are practical values for use in chemical thermodynamic calculations.

High temperature enthalpy determinations on TlBr have been reported by Goodwin and Kalmus (*6*) and recently on TlBr and TlI by Cubicciotti and Eding (*3*). The heat capacity equation derived by the latter investigators is represented by the following equations:

$$\text{TlBr: } C_p = 9.95 + 7.10 \times 10^{-3}T$$

$$\text{TlI: } C_p = 11.56 + 3.32 \times 10^{-3}T$$

These equations yield values of C_{p298} of 12.07 and 12.55 cal. per (g.f.m. ° K.) for TlBr and TlI, respectively. Kelley and King (*8*) estimated the values of entropy at 298.15° K. for TlBr and TlI as 29.5 ± 1.0 and 31.0 ± 1.0 cal. per (g.f.m. ° K.). The present results on TlI are consistent with the value of Cubicciotti (*2*). His sublimation pressure data obtained by the quasi-state method of Rodebush as well as by the transpiration method, combined with the entropy of the gas based on molecular constants gives $S^{\circ}_{298.15} = 30.7$ cal. per (g.f.m. ° K.).

The crystal structure of TlI is reported to be orthorhombic ("TlI-type" structure) below 448° K. (*13*). This structure, characteristic of NaOH, KOH, and RbOH crystals at ordinary temperatures, is a rhombohedrally distorted NaCl-type structure, rather than a CsI-type structure (*11*).

Thermodynamics of Formation. The enthalpy of formation of TlBr and TlI have been reported (*10*) as −41.2 ± 0.7 kcal. per (g.f.m.) and −29.7 ± 0.6 kcal. per (g.f.m.), respectively. Combining these values with the entropies of thallium, bromine, and iodine (*8, 9*), and the data from present work yields entropies of formation (ΔSf°) and Gibbs energies of formation (ΔGf°) of −4.3 ± 0.2 cal. per (g.f.m. ° K.) and −39.9 ± 0.8 kcal. per (g.f.m) for TlBr, and of 1.3 ± 0.1 cal. per (g.f.m. ° K.) and −30.1 ± 0.7 kcal. per (g.f.m.) for TlI, respectively, at 298.15° K.

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Osmotic and Activity Coefficients of Tris(hydroxymethyl)aminomethane and Its Hydrochloride in Aqueous Solution at 25° C.

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The isopiestic vapor pressure method has been used to determine the osmotic and activity coefficients of tris(hydroxymethyl)aminomethane and its hydrochloride in aqueous solution at 25° C. The base is an almost ideal solute while the hydrochloride resembles ammonium chloride in behavior.

A BASE of considerable use both as an acidimetric standard and as a biological buffer is 2-amino-2-(hydroxymethyl)-1,3-propanediol or tris(hydroxymethyl)aminomethane, sometimes abbreviated to tris. Its hydrochloride also finds use as a component of buffer solutions.

Bates and Hetzer (*2*) found that tris had an acidic dissociation constant of 8.075 (in pK units) at 25° while Datta, Grzybowski, and Wilson (*4*) found pK = 8.069. The former measurements were made with solutions containing only tris and its hydrochloride, and the results indicated a zero value of the ion-size parameter in the Debye-Hückel equation. This suggests that there is some ion-pair formation in the hydrochloride. The measurements of Datta, Grzybowski, and Wilson, however, were made in potassium chloride and indicated a normal value of the ion-size parameter of about 3 A.

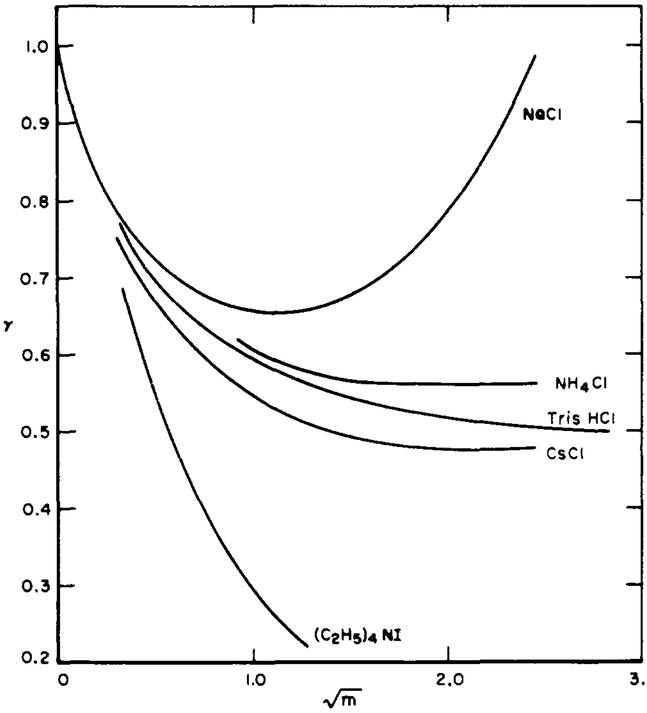

Figure 1. Activity coefficients of NaCl, NH_4Cl, tris HCl, CsCl, and $N(C_2H_5)_4$ I

Isopiestic vapor pressure measurements have now been made with both the base and its hydrochloride, using sodium chloride as the reference salt. Osmotic coefficient data for sodium chloride have been tabulated (*6*). The base was primary acidimetric standard grade material and had a purity of 99.91% by titration with standard hydrochloric acid. The hydrochloride was prepared from the base and hydrochloric acid; precipitation with silver nitrate indicated a purity of 99.92%. Table I gives the molalities of tris solutions in isopiestic equilibrium with sodium chloride solutions and also the osmotic coefficient of the tris solutions. A plot of osmotic coefficient against molality of tris shows some scatter of the points, possible owing to absorption of carbon dioxide (*1*). Nevertheless, the results indicate that, except at the highest concentrations, the departure from ideality is less than 1%. The osmotic coefficients can be expressed by the equation

$$\phi = 1 - 0.00314 m_C + 0.00016 m_C^3$$

where m_C is the molality of tris.

Its activity coefficient can therefore be expressed by the equation

$$\log \gamma = -0.00273 m_C + 0.00009 m_C^3$$

Table II gives the molalities of isopiestic solutions of sodium chloride and tris hydrochloride, and Table III gives the osmotic and activity coefficients of tris hydrochloride calculated from these isopiestic measurements. The osmotic coefficients of tris hydrochloride and ammonium chloride are almost the same in dilute solution and, therefore, the activity coefficients of tris hydrochloride are reported relative to $\gamma = 0.770$ at $0.1m$, the value for ammonium chloride at this concentration.

Table I. Molalities of Isopiestic Solutions of Sodium Chloride and Tris. Osmotic Coefficients of Tris Solutions at 25°

m_B	m_C	ϕ_C
0.2731	0.5035	1.001
0.5119	0.9438	0.999
0.9773	1.844	0.991
1.494	2.881	0.992
1.852	3.619	0.998
2.248	4.481	1.001
2.881	5.889	1.015

B = sodium chloride, C = tris.

Table II. Molalities of Isopiestic Solutions of Sodium Chloride and Tris Hydrochloride at 25°

m_B	m_D	m_B	m_D
0.2731	0.2781	3.056	3.548
0.5119	0.5276	3.317	3.905
0.9773	1.031	4.054	4.972
1.494	1.613	4.487	5.655
1.852	2.030	5.000	6.490
2.248	2.516	5.082	6.640
2.881	3.323	5.752	7.805

B = sodium chloride, D = tris hydrochloride.

Table III. Osmotic and Activity Coefficients of Tris Hydrochloride in Aqueous Solution at 25°

m	ϕ	γ	m	ϕ	γ
0.1	0.927	0.770	2.0	0.889	0.549
0.2	0.911	0.717	2.5	0.892	0.538
0.3	0.904	0.685	3.0	0.897	0.529
0.4	0.899	0.662	3.5	0.902	0.524
0.5	0.894	0.644	4.0	0.906	0.520
0.6	0.892	0.630	4.5	0.910	0.516
0.7	0.890	0.619	5.0	0.912	0.512
0.8	0.888	0.609	5.5	0.914	0.509
0.9	0.887	0.600	6.0	0.916	0.506
1.0	0.886	0.592	6.5	0.918	0.504
1.2	0.886	0.580	7.0	0.920	0.502
1.4	0.886	0.570	7.5	0.921	0.500
1.6	0.886	0.561	8.0	0.922	0.498
1.8	0.887	0.555			

Figure 1 offers a comparison of the activity coefficients of some 1-to-1 electrolytes. Sodium chloride is a typical, fully dissociated, 1-to-1 electrolyte, and the variation of its activity coefficient with concentration can be explained (*7*) by assuming that its ion-size parameter in the Debye-Hückel equation is 4 A. and that the sodium ion is hydrated to the extent of three or four water molecules. In the case of ammonium chloride, however, the ion-size parameter is smaller, 3.75 A, and the ammonium ion is hydrated with, on the average, only 1.6 water molecules (*8*); both effects lower the activity coefficient. Cesium chloride has a large cation (ionic radius 1.69 A.), too large to be hydrated, and the activity coefficient of this salt is lower than that of ammonium chloride. The curve for tetraethylammonium iodide (*3*) is typical for a salt with extensive ion-pair formation which, it has been suggested (*5*), occurs when both ions are large and are forced together in order to maintain the water structure.

The osmotic coefficients of ammonium chloride and of tris hydrochloride are very similar up to $1m$ and do not differ much even in concentrated solutions. It can be concluded that ion-pair formation does not occur to any marked extent.

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