

X_{AO}	mole fraction of component A at interface
X_{AL}	mole fraction of component A at end of tube
X_2, X_3	mole fraction of components 2 and 3, in eq 4 and 5
X_2^i	ideal solubility, mole fraction
Z, Z_k	volume fraction, volume fraction of k th component
α_{solvent}	hydrogen bonding factor, dimensionless ($= x/x_2^i$)
η, η_M, η_2	viscosity, cP
μ_B	viscosity of component B, cP
ξ_A	geometric parameter component A, dimensionless
ρ	average total mass concentration, g/cm ³
ρ_A	mass concentration component A, g/cm ³
σ	collision diameter, Å
ω_{AO}	mass fraction component A at interface
ω_{AL}	mass fraction component A at end of tube

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Standard Enthalpy of Formation of Tetrapotassium Pyrophosphate

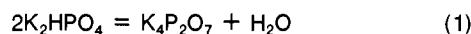
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The standard enthalpy of formation of tetrapotassium pyrophosphate is $-773.3 \text{ kcal mol}^{-1}$; it was determined from the enthalpies of solution of K_2HPO_4 , H_2O , and $\text{K}_4\text{P}_2\text{O}_7$ in 10 *m* HCl at 40 °C and from the heat capacities of these compounds and the standard enthalpies of formation of K_2HPO_4 and H_2O .

Introduction

The enthalpy of formation of tetrapotassium pyrophosphate is an important quantity in the development of processes for the manufacture of potassium phosphate fertilizers. It was determined from the enthalpies of formation of K_2HPO_4 and H_2O and the enthalpy of the reaction



at 25 °C.

Materials. Reagent-grade dipotassium orthophosphate, K_2HPO_4 (gram formula weight = 174.1834), was recrystallized from distilled water and dried by vacuum desiccation over MgClO_4 . Chemical analysis showed it to contain 40.7% P_2O_5 and 54.1% K_2O (stoichiometry: 40.75% P_2O_5 and 54.08% K_2O).

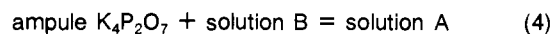
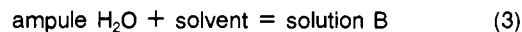
Tetrapotassium pyrophosphate, $\text{K}_4\text{P}_2\text{O}_7$ (gram formula weight = 330.3514), was prepared by heating reagent-grade dipotassium orthophosphate in a platinum dish at 600 °C for 21 h and allowing the product to cool to room temperature in a desiccator over MgClO_4 . Chemical analysis showed the material to contain 57.1% K_2O and 42.98% P_2O_5 (stoichiometry: 57.03% K_2O and 42.97% P_2O_5). None of the P_2O_5 was in the

ortho form. The calorimetric solvent was prepared by diluting reagent-grade hydrochloric acid with water to 9.93 *m* HCl as determined by alkalimetric titration.

Calorimeter. The solution calorimeter, the method of measurement, and the corrections applied have been described (1, 3). The defined thermochemical calorie (1 cal = 4.1840 absolute J) was used to convert electrical energy to thermal energy.

Procedure. In a preliminary run in which samples of the solution taken at 10-min intervals were analyzed for total and orthophosphate P_2O_5 , the results showed that 8.5 g of $\text{K}_4\text{P}_2\text{O}_7$ was completely hydrolyzed in 30 min at 40 °C in 850 mL of 10 *m* HCl.

The enthalpy of reaction of eq 1 at 40 °C was determined by the scheme



and

$$\Delta H_1 = 2(\Delta H_2) - \Delta H_3 - \Delta H_4 \quad (5)$$

where ΔH_1 is the enthalpy of reaction 1 in calories and ΔH_2 , ΔH_3 , and ΔH_4 are the enthalpies of reactions 2, 3, and 4, 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 tetrapotassium pyrophosphate and thus, by stoichiometry, the sample size of dipotassium orthophosphate. The stoichiometric amount of water

Table I. Enthalpy of Solution of K_2HPO_4 in 9.93 *m* HCl at 40 °C

sample wt, g	cor temp rise, °C	-enthalpy of soln, cal/sample	$-\Delta H_2^a$, cal/mol
8.442 60	0.6527	463.8	9570
8.647 70	0.6690	475.1	9570
8.828 08	0.6820	484.5	9560
9.024 76	0.6969	496.3	9578
9.224 17	0.7128	506.7	9568

^a $\Delta H_2 = -9550 - 2.13w$, std dev = 7, $w = 8.904\ 98$, $\Delta H_2 = -9569$ cal/mol.

Table II. Enthalpy of Solution of H_2O in 9.93 *m* HCl at 40 °C

sample wt, g	cor temp rise, °C	-enthalpy of soln, cal/sample	$-\Delta H_3^a$, cal/mol
4.944 40	0.1768	125.4	457.0
7.965 80	0.2825	201.6	456.0
10.999 52	0.3882	278.6	456.3
14.008 15	0.4898	352.9	453.8
17.043 63	0.5913	428.3	452.7

^a $\Delta H_3 = -459.1 + 0.357w$, std dev = 0.7, $w = 0.460\ 48$, $\Delta H_3 = -458.9$ cal/mol.

Table III. Enthalpy of Solution of $K_4P_2O_7$ in 9.93 *m* HCl + Stoichiometric H_2O at 40 °C

sample wt, g	cor temp rise, °C	-enthalpy of soln, cal/sample	$-\Delta H_4^a$, cal/mol
8.405 38	1.0012	711.94	27 981
8.410 33	0.9991	710.97	27 926
8.444 30	1.0059	716.18	28 018
8.445 04	1.0066	715.24	27 979
8.517 45	1.0134	721.13	27 969

^a $\Delta H_4 = -27974 - 0.110w$, std dev = 38, $w = 8.444\ 50$, $\Delta H_4 = -27\ 975$ cal/mol.

was too small to determine accurately its enthalpy of solution so the sample size of water was varied over a range several times greater than the stoichiometric amount.

Results of determinations of ΔH_2 , ΔH_3 , and ΔH_4 are listed in Tables I, II, and III, respectively. Straight line equations of the enthalpies of solution as a function of sample weight, w ,

were fitted to the observed values by the "least-squares" method. These equations were solved where w was the average weight of $K_4P_2O_7$ or the stoichiometric amount of H_2O or K_2HPO_4 corresponding to that weight. The equations along with the standard deviations and the values of ΔH_2 , ΔH_3 , and ΔH_4 for the specified values of w also are listed in Tables I, II, and III. Substitution of these calculated values of the enthalpies of solution in eq 5 gives 9296 ± 39 cal (standard deviation) for the enthalpy of reaction 1 at 40 °C. This value was adjusted by -154 ± 2 cal (standard deviation) to give 9142 ± 39 cal (standard deviation) for the enthalpy of reaction 1 at 25 °C according to the equation

$$\Delta H_1(25\ ^\circ\text{C}) = \Delta H_1(40\ ^\circ\text{C}) + \int_{40\ ^\circ\text{C}}^{25\ ^\circ\text{C}} \Delta C_p dT \quad (6)$$

where ΔC_p is the difference in heat capacity between the products and the reactants, and T is the temperature in °C. The heat capacity equations were derived from the data of Osborne et al. (5) for water and the data of Luff and Reed (2, 4) for K_2HPO_4 and $K_4P_2O_7$.

The standard enthalpy of formation of $H_2O(l)$ (6) is -68.315 kcal/mol and the standard enthalpy of formation of $K_2HPO_4(c)$ (3) is -425.4 kcal/mol. Substituting these enthalpies of formation and the enthalpy of reaction 1 at 25 °C in the equation

$$\Delta H_f^\circ(K_4P_2O_7) = 2\Delta H_f^\circ(K_2HPO_4) - \Delta H_f^\circ(H_2O) + \Delta H_1 \quad (7)$$

gives -773.3 kcal/mol as the standard enthalpy of formation of $K_4P_2O_7$.

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Low-Temperature Heat Capacity and Entropy of Tetrapotassium Pyrophosphate

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In a continuing program of measurement of thermochemical properties of materials of interest in fertilizer technology, the heat capacity of tetrapotassium pyrophosphate, $K_4P_2O_7$, was measured by adiabatic calorimetry over the temperature range 10–317 K. Related thermodynamic properties were derived.

Materials and Apparatus

Tetrapotassium pyrophosphate was prepared by heating reagent-grade dipotassium orthophosphate in a platinum dish

at 600 °C for 21 h and allowing it to cool in a desiccator over $MgClO_4$. Chemical analysis showed the material to contain 57.1% K_2O and 42.98% P_2O_5 (stoichiometry: 57.0% K_2O and 42.97% P_2O_5). None of the P_2O_5 was in the ortho form. The calorimeter was charged with 88.3417 g or 0.267589 mol. The weight was corrected for buoyancy in air on the basis of a density of $2.61\ \text{g/cm}^3$ (7), and the gram formula weight was taken as 330.3514. Its heat capacity ranged from 46% of the total at 10 K to 60% at 300 K. Air in the calorimeter was removed and replaced with the same mass of helium used in measurements on the empty calorimeter; the helium facilitated heat transfer and thermal equilibrium.