ences were important, temperatures were measured to four decimal places, but these were rounded to two decimal places in the final tabulation. The heat capacities below 10 K were read from a large scale plot of C_p/T against T^2 that extrapolated smoothly to 0 K. Observed molal heat capacities are shown in Table I.

Results and Discussion

Smoothed heat capacities and derived functions at round values of temperature are shown in Table II. The heat capacity curve had the normal sigmate shape and showed no thermal anomalies. The deviations of the observed heat capacity values from the smoothed curve are shown in the figure.

Literature Cited

(1) Lehr, J. R., Brown, E. H., Frazier, A. W., Smith, J. P., Thrasher, R. D., *Tenn. Val. Auth. Chem. Eng. Bull.*, **No. 6** (1967).

(2) Luff, B. B., Reed, R. B., Nash, R. H., *J. Chem. Eng. Data*, **21**, 418 (1976).

(3) Scott, R. B., Meyers, C. H., Rands, R. D., Jr., Brickwedde, F. G., Bekkedahl, N., *J. Res. Natl. Bur. Stand.*, **35**, 39-85 (1945).

(4) Wakefield, Z. T., Luff, B. B., Kohler, J. J., *J. Chem. Eng. Data*, **17**, 94 (1972).

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Standard Enthalpies of Formation of Monopotassium and Dipotassium Orthophosphate

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The standard enthalpies of formation of monopotassium orthophosphate, KH_2PO_4, and dipotassium orthophosphate, K_2HPO_4, are −376.1 and −425.4 kcal mol^{-1}, respectively. They were determined from the enthalpies of solution of KCl, $H_3PO_4 \cdot 13.88H_2O$, $H_3PO_4 \cdot 1.51H_2O$, KH_2PO_4, K_2HPO_4, and H_2O in 4 *m* HCl at 25 °C, the standard enthalpies of formation of KCl, aqueous HCl, and $H_3PO_4 \cdot 100H_2O$, and the enthalpies of dilution of H_3PO_4 solutions.

The enthalpies of formation of monopotassium and dipotassium orthophosphate are important quantities in the development of processes for the manufacture of potassium phosphate fertilizers. These values were determined from published enthalpies of formation of KCl, $H_3PO_4 \cdot 100H_2O$, and aqueous HCl, enthalpies of dilution of H_3PO_4, and the enthalpies of reaction

$$KCl + H_3PO_4 \cdot 13.88H_2O = KH_2PO_4 + HCl \cdot 13.88H_2O \quad (1)$$

and

$$K_2HPO_4 + H_3PO_4 \cdot 1.51H_2O = 2KH_2PO_4 + 1.51H_2O \quad (2)$$

at 25 °C.

Materials

Reagent monopotassium orthophosphate, KH_2PO_4 (gram formula weight = 136.0893), dipotassium orthophosphate, K_2HPO_4 (gram formula weight = 174.1834), and potassium chloride, KCl (gram formula weight = 74.555), were recrystallized from distilled water and dried by vacuum desiccation over $MgClO_4$. Chemical analyses of the products along with the stoichiometric values are listed in Table I. Recrystallized reagent phosphoric acid was diluted to yield $H_3PO_4 \cdot 1.51H_2O$ (gram formula weight = 125.2158, 56.68% P_2O_5 by chemical analysis) and $H_3PO_4 \cdot 13.88H_2O$ (gram formula weight = 348.0741, 20.39% P_2O_5 by chemical analysis). The calorimetric solvent was prepared by diluting reagent-grade hydrochloric acid with distilled water to 4.001 *m* (12.73%) HCl as determined by alkalimetric titration.

Table I. Chemical Analyses of Salts Used in Enthalpy of Solution Measurements

	Composition, %					
	P_2O_5		K_2O		Cl	
Salt	Anal.	Stoich	Anal.	Stoich	Anal.	Stoich
KH_2PO_4	52.1	52.15	34.6	34.61		
K_2HPO_4	40.7	40.75	54.1	54.08		
KCl			63.4	63.18	47.5	47.55

Table II. Enthalpy of Solution of $H_3PO_4 \cdot 13.88H_2O$ in 4.001 *m* HCl at 25 °C

Sample wt, g	Cor temp rise, °C	Enthalpy of soln, cal/sample	ΔH_3,[a] cal/mol
21.148 46	−0.0264	22.55	371
21.578 10	−0.0270	23.04	372
21.854 01	−0.0281	23.93	381
21.883 38	−0.0278	23.71	377
22.287 33	−0.0284	24.24	379

[a] $\Delta H_3 = 199 + 8.14w$, std dev = 3, $w = 21.75026$, $\Delta H_3 = 376$.

Calorimeter

The solution calorimeter, the method of measurement, and the corrections applied have been described (*2*), with the exception that the Wenner potentiometer and Aryton shunt were replaced by a digital voltmeter (Hewlett-Packard, Model 3490A) that measured the voltage drop directly across the calorimeter heater as well as across a standard resistor in series with the heater. The defined thermochemical calorie (1 cal = 4.1840 absolute J) was used to convert electrical energy to thermal energy.

Procedure

The enthalpy of reaction 1 was determined by the scheme

$$\text{ampule } H_3PO_4 \cdot 13.88H_2O + \text{solvent} = \text{solution D} \quad (3)$$

$$\text{ampule KCl} + \text{solution D} = \text{solution E} \quad (4)$$

$$\text{ampule } HCl \cdot 13.88H_2O + \text{solvent} = \text{solution F} \quad (5)$$

$$\text{ampule } KH_2PO_4 + \text{solution F} = \text{solution E} \quad (6)$$

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and

$$\Delta H_1 = \Delta H_3 + \Delta H_4 - \Delta H_5 - \Delta H_6 \qquad (7)$$

where ΔH_1 is the enthalpy of reaction 1 in calories and ΔH_3, ΔH_4, ΔH_5, and ΔH_6 are the enthalpies of reactions 3, 4, 5, and 6, respectively, in cal/mol of the materials in the ampules.

Bulb volume limited the amount of $H_3PO_4 \cdot 13.88H_2O$ and thus, by stoichiometry, the amounts of other materials in reaction 1. The concentration of H_3PO_4 chosen was such that the last term of reaction 1 would be exactly the same concentration as the calorimetric solvent, and ΔH_5 would be zero. Sample weights were corrected for buoyancy.

The observed enthalpies of solution of $H_3PO_4 \cdot 13.88H_2O$ in 4.001 *m* HCl (ΔH_3), of KCl in 4.001 *m* HCl to which the stoichiometric amount of $H_3PO_4 \cdot 13.88H_2O$ had been added (ΔH_4), and of KH_2PO_4 in 4.001 *m* HCl to which the stoichiometric amount of $HCl \cdot 13.88H_2O$ had been added (ΔH_6) are listed in Tables II, III, and IV, respectively. Straight line equations of the enthalpies of solution as a function of sample weight, *w*, were fitted to the observed values, and these equations were solved where *w* was the average weight of $H_3PO_4 \cdot 13.88H_2O$ or the stoichiometric amount of KCl or KH_2PO_4 corresponding to that weight. The equations along with the standard deviations and the values of ΔH_3, ΔH_4, and ΔH_6 for the specified values of *w* also are listed in the tables.

Substitution in eq 7 of the enthalpies of solution for the stoichiometric amounts of the compounds gives −1634 cal for ΔH_1.

The enthalpy of reaction 2 was determined by the scheme

$$\text{ampule } H_3PO_4 \cdot 1.51H_2O + \text{solvent} = \text{solution A} \qquad (8)$$

$$\text{ampule } K_2HPO_4 + \text{solution A} = \text{solution B} \qquad (9)$$

$$\text{ampule } H_2O + \text{solvent} = \text{solution C} \qquad (10)$$

$$\text{ampule } KH_2PO_4 + \text{solution C} = \text{solution B} \qquad (11)$$

and

$$\Delta H_2 = \Delta H_8 + \Delta H_9 - 1.51(\Delta H_{10}) - 2(\Delta H_{11}) \qquad (12)$$

where ΔH_2 is the enthalpy of reaction 2 in calories and ΔH_8, ΔH_9, ΔH_{10}, and ΔH_{11} are the enthalpies of reactions 8, 9, 10, and 11, respectively, in cal/mol of the materials in the ampules.

Temperature changes during dissolution were arbitrarily limited to 1 °C, which determined the sample size of monopotassium orthophosphate and thus, by stoichiometry, the amounts of other materials in reaction 2.

The observed enthalpies of solution of $H_3PO_4 \cdot 1.51H_2O$ in 4.001 *m* HCl (ΔH_8), of K_2HPO_4 in 4.001 *m* HCl to which the stoichiometric amount of $H_3PO_4 \cdot 1.51H_2O$ had been added (ΔH_9), and of KH_2PO_4 in 4.001 *m* HCl to which the stoichiometric amount of H_2O had been added (ΔH_{11}) are listed in Tables V, VI, and VII, respectively. Straight line equations of the enthalpies of solution as a function of sample weight, *w*, were fitted to the observed values, and these equations were solved where *w* was the average weight of KH_2PO_4 or the stoichiometric amount of $H_3PO_4 \cdot 1.51H_2O$ or K_2HPO_4 corresponding to that weight. The equations along with the standard deviations and the values of ΔH_8, ΔH_9, and ΔH_{11} for the specified values of *w* also are listed in the tables.

Table III. Enthalpy of Solution of KCl in 4.001 *m* HCl + Stoichiometric $H_3PO_4 \cdot 13.88H_2O$ at 25 °C

Sample wt, g	Cor temp rise, °C	Enthalpy of soln, cal/sample	ΔH_4,[a] cal/mol
3.993 65	−0.2830	231.35	4319
4.308 57	−0.3054	249.78	4322
4.907 85	−0.3468	284.50	4322
5.208 38	−0.3665	301.02	4309
5.516 19	−0.3878	318.90	4310

[a] $\Delta H_4 = 4352 - 7.49w$, std dev = 5, $w = 4.65816$, $\Delta H_4 = 4317$.

Table IV. Enthalpy of Solution of KH_2PO_4 in 4.001 *m* HCl + Stoichiometric $HCl \cdot 13.88H_2O$ at 25 °C

Sample wt, g	Cor temp rise, °C	Enthalpy of soln, cal/sample	ΔH_6,[a] cal/mol
7.482 99	−0.4262	348.30	6334
7.910 92	−0.4505	367.73	6326
8.322 62	−0.4742	387.06	6329
8.709 93	−0.4956	404.92	6327
9.510 41	−0.5385	441.67	6320

[a] $\Delta H_6 = 6376 - 5.85w$, std dev = 3, $w = 8.50279$, $\Delta H_6 = 6327$.

Table V. Enthalpy of Solution of $H_3PO_4 \cdot 1.51H_2O$ in 4.001 *m* HCl at 25 °C

Sample wt, g	Cor temp rise, °C	−Enthalpy of soln, cal/sample	$-\Delta H_8$,[a] cal/mol
8.190 28	0.0986	77.84	1190
8.379 04	0.1007	79.50	1188
8.590 58	0.1038	82.03	1196
8.819 13	0.1064	84.18	1195
9.011 75	0.1090	86.31	1199

[a] $\Delta H_8 = -1088 - 12.26w$, std dev = 2, $w = 8.50560$, $\Delta H_8 = -1192$.

Table VI. Enthalpy of Solution of K_2HPO_4 in 4.001 *m* HCl + Stoichiometric $H_3PO_4 \cdot 1.51H_2O$ at 25 °C

Sample wt, g	Cor temp rise, °C	−Enthalpy of soln, cal/sample	$-\Delta H_9$,[a] cal/mol
11.448 01	0.5196	416.40	6336
11.632 45	0.5277	423.22	6337
12.024 96	0.5452	437.41	6336
12.214 91	0.5541	444.52	6339
12.430 61	0.5644	452.65	6343

[a] $\Delta H_9 = -6270 - 5.71w$, std dev = 2, $w = 11.83288$, $\Delta H_9 = -6337$.

Table VII. Enthalpy of Solution of KH_2PO_4 in 4.001 *m* HCl + Stoichiometric H_2O at 25 °C

Sample wt, g	Solvent wt, g	Cor temp rise, °C	Enthalpy of soln, cal/sample	ΔH_{11},[a] cal/mol
18.459 59	901.7175	−1.0582	850.93	6273
18.470 25	901.1980	−1.0615	851.71	6275
18.487 27	901.6915	−1.0627	852.79	6278
18.499 04	901.6184	−1.0605	852.55	6272
18.533 98	901.0869	−1.0629	854.41	6274

[a] $\Delta H_{11} = 6555 - 15.16w$, std dev = 3, $w = 18.49003$, $\Delta H_{11} = 6274$.

The average weights of KH_2PO_4 (18.4900 g) and of 4.001 *m* HCl (901.4625 g) in Table VII were used to calculate the stoichiometric amount of H_2O (1.8484 g) in reaction 2 and the change in concentration of HCl brought about by the addition of this amount of H_2O. The enthalpy of solution of 1.8484 g (0.10260 mol) of H_2O, ΔH_{11}, in 901.4625 g (3.1473 mol) of 4.001 *m* HCl ($HCl \cdot 13.88H_2O$)

$$3.1473(HCl \cdot 13.88H_2O) + 0.10260H_2O = 3.1473(HCl \cdot 13.91H_2O) \qquad (13)$$

calculated from an equation that fitted the published enthalpies of formation of HCl solutions (*4*) with a standard deviation of 3 cal/mol is −61 cal/mol of H_2O.

Substitution in eq 12 of the enthalpies of solution for the stoichiometric amounts of the compounds gives −19 985 cal for ΔH_2.

The standard enthalpy of formation of KCl(c) (*3*) is −104.175 kcal/mol. The standard enthalpy of formation of $HCl\cdot 13.88H_2O$ calculated from the same data used in solving eq 13 is −13.899 kcal/mol. The standard enthalpy of formation of $H_3PO_4\cdot 100H_2O$ (*5*) was combined with the enthalpies of solution of H_3PO_4 solutions (*1*) to calculate the standard enthalpies of formation of $H_3PO_4\cdot 1.51H_2O$ and $H_3PO_4\cdot 13.88H_2O$ as −306.8 and −309.2 kcal/mol, respectively. Substituting these enthalpies of formation and the enthalpies of reactions 1 and 2 in the equations

$$\Delta H_f^\circ(KH_2PO_4) = \Delta H_1 + \Delta H_f^\circ(KCl) + \Delta H_f^\circ(H_3PO_4\cdot 13.88H_2O) - \Delta H_f^\circ(HCl\cdot 13.88H_2O) \quad (14)$$

and

$$\Delta H_f^\circ(K_2HPO_4) = 2(\Delta H_f^\circ(KH_2PO_4)) - \Delta H_f^\circ(H_3PO_4\cdot 1.51H_2O) - \Delta H_2 \quad (15)$$

gives −376.1 kcal/mol as the standard enthalpy of formation of KH_2PO_4 and −425.4 kcal/mol as the standard enthalpy of formation of K_2HPO_4.

Literature Cited

(1) Egan, E. P., Jr., Luff, B. B, *J. Phys. Chem.*, **65**, 523 (1961).
(2) Luff, B. B., Reed, R. B., *J. Chem. Eng. Data*, **20**, 420 (1975).
(3) *Natl. Bur. Stand.* (*U.S.*), *Circ.* **No. 500** (1952).
(4) *Natl. Bur. Stand.* (*U.S.*), *Tech. Note*, **No. 270-3** (1968).
(5) Schumm, R. H., Prosen, E. J., Wagman, D. D., *J. Res. Natl. Bur. Stand., Sect. C*, **78**, 375 (1974).

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Thermodynamic Properties of Toluene–1,1,2,2-Tetrachloroethane

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Data on heats of mixing at 298.15 and 308.15 K, vapor-liquid equilibria, latent heats of vaporization at 686 mmHg, and vapor pressures for the system toluene–1,1,2,2-tetrachloroethane are presented. The effect of alkyl substitution on heats of mixing is discussed.

Thermodynamic properties of liquid mixtures have an important place in industrial and academic work. Aromatic hydrocarbons and chlorinated hydrocarbons are one such class of important substances. This laboratory has embarked on a program of collecting experimental data on vapor pressure, vapor–liquid equilibria, heats of mixing, and latent heats of vaporization of aromatic hydrocarbon–chloroethane mixtures. The data for toluene–1,2-dichloroethane have been reported (*12*). This paper presents the data for toluene–1,1,2,2-tetrachloroethane.

Materials Used and Purification

Analar toluene supplied by British Drug House, Bombay, and laboratory grade 1,1,2,2-tetrachloroethane supplied by BDH Chemicals, England, were purified by the methods described by Weissburger (*14*) and Riddick and Bunger (*10*). The refractive index and density of the chemicals used along with literature values (*4*) are reported in Table I. Vapor-phase chromatographs were obtained for the liquid using the AIMIL-NCL dual column gas chromatograph using silicone gum rubber S.E. 30 as column material. A single peak was obtained for both the liquids. Because of the excellent agreement of refractive index and density and the vapor phase chromatograph, the purity of the substances can be taken as 99.9 mol %.

Vapor Pressure Data

The present data for 1,1,2,2-tetrachloroethane reported in Table II fitted the equation

$$\log P_2 = 7.88347 - (2096.8606/T) \quad (0.25, 0.8) \quad (1)$$

The values in parentheses denote the percent average absolute deviation and maximum deviation, respectively. The vapor pressure at the normal boiling point calculated from eq 1 deviated from the data reported by Driesbach (*4*) by 0.6%. The present data compare with the data of Nelson (*8*) and Matthews (*7*) with average absolute deviations of 2.5 and 3%, respectively. The rather large deviations may be due to the purity of the chemicals.

The experimental vapor pressures of toluene agreed with those calculated from the Antoine equation reported in the A.P.I. Tables (*11*) with an average absolute deviation of 0.1% and a maximum deviation of 0.3%.

Heats of Mixing

A new calorimeter with negligible vapor space described elsewhere (*13*) was used in the present work. The data on heats of mixing at 298.15 and 308.15 K given in Table III were fitted to eq 2 and 3, respectively.

$$H^E/x_1x_2 = -6680.2 + 5115.5(2x_1 - 1) - 2155.8(2x_1 - 1)^2 - 2555.2(2x_1 - 1)^3 + 3917.7(2x_1 - 1)^4 \quad (0.8, 2.2) \quad (2)$$

$$H^E/x_1x_2 = -6194.5 + 6142.3(2x_1 - 1) - 2347.2(2x_1 - 1)^2 - 5349.9(2x_1 - 1)^3 - 5744.4(2x_1 - 1)^4 + 43.3(2x_1 - 1)^5 \quad (1.0, 3.0) \quad (3)$$

Effect of Alkyl Substitution on Heats of Mixing

The heat of mixing of benzene–1,1,2,2-tetrachloroethane at 308.15 K and 0.5 mole fraction has been reported (*9*) as −570 J mol^{-1}. The value under similar conditions for toluene–1,1,2,2-tetrachloroethane is −1550 J mol^{-1}. These systems are similar to benzene and toluene with carbon tetrachloride. Here, alkyl substitution to benzene increases exothermicity, with the aromatic group acting as an electron donor. It is known that on

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