55. *Thermodynamics of Ion Association. Part III.*[1] *Some Thallous Ion Pairs with Univalent Anions.*

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Measurements are reported of the solubilities of thallous iodate and bromide in various salt solutions and of the conductivities of thallous chloride and bromide solutions. Thermodynamic association constants are derived for the formation of the ion pairs TlN_3 at 10°, 25°, and 40°; $TlNO_3$ at 0°, 25°, and 40°; TlBr at 25° and 40°; and TlCl at 40°. ΔH, ΔG, and ΔS are evaluated for the ion association $Tl^+ + X^- \rightleftharpoons TlX$ and hydration entropies of these and similar ion pairs are calculated.

IN previous papers [1,2] on the formation of ion pairs carrying a residual charge it was shown that the entropy of hydration of the ion pair is linearly related to the reciprocal of the sum of the radii of cation and anion. In present work the thermodynamics of association reactions involving ions of the same valency is studied: for these uncharged ion pairs a similar relation is found, the only exceptions being those formed with the linear azide and thiocyanate anions.

Bell and George [3] studied the solubility of thallous iodate in salt solutions at varying temperature and gave values for the association constants for the ion pairs TlCl, TlOH, and TlCNS. A similar method has been used in this paper for TlN_3 and $TlNO_3$. The solubility of thallous bromide in potassium nitrate and sodium perchlorate solutions, combined with conductivity measurements of saturated solutions in water, has enabled us to calculate thermodynamic properties for TlBr. The association entropy for TlCl obtained conductometrically is in good agreement with the value derived from solubilities.[3]

The work was undertaken in order to extend the number of relatively simple uncharged thallous ion pairs to which previously developed methods of calculating entropy terms could be applied.[1,2,4]

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[1] Part II, Nancollas, *J.*, 1956, 744.

[2] *Idem, J.*, 1955, 1458.

[3] Bell and George, *Trans. Faraday Soc.*, 1953, **49**, 619.

[4] Evans and Nancollas, *ibid.*, 1953, **49**, 363.

EXPERIMENTAL

Conductivity water, prepared by mixed-bed deionization,[5] was used throughout. Grade A glassware was used in all the solubility experiments. "AnalaR" materials were employed where available.

Thallous iodate was prepared by Bell and George's method.[3] Thallous bromide and chloride were prepared by adding equivalent proportions of potassium bromide solution and hydrochloric acid respectively to solutions of thallous sulphate at room temperature. The precipitates were washed free from sulphate, recrystallised four times from conductivity water, and dried at 110°.

Sodium azide was recrystallised three times from conductivity water and dried at 110°. Stock solutions of sodium perchlorate were prepared by exact neutralisation of sodium hydroxide with perchloric acid.

Saturators of the type described by Davies [6] were used for solubility measurements. The column of thallous salt was washed four times before each determination with the solution being used. Solutions were brought to the thermostat temperature and repeated tests showed complete saturation after passing twice through the column. Solutions were analysed volumetrically by treatment with excess of potassium iodide and removal of the precipitated thallous iodide by centrifugation, the precipitate being washed thoroughly. The iodine liberated on the addition of 2N-sulphuric acid was titrated against 0·01N-thiosulphate, the final addition being made with a microburette. Owing to uncertainties in estimating the densities of the solutions this method was found to be preferable to the weight titration procedure employed by Bell and George.[3]

Thallous bromide solutions were estimated by Mohr's method, the precipitated thallous chromate being removed by centrifuging. Dulplicates of all solubility determinations agreed to within 0·1%.

Conductivity measurements were made with a screened A.C. bridge [7] and, for thallous chloride, a cell of the type recommended for use with moderately concentrated solutions by Jones and Bollinger.[8] It was calibrated at 25° with a 0·01 D solution * of potassium chloride.[9]

The conductivity of saturated solutions of thallous bromide was determined with a cell of the Hartley–Barrett type incorporating an efficient stirrer and calibrated by Davies's method.[10] An aqueous suspension of thallous bromide crystals was added to the cell which contained conductivity water in equilibrium with carbon dioxide-free air. A correction for traces of impurity in the seed suspension was obtained by adding further amounts of suspension after equilibrium had been attained and noting any resulting change in the conductivity; this correction never exceeded 0·08% of the observed conductivity.

Results.—Solubility experiments with thallous iodate and bromide are summarised in Tables 1 and 2; S is the solubility and concentrations are in mmoles/l. The solubilities in pure water agree well with those reported by other workers. For thallous iodate, La Mer and Goldman [11] give 1·844; Bell and George,[3] 1·838 mmoles/l. at 25° (and 0·650 at 0° and 3·043 at 40°). For thallous bromide, Keefer and Reiber [12] give 2·007 mmoles/l. at 25°.

The concentrations of ionic species in saturated solutions of the salt TlY in the presence of added electrolyte, MX, were calculated by successive approximations by using the expressions:

Activity product, $$K_s = [\text{Tl}^+][\text{Y}^-]f_1^2 \qquad (1)$$

Total concentration of MX, $$T(\text{MX}) = [\text{X}^-] + [\text{TlX}] = [\text{M}^+] + [\text{MY}] \qquad (2)$$

Dissociation constant of MY, $$[\text{M}^+][\text{Y}^-]f_1^2/[\text{MY}] \qquad (3)$$

Electroneutrality condition, $$[\text{M}^+] + [\text{Tl}^+] = [\text{X}^-] + [\text{Y}^-] \qquad (4)$$

In the calculation of the activity product K_s (TlIO_3), a correction was made for incomplete dissociation using the dissociation constant at the appropriate temperature given by Bell and

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* See footnote, *J.*, 1956, 4464.

[5] Davies and Nancollas, *Chem. and Ind.*, 1950, **7**, 129.
[6] Davies, *J.*, 1938, 277.
[7] Jones and Joseph, *J. Amer. Chem. Soc.*, 1928, **50**, 1049.
[8] Jones and Bollinger, *ibid.*, 1931, **53**, 411.
[9] Jones and Bradshaw, *ibid.*, 1933, **55**, 1780.
[10] Davies, *Trans. Faraday Soc.*, 1929, **25**, 129.
[11] La Mer and Goldman, *J. Amer. Chem. Soc.*, 1929, **51**, 2632.
[12] Keefer and Reiber, *ibid.*, 1941, **63**, 3504.

George[8] who also quote values for KIO_3. The dissociation constant of $NaIO_3$ at 25° is 3·0;[13] values at 10° (3·4) and 40° (2·6) were obtained by Bjerrum's method.[14] The small constant concentration of $TlIO_3$ in saturated solutions were 0·001, 0·002, 0·006, 0·017 mmole/l. respectively at 0°, 10°, 25°, and 40°.

Activity coefficients were obtained from the Davies equation[15]

$$-\log f_z = Az^2\{I^{\frac{1}{2}}(1 + I^{\frac{1}{2}})^{-1} - 0{\cdot}2I\}$$

in which $A = 0{\cdot}49$ at 0° and 10°, 0·50 at 25° and 0·52 at 40°, I is the ionic strength and z the valency of the ions. Association constants $K = [TlX]/[Tl^+][X^-]\,f_1^2$ are given in Tables 1 and 2.

TABLE 1. *Solubility of thallous iodate in salt solutions, concns. in mmoles/l.*

$T(NaN_3)$	S	I	$NaIO_3$	Tl^+	N_3^-	TlN_3	K	K (mean)
			Sodium azide at 10°					
—	1·016	1·014	—	1·014	—	—	—	
17·93	1·144	19·02	0·005	1·100	17·89	0·043	2·83	
20·24	1·155	21·34	0·005	1·105	20·19	0·048	2·84	
27·24	1·182	28·35	0·007	1·118	27·17	0·062	2·81	
30·35	1·193	31·46	0·008	1·123	30·28	0·068	2·77	
36·40	1·214	37·52	0·009	1·131	36·32	0·081	2·81	2·81
			Sodium azide at 25°					
—	1·842	1·836	—	1·836	—	—	—	
6·49	1·935	8·42	0·004	1·927	6·49	0·002	(1·89)	
9·12	1·973	11·05	0·005	1·936	9·09	0·031	(2·18)	
12·11	2·004	14·05	0·006	1·954	12·06	0·045	2·41	
14·81	2·029	16·77	0·008	1·967	14·76	0·056	2·48	
20·23	2·072	22·21	0·010	1·992	20·15	0·073	2·41	
23·71	2·097	25·71	0·012	2·005	23·63	0·087	2·48	
27·05	2·119	29·05	0·014	2·016	26·95	0·097	2·46	2·44
			Sodium azide at 40°.					
—	3·048	3·031	—	3·031	—	—	—	
15·98	3·350	19·21	0·015	3·246	15·90	0·087	2·24	
21·80	3·423	25·07	0·021	3·288	21·68	0·118	2·26	
26·89	3·477	30·19	0·025	3·317	26·75	0·140	2·22	
32·07	3·536	35·40	0·030	3·343	31·89	0·176	2·37	
34·28	3·554	37·60	0·032	3·357	34·10	0·180	2·28	
41·72	3·621	45·08	0·038	3·390	41·51	0·214	2·26	
47·11	3·664	50·48	0·043	3·413	46·88	0·233	2·21	2·26
$T(KNO_3)$	S	I	KIO_3	Tl^+	NO_3^-	$TlNO_3$	K	K (mean)
			Potassium nitrate at 0°					
—	0·656	0·655	—	0·655	—	—	—	
32·76	0·778	33·49	0·007	0·737	32·72	0·040	2·33	
47·84	0·808	48·58	0·010	0·750	47·78	0·058	2·37	
50·92	0·813	51·66	0·011	0·752	50·86	0·060	2·32	
57·24	0·826	57·99	0·012	0·755	57·17	0·070	2·45	
59·80	0·830	60·55	0·013	0·757	59·73	0·072	2·42	2·38
			Potassium nitrate at 25°					
20·68	2·073	22·66	0·016	2·001	20·61	0·066	2·16	
28·64	2·127	30·64	0·022	2·031	28·55	0·089	2·15	
38·46	2·178	40·50	0·028	2·061	38·35	0·117	2·14	
39·58	2·195	41·61	0·029	2·061	39·45	0·127	2·15	
42·79	2·207	44·83	0·032	2·071	42·66	0·130	2·15	2·15
			Potassium nitrate at 40°					
20·56	3·408	23·82	0·030	3·290	20·46	0·101	2·09	
24·46	3·454	27·74	0·035	3·315	24·33	0·122	2·04	
30·44	3·517	33·75	0·043	3·352	30·30	0·148	2·07	
38·24	3·590	41·58	0·054	3·394	38·06	0·179	2·04	
39·39	3·600	42·73	0·055	3·399	39·20	0·184	2·04	
42·54	3·631	45·89	0·059	3·410	42·34	0·204	2·10	2·06

The conductivity of thallous chloride solutions at 40° is given in Table 3. The degree of dissociation, α, at each concentration was calculated by successive approximations from the

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[13] Davies, *Trans. Faraday Soc.*, 1927, **23**, 351.

[14] Bjerrum, *Kgl. danske vid. Selsk. Math.-fys. Medd.*, 1926, **7**, 9.

[15] Davies, *J.*, 1938, 2093.

TABLE 2. *Solubility of thallous bromide in salt solutions.*

$T(\mathrm{KNO_3})$	S	I	$\mathrm{TlNO_3}$	$\mathrm{Tl^+}$	$\mathrm{Br^-}$	K	K (mean)
			Potassium nitrate at 25°				
—	2·009	1·981	—	1·981	1·981	7·81	
(5·01)	(2·096)	7·06	0·019	2·050	2·068	7·81	
(10·01)	(2·159)	12·11	0·036	2·095	2·131	7·81	
(15·02)	(2·203)	17·14	0·053	2·122	2·175	7·81	
21·40	2·267	23·56	0·075	2·165	2·240	7·69	
26·49	2·320	28·69	0·092	2·201	2·292	7·58	
32·65	2·344	34·86	0·109	2·207	2·316	7·69	
37·77	2·385	40·00	0·125	2·232	2·357	7·63	7·67
			Sodium perchlorate at 25°.				
$T(\mathrm{NaClO_4})$	S	I	$\mathrm{Tl^+}$	$\mathrm{Br^-}$		K	
5·21	2·095	7·28	2·067	2·067		7·81	
11·69	2·224	13·89	2·197	2·197		7·31	
16·50	2·228	18·70	2·201	2·201		7·52	
17·78	2·232	19·98	2·204	2·204		7·58	
			Potassium nitrate at 40°				
$T(\mathrm{KNO_3})$	S	I	$\mathrm{TlNO_3}$	$\mathrm{Tl^+}$	$\mathrm{Br^-}$	K	
—	3·492	3·428	—	3·428	3·428	6·21	
21·27	3·760	24·85	0·115	3·581	3·696	6·62	
26·34	4·000	30·13	0·146	3·790	3·936	6·02	
32·46	4·035	36·26	0·175	3·796	3·971	6·17	
37·56	4·123	41·41	0·200	3·859	4·059	6·02	
			Sodium perchlorate at 40°				6·32
$T(\mathrm{NaClO_4})$	S	I	$\mathrm{Tl^+}$	$\mathrm{Br^-}$		K	
11·62	3·597	15·16	3·533	3·533		6·62	
16·41	3·691	20·03	3·626	3·626		6·49	
20·25	3·732	23·92	3·661	3·661		6·49	

TABLE 3. *Conductivity of thallous chloride at* 40°.

10^3m	$10^2m^{\frac{1}{2}}$	$\Lambda_{\text{obs.}}$	10^3I	α	K	10^3m	$10^2m^{\frac{1}{2}}$	$\Lambda_{\text{obs.}}$	10^3I	α	K
4·2136	6·4912	188·38	4·172	0·9902	2·74	8·3249	9·1241	183·40	8·169	0·9813	2·84
4·8361	6·9542	187·25	4·775	0·9873	3·13	13·505	11·620	179·09	13·160	0·9746	2·52
6·1021	7·8116	185·73	6·010	0·9849	3·01	15·637	12·505	177·34	15·180	0·9709	2·55
6·4491	8·0306	185·39	6·350	0·9846	2·93	16·222	12·736	176·91	15·760	0·9701	2·54

Mean $K = 2{\cdot}78$

relation $\alpha = \Lambda/[198{\cdot}6 - 129{\cdot}4\ (\alpha m)^{\frac{1}{2}}]$ where 198·6 is the Λ° value obtained by extrapolation of the conductivity data, and m is the molarity. Using the values at 40°, $\Lambda^\circ\ (\mathrm{Cl^-}) = 100{\cdot}6$ and $\Lambda^\circ\ (\mathrm{Br^-}) = 102{\cdot}4$, obtained by interpolation of Benson and Gordon's mobility data,[16] we find $\Lambda^\circ\ (\mathrm{Tl^+}) = 98{\cdot}0$. Association constants given in Table 3 have been derived from the equation

$$\log K = \log\,[(1 - \alpha)/\alpha^2 m] + 1{\cdot}04\ [I^{\frac{1}{2}}(1 + I^{\frac{1}{2}})^{-1} - 0{\cdot}2I]$$

Thallous bromide is too insoluble to permit of conductometric measurements similar to those of the chloride. Experimental conductivities of saturated solutions at 25° (146·84) and 40° (189·26) were therefore used to calculate the degree of dissociation from the expressions

$$\alpha = \Lambda/[153{\cdot}11 - 94{\cdot}58\ (\alpha m)^{\frac{1}{2}}] \text{ at } 25^\circ \text{ and } \alpha = \Lambda/[200{\cdot}4 - 129{\cdot}8\ (\alpha m)^{\frac{1}{2}}] \text{ at } 40^\circ$$

These, together with the observed solubilities in pure water enable the concentrations of TlBr in saturated solutions to be calculated as 0·028 at 25° and 0·064 mmole/l. at 40°. Allowing for incomplete dissociation of $\mathrm{TlNO_3}$, the association constants for TlBr given in Table 2 were evaluated from the solubilities in potassium nitrate and sodium perchlorate solutions. It is seen that concordant values are obtained with the two electrolytes. Keefer and Reiber[12] measured the solubility of thallous bromide in potassium nitrate solutions and some of their results are included in parentheses in Table 2.

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[16] Benson and Gordon, *J. Chem. Phys.*, 1945, **13**, 473.

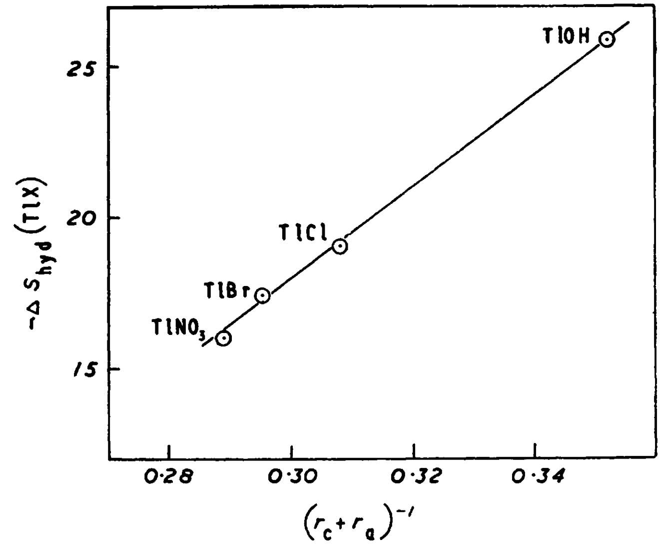
Discussion

Heats of association have been derived from the linear plots of log K against $1/T$. ΔG, ΔH, and ΔS values are given in Table 4 together with data for TlCl, TlOH, and TlCNS.[3]

TABLE 4. *Thermodynamic properties.*

Reaction	ΔG at 25° (kcal. mole^{-1})	ΔH (kcal. mole^{-1})	ΔS (cal. deg.$^{-1}$ mole^{-1})	S_{gas} (TlX) (cal. deg.$^{-1}$ mole^{-1})	ΔS_g (cal. deg.$^{-1}$ mole^{-1})	ΔS_{hyd} (TlX) (cal. deg.$^{-1}$ mole^{-1})	$r_c + r_a$ (Å)
Tl^+, OH^-	−1·12	+0·37	+5·1	58·8	−24·3	−25·9	2·84
Tl^+, Cl^-	−0·93	−1·43	−1·7	60·9	−17·7	−19·0	3·25
Tl^+, Br^-	−1·2	−2·45	−4·2	62·8	−18·3	−17·4	3·39
Tl^+, NO_3^-	−0·45	−0·65	−1·0	80·4	−19·8	−16·0	3·46
Tl^+, CNS^-	−1·09	−2·96	−6·4	69·8	−32·6	−10·0	*ca.* 3·3
Tl^+, N_3^-	−0·53	−1·33	−2·7	66·7	−25·2	− 7·0	*ca.* 3·1

Recalculation of conductivity data at 25° for thallous chloride [17] with Davies's activity coefficient expression gives $K = 3{\cdot}09$. This, in conjunction with our value at 40°, gives ΔS (association) $= -1{\cdot}8$ cal./(deg. mole), in good agreement with the value obtained from solubilities [3] [$-1{\cdot}7$ cal./(deg. mole)]. In view of this, we feel justified in comparing our entropy value for TlBr with those obtained for the other ion pairs from solubility data.



Plots of ΔS_{hyd}(TlX) *against* $(r_c + r_a)^{-1}$.

The entropy of association may be written

$$\Delta S = \Delta S_g + \Delta S_{hyd}(TlX) - \Delta S_{hyd}(Tl^+) - \Delta S_{hyd}(X^-) \quad . \quad . \quad . \quad . \quad (5)$$

where ΔS_g and ΔS_{hyd} represent gaseous and hydration entropies respectively. $\Delta S_{hyd}(Tl^+)$ and $\Delta S_{hyd}(X^-)$ were obtained from known gas-phase and standard entropies.[18]

$$\Delta S_g = S_{trans}(TlX) - S_{trans}(Tl^+) - S_{trans}(X^-) - S_{rot}(X^-) + S_{rot}(TlX)$$

The calculation of S_{trans} and S_{rot} has been described elsewhere for nitrate [2] and azide [4] ions. By analogy with known structures of azides [19] and cyanates,[20] the angles between the axes of the linear azide and thiocyanate ions and the Tl···X bond were taken as 120° and 130° respectively.

[17] Bray and Winninghof, *J. Amer. Chem. Soc.*, 1911, **33**, 1663; Garrett and Vellenga, *ibid.*, 1945, **67**, 225.

[18] Latimer, " Oxidation Potentials," Prentice-Hall, New York, 1952.

[19] Pauling and Brockway, *J. Amer. Chem. Soc.*, 1937, **59**, 13.

[20] Eyster, Gillette, and Brockway, *ibid.*, 1940, **62**, 3236.

ΔS_{hyd}(TlX) values were obtained by substitution of the calculated entropies in equation (5); these are given in Table 4 together with $(r_c + r_a)$, the sum of the cationic and anionic radii. The figure shows the good linear relationship between ΔS_{hyd}(TlX) and $(r_c + r_a)^{-1}$. ΔS_{hyd} values for TlN_3 and TlCNS are considerably lower than would be expected. There is some doubt about the aqueous entropies of azide and thiocynate ions but it is unlikely that they will be in error by more than 2 or 3 cal./(deg. mole). Also, contributions to entropy due to bending vibrations will account for some of the discrepancy.

It is of interest to determine whether a similar entropy relationship can be applied to uncharged ion pairs of higher valency type. Jones and Monk [21] from e.m.f. measurements give ΔS (association) for $MgSO_4$ as 31 cal./(deg. mole); the value for calcium sulphate from solubilities is 16·1 cal./(deg. mole).[3] Similar entropy calculations give values for $-\Delta S_{\text{hyd}}(MgSO_4)$ of 61·3 and 62·5 cal./(deg. mole) respectively: the corresponding $(r_c + r_a)^{-1}$ values are 0·35 and 0·32 Å^{-1}. The value for magnesium sulphate appears to be rather low and similar results were obtained with the acetate and formate.[1] It is possible that the small cation again retains part of its hydration shell in the ion pair. In view of the lack of accurate data over a large range of temperature for sulphates of other bivalent cations, further investigations are being made by precise e.m.f. methods over a wide temperature range.

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[21] Jones and Monk, *Trans. Faraday Soc.*, 1952, **48**, 929.