Electrolytic Conductivity of Aqueous Solutions of Potassium and Sodium Phosphates to 325 °C

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The electrolytic conductivities of aqueous solutions of potassium and sodium phosphates were measured over the temperature range 25–325 °C for phosphate concentrations of 0.0005–0.0100 M. The salts investigated were potassium dihydrogen phosphate, potassium monohydrogen phosphate, and potassium phosphate, and the corresponding sodium salts. At all temperatures and concentrations investigated, the conductivities of the potassium salts were higher than those of the sodium salts.

Introduction

The use of phosphate salts in boiler water to maintain pH and to prevent corrosion has prompted many studies on the high-temperature/pressure properties of aqueous solutions of these materials (*1–4*). Most of these studies deal with the equilibrium properties of phosphate solutions, such as dissociation (*1, 3*) and solubility (*2*). For high temperatures along the saturation line, there are few data for transport properties (*5–7*), and those are reported only for phosphoric acid rather than for the alkali-metal salts. Since the electrolytic conductivity of dilute solutions of phosphate salts is important in determining the ionic condition of boiler water at the operating temperature of the steam generators, there is a need for accurate values for molar conductances. It was toward this end that conductance measurements were performed for aqueous potassium and sodium phosphate salt solutions in the concentration range 0.0005–0.0100 M at 25–325 °C.

Experimental Section

Apparatus. Solutions to be measured were held in a 0.5-L-capacity Inconel pressure vessel (Parr Instrument Co.) equipped with a magnetic overhead drive stirrer, a 20-MPa pressure gauge, a resistance temperature device (RTD) (Omega 499, 100-Ω Pt, α = 0.003 92) placed 4–5 mm adjacent to a conductance electrode (see below), and a J-type thermocouple connected to the temperature controller (Parr Model 4842 with 1 °C resolution and ±2 °C precision) for the 0.9-kW heater surrounding the vessel. The accuracy of the RTD meter (Omega Model 199B) was close to ±0.05%. The precision of the temperature measurements at the RTD with this combination was about ±0.2 °C over the range of interest. Tolerances for accuracy of the RTD elements resulted in uncertainties of ±0.4, ±0.5, and ±0.8 °C at 100, 200, and 300 °C, respectively.

A parallel plate design was used for the conductance electrode assembly. The plates (25 mm × 12.5 mm) were cut from 99.998% platinum with a thickness of 0.1 mm and spaced about 2 mm apart. The leads were drawn from 90% platinum/10% iridium into 0.508-mm-diameter wire and brazed to the plates with 99.998% gold. (All metals were obtained from Johnson Matthey.) The leads were sealed into a standard 1/8-in. compression fitting (Conax) with Lava (soapstone) packing wrapped in poly(tetrafluoroethylene) film. The plate housing was cut from a preformed 20-mm-diameter × 30-mm-height crucible with a 2-mm wall thickness of high-density (5200 kg·m⁻³) 99% pure zirconia stabilized with 6% calcia and 3% hafnia (Frialit-Degussit ZR23). This material was chosen because of its virtual lack of dimensional hysteresis

during heating/cooling cycles and because its thermal expansion coefficient is within 10% of that of platinum. Insulating spacers for the leads were fabricated from 10-mm-diameter disks (3 mm thick) of the same material. Before machining, the crucible and disks were cleaned by immersion in demineralized water and heating to 300 °C in a 1-L pressure vessel for 2–3 h. After assembly, the plates were platinized with 10% aqueous chloroplatinic acid stabilized with 0.1% lead acetate. The electrode was cleaned by heating to 325 °C for 1 h in demineralized water following platinization.

The frequency dependence of the electrode response was evaluated at 25, 125, 200, and 300 °C for 0.08, 1, and 3 kHz by measuring the conductance of a 0.004 M potassium chloride solution (at 25 °C) with a variable-frequency conductance analyzer (Orion Model 101). The weak frequency dependence, which spanned 0.9%/kHz at 25 °C to 0.09%/kHz at 300 °C, indicated that the electrode pair did not become significantly polarized during measurements over the temperature range. A conductance meter (YSI Model 34) with an oscillator frequency of 1 kHz was used for the remainder of the measurements (±0.4% precision at midscale). The potential across the electrode plates was also measured with a high input impedance digital multimeter (Keithley Model 192). Values for the electromotive force (emf) ranged from 0.5 mV at 25 °C to 2.5 mV at 300 °C. The electrode was calibrated over the temperature range 25–325 °C using 0.01000 M (at 25 °C) potassium chloride solutions (*8*). The cell constant (precise to within ±0.5%) exhibited a smooth temperature dependence with an average linear thermal coefficient of 0.0098%/°C (with a value of 0.0370 at 25 °C). The cell was periodically recalibrated between measurements, and only slight thermal hysteresis was observed (<0.2% after three heating/cooling cycles over 25–325 °C). The uncertainties in the conductivity measurements were estimated to be ±1–2% over the temperature range on the basis of the reported accuracies for the conductance values (*8*) which were used for electrode calibration.

Materials. Potassium chloride having a purity of 99.999% and phosphoric acid with 99.99% purity as 85% w/w (ACS reagent) were obtained from Aldrich Chemical Co. Sodium hydroxide and potassium hydroxide were obtained as pre-standardized 1.002–0.998 M solutions (Fisher certified reagents) from Fisher Scientific. Demineralized water (Barnstead NANOPure) had a resistance of >18 MΩ.

Conductance Experiments. Solutions of the salts were prepared at room temperature (ca. 25 °C) under nitrogen in a glovebox by titration of dilutions of phosphoric acid with aqueous sodium or potassium hydroxide solutions which had been prestandardized. Five concentrations in the range 0.0005–0.0100 M (corrected to 25 °C) were prepared for each

Table 1. Conductivity κ of 0.002 M (at 25 °C) Na$_2$HPO$_4$ upon Heating and Cooling

	$\kappa/(\mu S \cdot cm^{-1})$			$\kappa/(\mu S \cdot cm^{-1})$	
$t/°C^a$	heating	cooling	$t/°C^a$	heating	cooling
25	412 ± 10[b]	395 ± 10	200	2326 ± 35	2292 ± 26
75	947 ± 11	897 ± 18	250	2682 ± 34	2680 ± 28
100	1238 ± 13	1212 ± 20	300	2667 ± 85	2742 ± 25
150	1824 ± 13	1801 ± 10	325	2486 ± 68	2474 ± 75

[a] See text for experimental uncertainties in the temperature.
[b] Precision based on the results for three experimental runs.

of the three sodium and three potassium salts. The uncertainties in the concentrations were about ±0.2%, on the basis of the standardized hydroxide solutions. Measured pH values for the solutions generally agreed to within 0.05 pH unit with values calculated from a knowledge of the dissociation constants.

Temperatures chosen for the potassium and sodium monohydrogen and dihydrogen phosphate studies were 25, 100, 150, 200, 250, 300, and 325 °C. A change in experimental design resulted in selecting temperatures of 25, 100, 150, 200, 225, 245, 265, 285, 305, and 325 °C for the measurements on the trisodium and tripotassium salts. This change in temperature interval permitted better interpolation of the conductivity values in the temperature range 200–300 °C for these salts.

The conductance experiments were performed using a technique similar to that of Noyes (5). Conductance measurements were made for a single concentration as a function of temperature. The pressure vessel was charged with the solution of interest under nitrogen at room temperature and heated. Conductance values were recorded as each temperature was attained during continued heating. Heating was relatively rapid and 325 °C was attained within 40–50 min from approximately 25 °C for a vessel charged with about 0.250 L of solution. The high heating rate was used so that the experiments could be performed quickly to mitigate the effects of potential corrosion of the vessel and possible decomposition of the solutes. Although the contents of the vessel were stirred during heating, there remained the question of whether thermal equilibrium was attained between the conductance electrode and the RTD as the data were recorded.

To aid in assessing the quality of the data obtained using this method, conductance measurements were made for a solution having a representative "midrange" concentration during vessel cooling. Vessel cooling generally required several hours after termination of the experiment (at 325 °C), so that thermal equilibrium at any given temperature of interest was more likely to be attained than upon heating. Three runs with heating and cooling cycles were performed with 0.002 M solutions (at 25 °C) of disodium hydrogen phosphate. The results are reported in Table 1. Agreement of the conductivity values is good among the three runs (2–3%) and between the heating and cooling cycles for each run (2–5%). The results of these experiments provide a good estimate of the precision involved for the technique.

The accuracy of the experimental technique was evaluated by determining limiting molar conductances for potassium chloride at 25, 100, 200, and 300 °C by extrapolation of plots of the molar conductance for ca. 0.0001–0.010 M solutions to zero concentration. The values obtained are in agreement with accepted values (9) to within 0.7, 0.9, 0.5, and 0.7%, respectively.

Results

The results of the conductance experiments, reported as conductivities, κ, for the potassium and sodium phosphate

Table 2. Conductivity κ of Aqueous Solutions of KH$_2$PO$_4$ and NaH$_2$PO$_4$

	$\kappa/(\mu S \cdot cm^{-1})$					
C/M^a	KH$_2$PO$_4$	NaH$_2$PO$_4$	KH$_2$PO$_4$	NaH$_2$PO$_4$	KH$_2$PO$_4$	NaH$_2$PO$_4$
	$t = 25$ °C		$t = 100$ °C		$t = 150$ °C	
0.0005	60.4	45.5	155	135	214	194
0.0010	118	86.6	318	263	444	378
0.0020	221	163	597	505	823	724
0.0050	508	400	1345	1211	1873	1757
0.0100	971	792	2575	2270	3581	3312
	$t = 200$ °C		$t = 250$ °C		$t = 300$ °C	
0.0005	275	271	336	302	363	306
0.0010	549	489	659	604	692	663
0.0020	1033	951	1234	1152	1324	1189
0.0050	2366	2269	2828	2741	2984	2913
0.0100	4414	4235	5094	5039	5225	4874
	$t = 325$ °C					
0.0005	333	314				
0.0010	665	623				
0.0020	1245	1165				
0.0050	2759	2743				
0.0100	4993	4523				

[a] Molar concentration at 25 °C. Concentrations of potassium and sodium salt solutions are identical to within ±0.2%. For estimates of other uncertainties see Table 1.

Table 3. Conductivity κ of Aqueous Solutions of K$_2$HPO$_4$ and Na$_2$HPO$_4$

	$\kappa/(\mu S \cdot cm^{-1})$					
C/M^a	K$_2$HPO$_4$	Na$_2$HPO$_4$	K$_2$HPO$_4$	Na$_2$HPO$_4$	K$_2$HPO$_4$	Na$_2$HPO$_4$
	$t = 25$ °C		$t = 100$ °C		$t = 150$ °C	
0.0005	127	110	371	338	536	531
0.0010	241	224	690	658	1010	961
0.0020	481	411	1339	1249	1905	1807
0.0050	1109	1090	2967	2923	4304	4144
0.0100	2080	1821	5624	5274	7673	7323
	$t = 200$ °C		$t = 250$ °C		$t = 300$ °C	
0.0005	697	689	831	818	867	851
0.0010	1288	1270	1527	1451	1612	1606
0.0020	2422	2344	2919	2804	2995	2885
0.0050	5390	5193	6202	5782	6186	5511
0.0100	9117	8866	10317	9634	10435	9297
	$t = 325$ °C					
0.0005	809	773				
0.0010	1531	1441				
0.0020	2746	2469				
0.0050	5652	4826				
0.0100	9113	7766				

[a] Molar concentration at 25 °C. Concentrations of potassium and sodium salt solutions are identical to within 0.2%. For estimates of other uncertainties see Table 1.

systems at 25–325 °C are presented in Tables 2–4. The data in the tables refer only to the pure potassium or sodium dihydrogen (Table 2), hydrogen (Table 3), or trivalent (Table 4) phosphate. No mixed alkali-metal salts were investigated. In the tables, only the molar concentration is reported for any given pair (i.e., potassium and sodium) of solutions at 25 °C. If the molar concentrations at any particular temperature are desired, it is possible to assume the densities of the dilute solutions to be equivalent to that of pure water and use the appropriate density values for water. Values in the tables are reported as raw conductivities rather than as molar conductances to avoid ambiguity and the assumption of any particular density function for water. Computation of the molar conductances is straightforward after obtaining the concentrations at the temperature of interest if one so desires. Estimates of precision in the conductivity data (and the temperature) can be made using the deviations reported in Table 1.

Table 4. Conductivity κ of Aqueous Solutions of K₃PO₄ and Na₃PO₄

	$\kappa/(\mu S \cdot cm^{-1})$					
C/M^a	K₃PO₄	Na₃PO₄	K₃PO₄	Na₃PO₄	K₃PO₄	Na₃PO₄
	$t = 25$ °C		$t = 100$ °C		$t = 150$ °C	
0.0005	253	232	660	644	918	868
0.0010	484	451	1280	1212	1721	1633
0.0020	943	871	2461	2301	3314	3084
0.0050	2130	1954	5486	5043	7213	6941
0.0100	3866	3431	9557	8455	12127	11537
	$t = 200$ °C		$t = 225$ °C		$t = 245$ °C	
0.0005	1154	1091	1288	1164	1274	1239
0.0010	2114	2062	2270	2257	2353	2346
0.0020	4000	3882	4248	3995	4391	4159
0.0050	8433	8237	8807	8636	8973	8699
0.0100	13822	13440	14159	13790	14267	14114
	$t = 265$ °C		$t = 285$ °C		$t = 305$ °C	
0.0005	1302	1272	1300	1230	1257	1130
0.0010	2385	2344	2352	2545	2251	2171
0.0020	4412	4205	4358	4166	4170	3762
0.0050	8967	8532	8665	8130	8140	7580
0.0100	14184	13991	13581	12882	12656	11956
	$t = 325$ °C					
0.0005	1196	1131				
0.0010	2123	2045				
0.0020	3892	3470				
0.0050	7392	6868				
0.0100	11539	10749				

^{a} Molar concentration at 25 °C. Concentrations of potassium and sodium salt solutions are identical to within 0.2%. For estimates of other uncertainties see Table 1.

Discussion

As a more stringent test to assess the overall quality of the conductivity data as a function of temperature, it was decided to compare the differences between limiting molar conductance values, $\lambda°$, of the potassium and sodium ions derived from the experiments for the dihydrogen phosphate solutions with the differences obtained using accepted literature values (9). The differences between the limiting molar conductances for potassium and sodium were determined by calculating the differences between the molar conductances for pairs of solutions having the same phosphate concentrations at a particular temperature. (All of the solutions in this work were prepared such that the concentrations of both potassium and sodium salts were identical to within ±0.2%.) The derived differences were then plotted as a function of ionic strength I. The ionic strength was computed by first obtaining an estimate of the hydrogen ion concentration of the solution via iterative solution of the charge balance equation

$$\sum_i C_i Z_i = 0 \tag{1}$$

where the sum is over the concentrations C_i of all ions having charge Z_i using the known total concentration of phosphate and alkali metal along with the dissociation constants for the phosphate system (1) and water (10). Once the hydrogen ion

Table 5. Difference between Limiting Molar Conductances of Potassium and Sodium Ions: Comparison between Literature Values and Values Derived from Experimental Results for Dihydrogen Phosphate Solutions

	$[\lambda°(K^+) - \lambda°(Na^+)]/$ $(10^{-4} \, S \cdot m^2 \cdot mol^{-1})$			$[\lambda°(K^+) - \lambda°(Na^+)]/$ $(10^{-4} \, S \cdot m^2 \cdot mol^{-1})$	
$t/°C$	ref 9	this work	$t/°C$	ref 9	this work
25	23.4	26 ± 3	250	52	46 ± 3
100	44	41 ± 4	300	45	50 ± 12
150	53	45 ± 4	325	41	48 ± 3
200	60	40 ± 10			

concentration was estimated, it was a straightforward matter to obtain an initial estimate for the ionic strength. Once this estimate was obtained, activity coefficients were then computed to correct for the effect of ionic strength on the dissociation constants, and then a new estimate of the hydrogen ion concentration was made, which was then used to recalculate the concentrations of the charged species, the ionic strength, and so on. Convergence to within 0.01 pH unit was attained after two iterations. A modified Debye–Huckel equation was used to estimate activity coefficients (11) from values of the dielectric constant of water (12). All concentrations were computed assuming that solution densities as a function of temperature were identical to that of pure water (13).

Extrapolation to zero ionic strength provided an "experimental" value for the difference between the limiting molar conductances of potassium and sodium. The results, presented in Table 5, indicate that there are relatively large discrepancies between the literature values and those obtained from these conductance experiments. However, it must be noted that these results are reflective of uncertainties accumulating in a single value which was derived from 20 or so experimental measurements, each with its associated error. Thus, the test is a stringent one for data quality.

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