the stoichiometrical equilibrium constant is $K_m = m/P$, where P is the pressure in atmospheres and m is the molality. The equilibrium constant is $K = a_2(aq)/a_2(g)$. For gases dissolved in pure water, $a_2(aq) = \gamma m = m$ as the solutions are so dilute that γ, the activity coefficient, is unity, and for gases at moderate pressures, within the limits of the experimental error, $a_2(g) = P$. Hence in pure water we may take $K_m = K$.

In any solution, $K = a_2(aq)/a_2(g) = \gamma m/P = \gamma K_m$. Thus, to obtain γ, for oxygen dissolved in a salt solution, we need only to know K_m in pure water, which is equal to K and also K_m in the salt solution, whence,

$$\gamma \text{ (in salt solution)} = K/K_m \text{ (in salt solution)} \tag{2}$$

The activity of the gas has been taken equal to the partial pressure in atmospheres. This is not always justified, for in case of carbon dioxide at one atmosphere $a(g)/P = 0.99$. But since a series of measurements is made at approximately the same pressure the error of this assumption cancels out.

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[2] The authors studied the solubility of helium in water and ascribed the supersaturation to the effect of hammering and of small bubbles.

The concentration in the liquid phase is always expressed as mols per 1000 grams water. In almost all cases it was necessary to transform the data from mols per liter to mols per 1000 grams water. This transformation was made by assuming (approximately) that $(m/c) = 1 + k\, c'$, where m is the molality of the salt or gas, c is the concentration of salt or gas in mols per liter, c' the concentration of the salt in mols per liter, and k a constant which varies from salt to salt, but is the same for solutions of one salt of varying concentration.

Most of these measurements (10) were made by shaking the salt solution in a flask connected by means of a metal capillary to a manometer, measuring the change in pressure and volume, and reducing the volume of absorbed gas to standard conditions. Abegg and Riesenfeld used a dynamic method with ammonia. McLauchlan saturated his solutions with hydrogen sulfide and then titrated them.

The data are summarized in the tables. The first column gives the salt used. The second gives the ionic strength μ, which equals the molality for uni-uni, is 3 times the molality for uni-bi, 4 times the molality for bi-bi, 9 times the molality for uni-tri and 15 times the molality for bi-trivalent salts.[3] The third column gives the activity coefficient of the gas dissolved in the salt solution, and the fourth the quotient, $(\log \gamma)/\mu$.

DISCUSSION

As previously mentioned[2] (9), there may be relatively large absolute errors in the solubility measurements. But the relative error in any series is not great as is shown by the agreement between different authors in a few cases.

We have plotted, in figures 1 and 2, the values of the quotients of $\log \gamma$ by the ionic strengths against the square roots of the ionic strengths for those concentrations below ionic strength of 4 M. The values at 15° are shown by dotted, those at 20° by broken, and those at 25° by solid, lines. In many cases the values

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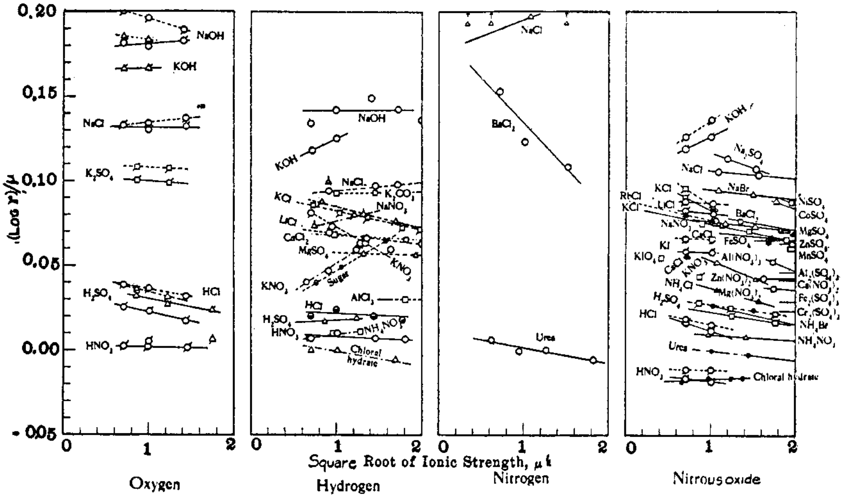
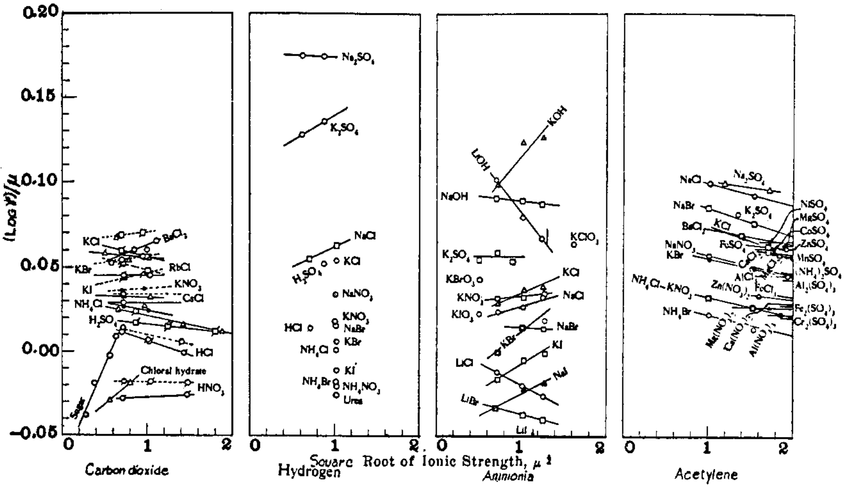
[3] In the case of added non-electrolytes the molality is used instead of the ionic strength.



Oxygen Hydrogen Nitrogen Nitrous oxide

FIG. 1. SALTING-OUT EFFECT OF SALTS ON GASES



Carbon dioxide Hydrogen Ammonia Acetylene

FIG. 2. SALTING-OUT EFFECT OF SALTS ON GASES

of (log γ)/μ are far from constant, increasing or decreasing as the salt concentration is increased. For the most part, however, the variations lie within the probable experimental error, and are of a random character. Although we have drawn the curves in the figures with definite slopes, we would probably be justified in taking the values of (log γ)/μ to be constants, and use the arithmetical mean of the values given in tables 1 to 8.

TABLE 1

Activity coefficient of oxygen[d] *in aqueous solutions**

Solubility in water = 0.00162 M at 15°—0.00138 M at 25°

SALT	μ	γ	(log γ)/μ	SALT	μ	γ	(log γ)/μ
HCl, 15°	0.505	1.046	0.0386	NaOH, 25°	0.500	1.232	0.1812
	1.019	1.090	0.0367		1.000	1.510	0.1790
	2.080	1.167	0.0322		2.000	2.316	0.1824
HCl, 25°	0.505	1.030	0.0253	NaCl, 15°	0.505	1.167	0.1330
	1.019	1.055	0.0229		1.018	1.370	0.1340
	2.080	1.108	0.0173		2.072	1.921	0.1368
H_2SO_4, 15°	0.758	1.065	0.0361	NaCl, 25°	0.505	1.167	0.1328
	1.527	1.117	0.0314		1.018	1.356	0.1299
	3.108	1.046	0.0063		2.072	1.878	0.1320
H_2SO_4, 25°	0.756	1.058	0.0324	KOH, 15°	0.503	1.239	0.1851
	1.527	1.100	0.0271		1.013	1.532	0.1829
	3.108	1.185	0.0237				
				KOH, 25°	0.503	1.212	0.1660
HNO_3, 15°	0.508	1.028	0.0023		1.013	1.474	0.1663
	1.030	1.049	0.0020				
	2.140	1.077	0.0015	K_2SO_4, 15°	0.760	1.210	0.1081
					1.563	1.470	0.1070
HNO_3, 25°	0.508	1.003	0.0025				
	1.030	1.013	0.0054	K_2SO_4, 25°	0.760	1.194	0.1006
	2.140	1.013	0.0026		1.563	1.426	0.0985
NaOH, 15°	0.500	1.260	0.2008				
	1.000	1.571	0.1962				
	2.000	2.388	0.1890				

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* The letter references in these tables correspond with the citations under reference (10).

TABLE 2

Activity coefficient of hydrogen in aqueous solutions

Solubility in water = 0.000886 M at 15°—0.000863 M at 25°C.

SALT	μ	γ	$(\log \gamma)/\mu$
HCl,[d] 25°	0.505	1.024	0.0204
	1.019	1.058	0.0240
	2.080	1.101	0.0201
	3.186	1.140	0.0179
$\mathrm{H_2SO_4}$,[d] 25°	0.757	1.030	0.0169
	1.527	1.070	0.0193
	3.110	1.140	0.0183
$\mathrm{HNO_3}$,[d] 25°	0.508	1.008	0.0069
	1.030	1.024	0.0100
	2.140	1.035	0.0069
	3.294	1.052	0.0066
$\mathrm{AlCl_3}$,[h] 15°	3.290	1.252	0.0297
	6.250	1.522	0.0292
	11.23	2.074	0.0282
	19.74	3.309	0.0263
$\mathrm{MgSO_4}$,[h] 15°	1.732	1.255	0.0570
	3.744	1.625	0.0563
	6.520	2.363	0.0572
	10.00	3.774	0.0577
$\mathrm{CaCl_2}$,[h] 15°	0.963	1.163	0.0681
	1.734	1.299	0.0655
	3.366	1.655	0.0650
	5.480	2.244	0.0640
	8.870	3.628	0.0630
LiCl,[h] 15°	0.848	1.145	0.0694
	1.861	1.329	0.0664
	3.999	1.776	0.0624
NaOH,[d] 25°	0.500	1.167	0.134
	1.000	1.386	0.142
	2.000	1.986	0.149
	3.000	2.675	0.142
	4.000	3.502	0.136
NaCl,[h] 15°	0.837	1.199	0.0942
	2.125	1.607	0.0970
	2.941	1.939	0.0978
	5.230	2.915	0.0889
$\mathrm{NaNO_3}$,[h] 15°	0.694	1.150	0.0875
	1.477	1.315	0.0805
	2.882	1.650	0.0755
	4.485	2.062	0.0701
	6.770	2.745	0.0647
$\mathrm{NaNO_3}$,[e] 20°	0.542	1.095	0.0728
	0.844	1.212	0.0990
	1.739	1.377	0.0800
KOH,[d] 25°	0.504	1.146	0.118
	1.013	1.338	0.125
KCl,[h] 15°	0.534	1.111	0.0855
	1.086	1.224	0.0809
	1.850	1.397	0.0785
	3.171	1.692	0.0720
	3.945	1.902	0.0708
$\mathrm{KNO_3}$,[h] 15°	0.492	1.096	0.0809
	0.912	1.164	0.0723
	1.643	1.270	0.0632
	1.962	1.333	0.0635
	2.685	1.444	0.0594
$\mathrm{KNO_3}$,[e] 20°	0.413	1.039	0.0403
	0.829	1.094	0.0471
	1.540	1.236	0.0596
$\mathrm{K_2CO_3}$,[h] 15°	1.031	1.245	0.0923
	2.103	1.567	0.0928
	4.264	2.400	0.0890
	6.804	3.875	0.0865
	14.37	10.70	0.0716
$\mathrm{NH_4NO_3}$,[e] 20°	0.436	1.007	0.0070
	0.907	1.021	0.0100
	1.631	1.041	0.0107
Chloral hydrate,[e] 20°	0.504	1.000	0.000
	1.030	1.000	0.000
	2.845	0.967	−0.0051
	6.000	0.872	−0.0099
Sugar,[h] 15°	0.594	1.056	0.0398
	1.263	1.153	0.0490
	2.481	1.446	0.0646

In making the plots of figures 1 and 2 we have used the square roots of the ionic strengths as the abscissae. This was done for convenience in evenly distributing the points, for since the values of $(\log \gamma)/\mu$ seem to be practically constant, even at very high ionic strengths (see table 8), the function used does not matter. But it is interesting that many of the curves in the figures are straight lines.

There seems to be a definite temperature coefficient, the value of $(\log \gamma)/\mu$ being slightly higher the lower the temperature in most cases.

TABLE 3

Activity coefficient of nitrogen in aqueous solutions at 25°[d]

Solubility in water = 0.000641 M at 25°

SALT	μ	γ	$(\log \gamma)/\mu$	SALT	μ	γ	$(\log \gamma)/\mu$
$BaCl_2$	0.509	1.196	0.153	Urea	0.389	1.013	0.0062
	1.070	1.355	0.123		0.912	0.999	−0.0005
	2.310	1.779	0.108		1.900	1.002	0.0005
					3.330	0.958	−0.0055
NaCl	0.115	1.096	0.346				
	0.372	1.259	0.269				
	1.170	1.698	0.197				
	2.270	2.920	0.205				

The value of the activity coefficient will depend upon the units chosen to express the concentrations. For thermodynamic purposes the molality or the mol fraction is much more useful than the concentration.

The quotient of the activity coefficient by the molality will also be constant, but by taking the quotient by the ionic strength the values of the function are brought to much closer values for similar substances, e.g., acids. In this respect equation 1 is justified.

But according to equation 1, for the same non-electrolyte in solutions of different salts the constant should vary inversely as the atomic radius of the salt.

The values of the mean ionic radius of such of the salts as can be calculated from the radii of combination given by Bragg and

TABLE 4

Activity coefficient of nitrous oxide in aqueous solutions

Solubility in water = 0.0348 M at 15°—0.0218 M at 25°

SALT	μ	γ	$(\log \gamma)/\mu$
HCl,^{d} 15°	0.505	1.022	0.0188
	1.018	1.036	0.0151
HCl,^{d} 25°	0.505	1.021	0.0178
	1.018	1.028	0.0118
H_2SO_4,^{d} 15°	0.757	1.050	0.0280
	1.527	1.093	0.0253
	3.108	1.165	0.0213
H_2SO_4,^{d} 25°	0.757	1.041	0.0433
	1.527	1.075	0.0206
	3.108	1.128	0.0168
HNO_3,^{d} 15°	0.508	0.987	−0.0112
	1.030	0.973	−0.0116
HNO_3,^{d} 25°	0.508	0.981	−0.0164
	1.030	0.958	−0.0180
$ZnSO_4$,^{g} 25°	3.850	1.758	0.0636
	7.564	3.062	0.0642
$Zn(NO_3)_2$,^{g} 25°	2.616	1.291	0.0423
	5.448	1.697	0.0421
$Cu(NO_3)_2$,^{g} 25°	2.127	1.456	0.0767
	4.377	1.813	0.0590
$MnSO_4$,^{g} 25°	3.834	1.708	0.0606
	8.088	2.993	0.0588
$FeSO_4$,^{g} 25°	2.902	1.554	0.0659
	5.852	2.423	0.0656
$Fe_2(SO_4)_3$,^{g} 25°	10.31	1.975	0.0286
	21.90	3.673	0.0257
$CoSO_4$,^{g} 25°	3.181	1.917	0.0888
	6.448	3.048	0.0750
$NiSO_4$,^{g} 25°	3.784	2.141	0.0873
	7.696	3.752	0.0746
$Cr_2(SO_4)_3$^{g}	9.075	1.582	0.0220
	19.41	2.620	0.0215
$Al_2(SO_4)_3$^{g}	7.916	2.328	0.0463
	12.73	3.805	0.0455
$Al(NO_3)_3$^{g}	2.972	1.428	0.0520
	6.144	1.702	0.0375
$MgSO_4$^{g}	3.633	1.794	0.0698
	7.280	3.290	0.0710
$Mg(NO_3)_2$^{g}	3.066	1.291	0.0361
	6.447	1.681	0.0349
$CaCl_2$^{g}	2.861	1.536	0.0652
	6.310	2.501	0.0631
$Ca(NO_3)_2$^{g}	4.422	1.532	0.0414
$BaCl_2$^{g}	1.898	1.395	0.0762
	4.122	1.953	0.0705
$LiCl$,^{d} 15°	0.505	1.107	0.0877
	1.019	1.226	0.0869
$LiCl$,^{d} 25°	0.505	1.100	0.0821
	1.019	1.208	0.0806
$NaCl$^{g}	1.178	1.333	0.1059
	2.426	1.782	0.1034
	4.761	2.805	0.0940
$NaBr$^{g}	1.161	1.287	0.0944
	2.306	1.625	0.0914
	5.098	2.625	0.0822
Na_2SO_4^{g}	1.409	1.444	0.1132
	3.006	2.098	0.1071
$NaNO_3$^{g}	1.120	1.214	0.0751
	1.370	1.266	0.0747
	2.334	1.480	0.0729
	3.350	1.730	0.0711
	4.894	2.115	0.0664

TABLE 4—*Continued*

SALT	μ	γ	$(\log \gamma)/\mu$
KOH,[d] 15°	0.503	1.158	0.1266
	1.013	1.375	0.1365
KOH,[d] 25°	0.503	1.149	0.1199
	1.013	1.344	0.1268
KCl,[d] 15°	0.508	1.118	0.0954
	1.031	1.226	0.0858
KCl,[d] 25°	0.508	1.111	0.0900
	1.031	1.213	0.0814
KCl,[g] 25°	0.800	1.148	0.0748
	1.301	1.248	0.0739
	2.112	1.406	0.0701
	3.570	1.708	0.0651
	4.632	1.938	0.0620
KBr,[d] 15°	0.510	1.095	0.0773
	1.041	1.192	0.0732
KBr,[d] 25°	0.510	1.086	0.0702
	1.041	1.177	0.0680
KBr,[g] 25°	1.160	1.187	0.0642
	2.339	1.396	0.0619
	4.992	1.813	0.0517
KI,[d] 15°	0.513	1.081	0.0660
	1.050	1.171	0.0653
KI,[d] 25°	0.513	1.071	0.0581
	1.050	1.149	0.0574
KIO_4,[g] 25°	0.164	1.021	0.0548
KNO_3,[g] 25°	1.068	1.136	0.0518
	2.374	1.250	0.0422
RbCl,[d] 15°	0.509	1.099	0.0806
	1.036	1.201	0.0767
RbCl,[d] 25°	0.509	1.094	0.0766
	1.036	1.188	0.0722
CsCl,[d] 15°	0.511	1.072	0.0591
CsCl,[d] 25°	0.511	1.069	0.0567
NH_4Cl,[g] 25°	1.118	1.094	0.0348
	2.470	1.181	0.0292
	5.185	1.275	0.0203
NH_4Br,[g] 25°	1.093	1.070	0.0269
	2.341	1.136	0.0236
	5.161	1.195	0.0150
NH_4NO_3,[g] 25°	0.933	1.021	0.0096
	2.045	1.038	0.0079
	4.463	1.059	0.0055
	11.95	1.072	0.0025
Chloral hydrate,[e] 20°	0.445	0.981	−0.0187
	0.942	0.964	−0.0169
	1.474	0.946	−0.0164
	1.911	0.930	−0.0165
Urea,[g] 25°	1.016	0.998	−0.0009
	2.139	0.987	−0.0026
	4.955	0.942	−0.0052
	7.995	0.883	−0.0067

Bragg (11) are given in Table 9. The values are obtained by means of the formula

$$r = \Sigma\ \nu_i\ z_i^2/\Sigma\ (\nu_i\ z_i^2/r_i), \qquad (3)$$

where r_i is the radius of combination of an ion of the i^{th} kind, and r is the mean atomic radius for the molecule, and ν_i and z_i have the same significance as in equation 1.

TABLE 5

Activity coefficient of carbon dioxide in aqueous solutions

Solubility in water = 0.0478 M at 15°—0.0370 M at 25°

SALT	μ	γ	$(\log \gamma)/\mu$
HCl,[d] 15°	0.522	1.017	0.0140
	1.028	1.021	0.0070
	2.000	1.029	0.0062
HCl,[d] 25°	0.505	1.015	0.0129
	1.019	1.014	0.0059
	2.080	0.998	−0.0004
H_2SO_4,[d] 15°	0.757	1.042	0.0236
	1.554	1.056	0.0153
	3.216	1.089	0.0116
H_2SO_4,[d] 25°	0.757	1.031	0.0176
	1.527	1.053	0.0147
	3.108	1.092	0.0123
HNO_3,[d] 15°	0.539	0.978	−0.0180
	1.086	0.956	−0.0180
	2.200	0.909	−0.0188
HNO_3,[d] 25°	0.508	0.968	−0.0278
	1.030	0.960	−0.0172
	2.140	0.880	−0.0259
$BaCl_2$,[c] 25°	0.345	1.042	0.0518
	0.718	1.106	0.0609
	1.010	1.151	0.0604
	1.239	1.204	0.0650
KCl,[d] 15°	0.488	1.080	0.0685
	0.897	1.157	0.0706
KCl,[d] 25°	0.508	1.072	0.0595
	1.031	1.143	0.0563
KCl,[c] 25°	0.248	1.034	0.0584
	0.414	1.066	0.0671
	0.626	1.081	0.0539
KCl,[c] 25°	1.031	1.141	0.0555
KBr,[d] 15°	0.493	1.064	0.0546
	0.914	1.125	0.0560
KBr,[d] 25°	0.510	1.054	0.0448
	1.041	1.113	0.0447
KI,[d] 15°	0.496	1.052	0.0444
	0.923	1.104	0.0466
KI,[d] 25°	0.513	1.040	0.0332
	1.050	1.082	0.0318
KNO_3,[d] 15°	0.503	1.043	0.0364
	0.946	1.084	0.0370
KNO_3,[d] 25°	0.511	1.032	0.0268
	1.043	1.060	0.0243
RbCl,[d] 15°	0.509	1.063	0.0521
	1.036	1.122	0.0483
CsCl,[d] 15°	0.511	1.041	0.0342
CsCl,[d] 25°	0.511	1.034	0.0284
NH_4Cl,[c] 25°	0.446	1.026	0.0251
	0.947	1.060	0.0267
	1.630	1.063	0.0163
	2.010	1.080	0.0166
	3.600	1.103	0.0118
Chloral hydrate,[c] 25°	0.317	0.979	−0.0290
	0.654	0.972	−0.0188
Sugar,[c] 25°	0.078	0.993	−0.0382
	0.157	0.993	−0.0191
	0.305	0.998	−0.0029
	0.396	1.009	0.0098

TABLE 6

Activity coefficient of hydrogen sulphide in aqueous solutions at 25°[f]

Solubility in water = 0.000135 *M* under pressure of 1 mm. Hg at 25°

SALT	μ	γ	$(\log \gamma)/\mu$	SALT	μ	γ	$(\log \gamma)/\mu$
HCl	0.505	1.016	0.0136	KBr	1.041	1.016	0.0062
H_2SO_4	0.758	1.095	0.0519	KI	1.050	0.972	−0.0117
NaCl	0.505	1.066	0.0550	K_2SO_4	0.377	1.118	0.1283
	1.018	1.160	0.0633		0.758	1.269	0.1365
NaBr	1.029	1.039	0.0161	KNO_3	1.043	1.050	0.0183
Na_2SO_4	0.377	1.164	0.1750	NH_4Cl	1.039	1.003	0.0013
	0.758	1.357	0.1749	NH_4Br	1.046	0.956	−0.0184
$NaNO_3$	1.032	1.084	0.0339	NH_4NO_3	1.064	0.950	−0.0209
KCl	1.031	1.137	0.0541	Urea	1.045	0.938	−0.0266

TABLE 7

Activity coefficient of ammonia in aqueous solutions at 25°[a]

Solubility in water = 0.00743 *M* under pressure of 1 mm. Hg. at 25°

SALT	μ	γ	$(\log \gamma)/\mu$	SALT	μ	γ	$(\log \gamma)/\mu$
LiOH	0.513	1.128	0.1019	KOH	0.516	1.139	0.1094
	1.025	1.207	0.0797		1.038	1.347	0.1246
	1.538	1.270	0.0674		1.566	1.580	0.1268
LiCl	0.517	0.986	−0.0117	KCl	0.520	1.036	0.0296
	1.044	0.951	−0.0208		1.056	0.093	0.0365
	1.580	0.909	−0.0262		1.605	1.155	0.0390
LiBr	0.520	0.961	−0.0332	$KClO_3$	0.260	1.039	0.0638
	1.053	0.914	−0.0370				
	1.601	0.861	−0.0405	KBr	0.523	1.006	0.0050
					1.066	1.038	0.0152
LiI	0.523	0.928	−0.0619		1.629	1.075	0.0193
	1.066	0.856	−0.0633				
	1.629	0.771	−0.0693	$KBrO_3$	0.259	1.026	0.0432
NaOH	0.513	1.114	0.0914	KI	0.525	0.981	−0.0158
	1.025	1.239	0.0908		1.075	0.988	−0.0048
	1.538	1.363	0.0874		1.650	1.000	0.0000
NaCl	0.517	1.029	0.0240	KIO_3	0.259	1.014	0.0231
	1.043	1.079	0.0276				
	1.578	1.128	0.0332	K_2SO_4	0.259	1.104	0.0553
					0.523	1.238	0.0590
NaBr	0.520	0.999	−0.0008		0.816	1.356	0.0540
	1.054	1.036	0.0146				
	1.602	1.052	0.0137	KNO_3	0.523	1.037	0.0302
					1.068	1.087	0.0338
NaI	0.523	0.961	−0.0331		1.634	1.143	0.0355
	1.066	0.947	−0.0221				
	1.629	0.935	−0.0179				

TABLE 8

Activity coefficient of acetylene in aqueous solutions at 25°[a]

Solubility in water = 0.0421 M at 25°

SALT	μ	γ	$(\log \gamma)/\mu$
$ZnSO_4$	3.704	1.701	0.0622
	7.536	2.878	0.0609
$Zn(NO_3)_2$	2.580	1.222	0.0337
	5.367	1.465	0.0308
$MnSO_4$	3.999	1.688	0.0568
	8.212	2.869	0.0557
$FeSO_4$	2.902	1.520	0.0626
	5.852	2.258	0.0604
$FeCl_3$	5.129	1.453	0.0316
	8.412	1.735	0.0284
$Fe_2(SO_4)_3$	10.31	1.979	0.0287
	21.90	3.761	0.0262
$CoSO_4$	3.219	1.589	0.0624
	6.528	2.484	0.0605
$NiSO_4$	2.966	1.571	0.0661
	5.980	2.452	0.0651
$Cr_2(SO_4)_3$	9.075	1.568	0.0215
	19.41	2.565	0.0210
$AlCl_3$	3.798	1.491	0.0456
	6.642	1.946	0.0435
$Al_2(SO_4)_3$	7.916	2.221	0.0437
	12.73	3.562	0.0433
$Al(NO_3)_3$	3.460	1.204	0.0232
	6.576	1.401	0.0222
$MgCl_2$	3.396	1.576	0.0581
	6.738	2.251	0.0523
$MgSO_4$	3.615	1.700	0.0637
	7.328	2.968	0.0644
$Mg(NO_3)_2$	2.998	1.207	0.0272
	6.333	1.421	0.0240
$CaCl_2$	2.938	1.518	0.0617
	6.513	2.273	0.0547
$Ca(NO_3)_2$	4.422	1.350	0.0294
	9.696	1.812	0.0266
$BaCl_2$	1.936	1.366	0.0699
	4.128	1.833	0.0637
$NaCl$	1.147	1.305	0.1007
	2.372	1.662	0.0930
	5.012	2.666	0.0849
$NaBr$	1.158	1.256	0.0854
	2.393	1.525	0.0765
	5.152	2.274	0.0692
$NaSO_4$	1.420	1.390	0.1007
	2.978	1.934	0.0962
$NaNO_3$	1.121	1.160	0.0575
	2.330	1.312	0.0506
	5.072	1.641	0.0424
KCl	1.956	1.361	0.0684
	4.176	1.736	0.0573
KBr	1.139	1.158	0.0559
	2.381	1.317	0.0502
	5.272	1.634	0.0404
K_2SO_4	1.834	1.415	0.0822
KNO_3	1.129	1.091	0.0334
	2.376	1.160	0.0271
NH_4Cl	1.137	1.091	0.0332
	2.381	1.154	0.0261
	5.254	1.215	0.0161
NH_4Br	1.125	1.061	0.0228
	2.372	1.078	0.0137
	5.323	1.104	0.0082
$(NH_4)_2SO_4$	4.533	1.638	0.0472
	8.181	2.201	0.0423

Thus the ratio of this constant for two given salts, say sodium chloride and potassium iodide, should be independent of the non-electrolyte whose activity coefficient is being measured. Or, for two different gases, say oxygen and nitrous oxide, in a solution of the same salt the ratio of the constants should be independent of the salt used. There seems to be a qualitative agreement with these demands in most cases, but not a quantitative one. In the case of ammonia the order of increasing salting out power (increase in the quotient) for salts of the alkali metals is that of increasing atomic radius rather than of increasing reciprocal of the atomic radius.

TABLE 9

Mean atomic radius of some halides ($\times 10^8$)

	H	Li	Na	K	Rb	Cs	Mg	Ca	Ba	Al	Fe^{+++}
Cl.	0.85	1.21	1.29	1.37	1.41	1.45	1.27	1.41	1.57	1.27	1.28
Br.	0.90	1.31	2.13	1.50	1.55	1.60					
I.	0.93	1.42	2.25	1.64	1.70	1.76					

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