aqueous solutions, and thus only half as many equivalents of C_6H_5I would be available for reduction as a result of the proposed disproportionation.

It is seen (Fig. 2) that at higher acidity β-chlorovinylphenyliodonium chloride is not completely reduced. Instead, the solvent decomposition (hydrogen wave) merely precedes and prevents formation of waves III and IV.

Quantitative Analysis of Iodonium Salts.— Diffusion currents of all the reduction waves were found to be proportional to concentration when tested between 5×10^{-4} M and 1×10^{-2} M in 50% alcohol as a solvent. The solubility of the diphenyliodonium salts limits the analytical determinations to concentrations in the region of 0.001 M. Acidities in the region pH 6–7 are recommended since higher acidities do not allow full development of all waves, and basic solutions decompose iodonium salts. Maxima in any of the waves are not particularly large or troublesome, see Fig. 3. These maxima are completely absent at iodonium salt concentrations around 0.001

M. At higher concentrations, the maxima are easily eliminated by the addition of small quantities of gelatin or long chain quaternary ammonium salts as suppressors. Gelatin is recommended since concentrations slightly in excess of the "Maximum Suppression Point" (M.S.P.)[9,21] do not alter the polarographic results. The use of, for example, lauryltrimethylammonium bromide introduces complications. The minimum concentration of quaternary ammonium salt necessary to eliminate the maximum in wave III (its M.S.P. value[21]) shifts the $E_{1/2}$ value of wave IV to an erroneous smaller negative voltage. Apparently, the RHg• free radicals, postulated in the reduction, result in another example of substantivity causing an anomalous[9,21] maxima suppression behavior.

Acknowledgment.—The support of this investigation by the Research Corporation is acknowledged with appreciation.

(21) E. L. Colichman, THIS JOURNAL, **72**, 4036 (1950).

PORTLAND, OREGON

The Iodine–Iodide Interaction

BY MANSEL DAVIES AND EMRYS GWYNNE

The well-known equilibria in dilute aqueous iodide–iodine solutions have been re-examined systematically at a number of temperatures by the partition technique. The increase in heat content (ΔH_3) associated with the formation of the triiodide ion is found to be markedly temperature dependent. The next detectable step in polyiodide formation is the occurrence of $2I_3^- \rightleftharpoons I_6^-$. The structure and binding in the triiodide ion are discussed on the basis of an electrostatic model.

The equilibrium $I^- + I_2 \rightleftharpoons I_3^-$ has been one of the most frequently studied of ion–molecule interactions. The well-known distribution method was systematically applied to its study at 25° by Jakowkin[1]; his results and those of many later workers serve to show that the process is not confined to the triiodide stage. Most of the numerous determinations of the equilibrium constant (K_3) for the triiodide formation have been made at 25° and few explicit evaluations of the corresponding increase in heat content (ΔH_3) have been reported; in fact Dawson's[2a] and Jones and Kaplan's[2b] papers are exceptional in quoting K_3 values at two temperatures.[3] Although these authors did not calculate ΔH_3, this has been done by Moelwyn-Hughes.[4] On the practical side, the purpose of the present work was to make a systematic determination of ΔH_3 and also an examination of what further equilibria play a significant role in dilute solutions. For comparison with the former, a calculation of the expected net interaction energy arising principally from an ion-induced dipole term has been made.

(1) A. A. Jakowkin, Z. physik. Chem., **20**, 19 (1896).

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

(3) See, however, A. D. Awtrey and R. E. Connick, ibid., **73**, 1842 (1951).

(4) E. A. Moelwyn-Hughes, "The Kinetics of Reactions in Solution," 2nd Edition, Oxford University Press, 1947, p. 191.

Experimental

Distribution measurements between aqueous and carbon tetrachloride phases at 25.00 ± 0.02, 38.38 ± 0.03, 49.65 ± 0.05, $63.05 \pm 0.05°$ form the basis of the results presented. A. R. chemicals, appropriately dried when used as volumetric standards, were used throughout the work, together with calibrated weights and carefully standardized volumetric apparatus. In view of the numerous previous studies of this system, between which marked discrepancies are often found (see later), the experimental errors in our methods were evaluated at each stage. Equilibrium was established in an all-glass cell of the form sketched by Brown and Bury[5] and samples of the layers were displaced by air pressure with precautions against loss of volatile iodine. Such samples for analysis were weighed and concentrations converted to volume units largely on the basis of recorded densities[6] and, for aqueous KI + I_2 solutions at temperatures other than 25°, from our own determinations of a few points over the ranges involved. Frequently standardized thiosulfate was used for the I_2 estimations. The aqueous phase was throughout made 0.0010 M in H_2SO_4; this concentration of acid sufficing to ensure that the hydrolysis of I_2 to HIO is negligible.[7] It is worth mentioning that the presence of the acid led to significantly better reproducibility in the distribution ratio (K_1) for iodine itself between the two solvents. In each run with the potassium iodide solutions dilution was continued until the total titratable iodine reached the lower limit for accurate determination: accepting a maxi-

(5) F. S. Brown and C. R. Bury, Trans. Chem. Soc., **123**, 2430 (1923).

(6) "Landolt-Börnstein," 5th Edition, Vol. I, p. 430; "I.C.T.," Vol. III, p. 132.

(7) W. C. Bray and G. M. J. MacKay, THIS JOURNAL, **32**, 932 (1910); **33**, 1485 (1911).

mum uncertainty of 0.15%, this concentration was about 1.5×10^{-3} molar. This procedure led to a minimum extrapolation in the plots of K_3 against free iodine concentrations to zero concentration.

Results and Discussion

The Iodine Distribution.—For the distribution ratio

$$K_1 = \frac{\text{Molar concentration of } I_2 \text{ in } CCl_4 \text{ solution}}{\text{Molar concentration of } I_2 \text{ in } H_2O \text{ solution}} = \frac{C_c}{C_w}$$

the results at 25° are typical and are shown in Fig. 1. The *maximum* difference between duplicated K_1 values was found to be 0.61 unit, or 0.67%. The mean values plotted should be significantly better than ±0.5 unit. Regular variations of K_1 with concentration of the form shown, and of the same order, appear at other temperatures. Of previous estimates of K_1 at 25.00°, Linhart's values[8] are certainly amongst the most carefully determined, although he did not suppress the hydrolysis. At the lowest concentrations measured by him the hydrolysis of the aqueous I_2 exceeds 1%: with 0.0010 M H_2SO_4 this is reduced to less than 0.10%. Whilst Jakowkin's figures show a concentration dependence of the same type as ours, they are in the region 85 ∼ 88.[1] Bray and MacKay[9] chose a value $K_1 = 90$, although estimates as low as 82.6 have been reported.[10] The ratio of the solubilities in the pure solvents at 25° is quoted as 89.6.[11]

The small but real variation of K_1 with concentration arises, of course, from the non-ideality of the iodine solutions. The general features of iodine solutions have formed a particular topic in a number of Hildebrand's studies,[12] and the K_1 variation, whose form could be "explained" by an association of the iodine in the carbon tetrachloride (*cf.* Hildebrand and Jenks), has been discussed explicitly by Hildebrand and Scott.[11] The solubility relations of iodine in the individual solvents lead to a confident prediction of an increase in K_1 with increasing concentration.

In calculating the equilibrium constant K_3, we have used the K_1 value appropriate to the carbon tetrachloride concentration of iodine. As a check on the influence of ionic strength upon the activity of aqueous iodine, K_1 was determined at 25° in presence of potassium nitrate (a neutral salt unlikely to interact specifically with the halogen) up to the maximum ionic strength subsequently encountered. For $C_c = 4.8.10^{-2}$ M, and $[KNO_3]$ = 1.00 M, a value $K_1 = 90.5 \pm 0.3$ was found, showing no real deviation from the value with respect to water (90.6) at the same concentration. This absence of a general salt effect on the iodine activity agrees with numerous previous indications for the present and similar systems provided the aqueous halogen concentration is below 0.1 M.[1] It is given further considerable support by the

(8) G. A. Linhart, *ibid.*, **40**, 158 (1918).

(9) W. C. Bray and G. M. J. MacKay, *ibid.*, **32**, 1207 (1910).

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

(11) J. H. Hildebrand and R. L. Scott, "The Solubility of Non-Electrolytes," 3rd Edition, Reinhold Publishing Corp., New York, N. Y., 1950, p. 208.

(12) (a) J. H. Hildebrand and C. A. Jenks, THIS JOURNAL, **42**, 2180 (1920); (b) J. H. Hildebrand, *ibid.*, **51**, 66 (1929); (c) G. R. Negishi, L. H. Donnally and J. H. Hildebrand, *ibid.*, **55**, 4793 (1933).

degree of agreement in the K_3 values as $[I_2]$ tends to zero over a forty-fold concentration range of iodide.

To evaluate ΔH_1, *i.e.*, the heat content change for the transfer of one mole of iodine from aqueous to carbon tetrachloride solution, the value $K_1°$ for $C_w = 0$ was obtained by slight extrapolation of the smooth K_1-C_w curves. These values are

t, °C.	25.00	38.38	49.65	68.05
$K_1°$	89.9	92.6	95.5	98.6

The limits for ΔH_1 are $+490 \pm 25$ cal. per mole. This factor should, of course, equal the difference
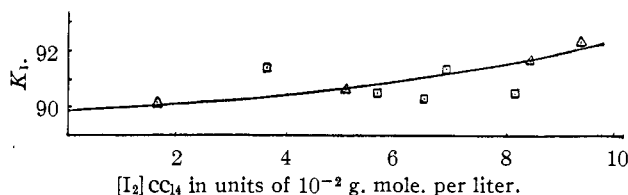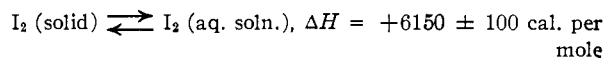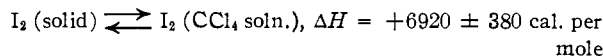

[I₂] CCl₄ in units of 10^{-2} g. mole. per liter.

Fig. 1.—△, present values; ▫, Linhart's values.

in the heats of solution of iodine in the two solvents at (ideally) zero concentration. From solubility data[13] the limiting values of the heats of solution at saturation (for the same mean temperature range as above) were evaluated as

I_2 (solid) $\rightleftharpoons$ I_2 (CCl₄ soln.), $\Delta H = +6920 \pm 380$ cal. per mole

I_2 (solid) $\rightleftharpoons$ I_2 (aq. soln.), $\Delta H = +6150 \pm 100$ cal. per mole

The difference of these figures, *i.e.*, $+770 \pm 480$ cal. per mole provides adequate agreement with the directly determined ΔH_1.

The Triiodide Equilibrium.—The constant for this is taken in the form

$$K_3 = \frac{[I_3^-]}{[I^-][I_2]} \times \frac{f_{I_3^-}}{f_{I^-} \times f_{I_2}}$$

Although Lewis and Randall[14] were of the opinion that the activity coefficient $f_{I_3^-}$ is less than f_{I^-}, Jones and Kaplan[2b] cite sufficient reasons for assuming them to be equal. As f_{I_2} has been shown not to vary with ionic strength over the range in which we are interested, it is taken as unity in the following calculations.

At 25° the distribution of iodine between CCl₄ and approximately 1.0, 0.10 and 0.025 M KI solutions was measured at a series of iodine concentrations. For the other temperatures only two KI concentrations were used, 0.025 M KI being omitted at 38 and 49°, and 1.0 M KI at 68°. Table I summarizes the data for 25.00 ± 0.02°, the terms being calculated on the assumption that I_3^- formation is the only interaction occurring; the units are moles (or g.-ions) per liter. The data at other temperatures are shown in Fig. 2.

It is seen that there are marked systematic trends in K_3, but that as $[I_2]$ tends to zero the various series at any one temperature converge to a common value. This means that, as antici-

(13) A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," 3rd Edition, D. Van Nostrand Co., Inc., New York, N. Y., 1941.

(14) G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, p. 526.

TABLE I

[I⁻] + [I₃⁻]	[I₂] × 10⁴	[I₃⁻]	K_2
1.069	6.766	0.4917	1287
1.059	4.167	.3300	1086
1.059	3.964	.3129	1058
1.039	2.520	.2016	954.1
1.032	1.991	.1577	906.1
1.014	1.212	.0960	862.8
1.008	0.594	.0456	798.1
1.004	0.230	.0178	783.6
0.1010	8.120	0.03954	791.1
.1002	1.807	.01253	772.6
.1001	0.920	.00660	767.6
.1000	.471	.00348	767.6
.1000	.205	.00155	767.0
.1000	.103	.00078	766.5
0.02482	7.794	0.009271	765.4
.02482	7.682	.009233	764.8
.02482	5.202	.007068	765.9
.02482	2.073	.003338	767.0
.02482	0.891	.001595	770.7
.02482	0.434	.000785	770.7
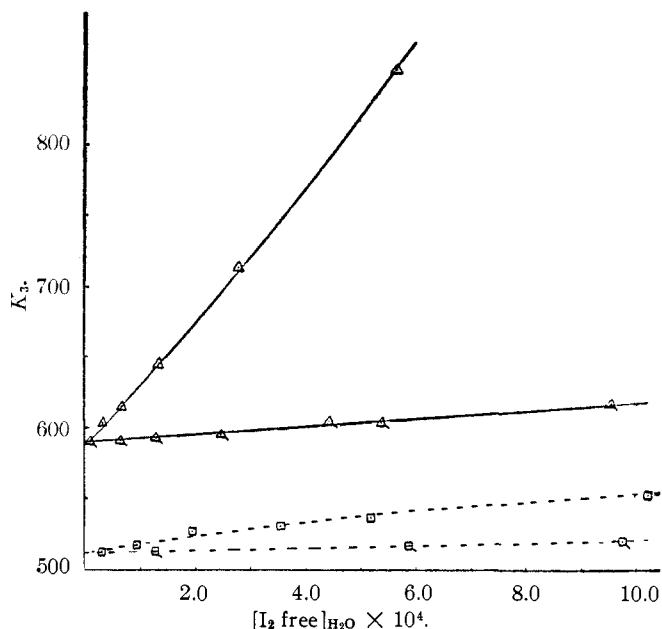
Fig. 2.—△ 1.0 M KI at 38.38°; ▲, 0.1 M KI at 38.38°; ▣ 0.1 M KI at 63.05°; ☐ 0.025 M KI at 63.05°. Subtract 100 from left-hand scale for results at 63°.

pated, at the lowest values of [I₂] only the I₃⁻ equilibrium is significant. The "best" values,

t, °C.	25.00	38.38	49.65	63.05
K_3°	768 ± 2	590 ± 2	490 ± 3	411.5 ± 2
K_3 (calcd.)	774	591	490	411

SOME OF THE MORE SIGNIFICANT PREVIOUS VALUES AT 25°

K_3 at 25°	Ref. No.	Remarks
715 ± 15	1	Early extensive data: no suppression of I₂ hydrolysis
769 ± 9	15	For HI + I₂ ⇌ HI₃: precise determin. with estimated total uncertainty
770	9	In presence dilute acid, i.e., hydrolysis suppressed
714	3	Distribution via vapor: no estimate of uncertainty given

(15) E. W. Washburn and E. K. Strachan, THIS JOURNAL, 35, 688 (1913).

K_3°, at each temperature were obtained by extrapolating the plots of K_3 to zero concentration of free iodine and the limits of uncertainty estimated by considering enlarged plots.

A point of major significance arises from the departure of the $\log_{10} K_3^\circ \sim 1/T$ plot from linearity, the points lying on a smooth curve. From the extreme slopes between 25 and 63° the range of ΔH_3 is -3215 ± 400 cal. per g. ion. Individual values (ΔH_m) from successive pairs of temperatures, i.e., corresponding to the mean temperatures (t_m, °C.); are

t_m, °C.	31.69	44.01	56.35
$-\Delta H_m$	3645	3272	2815

Jones and Kaplan's two values give $\Delta H_m = -4304$ for $t_m = 12.5°$. From Awtrey and Connick's account (which gives $\Delta H_3 = -5100$) it appears that they did not directly determine the equilibrium constant but assumed a value for 25° and calculated its change with temperature from their spectrophotometric data: their limits of 5% in K_3 appear to refer merely to the possible 1% error in the spectrophotometer readings. The agreement between our own observed K_3 and the integrated form of Kirchhoff's equation is shown by the K_3 (calcd.) values obtained from

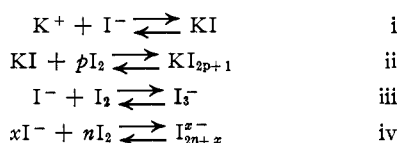$$\log_{10} K_3 = -48.622 + 16.725 \log_{10} T + 3018.8(1/T)$$

The temperature variation of ΔH_3 is well beyond the sum of the errors involved in determining the K_3°'s. Much the largest uncertainty in the latter arises from the possible error in K_1. For the dilute [I₂] range and with the least favorable iodide concentration, [KI] = 0.025 M at 25°, differences of ±0.5 unit in K_1 give changes in K_3 of ±6 (i.e., ±0.8%): significantly smaller changes in K_3 result for the other conditions. Assuming then the errors in K_3 to be ±0.8%, only by taking extreme values can at most three of the $\log_{10} K_3^\circ$ figures give a linear $1/T$ plot, e.g., those at 25, 38 and 49°. The line so defined would require K_3° at 63.05° to be 390: an error of ±0.8% confines it to 411 ± 3.

For the ΔC_P term the acceptable values are 33 ± 5 cal. per g. ion per °K. This large value for the simple interaction I⁻ + I₂ ⇌ I₃⁻ is very surprising. It is quite impossible to account for it by any consideration of the degrees of freedom which might be involved in the isolated three-particle change. However, many other examples of aqueous equilibria showing large ΔC_P terms are known.[16] The majority of these cases consist of ionization processes, e.g., of weak acids HA ⇌ H⁺ + A⁻, for which a mean value of ΔC_P of about −40 units is found. Accepting, for instance, Pitzer's evaluation of this factor, one can suggest that in the change from (I⁻ + I₂) to I₃⁻, a maximum of some four molecules of water are released from their role of hydration. As the molar volume of I₂ (∼ 60 cc.) is approximately four times that of H₂O, this figure is not unreasonable. There is, of course,

(16) K. S. Pitzer, ibid., 59, 2365 (1937); E. A. Moelwyn-Hughes, Trans. Faraday Soc., 34, 91 (1938); ref. (4) p. 191, et seq.

much uncertainty in the details of this interpretation as, indeed, in the whole explanation of the ΔC_P terms.

Further Equilibria.—Plausible associative equilibria which may occur in a potassium iodide–iodine solution are

$$K^+ + I^- \rightleftarrows KI \qquad\qquad i$$

$$KI + pI_2 \rightleftarrows KI_{2p+1} \qquad\qquad ii$$

$$I^- + I_2 \rightleftarrows I_3^- \qquad\qquad iii$$

$$xI^- + nI_2 \rightleftarrows I_{2n+x}^{x-} \qquad\qquad iv$$

i and ii are not considered here, as KI shows very little tendency to ion association at the concentrations involved.[17] iii, being the simplest version of iv, has already been evaluated. The problem remains of determining x and n for the process playing the next most important role in the solutions measured. In doing this the "best" (*i.e.*, extrapolated) value of K_3 is assumed to apply over the measured range and the deviations from it at the higher concentrations are to be accounted for in terms of K_{2n+x}. Various general practical methods have been developed for calculating simple successive equilibria,[18] but none of these is immediately useful in the present instance.

The distribution data are insufficient to provide an explicit solution of the problem, and a systematic trial is involved. Consider first $x = 2$ *i.e.*, $2I^- + nI_2 \rightleftarrows I_{2n+2}^=$

$$K_{2n+2} = [I_{2n+2}^=]/[I^-]^2 \times [I_2]^n \times f_{I_{2n+2}^=}/f_{I^-}^2 \times f_{I_2}^n$$

Evidence has already been quoted for writing $f_{I_2} = 1.00$. Attempts to calculate the two remaining ion activity coefficients would necessarily involve a number of assumptions. We propose to neglect the correcting factor $f_{I_{2n+2}^=}/f_{I^-}^2$; thus a reference to typical experimental values[19] shows that at the ionic strengths involved, the approximation $f_{Y^-} = f_{X^-}^2$ is reasonable. More relevant, however, is the consideration that, owing to the very low values of $[I_{2n+2}^=]$, the variations in ionic strength in any one series of results are negligible, so that the factor should remain a constant one. As the three relations available from the experimental data

$$[K^+] = [I^-] + [I_3^-] + 2[I_{2n+2}^=]$$

$$[I_2]_t = \text{total titratable iodine in aqueous phase}$$
$$= [I_2] + [I_3^-] + n[I_{2n+2}^=]$$
$$[I_{2n+2}^=] = K_{2n+2}[I^-]^2 \cdot [I_2]^n$$

have four unknowns ($[I^-]$, $[I_{2n+2}^=]$, K_{2n+2}, n) a solution must be sought by taking various values of n in turn.

Commencing with the results at 25° and molar KI it is quickly found that the *next* step in the equilibria is best represented in terms of $I_6^=$ or

(17) See the conductivity values and slopes: C. W. Davies, "The Conductivity of Solutions," 2nd Edition, Chapman and Hall, London, 1933, pp. 79, 85; H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1943; ref. (7).

(18) J. Kreuzer, *Z. physik. Chem.*, **B53**, 213 (1943): K. L. Wolf and G. Metzger, *Ann.*, **563**, 157 (1948): J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

(19) H. S. Harned and B. B. Owen, ref. 17.

I_6^-, *i.e.*, $n = 2$ above. Consideration of the much smaller deviations from iii for 0.1 M KI favored $I_6^=$ formation; see Table II. This choice was confirmed by the results at 38 and 49°.

TABLE II

[K⁺]	[I₂] × 10⁴	K₅ × 10⁻⁶	K₆ × 10⁻⁵
1.0	6.776	2.5	6.1
	3.964	3.0	4.9
	1.991	3.5	4.4
	0.230	3.6	3.8
0.10	8.120	0.11	2.5
	1.807	0.57	7.2

For the *lowest* iodine concentrations where the uncertainty is greatest, the limits of K_6 for molar KI are ±30%. Accordingly, it was impracticable to extrapolate K_6 to $[I_2] = 0$, and ΔH_6 was estimated from values of K_6, each uncertain to ±0.25 units. at some common concentration of free iodine; thus, at $[I_2] = 6.75 \cdot 10^{-4}$ molar

| t, °C.	25.00	38.38	49.65
$K_6 \cdot 10^{-5}$	6.2	3.8	2.2

These and other similar figures give a best estimate of $\Delta H_6 = -7200 \pm 600$ cal. per g. ion.

Rewriting the equilibrium $2I^- + 2I_2 = I_6^=$ in terms of $2I_3^- \rightleftarrows I_6^=$, the equilibrium constant for the latter (K_6') is $K_6' = K_6/K_3^2$, and also, $\Delta H_6' = \Delta H_6 - 2\Delta H_3$. Whence $\Delta H_6' = -770$ cal. per g. ion.

Linhart[8] interpreted the data for KI solutions saturated with respect to I_2 on the sole basis of I_3^- and $I_{14}^=$ equilibria, *i.e.*, $I^- + I_2 \rightleftarrows I_3^-$, and $2I_3^- + 4I_2 \rightleftarrows I_{14}^=$. Whilst this may well be the best representation of the results for saturated solutions in terms of only two interactions, it appears kinetically unlikely that the second of these would be the next significant stage after I_3^- formation when the concentrations are increased gradually. Linhart's deduction of $I_{14}^=$ formation, however, may be taken as an indication of the degree of complexity which is involved in the saturated solutions, and it is significant that this ion is of a similar type $(2I^- + nI_2)$ to that adduced above.[20] The evidence in favor of this type rather than the $(Br^- + nBr_2)$ probable in bromine solutions is considerable (*e.g.*, Linhart, ref. 8).

A Calculated Interaction Energy for I_3^- Formation.—A calculation, based on simple electrostatic principles, for the potential energy of the iodine–iodide system can be made as follows. With ϵ = electronic charge; α = polarizability of I_2; α' = polarizability of I^- ion; the distances as represented in the figure, the net interaction energy may be written

$$U_1(r) = \epsilon^2\alpha[\beta/r^n - 1/2(r + r_1)^4 - 2\alpha\alpha'/(r + r_1)^{10}]$$
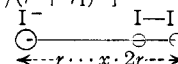
For the repulsive field it is necessary to assume a value for n, but the result is not sensitive to this choice[21] and the conditions near the equilibrium configuration have been represented by $n = 7$. The above expression treats the moment induced in I_2 as a point dipole at the center of the molecule. The other extreme from this assumption,

(20) See also T. R. Briggs, W. F. Geigle and J. L. Eaton, *J. Phys. Colloid Chem.*, **45**, 595 (1941).

(21) G. Briegleb, *Z. physik. Chem.*, **B51**, 9 (1941); M. M. Davies, *J. Chem. Phys.*, **15**, 739 (1947); *ibid.*, **17**, 374 (1949).

i.e., that the induced charges in I_2 are separated by $2r_1$ would give the second term in $U(r)$ as $-e^2\alpha/2r(r + r_1)^2 \cdot (r + 2r_1)$. The interaction energy, $U_2(r)$, calculated on this latter basis is given the suffix 2. The resultant energy of interaction will also include a term due to the work done in stretching the I_2 bond from its normal equilibrium value to that $(2r_1)$ obtaining in the triiodide ion. Representing this (small) extension by x, the work done in stretching is $U_s(x) = \frac{1}{2!}\times U^{11} \times x^2 + \frac{1}{3!} \times U^{111} \times x^3 + \frac{1}{4!} \times U^{IV} \times x^4 + \ldots$, see ref. 22; the necessary values are tabulated by Herzberg.[23] Thus a theoretical ΔE_0 for $T = 0°K$. is given by $U(r_{eq.}) + U_s(x)$.

TABLE III

$r_{eq.}$ Å. units	$2r_1$	$-U_1$ $(r_{eq.})$	$-U_2$ $(r_{eq.})$	U_s (x)	$-\Delta E_1$	$-\Delta E_2$
		erg per ion × 10^{13}			cal. per g. ion	
a 3.23	2.68	2.00	2.30	0.00	2880	3310
b 3.15	2.76	2.08	2.43	0.61	2120	2630
c 3.09	2.82	2.13	2.51	1.55	840	1380
d 2.95	2.96	2.35	2.85	4.61	−3250	−2570

(22) See, W. Jevons, "Report on Band Spectra of Diatomic Molecules," The Physical Society, London, 1932, p. 27.

(23) G. Herzberg, "Molecular Spectra," Vol. I, Prentice-Hall Inc., New York, N. Y., 1939, p. 482, *et seq.*

Mooney's X-ray study[24] of the ammonium triiodide crystal structure provides the most direct estimates of $r_{eq.}$ and $2r_1$; these are given as 3.10 and 2.81 Å., as compared with the 2.67 Å. interatomic distance in the normal I_2 molecule. A number of values of ΔE_1 and ΔE_2 have been calculated, keeping $(r_{eq.} + 2r_1) = 5.91$ Å. These range from (a) where the I_2 molecule is unstretched during the interaction, to (d), which is a symmetrical I_3^- structure; (c) represents the distances proposed by Mooney.

The electrostatic calculation arrives at an energy close to the measured ΔH_T, but distinctly smaller than the present estimate, based on results between 298 and 336°K. only, of the more strictly comparable ΔH_0. The pronounced temperature variation of ΔH_T has been taken to indicate that hydration effects play an important part during ion association in solution. This practical feature is one obvious item vitiating the agreement between calculated and experimental energy terms. Again, the simple treatment entirely neglects any contribution by electron sharing (*i.e.*, by exchange forces) which, clearly, may be a serious omission.

Acknowledgment.—One of us (E. G.) is indebted to the Department of Scientific and Industrial Research for a maintenance grant.

(24) R. C. L. Mooney, *Z. Kristal.*, **90**, 143 (1935).

ABERRYSTWYTH, WALES

The System Cobaltous Chloride–Water–Acetone at 25°

BY LEONARD I. KATZIN AND JOHN R. FERRARO

The phase diagram of the system cobaltous chloride–water–acetone at 25° is depicted. $CoCl_2 \cdot 4H_2O$ and $CoCl_2 \cdot 3H_2O$ are shown to exist over narrow ranges of water activity, in addition to the more generally accepted hydrates (hexahydrate, dihydrate, and probably monohydrate). The data do not determine the exact nature of the anhydrous cobalt chloride in the system, which could contain one or two molecules of acetone per cobalt chloride.

Cobaltous nitrate has been shown to form hydrates with six, four, three and two moles of water per mole of salt.[1] The literature on the hydrates of cobaltous chloride shows general agreement on the existence of hexahydrate and dihydrate, as well as a monohydrate. No trihydrate has been reported, and although descriptions of a tetrahydrate

SYSTEM
$CoCl_2 - H_2O - CH_3COCH_3$
(25 °C.)

Fig. 1.

and its preparaton have been given,[2–5] other workers have failed[6–8] to find the tetrahydrate except[9] as mixed crystals with manganous chloride. Cobaltous chloride tetrammine[10] and tetrapyridine[11] are known, lending support to the thesis that a tetrahydrate exists. Since previous experience has shown the salt–water–acetone ternary system to be very favorable for detecting hydrates with narrow stability ranges,[1,12] investigation was made of the cobaltous chloride–water–acetone system.

The results of the studies at 25° using the method of "wet residues" (Fig. 1 and Table I), taken together with the distinctive colors of those compositions, show the definite existence of $CoCl_2 \cdot 4H_2O$, and give evidence for the hitherto unreported trihydrate, $CoCl_2 \cdot 3H_2O$. Both have narrow stabil-
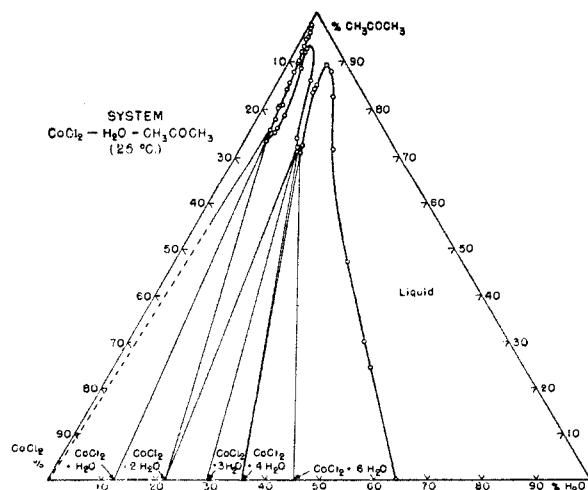
(2) J. Bersch, *Sitzungsber. Akad. Wiss. Wien*, **56**(II), 724 (1867).

(3) W. O. de Coninck, *Bull. acad. roy. Belg.*, 803, 1170 (1904).

(4) A. Neuhaus, *Chem. Erde*, **5**, 578 (1930).

(5) H. Benrath, *Z. anorg. allgem. Chem.*, **220**, 142 (1934).

(6) H. W. Foote, THIS JOURNAL, **45**, 663 (1923).

(7) A. Benrath, *Z. anorg. allgem. Chem.*, **163**, 396 (1927).

(8) H. Bassett and H. H. Croucher, *J. Chem. Soc.*, 1784 (1930).

(9) W. Stortenbeker, *Z. physik. Chem.*, **16**, 250 (1895).

(10) G. L. Clark, A. J. Quick and W. D. Harkins, THIS JOURNAL, **42**, 2483 (1920).

(11) Gmelin's "Handbuch der anorganischen Chemie," "Cobalt", (Sys. No. 58), 8th Ed., Verlag Chemie, Berlin, 1932, Abt. A, p. 294.

(12) L. I. Katzin and J. C. Sullivan, *J. Phys. Colloid Chem.*, **55**, 346 (1951).

(1) L. I. Katzin and J. R. Ferraro, THIS JOURNAL, **72**, 5451 (1950).