Discussion of Results

Heat Capacities.—Hirabayashi, *et al.*[16–18] and Khomyakov, *et al.*,[19] have measured the heat capacity of various alloys with compositions fairly near to MgCd. Both investigators employed adiabatic calorimetry, but they used the continuous heating technique. Their results agree with the present data in regard to the first degree nature of the transition at about 251° which is superimposed upon the broad second degree "order-disorder" transition. Table IV shows that the exact transition temperature and transition energy depend upon the composition. Composition differences make a detailed quantitative comparison of heat capacities seem unwarranted.

An integration of the data reported by Khomyakov, *et al.*, from 298.16 to 543.16°K. for the 1:1 alloy results in an entropy value of 5.08 e.u., which is slightly lower than the 5.13 e.u. obtained in the present investigation. This difference might be attributed to the continuous heating technique which, when applied to systems exhibiting order–disorder transformations, tends to displace energy to higher temperatures and thus lower the observed entropy.

TABLE IV

COMPARISON OF ΔH OF TRANSITION AND TRANSITION TEMPERATURES FOR VARIOUS COMPOSITIONS

Compn., at % Cd	Present data $\Delta H_{\text{Trans.}}$, T_{Trans}	Hirabayashi ΔH_{Trans},	T_{Trans}	Khomyakov ΔH_{Trans}, T_{Tran}
51.0		360		
50.8			250°	
50.52 ± 0.04	357.0, 251.30°			
50.00			251.84°	362, 251.5°
49.5		400		
49.44				362, 250.2°

The present data join smoothly below 280°K. to that reported earlier[3] for the low temperature region. Above 280°K. the earlier data are slightly higher, reaching a maximum deviation of 0.24% at 300°K. The earlier data were taken with the original version of the low temperature calorimeter developed in this Laboratory. Heat capacities of cadmium measured in the same calorimeter were also shown to be high in the upper range of the instrument. The discrepancy was explained by Craig, *et al.*,[11] as resulting from faulty design of the earlier calorimeter which permitted some heat to be lost from the sample *via* the lead wires. All other heat capacity measurements on Mg–Cd alloys in this Laboratory have been made with an improved version of the calorimeter in which this fault has been corrected.

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, CLARKSON COLLEGE OF TECHNOLOGY AND UNIVERSITY OF NORTH CAROLINA]

Correlation of Turbidity and Activity Data for Aqueous Solutions of the Tungstophosphoric Acids[1]

BY J. B. GOEHRING, M. KERKER, E. MATIJEVIĆ AND S. Y. TYREE, JR.

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Good agreement was obtained between the turbidities of 9- and 12-tungstophosphoric acid from light scattering and those calculated from activity data. The activity data were obtained from isopiestic vapor pressure measurements. Turbidities calculated on the basis of ideal behavior are considerably different.

Introduction

In an earlier light scattering study[2] of 9- and 12-tungstophosphoric acids, the usual Debye Hc/τ *versus* c extrapolation[3] led to molecular weights in agreement with the dimeric formulation of the 9-acid ($H_6P_2W_{18}O_{62}$), and the monomeric formulation of the 12-acid, ($H_7PW_{12}O_{42}$), when organic solvents were used.

However, in aqueous solution,[2,4] the apparent molecular weights obtained were only a fraction of the empirical formula weights. This difference may be attributed to the dissociation of these acids to highly charged ions in aqueous solution,[5,6] leading to deviations from ideality. Accordingly, the approximations used in the Debye treatment are no longer applicable.

In order to interpret the turbidity of such systems it is necessary to use activity data. We have determined the vapor pressure over these solutions by the isopiestic method from which the activity of water was obtained. When these results were used in the appropriate expression for the turbidity, the calculated and experimental turbidities were in good agreement.

Experimental

The tungstophosphoric acids were prepared and purified as described earlier.[4] The density data were obtained at 25° with a Gay-Lussac type specific gravity bottle. Earlier data obtained by Soboleff[7] could not be utilized.

The isopiestic vapor pressure data were obtained using equipment and technique previously described.[8]

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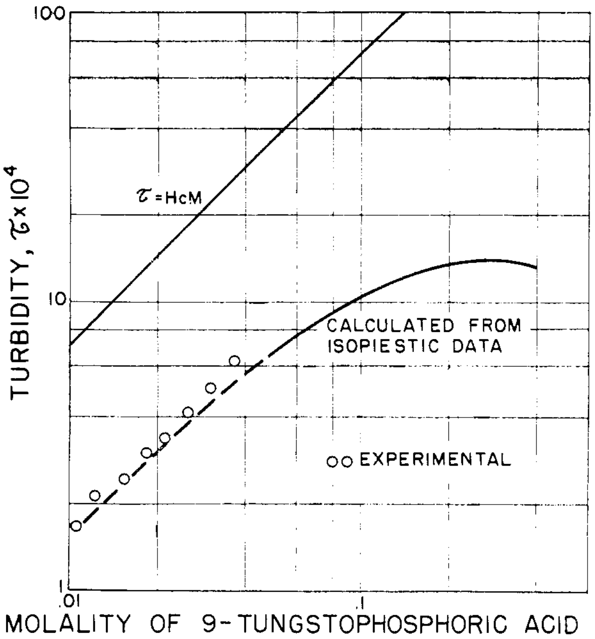

Fig. 1.—Comparison of experimental turbidities of aqueous solutions of 9-tungstophosphoric acid with those calculated from isopiestic data and from $\tau = HcM$. Dotted line is from extrapolated isopiestic data.

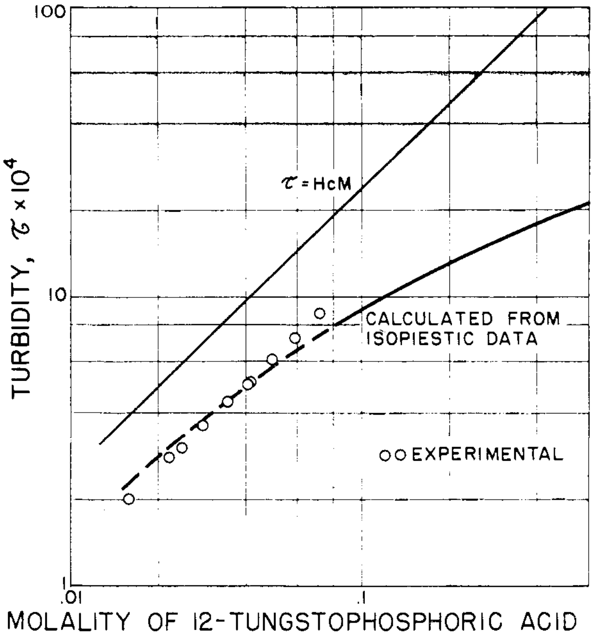

Fig. 2.—Comparison of experimental turbidities of aqueous solutions of 12-tungstophosphoric acid with those calculated from isopiestic data and from $\tau = HcM$. Dotted line is from extrapolated isopiestic data.

Results and Discussion

The excess turbidity of a solution due to concentration fluctuations is given by[9]

$$\tau = \frac{8\pi^3}{3\lambda' N} \frac{RT\bar{V}_0 c}{(-\partial\mu_0/\partial c)} \left(\frac{\partial\epsilon}{\partial c}\right)^2 \qquad (1)$$

which may be alternatively expressed as

$$\tau = \frac{8\pi^3}{3\lambda^4 N} \frac{\bar{V}_0 c}{(-\mathrm{d}\ln a_0/\mathrm{d}c)} \left(\frac{\partial n^2}{\partial c}\right)^2 \qquad (2)$$

$$= \frac{H\bar{V}_0 c}{(-\mathrm{d}\ln a_0/\mathrm{d}c)}$$

where

λ = wave length of incident light *in vacuo* (results reported in this paper are for 4361 Å.)
N = Avogadro's number
V_0 = partial molar volume
R = molal gas constant
T = Kelvin temperature
c = concentration (g./ml.)
μ_0 = chemical potential of solvent
ϵ = dielectric constant of soln.
a_0 = activity of solvent
n = index of refraction of soln.

The partial molal volume of water was calculated from the density data, given in Table I, and was found to be approximately that of pure water, *viz.*, $\bar{v}_0$ = 18.0 ± 0.1 ml. From the isopiestic molalities and activities[10] given in Table II a curve of ln a_0 *versus* c was obtained. The quantity (d ln a_0/dc) was determined from this curve by graphical differentiation using the chord area method and the results are given in Table III. In calculation of turbidities from equation 2 the approximation (3) usually is employed

$$\frac{\mathrm{d}n^2}{\mathrm{d}c} \cong 2n_0 \frac{\mathrm{d}n}{\mathrm{d}c} \qquad (3)$$

where n_0 is the refractive index of the pure solvent. However, Maron and Lou[11] have pointed out that this is not valid for concentrated solutions and we have accordingly used their method for calculating this quantity. The factor H is given in Table III. Although it is usually treated as constant in dilute

TABLE I

DENSITY OF TUNGSTOPHOSPHORIC ACIDS AT 25°

Molality	9-Tungstophosphoric acid	12-Tungstophosphoric acid
0.02	1.0705	1.0484
.04	1.1405	1.0996
.06	1.2086	1.1508
.08	1.2650	1.2010
.10	1.3402	1.2516
.15	1.4964	1.3735
.20	1.6480	1.4940
.30		1.650
.40		1.912
.50		2.116
.60		2.308
.70		2.804

TABLE II

ISOPIESTIC MOLALITIES

KCl	9-Tungstophosphoric acid	12-Tungstophosphoric acid	Activity of water
0.2	0.070_2	0.122_0	0.993443
.4	$.128_2$	$.238_4$	.98709
.6	$.181_2$	$.342_2$	.98078
.8	$.226_0$	$.426_0$	.97448
1.0	$.267_0$	$.505_8$	.96818
1.2	$.304_4$	$.583_0$	.9619
1.4	$.338_0$	$.656_0$	.9556
1.6	$.371_8$		.9492
1.8	$.404_2$		.9428

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TABLE III

Molality	9-Tungstophosphoric acid c	(d ln a_0/dc)	$H \times 10^6$	12-Tungstophosphoric acid c	(d ln a_0/dc)	$H \times 10^6$
0.02	0.086	−0.020	3.93	0.058	−0.011	2.96
.04	.170	.022	3.96	.115	.013	2.98
.06	.251	.023	3.99	.171	.014	2.99
.08	.328	.026	4.01	.227	.016	3.00
.10	.407	.028	4.04	.283	.017	3.02
.15	.597	.035	4.11	.418	.020	3.04
.20	.769	.042	4.17	.550	.023	3.07
.30	1.078	.059	4.25	.770	.029	3.13
.40	1.36	.080	4.39	1.029	.034	3.18
.50				1.26	.038	3.23
.60				1.47	.042	3.29
.70				1.88	.044	3.34

solutions, this is not the case for concentrated solutions. The turbidities were calculated from the tabulated quantities using equation 2. They are plotted together with the experimental turbidities obtained previously[2,4] in Figs. 1 and 2. Also shown in these figures are the turbidities calculated on the assumption of ideal behavior, from

$$\tau = \frac{8\pi^3}{3\lambda^4 N} cm \left(\frac{dn^2}{dc}\right)^2 = HcM \qquad (4)$$

where M is the molecular weight of the solute.

The agreement between the experimental turbidities and those calculated from activity data is quite satisfactory. In the concentration range where the results by the two methods overlap, the agreement is within 10%, which is approximately the combined uncertainty in determining (d ln a_0/dc) at these very low molalities and the experimental turbidity. The difference between the experimental turbidities and those calculated from equation 4 is quite striking, indicating the failure of the approximations based on ideal behavior for these systems.

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The Effects of Some Organic Oxy-acids on the Electron Exchange Reaction between Thallium(I) and (III) in Aqueous Perchloric Acid

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The effects of these various oxy-acids: oxalic, acetic, malonic, succinic, malic and tartaric, on the Tl(I)–Tl(III) exchange in 3.50 M $HClO_4$ were studied. With oxalic, malonic, malic and tartaric, reduction of Tl(III) proceeded at a rate comparable to or faster than the exchange. Acetic and succinic acids retard the exchange; the exchange rate reflects the loss of exchangeable species through competition of the acetate or succinate complexes.

The thallium(I)–(III) electron transfer reaction in perchloric acid has been studied by Dodson and co-workers,[2] Prestwood and Wahl[3] and Rossotti[4] and the effects of chloride, cyanide and sulfate have been examined by various workers.[5–7] In view of suggestions that anion bridges might accelerate exchange[6,7] and in view of the contrasting effects of various anions on the exchange, we decided to examine the exchange in perchloric acid in the presence of various added organic oxy-acids.

Experimental

Experimental procedures were the same as have been reported in earlier papers,[6] except that glass filters, with fritted discs and removable glass chimneys, replaced the steel models. The reactions were run at 25.0°.

Reagents, except for the Oak Ridge Tl 204, were from Merck and Company (Germany).

Since all the organic acids employed (oxalic, acetic, malonic, succinic, malic and tartaric) are weak acids, these were simply added to the $TlClO_4$, $Tl(ClO_4)_3$ and $HClO_4$ (3.50 M) and it was assumed the change in ionic strength caused by the addition was negligible compared to 3.68; *i.e.*, $\mu = {}^1/_2 [(Tl(I)) + 9(Tl(III)) + (Na^+) + (H^+) + (ClO_4^-)]$. $NaClO_4$ was used, when necessary, to maintain $\mu = 3.68$ M.

Results

Exchange between thallium(I) (0.0104 M) and thallium(III) (0.0100 M) in 3.50 M perchloric acid was found to proceed with a half-life of 205 hours, which agrees reasonably well with previous experiments.[3,6]

There was some problem in keeping the Tl^{204}-$(ClO_4)_3$ tracer. It was stored in 3.50 M perchloric acid, but was reduced slowly, so that apparent induced exchange rose from about 5%, when fresh tracer was used, to about 12% in two months. When enough reduction had occurred to give an apparent 12% induced exchange, a new tracer solution was prepared. Probably some trace of reducing agent in the distilled water or perchloric acid was responsible.

It was found that small amounts of acid [(acid)/(Tl^{III}) $\geq$ 0.5] caused reduction of thallium(III) when oxalic, malonic, malic and tartaric acids were added to the system. The reduction showed up not only in the MacKay plots log $(1 - F)$ *vs.* time, where F is the fraction exchanged, but also in the increasing weights of the Tl_2CrO_4 precipitates. As an example, the data for one reaction with

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