

Figure 1. Comparison of density data with those of Lewis.

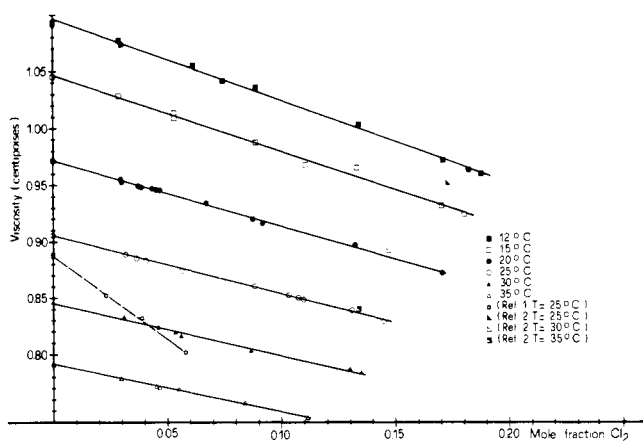


Figure 2. Comparison of viscosity data with those of Lewis and Mann

Table II. Empirical Equations from Linear Regression Model: $y = B_0 + B_1x$

$T, ^\circ\text{C}$	y	B_0	B_1	N	Student's t^2 value at 97.5%	ΔB_1
12	ρ	1.6093	-0.0422	10	2.306	± 0.0010
	ν	0.6816	-0.4333			± 0.0178
	μ	1.0968	-0.7221			± 0.0274
15	ρ	1.6036	-0.0429	9	2.365	± 0.0009
	ν	0.6529	-0.4029			± 0.0316
	μ	1.0469	-0.6710			± 0.0507
20	ρ	1.5940	-0.0440	13	2.201	± 0.0008
	ν	0.6097	-0.3501			± 0.0112
	μ	0.9718	-0.5824			± 0.0177
25	ρ	1.5845	-0.0451	11	2.262	± 0.0015
	ν	0.5711	-0.3111			± 0.0112
	μ	0.9049	-0.5164			± 0.0176
30	ρ	1.5747	-0.0461	8	2.447	± 0.0019
	ν	0.5364	-0.2805			± 0.0238
	μ	0.8446	-0.4643			± 0.0399
35	ρ	1.5649	-0.0471	7	2.571	± 0.0028
	ν	0.5056	-0.2603			± 0.0193
	μ	0.7911	-0.4300			± 0.0299

^a Key: x = molar fraction, N = number of experimental points, ρ = density (g/cm^3), ν = kinematic viscosity (cSt), μ = viscosity (cP), ΔB_1 = estimated error at 97.5% confidence interval.

from the liquid samples. The low values reported by Lewis are expected since in his experiments an atmosphere of chlorine was used above the liquid samples tested so that mass transfer would be taking place continuously during measurement.

Literature Cited

- (1) Lewis, J. R., *J. Am. Chem. Soc.*, **47**, 626 (1925).
- (2) Clegg G. T., Mann R., *Chem. Eng. J.*, **4**, 243 (1972).

Received for review April 7, 1977. Accepted September 7, 1977.

Solubility of Thallium(III) Sulfate in Aqueous Sulfuric Acid Solutions

Sanjay I. Amin

The Upjohn Company, Kalamazoo, Michigan 49001

The solubility of thallium(III) sulfate ($\text{HTl}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$) in aqueous sulfuric acid solutions (30–50% sulfuric acid by weight) was determined over the temperature range 0–25 °C. The data were correlated to show that the logarithm of solubility was a linear function of the absolute temperature and acid concentration. The correlation coefficient was found to be 0.9.

As a part of an ongoing study, it was necessary to know the solubility of thallium(III) sulfate in aqueous sulfuric acid solutions. There is no mention of this information in the literature, except for an article by Meyer (1). Meyer studied the solubility of $\text{HTl}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ at 25 °C and in 50–70 wt % sulfuric acid solutions, which was beyond our range of use. Meyer found that $\text{HTl}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ is hydrolyzed to Tl_2O_3 in sulfuric acid solutions having a concentration less than 10 wt %.

Table I. Solubility of Thallium(III) Sulfate [$\text{HTl}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$] in Aqueous Sulfuric Acid Solutions

Temp, °C	Wt % acid in water			
	30	40	50	70
0	12.37	0.76	0.288	
25	18.8	1.8	0.414 [0.1] ^a	0.34 ^a

^a Reference 1.

Experimental Section

Thallium(III) sulfate was made by reacting freshly prepared Tl_2O_3 (reaction between $\text{Tl}(\text{I})\text{SO}_4$ and H_2O_2 in basic media) with 50% sulfuric acid at 60–65 °C and cooling the solution to 5 °C on an ice bath. The precipitated flaky crystals of $\text{HTl}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ were filtered and stored wet in an airtight bottle, to prevent de-

composition. $\text{HTl}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ decomposes to $\text{Tl}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ if left exposed to air at room temperature (2).

Weighed amounts of $\text{HTl}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ and premixed sulfuric acid solution were taken in a closed Erlenmeyer flask and agitated with a magnetic stirrer in an oil bath ($\pm 0.5^\circ\text{C}$) for 2 h, until all the salt dissolved. The solution was slowly cooled and allowed to equilibrate (until no change in concentration in the supernatant was observed) at the temperature under consideration (25 or 0°C). An ice bath was used for regulating the lower temperature ($\pm 1^\circ\text{C}$). The amount of $\text{HTl}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ in the saturated solution was determined by an iodometric titration using KI and $\text{Na}_2\text{S}_2\text{O}_3$. Thallium salts are extremely toxic and must be handled very carefully.

Results and Discussion

The results are given in Table I. The solubility of $\text{HTl}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ is expressed as grams of the salt dissolved in 100 g of the premixed acid solution. Also presented in Table I are the data

of Meyer. The data were correlated by the following least-squares expression

$$\ln(s) = 13.02 - ((1314/T) + 0.19a)$$

with a correlation coefficient of 0.9. The solubility of $\text{HTl}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ seems to be very dependent on the acid concentration.

Glossary

- s* solubility, g of salt/100 g of acid solution
T absolute temperature, K
a acid concentration, %

Literature Cited

- (1) Meyer, J., *Recl. Trav. Chim Pays-Bas*, **42**, 614 (1923).
 (2) Tudo, T. et al., *C. R. Hebd. Seances Acad. Sci., Ser. C*, **283**, 739 (1976).

Received for review April 25, 1977. Accepted July 27, 1977.

Enthalpy of Solution of Dipotassium Orthophosphate at 25°C

Basil B. Luff* and Robert B. Reed

Division of Chemical Development, Tennessee Valley Authority, Muscle Shoals, Alabama 35660

Measurements were made of the enthalpy of solution at 25°C of dipotassium orthophosphate in water over the concentration range 0.06–2.33 *m*. Measurements also were made of the enthalpies of dilution to near infinite dilution of dipotassium orthophosphate solutions ranging from 3.12 to 9.99 *m*. The results were combined to determine the enthalpy of solution over the entire concentration range, and the partial molal heat contents were derived.

The integral enthalpy of solution of dipotassium orthophosphate was measured as part of a possible refinement of the entropies of aqueous phosphate ions. Relative partial molal quantities were calculated from the enthalpy of solution.

Materials and Apparatus

Reagent-grade dipotassium orthophosphate was recrystallized from distilled water. The crystals were filtered by suction on fritted glass and dried under vacuum desiccation over magnesium perchlorate for several days. Then, they were ground lightly to pass a 20-mesh screen and dried to constant weight under vacuum over magnesium perchlorate. Chemical analysis of the product showed it to contain 54.1% K_2O and 40.7% P_2O_5 (stoichiometric, 54.08% K_2O and 40.75% P_2O_5).

The dipotassium orthophosphate solutions were prepared by dissolving the recrystallized salt in distilled water. The concentrations of these solutions are shown in Table I.

The saturated solution was prepared by dissolving the recrystallized salt in distilled water at 70°C until no more would dissolve readily. The solution was allowed to cool to room temperature in a capped plastic bottle with periodic stirring. After several days the supernatant liquid was decanted from the rather large crystals that had developed. All solutions were stored in capped plastic bottles until used.

The solution calorimeter has been described (2). The initial bulk charge of liquid for each experimental run was weighed and placed in the calorimeter. Each addition to the bulk liquid was

Table I. Dipotassium Orthophosphate Solutions

Composition, %		$[\text{K}_2\text{HPO}_4], m$
K_2O	P_2O_5	
19.1	14.29	3.119
22.0	16.49	3.924
24.7	18.63	4.832
27.8	20.83	6.048
29.6	22.48	6.995
32.4	24.26	8.526
34.6	25.64	9.988 ^a

^a Saturated solution.

contained in a thin-walled glass bulb that was suspended from a glass rod inside the hollow stirrer shaft. The bulb was crushed against the bottom of the Dewar flask to start the solution period.

The calorimeter system was calibrated electrically immediately before and after each measurement. The platinum resistance thermometer was calibrated by the National Bureau of Standards. The Wenner potentiometer, Ayrton shunt, and standard resistors used in the energy measurements were calibrated against standard resistors and a potentiometer calibrated by the Redstone Arsenal, Huntsville, Ala., and traceable to the National Bureau of Standards. The defined calorie was taken as 4.1840 absolute J.

Conventional "normal" and "reverse" readings of the resistance of the platinum resistance thermometer on a Leeds and Northrup G-2 Mueller bridge were made during rating periods to establish heat-leak corrections. Only normal readings were taken during the solution period, and to these were applied both the usual bridge corrections and an adjustment to compensate for the absence of reverse measurements. The observed temperature rise was the difference between the temperatures at the end and at the beginning of the solution period as calculated from linear equations for the rating periods. The correction to the observed temperature rise for heat leak was calculated by in-