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APPARENT MOLAR HEAT CAPACITIES AND VOLUMES OF SILVER NITRATE AND SILVER PERCHLORATE IN AQUEOUS SOLUTION AT 298 K

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ABSTRACT

We have made calorimetric and density measurements leading to apparent molar heat capacities and volumes of dilute aqueous solutions of silver nitrate and silver perchlorate at 298 K. Resulting apparent molar properties at infinite dilution are the following: $\phi_C^\circ(AgNO_3) = -36.8$ J K^{-1} mol^{-1}, $\phi_V^\circ(AgNO_3) = 29.1$ cm^3 mol^{-1}, $\phi_C^\circ(AgClO_4) = 11.0$ J K^{-1} mol^{-1}, and $\phi_V^\circ(AgClO_4) = 43.5$ cm^3 mol^{-1}.

INTRODUCTION

Heat capacities of pure solids, liquids, and gases have been used for a long time in thermodynamic calculations based on $(d\Delta H/dT)_p = \Delta C_p$. Calculations of the same kinds with partial molar heat capacities of aqueous solutes have not been carried out very often because of the paucity of needed heat capacity values. Recent developments in flow calorimetry now make it practical to obtain these heat capacities that are needed for calculation of the effects of temperature on a variety of thermodynamic properties of systems that involve aqueous solutions.

Just as standard state partial molar heat capacities are needed for calculation of the effects of temperature on thermodynamic properties, standard state partial molar volumes are needed for analogous calculations of the effects of pressure on thermodynamic properties.

As part of our program for determination of thermal and volumetric properties of many aqueous solutions, we have made calorimetric measurements leading to apparent molar heat capacities and density measurements leading to apparent molar volumes of silver nitrate and of silver perchlorate in aqueous solution at 298 K. Results of these measurements and our thermodynamic calculations are reported in this paper.

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EXPERIMENTAL

Heat capacity measurements were made with a Picker flow calorimeter that has been described previously[1]; the apparatus for measurements of densities has also been described[2]. All of our results refer to 298.15 ± 0.10 K.

Reagent grade silver nitrate was further purified by recrystallization from water. One sample was air-dried on a sintered glass filter for 30 min and then further dried for one hour in an oven maintained at 110°C. Another sample was dried in the same oven for 20 min, removed from the oven and gently ground to yield small crystals, and then dried in the oven again for 40 min. Both samples were stored in a desiccator with silica gel for three days before being used. Solutions of known molalities were then prepared from known masses of silver nitrate and water.

Stock solutions of silver perchlorate were prepared as follows. Reagent grade sodium carbonate was added to a solution of silver nitrate to yield a precipitate of silver carbonate, which was recovered and thoroughly washed on a filter before being dissolved in perchloric acid to yield the desired solutions with pH = 5. These stock solutions were standardized by gravimetric determination of silver as AgCl; other solutions were prepared by dilution of the stock solutions.

All operations with these silver compounds were carried out in a darkened room.

RESULTS AND CALCULATIONS

Apparent molar properties of solutions (ϕ_Y) are defined by the expression

$$\phi_Y = [Y(\text{sol'n}) - n_1 Y_1^\circ]/n_2 \quad (1)$$

in which the symbols have the following meanings: Y is the extensive property (heat capacity or volume here) of a specified quantity of solution, n_1 is the number of moles of solvent in this specified quantity of solution, Y_1° is the property (heat capacity or volume) of one mole of pure solvent, and n_2 is the number of moles of solute in the specified quantity of solution. Our experimental results (compositions of solutions, heat capacities, densities) have been used to obtain the apparent molar heat capacities (ϕ_C) and apparent molar volumes (ϕ_V) that are listed in Tables 1 and 2. In making these calculations, we have taken the heat capacity and density of pure water to be 4.1793 J K^{-1} g^{-1} and 0.997044 g cm^{-3}, respectively. Heat capacities of solutions (expressed in J K^{-1} g^{-1}) can be recovered from tabulated ϕ_C values and corresponding molalities by way of

$$c_p = (m\phi_C + 4179.3)/(1000 + mM_2) \quad (2)$$

Similarly, densities of solutions can be recovered from tabulated ϕ_V values and corresponding molalities by way of

$$d = [(1000 + mM_2)d_1^\circ]/[1000 + md_1^\circ\phi_V] \quad (3)$$

in which M_2 is the molecular weight of the solution and d_1° is the density of pure water cited above.

TABLE 1

APPARENT MOLAR HEAT CAPACITIES AND VOLUMES OF AQUEOUS $AgNO_3$ AT 298 K

m (*mol kg*$^{-1}$)	ϕ_C (*J K*$^{-1}$ *mol*$^{-1}$)	ϕ_V (*cm*^{3} *mol*$^{-1}$)
0.04518	-29.2_7	29.3_9
0.08627	-24.5_0	29.6_5
0.10964	-22.6_3	29.5_7
0.12050	-22.2_4	29.4_4
0.15138	-19.4_6	29.7_6
0.18224	-17.6_0	29.6_2

TABLE 2

APPARENT MOLAR HEAT CAPACITIES AND VOLUMES OF AQUEOUS $AgClO_4$ AT 298 K

m (*mol kg*$^{-1}$)	ϕ_C (*J K*$^{-1}$ *mol*$^{-1}$)	ϕ_V (*cm*^{3} *mol*$^{-1}$)
0.0400	16.7_6	43.4_1
0.0656	20.8_0	44.3_6
0.0755	21.8_6	44.0_2
0.0989	22.7_6	43.2_9
0.1102	24.0_7	44.1_5
0.1265	25.4_5	44.5_0
0.1314	25.1_7	44.0_3
0.1583	27.9_0	44.2_1
0.1985	30.0_7	43.8_4
0.2200	30.6_5	44.0_5
0.2543	33.9_0	44.6_0
0.3326	37.7_0	44.0_7

TABLE 3

PARAMETERS FOR EQUATION (4)

Solute	ϕ_C^0 (*J K*$^{-1}$ *mol*$^{-1}$)	B_C (*J K*$^{-1}$ *mol*$^{-2}$ *kg*)	ϕ_V^0 (*cm*^{3} *mol*$^{-1}$)	B_V (*cm*^{3} *mol*$^{-2}$ *kg*)
$AgNO_3$	−36.8	39.0	29.1	−1.2
$AgClO_4$	11.0	30.7	43.5	−0.8

Apparent molar properties of dilute solutions of electrolytes are accurately described by equations of the form of

$$\phi_Y = \phi_Y^\circ + A_Y(d_1^\circ m)^{\frac{1}{2}} + B_Y m \tag{4}$$

in which ϕ_Y° is the value of ϕ_Y at infinite dilution, A_Y is the limiting slope derived from the Debye-Hückel theory, m is the molality, and B_Y is an adjustable parameter. Our principal interest in this work has been in determining ϕ_Y° values that are identical with the corresponding partial molar properties at infinite dilution ($\bar{Y}_2^\circ$). For our calculations leading to these values we have used $A_C(d_1^\circ)^{\frac{1}{2}} = 28.95$ J K^{-1} mol$^{-\frac{3}{2}}$ kg$^{\frac{1}{2}}$ and $A_V(d_1^\circ)^{\frac{1}{2}} = 1.865$ cm^3 mol$^{-\frac{3}{2}}$ kg$^{\frac{1}{2}}$ as reported previously[3]. Our ϕ_Y° and B_Y values based on least squares fitting of the results in Tables 1 and 2 to equations of the form of (4) are given in Table 3.

We do not know of any previous measurements of heat capacities of solutions of silver perchlorate with which to compare our results. Parker's excellent review[4] and analysis of such measurements on many other solutions led her to select $\phi_C^\circ = -64.8$ J K^{-1} mol^{-1} as the best value then available for aqueous silver nitrate. On the basis of previous experience and the consistency tests described below, we suggest that our $\phi_C^\circ = -37.2$ J K^{-1} mol^{-1} for aqueous silver nitrate is now the best available value.

Using our results from Table 1 leads to

$$\phi_C^\circ(AgClO_4) - \phi_C^\circ(AgNO_3) = 11.0 - (-36.8) = 47.8 \text{ J K}^{-1}\text{ mol}^{-1} \tag{5}$$

Our[5–7] previously obtained ϕ_C° values for other electrolytes lead to the following:

$$\phi_C^\circ(HClO_4) - \phi_C^\circ(HNO_3) = -27.1 - (-72.1) = 45.0 \text{ J K}^{-1}\text{ mol}^{-1} \tag{6}$$

$$\phi_C^\circ(NaClO_4) - \phi_C^\circ(NaNO_3) = 15.9 - (-28.9) = 44.8 \text{ J K}^{-1}\text{ mol}^{-1} \tag{7}$$

If all of our ϕ_C° values were exactly correct, the $\Delta\phi_C^\circ$ values from the three calculations above would be identical. We see that the spread in these $\Delta\phi_C^\circ$ values amounts to only 3 J K^{-1} mol^{-1}, which is about what could be expected on the basis of earlier assessments of uncertainties of about 3 J K^{-1} mol^{-1} in these values.

Millero's extensive review[8] of earlier investigations of volumetric properties of electrolytes cites $\phi_V^\circ = 28.02$ and 28.78 cm^3 mol^{-1} for aqueous silver nitrate, to be compared with our $\phi_V^\circ = 29.1$ cm^3 mol^{-1}. Millero[8] has not cited any previous investigations of silver perchlorate, but his selected $\phi_V^\circ = -0.7$ cm^3 mol^{-1} for Ag^+(aq) with his $\phi_V^\circ = 44.1$ cm^3 mol^{-1} for ClO_4^-(aq) permits us to calculate $\phi_V^\circ(AgClO_4) = 43.4$ cm^3 mol^{-1}, which is in excellent agreement with our $\phi_V^\circ = 43.5$ cm^3 mol^{-1} as listed in Table 3.

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