

agreement between calculated and observed barriers is best in those cases where the internuclear distances involved are smallest. Multipole interactions, dipole-dipole, dipole-quadrupole and quadrupole-quadrupole, fall off less rapidly with distance than do van der Waals repulsions, so that the van der Waals forces would be expected to be relatively more important at small internuclear distances. The uncertainties in bond moments are such^{3,10} that the above must be considered only speculation, however.

The model used in the present investigation is highly simplified, and a number of effects have been ignored which should be taken into account in a more rigorous treatment. Two effects which may be important are deformation of the bond angles and

interactions of atoms with unshared pairs of electrons on other atoms. These latter occur in methanol and the various methylamines. Nevertheless, the model seems capable of giving semi-quantitative results and it is hoped that the force laws for interactions between non-bonded atoms given in this paper will prove useful in the calculation of other types of steric effects.

Acknowledgments.—The authors acknowledge with thanks a number of stimulating and helpful conversations with Dr. J. G. Aston. They also wish to express their appreciation to Dr. J. O. Hirschfelder and Dr. K. S. Pitzer for several helpful comments.

UNIVERSITY PARK, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

The Iodide-Iodine-Triiodide Equilibrium and Ion Activity Coefficient Ratios¹

BY LEONARD I. KATZIN AND ELIZABETH GEBERT

RECEIVED JUNE 27, 1955

The triiodide dissociation constant is determined at 20, 25 and 30° by measuring the solubility of iodine in iodide solutions. It is demonstrated that the activity coefficient ratio of iodide and triiodide ions in the same solution is a function of solution composition, and the differences between different media are greater at higher ionic strengths. Entropy data for the three reactions, $X^- + I_2 \cdot H_2O = XI_2^- + H_2O$ are shown to be consistent with this formulation.

A recent spectrophotometric study of the iodide-iodine-triiodide equilibrium² seemed to indicate that in 1 *M* acid the stability of the triiodide is greater at higher temperature than at lower, a reversal of the temperature coefficient determined by other techniques^{3,4} for non-acid solutions. Verification by other methods seemed required. The approach chosen was the measurement of the change in solubility of iodine in water as a function of potassium or sodium iodide concentration. With the activity of the iodine fixed by the presence of solid phase, the increased iodine content is a direct measure of the triiodide formed in a solution of known total iodide concentration. This paper presents the findings of experiments using this technique.

Experimental

The equilibration vessels used were 125-ml. glass-stoppered erlenmeyer flasks sealed with paraffin. They were shaken in a commercial shaking device in air for several hours, then transferred to a less efficient form of shaker mounted in a constant temperature water-bath, whose temperature was fixed to $\pm 0.15^\circ$. Solutions containing iodide came to apparent equilibrium in 24 hours; solutions without iodide added changed slowly in iodine concentration over periods up to a week in length. This period was shorter at higher perchloric acid concentrations.

Three series of solutions, containing 1 *M*, 0.01 *M* and no added perchloric acid were investigated at three temperatures, 20, 25 and 30°. Effects of ionic strength as such were tested using sodium perchlorate. When a solution was to contain KI or NaI, the solid C.P. salt was weighed out and made up to 100 ml. with the appropriate addition of

1 *M* stock sodium perchlorate and perchloric acid solutions. The resulting solutions were then transferred to the equilibration flasks together with excess solid sublimed iodine, and the flasks were sealed.

When equilibration was completed, aliquots were pipetted through glass wool filters and titrated with thiosulfate solution. The latter was standardized daily against potassium iodate, using the iodate-iodide reaction,⁵ and starch indicator end-point. The end-points of iodine solutions not containing iodide were found to be sharpened considerably by adding KI to the titration flask; the starch-triiodide color was considerably more intense than the simple starch-iodine color.

Iodine Solubility.—The solubility of iodine was determined in water and the several base solutions to be used in the experiments. The average values found in a series of determinations are given in Table I. Our determination of the solubility of iodine in water at 25° agrees quite satisfactorily with the consensus of the literature determinations.⁶⁻¹⁷ At 20 and 30° there is good agreement with the values read from a composite plot of the published solubilities over a temperature range.¹⁸ The water equilibria to give oxyiodine products are apparently not sufficient to

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) L. I. Katzin and E. Gebert, *THIS JOURNAL*, **76**, 2049 (1954).

(3) (a) H. M. Dawson, *J. Chem. Soc.*, **79**, 238 (1901); (b) G. Jones and B. B. Kaplan, *THIS JOURNAL*, **50**, 1845 (1928).

(4) C. Winther, *Z. physik. Chem.*, [B] **3**, 299 (1929).

(5) H. H. Willard and N. H. Furman, "Elementary Quantitative Analysis," D. Van Nostrand Co., Inc., New York, N. Y., 1940, p. 269.

(6) A. A. Jakowkin, *Z. physik. Chem.*, **18**, 585 (1895).

(7) A. A. Noyes and J. Seidensticker, *ibid.*, **27**, 357 (1898).

(8) V. Sammet, *ibid.*, **53**, 641 (1905).

(9) H. Hartley and N. P. Campbell, *J. Chem. Soc.*, **93**, 741 (1908).

(10) E. Oliveri-Mandala and A. Angenica, *Gazz. chim. ital.*, **50**, [I] 273 (1920).

(11) J. N. Pearce and W. G. Eversole, *J. Phys. Chem.*, **28**, 245 (1924).

(12) J. S. Carter, *J. Chem. Soc.*, **127**, 2861 (1925).

(13) J. S. Carter, *ibid.*, 2227 (1928).

(14) A. v. Kiss and A. Urmanczy, *Z. anorg. allgem. Chem.*, **202**, 172 (1931).

(15) V. K. LaMer and M. H. Lewinsohn, *J. Phys. Chem.*, **38**, 171 (1934).

(16) I. M. Korenman, *J. Gen. Chem. (U.S.S.R.)*, **17**, 1608 (1947).

(17) I. M. Korenman, *C. A.*, **42**, 4026 (1948).

(18) A. Seidell, "Solubilities of Inorganic and Metal-Organic Compounds," Vol. I, D. Van Nostrand Co., Inc., New York, N. Y., 1940, 3rd Ed., p. 654.

modify the iodine solubility value at these temperatures, since there is no certain difference between the values for water and for 0.01 *M* acid.

TABLE I
IODINE SOLUBILITIES^a

Medium	Temp., °C.		
	20	25	30
H ₂ O	1.127	1.320	1.526
0.01 <i>M</i> HClO ₄	1.129	1.310	1.520
1.0 <i>M</i> HClO ₄	1.053	1.27	1.465
0.09 <i>M</i> NaClO ₄ + 0.01 <i>M</i> HClO ₄	1.093	1.269	1.36
0.1 <i>M</i> NaClO ₄	1.126	1.275	1.46
1.0 <i>M</i> NaClO ₄	0.834	1.039	1.15
0.99 <i>M</i> NaClO ₄ + 0.01 <i>M</i> HClO ₄	...	0.965	...

^a In units of $1 \times 10^{-3} M$.

The presence of sodium perchlorate does make a consistent difference: the iodine solubility in 0.1 *M* NaClO₄ is consistently lower than for the corresponding acid concentration. Further, if acid is mixed with the sodium perchlorate, the iodine titer is depressed still more. This suggests that in the presence of even 0.1 *M* salt the iodine-water reactions are promoted sufficiently that the addition of acid to 0.01 *M* concentration lowers the equilibrium titer detectably. Perchloric acid at 1 *M* concentrations shows a slightly lower iodine solubility than does water, but 1 *M* NaClO₄ lowers the iodine solubility 25% or more. The effects of NaClO₄ are in line with the action of other salts, which salt-out iodine from aqueous solution.^{12,14,15} The salting-out power of perchloric acid is obviously much less.

Triiodide Dissociation Constants.—To avoid complications from possible formation of higher polyiodides, the maximum KI concentrations used were about 0.08 *M*. To minimize fluctuations due to small errors in iodine concentration determination at low iodide concentrations, a practical minimum of about 0.02 *M* iodide was established. The concentration of triiodide is given by the total iodine titer *T* minus the titer *t* for solutions without iodide. The equilibrium iodide concentration is the initial formal concentration *F* minus the equilibrium triiodide. The computation of the equilibrium constant can be represented by the equation

$$K_o = (I_2)(I^-)/(I_3^-) = t(F - (T - t))/(T - t) \quad (1)$$

The values for *K_o* calculated by this equation are given in Table II as "*K_o*."

The quotation marks around *K_o* acknowledge that the use of the iodide-free solution titer as the value for uncombined iodine involves an approximation. The potassium iodide and triiodide in the equilibrium solutions can be expected to exert a salting-out effect on the iodine, just as is shown by the sodium perchlorate, and to a lesser extent by the perchloric acid. The use of the iodide-free titer for the free iodine is not exactly correct for any KI concentration *F*, and is less nearly correct for the higher concentrations than the lower. Both *t* and (*F* - (*T* - *t*)) should become smaller, and (*T* - *t*) larger, with increasing *F*. For the dilute solutions considered, the effect on the constant calculated is closely proportional to the changes in *t*, as the iodide-triiodide ratio is close to unity.

The salting-out effects can be estimated with the aid of the conventional salting-out approximation

$$\log t = \log t_0 - kC \quad (2)$$

From the solubilities of iodine in 1 *M* NaClO₄, *k* for this salt is about 0.13. The corresponding *t*/*t*₀ value at 0.1 *M* salt is 0.971, at 0.05 *M*, 0.985, and at 0.001 *M*, 0.997. There are no direct values for the salting coefficient of KI on iodine, but the constants for other potassium salts^{14,15} are KNO₃, 0.11; KCl, 0.16; and KBr, 0.15. A reasonable approximation for our purposes is to use the sodium perchlorate salting coefficient and *t*/*t*₀ values. We may therefore expect the "*K_o*" values at our lowest KI concentrations to differ from true *K_o* values by 1%, and to be off perhaps 3% at the highest concentrations, with a mean calculated over the entire concentration range to be about 1.5% too high. *K_o* values illustrating this are shown as the last column of Table II, for the systems water-iodide-iodine.

Though it is small, and sometimes masked by experimen-

tal variation, there seems apparent a trend of *K_o* toward smaller values with increasing iodide. This could be ascribed to a constancy of the iodide-triiodide ratio, and the changing iodine concentration with salting-out, were it not for the circumstances that in the 1 *M* perchlorate solutions, where the stoichiometric iodine concentration may be only 75% that of water, the "*K_o*" values differ very little from those for water. The iodide-triiodide ratio therefore cannot be constant, and it is instructive to consider this ratio and its relation to the activity equilibrium constant, *K_a*, whose isothermal value is constant by definition, and to ion activity coefficients.

The relationships between *K_a* and *K_o* are indicated in equation 3

$$K_a = a_{I_2} \times a_{I^-}/a_{I_3^-} = K_o \times f_{I_2} \times f_{I^-}/f_{I_3^-} \quad (3)$$

Qualitatively, if the iodide-triiodide activity coefficient ratio is constant, *K_o* and *f*_{I₂} will vary inversely (constant temperature assumed throughout). The assumption is often casually made that the iodide-triiodide activity coefficient ratio is constant at unity.^{11,16,20} This is an extrapolation of the Brönsted approximation.²¹ The danger of such an assumption can be illustrated by rearranging equation 3 into the form

$$f_{I^-}/f_{I_3^-} = K_a/a_{I_2} \times (I_3^-)/(I^-) \quad (4)$$

In our systems, which have constant iodine activity, the triiodide-iodide concentration ratio is therefore a direct measure of the iodide-triiodide activity coefficient ratio. Values of the concentration ratio are given in the penultimate columns of Table II, and arithmetic means for a given system are assembled in Table III. It is seen that at $\mu = 1.0$ the ratio is a function of iodide concentration, and at lower ionic strengths is visibly a function of solution composition. To translate the concentration ratios directly into activity coefficient ratios demands a value for *K_a* obtained by extrapolation of dilute solution experiments to infinite dilution. It is doubted that sufficient precision could be obtained, in view of the difficulties with the iodine solubility values, which become crucial.

Bray and MacKay,²² in a rather neglected paper, conclude from conductivity studies on KI-saturated iodine solutions that the change in triiodide-iodide ratio from infinite dilution to 0.1 *M* is 8%. V. Kiss and Urmanczy,¹⁴ in another paper whose implications have been overlooked, though repeated in part by LaMer and Lewinsohn,¹⁵ have shown that the ratio changes strongly in concentrated salt solutions. Our data, for the range 0.02-0.08 *M* KI, suggest at most a variation of about 2% for the triiodide-iodide ratio, which is consistent with Bray and MacKay,²² most of the change taking place below 0.01 *M*. More significant is the difference (Table III) between KI and NaI even in the 0.02-0.08 *M* range, which is more marked at the lower temperatures. At ionic strength 0.1 (NaClO₄ + KI) there is a difference from the KI solutions which approaches 3% at the higher temperatures, even with almost half the cation concentration being K⁺. At ionic strength 1.0, whereas with HClO₄ as the bulk electrolyte the triiodide-iodide ratios are slightly higher than for the dilute KI solutions, with NaClO₄ as the bulk electrolyte, the ratios are as much as 25% smaller than for the dilute KI systems. This behavior makes it clear that a *priori* assumptions of activity coefficient relations in quantitative calculations represent a considerable risk of error, and that this error is potentially larger, the higher the salt concentration. Constancy of ionic strength is clearly no guarantee of constant activity coefficients even at 0.1 *M* and uni-univalent salts. It should therefore not be surprising that with the hydrolysis of ferric ion, dealing with both triply and doubly charged ions, and with electrolytes containing univalent, bivalent and even trivalent cations, Olson and Simonson²³ should have found results demonstrating that the activity coefficients of the iron ions varied at constant ionic strength. With more investigations using techniques that measure concentrations rather than activities, such reports should be more frequent.

(19) G. Jones and B. B. Kaplan, *THIS JOURNAL*, **50**, 1845 (1928).

(20) M. Davies and E. Gwynne, *ibid.*, **74**, 2748 (1952).

(21) J. N. Brönsted, *ibid.*, **42**, 761 (1920).

(22) W. C. Bray and C. M. J. MacKay, *ibid.*, **32**, 914 (1910).

(23) A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 1322 (1949).

TABLE II
STOICHIOMETRIC DISSOCIATION CONSTANTS OF TRIIODIDE AS FUNCTION OF MEDIUM AND TEMPERATURE

Medium	Iodide	Titer	KI		NaI		Iodide	Titer	$\frac{K_c}{(I^-)}$	$\frac{K_c}{\times 10^3}$	
			$\frac{K_c}{\times 10^3}$	$\frac{(I_3^-)}{(I^-)}$	$\frac{K_c}{\times 10^3}$	$\frac{(I_3^-)}{(I^-)}$					
20°											
H ₂ O	0.01535	0.00851	1.21	0.928	1.21	0.02732	0.01426	1.22	0.927	1.21	
	.02051	.01111	1.19	.950	1.18	.03508	.01799	1.22	.926	1.20	
	.02112	.01131	1.21	.932	1.20	.04322	.02178	1.23	.917	1.21	
	.02588	.01362	1.21	.934	1.20	.04782	.02414	1.22	.929	1.19	
	.03276	.01694	1.21	.934	1.20	.06242	.03139	1.20	.942	1.17	
	.03631	.01866	1.21	.935	1.19	.06758	.03346	1.23	.919	1.20	
	.03711	.01922	1.18	.953	1.17						
	.03813	.01963	1.19	.944	1.18						
	.04223	.02152	1.19	.935	1.19						
	.04304	.02200	1.20	.943	1.18						
	.04468	.02285	1.19	.948	1.17						
	.04890	.02472	1.21	.934	1.19						
	.05067	.02568	1.20	.941	1.18						
	.05500	.02784	1.19	.946	1.17						
	.06884	.03494	1.17	.967	1.14						
	.07302	.03707	1.16	.971	1.14						
	.08090	.04087	1.17	.967	1.14						
	0.01 M HClO ₄	0.01500	0.00843	1.19	0.951	1.18					
		.01720	.00958	1.17	.967	1.16					
		.02086	.01117	1.22	.930	1.21					
.02453		.01312	1.18	.958	1.17						
.02745		.01454	1.18	.957	1.17						
.03073		.01598	1.21	.936	1.19						
.03124		.01627	1.20	.942	1.19						
.03449		.01801	1.18	.959	1.16						
.03505		.01808	1.20	.938	1.19						
.03767		.01953	1.18	.957	1.16						
.04240		.02160	1.21	.935	1.19						
.04361		.02230	1.19	.945	1.18						
.05055		.02595	1.17	.966	1.15						
.05110		.02620	1.17	.965	1.15						
.05422		.02722	1.22	.929	1.19						
.05589		.02845	1.18	.958	1.16						
.06719	.03361	1.20	.937	1.18							
.07333	.03715	1.17	.967	1.14							
1 M HClO ₄	0.02625	0.01393	1.09	0.963		0.02853	0.01505	1.09	0.964		
	.03076	.01617	1.09	.967		.03525	.01849	1.08	.979		
	.03771	.01939	1.11	.947		.04159	.02167	1.07	.983		
	.04333	.02214	1.11	.948		.04780	.02495	1.05	1.000		
	.04879	.02493	1.10	.959		.06047	.03124	1.06	0.997		
	.05607	.02851	1.10	.960		.07552	.03896	1.05	1.008		
	.06702	.03377	1.10	.954							
$\mu = 0.1$	0.02661	0.01402	1.16	0.945							
H ⁺ = 0.01	.03032	.01582	1.16	.945							
Na ⁺ = 0.09 --	.03312	.01701	1.18	.927							
KI	.03635	.01882	1.15	.952							
ClO ₄ ⁻ = 0.1 --	.04114	.02110	1.15	.947							
KI	.04993	.02518	1.17	.932							
	.05279	.02685	1.15	.953							
	.05678	.02896	1.13	.964							
$\mu = 0.1$	0.02577	0.01337	1.20	0.910							
NaClO ₄ =	.03053	.01564	1.20	.910							
0.1 -- KI	.03462	.01748	1.22	.899							
	.03668	.01842	1.22	.896							
	.04083	.02060	1.19	.915							
	.04295	.02164	1.19	.917							
	.04618	.02343	1.17	.937							
1 M NaClO ₄						0.02806	0.01261	1.16	0.724		
						.03459	.01542	1.15	.730		
						.04090	.01812	1.14	.732		

TABLE II (Continued)

Medium	Iodide	Titer	$\frac{KI}{K_e''} \times 10^3$	$\frac{(I_3^-)}{(I^-)}$	$K_e \times 10^3$	Iodide	Titer	$\frac{NaI}{K_e''} \times 10^3$	$\frac{(I_3^-)}{(I^-)}$	$K_e \times 10^3$
						.04917	.02175	1.13	.741	
						.05448	.02395	1.14	.737	
						.06036	.02668	1.12	.749	
						.06716	.02973	1.11	.755	
						.07431	.03273	1.11	.752	
$\mu = 1.0$						0.02801	0.01255	1.17	0.718	
$H^+ = 0.01$.03695	.01651	1.14	.736	
$Na^+ = 0.99$.04271	.01898	1.13	.738	
						.04706	.02123	1.10	.765	
						.06207	.02747	1.11	.751	
$ClO_4^- = 1.0 -$ NaI						.06844	.03043	1.10	.762	
						.07534	.03376	1.08	.776	
25°										
H_2O	0.02051	0.01151	1.34	0.989	1.33	0.02830	0.01525	1.36	0.971	1.35
	.03711	.01963	1.36	.975	1.34	.03385	.01799	1.36	.971	1.35
	.04304	.02258	1.35	.978	1.33	.04220	.02199	1.38	.962	1.35
	.05067	.02655	1.33	.993	1.31	.04783	.02496	1.35	.979	1.33
	.05463	.02822	1.36	.972	1.34	.02784	.01497	1.37	.963	1.36
	.06884	.03545	1.34	.985	1.31	.03490	.01852	1.36	.973	1.34
	.07302	.03789	1.32	1.005	1.29	.04984	.02596	1.35	.979	1.33
	.08090	.04190	1.31	1.008	1.28	.05404	.02804	1.35	.979	1.33
						.06031	.03114	1.35	.979	1.32
						.06673	.03440	1.35	.984	1.32
						.07335	.03764	1.35	.982	1.32
0.01 M $HClO_4$	0.02745	0.01503	1.32	0.999	1.31					
	.03505	.01881	1.32	.997	1.31					
	.04361	.02312	1.32	1.001	1.30					
	.05422	.02811	1.35	0.978	1.33					
	.07333	.03816	1.31	1.011	1.28					
1 M $HClO_4$	0.02625	0.01448	1.30	1.013		0.02980	0.01607	1.29	0.987	
	.03076	.01644	1.36	0.973		.04069	.02172	1.26	1.010	
	.03771	.02004	1.33	.991		.04879	.02567	1.27	1.000	
	.04333	.02282	1.33	.989		.02707	.01484	1.26	1.005	
	.04879	.02557	1.33	.992		.03483	.01873	1.26	1.005	
	.05607	.02926	1.32	.997		.04086	.02165	1.28	0.995	
	.06702	.03459	1.34	.989		.04777	.02512	1.27	.997	
	.07337	.03767	1.34	.985		.05333	.02769	1.29	.982	
						.06043	.03151	1.27	1.002	
						.06754	.03537	1.25	1.020	
						.07379	.03850	1.25	1.018	
$\mu = 0.1$	0.02622	0.01408	1.38	0.955						
$H^+ = 0.01$.02992	.01590	1.38	.957						
$Na^+ = 0.09 -$ KI	.03378	.01783	1.37	.962						
	.04796	.02494	1.36	.975						
$ClO_4^- = 0.1 -$ KI	.05207	.02694	1.36	.972						
	.05452	.02825	1.35	.980						
$\mu = 0.1$	0.02412	0.01300	1.39	0.947						
$Na^+ = 0.10 -$ KI	.02803	.01496	1.38	.955						
	.03092	.01632	1.39	.948						
$ClO_4^- = 0.1 -$ KI	.03736	.01950	1.38	.955						
	.04128	.02148	1.38	.959						
	.05636	.02896	1.37	.966						
1 M $NaClO_4$						0.02818	0.01309	1.39	0.747	
						.03561	.01640	1.37	.759	
						.04124	.01888	1.36	.762	
						.04888	.02232	1.35	.771	
						.05505	.02502	1.35	.772	
						.06159	.02787	1.35	.772	
						.06798	.03074	1.37	.760	
						.07460	.03380	1.33	.783	
						.02856	.01307	1.43	.728	
						.03342	.01515	1.42	.731	

TABLE II (Concluded)

Medium	Iodide	Titer	KI "K ₀ " × 10 ³	(I ₃ ⁻) (I ⁻)	K ₀ × 10 ³	Iodide	Titer	NaI "K ₀ " × 10 ³	(I ₃ ⁻) (I ⁻)	K ₀ × 10 ³
Na ⁺ = 0.99						0.04073	0.01927	1.41	0.803	
ClO ₄ = 1.0 -						.04642	.02190	1.40	.810	
NaI						.05349	.02507	1.40	.810	
						.06090	.02851	1.39	.817	
						.06523	.03043	1.39	.815	
						.07335	.03378	1.41	.802	

TABLE III

Medium	Iodide	MEAN EQUILIBRIUM (I ₃ ⁻)/(I ⁻) RATIOS		
		20°	25°	30°
H ₂ O	KI	0.945	0.988	1.0
	NaI	.927	.975	1.040
0.01 M HClO ₄	KI	.950	.997	1.050
	NaI
1 M HClO ₄	KI	.957	.991	...
	NaI	.989	1.002	1.019
μ = 0.1 H ⁺ = 0.01	KI	.946	0.967	1.017
	NaI
μ = 0.1	KI	.946	.955	1.017
	NaI
1 M NaClO ₄	KI
	NaI75 → 0.78 or
μ = 1.0 H ⁺ = 0.01	KI	.72 → 0.75	.73 → .75	0.78 → 0.80
	NaI73 → .77	.8 → .82

Relation of Ion Activity Coefficients to Salting Out.—Equation 3 may be recast into the form

$$f_{I_3^-}/f_{I_2} = K_a/K_0 \times f_{I^-} \quad (5)$$

With K_a constant by definition, and K_0 approximately constant, as seen in Table I, the ratio of triiodide and iodine activity coefficients tends to be proportional to the iodide activity coefficient. Assuming the salt to be KI, and using γ_{\pm} as tabulated by Harned and Owen,²⁴ we see that it drops from 0.776 at 0.1 *M* to 0.639 at 1.5 *M* and rises only to 0.692 at 4.5 *M*. The general pattern of variation, though not the exact values of activity coefficients, is shown by most electrolytes. The effect of admixture with other electrolytes is essentially a geometric averaging of the values for the pure salts (*e.g.*, the data on HCl in other chlorides²⁴). The value of f_{I_2} , in contrast, will be a steadily increasing function of concentration with a salting-out electrolyte, and may reach values of 4 or 5. To maintain the relations of equation 5, therefore, $f_{I_3^-}$ must approximately follow the variations of f_{I_2} . Our data do not go above 1 *M* salt, but those of v. Kiss and Urmanczy¹⁴ illustrate the reality of this effect for concentrated salt solutions also.

The relations discussed above are rather general, and in their essence should apply to other reactions between a neutral molecule and an ion. If one considers a generalized equilibrium, $AB = A + B$, with

$$f_{AB}/f_B = K_a/K_0 \times f_A \quad (6)$$

(24) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950.

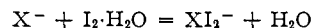
AB may be taken as a neutral molecule which dissociates into ions in solution (*e.g.*, a volatile inorganic acid, or an organic acid). Dr. A. J. Zielen has kindly brought to our attention data on the organic acids which follow this relation,²⁵ and more may be found in Harned and Owen.²⁴

An interesting (and perhaps unanswerable) theoretical question arises: to what extent is the normal concentration course (fall, minimum, then rise) of salt activity coefficients with concentration a reflection of salting-out of water and of possible molecular components in the equilibrium



Triiodide Dissociation Constant Temperature Coefficients.—The K_0 values shown in Table II of this paper increase with increasing temperature. This is in agreement with data in the literature,^{2-4,20} and contradicts the previous findings by spectrophotometric dilution measurement.¹ A calculation with the K_0 values found in this paper, and published extinction coefficients for triiodide and iodine,²⁸ indicates that the source of the discrepancy may have been losses of small fractions of the very dilute iodine in the preparation of the solutions.

Our data indicate, for the association reaction, $I^- + I_2 = I_3^-$, a ΔH value of -3600 cal., which agrees with the Davies and Gwynne²⁰ value for a corresponding temperature range, though their K_0 values are based on the activity coefficient ratio unity assumption. The ΔH values for the reactions $Cl^- + I_2 = ClI_2^-$ and $Br^- + I_2 = BrI_2^-$ are^{27,28} about 965 and -1600 cal. The entropy change values for the three reactions are, respectively, +1.1, +3.7 and -0.5 cal./deg. With the Ulich²⁹ value of 6 cal./deg. per solvate water molecule in mind, all three reactions are consistent with the formulation



on the assumption that the entropy values of the initial and product ions and neutral molecules are about equivalent, respectively.

LEMONT, ILLINOIS

- (25) A. J. Zielen, Dissertation, University of California, 1953.
 (26) A. D. Awtrey and R. E. Connick, THIS JOURNAL, **73**, 1842 (1951).
 (27) Fang-Hsun Lee and Hwei-Ching Chen, *Nanking J.*, **7**, 353 (1937); *C. A.*, **40**, 2375 (1946).
 (28) Fang-Hsun Lee and Hwei-Ching Chen, *J. Chinese Chem. Soc.*, **4**, 126 (1936); *C. A.*, **31**, 22 (1937).
 (29) H. Ulich, *Z. Elektrochem.*, **36**, 497 (1930).