The error is 0.30 or 0.51%.

Registry No. Xanthene, 92-83-1.

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Densities of Aqueous Solutions of 18 Inorganic Substances

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Densities of aqueous solutions of $Cd(NO_3)_2$, $Co(NO_3)_2$, H_2SiF_6, $K_3Fe(CN)_6$, $KMnO_4$, KNO_2, $Mg(ClO_4)_2$, NaH_2PO_4, Na_2HPO_4, Na_2MoO_4, Na_3PO_4, $Na_4P_2O_7$, Na_2SO_3, $Na_2S_2O_3$, Na_2WO_4, $NH_4Al(SO_4)_2$, $(NH_4)_2C_2O_4$, and NH_4CH_3COO for temperatures from 5 to 85 °C and concentrations up to near saturation determined pycnometrically are reported.

Introduction

The densities of aqueous solutions are frequently used in both physical chemistry and chemical engineering. In the latter case they are necessary in establishing material balance of a process using solutions as a medium and/or volume of technological equipment. For purposes of chemical engineering it seems advantageous when concentration and temperature dependence of solution density is represented by a single equation valid in the range 0–100 °C and up to saturation concentration.

Also reliable data covering the whole interval of concentrations and temperatures should be available in sufficient supply. Since for many inorganic systems data reported in the literature are restricted to a rather narrow temperature and concentration range, we have measured missing densities for 18 systems.

Theoretical Section

The apparent molar volume of solute in a binary solution is defined as (*1*)

$$\phi_V = (V - n_1 V_{m,1})/n_2 = \frac{1}{n_2}\left[\frac{n_1 M_1 + n_2 M_2}{\rho} - \frac{n_1 M_1}{\rho_1}\right] \qquad (1)$$

for constant temperature and pressure. If the solution composition is expressed by the number of moles of solute in 1 m^3 of solution, i.e., $n_2 = c$, $n_1 = (\rho - cM_2)/M_1$, then eq 1 acquires the form

$$\phi_V = (\rho_1 - \rho)/c\rho_1 + M_2/\rho_1 \qquad (2)$$

Combination of eq 2 with the relation after Masson (*2*)

$$\phi_V = \phi_V{}^\circ + s_{\mathrm{exptl}} c^{1/2} \qquad (3)$$

gives

$$\rho = \rho_1 + \alpha c - \beta c^{3/2} \qquad (4)$$

where

$$\alpha = M_2 - \rho_1 \phi_V{}^\circ \qquad (5)$$

$$\beta = s_{\mathrm{exptl}} \rho_1 \qquad (6)$$

Relation 4 describes the dependence of solution density on concentration at constant temperature. Introducing the temperature dependence of α and β in the form

$$\alpha(t) = A + Bt + Ct^2 \qquad (7)$$

$$\beta(t) = -(D + Et + Ft^2) \qquad (8)$$

into eq 4 and rearranging gives

$$\rho(t) = \rho_1(t) + Ac + Bct + Cct^2 + Dc^{3/2} + Ec^{3/2}t + Fc^{3/2}t^2 \qquad (9)$$

Relation 9 describing the concentration–temperature dependence of densities of binary aqueous solutions can thus be regarded as theoretically justified. Its application to aqueous binary solutions has been tested for over 300 systems and found very satisfactory (*3*). Moreover, the physical parameter of solute, $\phi_V{}^\circ$, calculated from constants of eq 9, is rather close to the theoretical values (*4*). Equation 9 can also be used for the estimation of the ternary system densities on the basis of data for binary systems (*5*).

Relations proposed in the literature for the description of the concentration and temperature dependences of densities of aqueous solutions are mostly of an empirical nature, e.g., ref *6–10*. Such equations have, however, several disadvantages compared with eq 9, mainly (i) narrower field of application due to their validity for either concentration or temperature dependence, (ii) less satisfactory description of the density depen-

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Table I. Experimentally Determined Densities of Solutions

concn, wt %	t, °C	ρ, kg·m^{-3}
	Cd(NO$_3$)$_2$	
10	65	1065.8
20	65	1164.5
30	65	1282.4
40	65	1422.8
50	65	1592.0
60	65	1800.9
70	65	2050.5
10	85	1053.9
20	85	1150.3
30	85	1265.8
40	85	1404.7
50	85	1573.0
60	85	1779.2
70	85	2036.0
	Co(NO$_3$)$_2$	
10	25	1083.1
20	25	1182.4
30	25	1297.4
40	25	1429.2
50	25	1583.3
10	40	1077.2
20	40	1175.1
30	40	1288.7
40	40	1419.1
50	40	1572.4
10	60	1066.5
20	60	1162.5
30	60	1275.7
40	60	1405.3
50	60	1556.8
60	60	1729.4
10	80	1054.3
20	80	1148.2
30	80	1261.5
40	80	1390.8
50	80	1540.7
60	80	1710.0
	K$_3$Fe(CN)$_6$	
5	65	1007.0
15	65	1062.8
25	65	1122.8
35	65	1187.9
5	75	1001.6
15	75	1057.0
25	75	1117.3
35	75	1182.2
5	85	995.4
15	85	1051.1
25	85	1111.8
35	85	1176.5
40	85	1212.3
	KMnO$_4$	
7	40	1038.5
10	40	1060.7
7	60	1029.6
10	60	1050.7
13	60	1072.4
15	60	1088.0
7	80	1016.9
10	80	1037.5
13	80	1058.9
15	80	1075.0
	KNO$_2$	
5	20	1028.9
15	20	1094.3
30	20	1201.5
45	20	1324.2
60	20	1463.7
75	20	1623.8
5	30	1026.1
15	30	1089.7
30	30	1196.1
45	30	1317.7
60	30	1456.3
75	30	1615.6
5	40	1021.9
15	40	1085.2
30	40	1190.0
45	40	1311.1
60	40	1448.7
75	40	1607.6
5	60	1012.5
15	60	1073.7
30	60	1177.4
45	60	1297.5
60	60	1434.1
75	60	1591.5
5	80	1001.0
15	80	1061.5
30	80	1163.3
45	80	1282.6
60	80	1417.8
75	80	1575.4
	Mg(ClO$_4$)$_2$	
10	25	1072.7
20	25	1157.9
30	25	1254.2
	Mg(ClO$_4$)$_2$	
45.72	25	1437.3
10	40	1065.6
20	40	1149.2
30	40	1244.6
45.72	40	1425.3
10	60	1054.6
20	60	1137.1
30	60	1230.6
45.72	60	1409.3
10	80	1042.1
20	80	1122.2
30	80	1215.4
45.72	80	1394.0
	NaH$_2$PO$_4$	
10	5	1071.0
20	5	1148.8
10	15	1068.5
20	15	1144.0
10	40	1058.6
20	40	1132.9
50	40	1396.2
10	60	1048.6
20	60	1122.3
50	60	1383.2
60	60	1482.8
10	80	1035.8
20	80	1108.7
50	80	1372.2
60	80	1469.9
	Na$_2$HPO$_4$	
5	40	1043.1
10	40	1097.6
20	40	1215.4
30	40	1350.4
5	60	1033.7
10	60	1087.1
20	60	1203.6
30	60	1337.6
5	80	1022.5
10	80	1076.0
20	80	1191.9
30	80	1325.1
	Na$_2$MoO$_4$	
5	25	1040.6
10	25	1087.1
20	25	1191.3
30	25	1311.5
35	25	1379.3
5	40	1035.4
10	40	1080.9
20	40	1184.6
30	40	1304.7
35	40	1372.0
5	60	1026.3
10	60	1071.9
20	60	1174.4
30	60	1292.9
35	60	1360.6
5	80	1014.3
10	80	1060.5
20	80	1162.3
30	80	1281.0
35	80	1347.2
	Na$_3$PO$_4$	
5	40	1047.3
10	40	1106.1
15	40	1166.5
5	60	1037.7
10	60	1095.5
15	60	1155.4
20	60	1221.5
25	60	1286.5
5	80	1025.5
10	80	1083.1
15	80	1141.6
20	80	1206.5
25	80	1270.6
30	80	1343.5
	Na$_4$P$_2$O$_7$	
3	25	1027.0
5	25	1046.9
3	40	1021.6
5	40	1041.3
7	40	1061.7
3	60	1012.3
5	60	1031.3
7	60	1051.5
10	60	1081.5
3	80	1000.8
5	80	1019.5
7	80	1039.4
10	80	1069.1
15	80	1123.6
	Na$_2$SO$_3$	
5	25	1044.6
10	25	1092.8
15	25	1143.3
20	25	1198.2
5	40	1039.4
10	40	1086.8
15	40	1137.1
20	40	1191.2
5	60	1029.9
10	60	1077.4
15	60	1126.9
20	60	1179.6
5	80	1017.4
10	80	1065.3
15	80	1113.7
20	80	1166.6
	Na$_2$S$_2$O$_3$	
10	25	1081.2
20	25	1172.1
30	25	1270.4
40	25	1379.5
10	40	1074.5
20	40	1164.2
30	40	1261.5
40	40	1370.2
50	40	1487.0
10	60	1063.3
20	60	1152.1
30	60	1248.9
40	60	1355.9
50	60	1473.5
60	60	1599.2
10	80	1051.7
20	80	1138.7
30	80	1235.3
40	80	1341.8
50	80	1458.8
60	80	1584.8
	Na$_2$WO$_4$	
10	20	1095.0
20	20	1210.2
30	20	1347.8
40	20	1516.6
10	40	1087.8
20	40	1201.9
30	40	1338.1
40	40	1505.7
10	60	1077.7
20	60	1190.6
30	60	1326.0
40	60	1492.5
10	80	1065.5
20	80	1178.0
30	80	1312.7
40	80	1478.4
	NH$_4$Al(SO$_4$)$_2$	
2	40	1011.3
4	40	1028.5
6	40	1046.6
8	40	1065.1
2	60	1000.8
4	60	1018.6
6	60	1035.9
8	60	1054.1
10	60	1073.0
2	80	988.2
4	80	1005.2
6	80	1021.8
8	80	1039.4
10	80	1057.9
14	80	1096.4
16	80	1115.8
18	80	1137.2
22	80	1179.9
	(NH$_4$)$_2$C$_2$O$_4$	
2	20	1008.1
3.5	20	1015.7
2	40	1001.9
3.5	40	1008.8
5	40	1015.7
6	40	1020.5
7	40	1024.7
2	60	992.8
3.5	60	999.7
5	60	1006.7
6	60	1011.2
7	60	1016.2
9	60	1024.7
10	60	1029.6
11.5	60	1035.7
2	80	980.9
3.5	80	988.3
5	80	994.7
6	80	999.6
7	80	1004.1
9	80	1013.7
10	80	1018.5
11.5	80	1025.0
	NH$_4$CH$_3$COO	
5	25	1006.7
10	25	1016.1
15	25	1025.1
20	25	1034.0
25	25	1042.5
5	40	1001.5
10	40	1010.3
15	40	1019.6
20	40	1027.6
25	40	1035.5
5	60	992.3
10	60	1001.3
15	60	1009.3
20	60	1017.5
25	60	1025.6
5	80	981.7
10	80	989.8
15	80	998.4
20	80	1006.3
25	80	1014.2
	H$_2$SiF$_6$	
3.11	25	1019.6
5.75	25	1041.3
11.14	25	1085.4
15.03	25	1120.8
3.13	40	1014.2
5.79	40	1035.6
11.20	40	1079.3
15.11	40	1114.1
3.16	60	1004.6
5.84	60	1025.5
11.31	60	1068.7
15.27	60	1102.6
3.20	80	993.1
5.61	80	1014.6
11.43	80	1057.3
15.43	80	1091.3

Table II. Calculated Constants of Eq 9[a]

substance	$10^{-2}A$	$10^{2}B$	$10^{4}C$	D	$10^{2}E$	$10^{4}F$	$10^{2}s_r$
$Co(NO_3)_2$	1.558	−13.55	11.59	−8.800	1.962	−2.246	10.4
$K_3Fe(CN)_6$	1.816	−19.25	22.98	−3.819	−22.49	12.79	2.1
$KMnO_4$	0.3883	202.3	−161.8	75.96	−239.4	186.3	3.3
KNO_2	0.5503	−11.05	7.335	−2.870	2.170	−1.328	3.3
$Mg(ClO_4)_2$	1.702	−35.08	16.30	−10.14	11.05	−2.298	2.3
NaH_2PO_4	0.8483	−14.92	13.13	−4.898	0.6584	−0.8450	13.6
Na_2HPO_4	1.591	−46.85	42.44	−17.86	19.73	−17.97	2.5
Na_2MoO_4	1.832	−27.81	29.17	−12.47	14.28	−14.54	2.6
Na_3PO_4	1.814	19.69	−18.51	−17.92	−16.31	14.14	7.9
$Na_4P_2O_7$	2.638	26.83	−38.68	−8.272	−127.8	130.5	3.4
Na_2SO_3	1.189	5.961	−5.013	−8.432	−10.16	8.247	4.3
$Na_2S_2O_3$	1.387	−25.96	18.57	−14.49	8.483	−5.674	3.6
Na_2WO_4	2.713	−23.75	20.42	−13.07	10.01	−7.156	2.2
$NH_4Al(SO_4)_2$	2.620	−74.85	−7.760	−110.6	185.2	−68.35	3.3
$(NH_4)_2C_2O_4$	0.7208	−18.22	4.987	−20.97	24.09	−4.520	2.4
NH_4CH_3COO	0.1803	−10.03	9.947	−1.733	1.632	−2.353	2.3
H_2SiF_6	1.206	−84.01	81.74	−9.503	58.45	−63.54	9.1

[a] When constants A–F are used in eq 9 with concentrations in mol·dm^{-3} and temperature in °C, calculated densities of solution are given in kg·m^{-3}.

dence over the whole range of temperatures and concentrations, and (iii) inapplicability for the estimation of densities of ternary systems.

Experimental Section

The densities of aqueous solutions were measured in a single-flask type pycnometer of 50-mL volume. Solutions of salts with predetermined concentrations were prepared by dissolving recrystallized AnalaR-grade chemicals in distilled water. Solutions of H_2SiF_6 were prepared by diluting the stock solution of the acid (15 wt %) to the required concentration. The exact concentration of a diluted acid was always determined analytically.

The pycnometer filled with a solution was kept for 2 h in a constant-temperature water bath and the meniscus of the liquid was adjusted several times during that period. Then the pycnometer was weighed. The weight of the same volume of water at the given temperature was determined similarly. Three independent measurements with the same solution at each temperature were carried out.

The relative density of the solution ($d = G_{soln}/G_{water}$) was calculated as the arithmetic mean of three values which differed, as a rule, by less than 0.5 kg·m^{-3}. The relative densities thus determined were converted to absolute values, ρ, by multiplying them with the water density at the given temperature calculated from

$$\rho_1 = 999.65 + 2.0438 \times 10^{-1}t - 6.1744 \times 10^{-2}t^{3/2} \qquad (10)$$

Equation 10 was obtained by correlating densities of water given in ref *11* for the temperature range 5–100 °C.

The density of water calculated from eq 10 differs within the temperature range 5–80 °C in the second decimal place from the precise value (*12*). Such precision is fully satisfactory in our case.

The accuracy of our data was assessed for KCl solutions since data for the system given in ref *11* both are internally consistent and fit eq 9 best among nearly 300 systems tested ($s_r = 4.2 \times 10^{-3}$) and thus can be regarded as reliable. Densities of KCl solutions with concentrations of 10 and 20 wt % at 20, 40, 60, and 80 °C from ref *11* and ours determined for the same conditions were tested by the test for significance of pair differences with the conclusion that the difference between the two sets of data is statistically insignificant. The average difference, however, between the two sets is 0.75 kg·m^{-3}, i.e., approximately 0.07 rel %. It leads us to the conclusion that also for other systems the deviation of our data from reality does not exceed 1 kg·m^{-3}.

Results

The densities of solutions of $Cd(NO_3)_2$, $Co(NO_3)_2$, H_2SiF_6, $K_3Fe(CN)_6$, $KMnO_4$, KNO_2, NaH_2PO_4, Na_2HPO_4, Na_2MoO_4, Na_3PO_4, $Na_4P_2O_7$, Na_2SO_3, $Na_2S_2O_3$, Na_2WO_4, $NH_4Al(SO_4)_2$, $(NH_4)_2C_2O_4$, and NH_4CH_3COO were determined in the concentration and temperature range not covered by the literature data. Experimentally determined values (unsmoothed) are given in Table I.

Constants A–F in eq 9 determined by the least-squares method are given in Table II. The relative standard deviation as a measure of data scatter around the calculated function defined as

$$s_r = 100[\sum(\rho_{exptl} - \rho_{calcd})^2/(N - l)]^{1/2}/\bar{\rho} \qquad (11)$$

is given in Table II for each correlation as well.

It should be emphasized that constants given in Table II are valid for the concentration and temperature ranges covered by reported data. They can safely be used for interpolation within the given range whereas extrapolation should be carried out with greater care.

Glossary

A, B, C, D, E, F	constants
c	molar concentration, mol·m^{-3}
l	number of constants
M	molecular weight, kg·mol^{-1}
n_i	amount of i-th component in mixture, mol
N	number of measurements
s_{exptl}	experimental slope of dependence $\phi_V = f(c^{1/2})$
s_r	relative standard deviation
V	volume of system, m^3
V_m	molar volume, m^3·mol^{-1}
ϕ_V	apparent molar volume, m^3·mol^{-1}
$\phi_V{}^\circ$	apparent molar volume at infinite dilution, m^3·mol^{-1}
ρ	density, kg·m^{-3}

Subscripts

1	solvent
2	solute
exptl	experimental
calcd	calculated

Registry No. $Cd(NO_3)_2$, 10325-94-7; $Co(NO_3)_2$, 10141-05-6; H_2SiF_6, 16961-83-4; $K_3Fe(CN)_6$, 13746-66-2; $KMnO_4$, 7722-64-7; KNO_2, 7758-09-0; $Mg(ClO_4)_2$, 13770-16-6; NaH_2PO_4, 7558-80-7; Na_2HPO_4, 7558-79-4; Na_2MoO_4, 7631-95-0; Na_3PO_4, 7601-54-9; $Na_4P_2O_7$, 7722-88-5; Na_2SO_3, 7757-83-7; $Na_2S_2O_3$, 7772-98-7; Na_2WO_4, 13472-45-2; $NH_4Al(SO_4)_2$, 7784-25-0; $(NH_4)_2C_2O_4$, 1113-38-8; NH_4CH_3COO, 631-61-8.

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Thermal Conductivity of Parahydrogen

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The paper presents new experimental measurements of the thermal conductivity of parahydrogen for eight isotherms at temperatures from 100 to 275 K with intervals of 25 K, pressures to 12 MPa, and densities from 0 to 12 mol/L. Three additional isotherms at 150, 250, and 275 K cover para-rich compositions with para percentages varying from 86% to 73%. For these three isotherms the pressures reach 70 MPa and the density a maximum of 30 mol/L. The data for all compositions are represented by a single thermal conductivity surface in which the differences in thermal conductivity for different ortho–para compositions are accounted for in the dilute-gas term. The new measurements are compared with previous data on parahydrogen through the new correlation. It is estimated that the overall uncertainty of both experimental and correlated thermal conductivity is 1.5% at the 3σ level.

Introduction

For the H_2 molecule, two spin isomers exist—orthohydrogen and parahydrogen. The differentiating feature is the relative orientation of the two nuclear spins of the molecule. The spins may be either parallel or antiparallel. Parahydrogen molecules have antiparallel nuclear spins, and even rotational quantum numbers; they are therefore in the lowest rotational energy state ($J = 0$) at low temperatures. In the absence of a catalyst, the rate of conversion between the two species is slow; hence, hydrogen can be thought of as a binary mixture of two different species of molecules differing from each other in physical properties. The equilibrium ortho–para composition in the mixture is temperature dependent. For example, at a temperature of about 20 K, the equilibrium composition is 99.79% para and 0.21% ortho. Near room temperature the composition is about 25% para and 75% ortho. This 25–75 composition is called normal hydrogen.

A search of the literature reveals a relative abundance of papers on the thermal conductivity of hydrogen (*1*). However, measurements on parahydrogen are rare (*2*, *3*). It is, therefore, not surprising that efforts to correlate the thermal conductivity surface of parahydrogen (*4*) are beset with difficulties and that the correlations are of doubtful accuracy. In this paper new experimental measurements are presented that cover the range 0–8 mol/L for every isotherm with a para percentage of 99.79%. Additional isotherms at 150, 250, and 275 K cover densities up to 30 mol/L at para-rich compositions with para percentages varying from 86% to 73%. For these three isotherms the pressures reach 70 MPa and the density a maximum of 30 mol/L. The results overlap our earlier measurements (*2*) and extend them to 300 K. The earlier measurements were done primarily at temperatures below 100 K. The present results are described by a new correlation for the thermal conductivity surface of hydrogen between 78 and 300 K for pressures up to 70 MPa (*5*). In this new correlation (*5*) differences in thermal conductivity for varying ortho–para compositions are accounted for in the dilute-gas term (*6*).

Experimental Section

The measurements were made with a new transient hot wire thermal conductivity apparatus (*7*). In the transient hot wire technique, a thin platinum wire, immersed in the fluid and initially in thermal equilibrium with it, is subjected at time $t = 0$ to a step voltage. The wire behaves as a line source of heat with constant heat generation. The physical arrangement closely models an ideal line source, and the working equation for the temperature increase in the wire, ΔT, is given by

$$\Delta T = \frac{q}{4\pi\lambda} \ln\left(\frac{4K}{a^2C}t\right) \qquad (1)$$

where q is the heat generated per unit length of wire of radius a, $K = \lambda/(\rho C_p)$ is the thermal diffusivity of the fluid at the reference temperature, and $\ln C = \gamma$, where γ is Euler's constant. K is nearly constant since the fluid properties do not change drastically with a small increase in temperature. Corrections to eq 1 have been fully described elsewhere (*8*), the most important one being the effect of the finite heat capacity of the wire.

Use of a Wheatstone bridge with both a long and a short hot wire provides end-effect compensation. Voltages are measured directly with a fast response digital voltmeter (DVM). The DVM is controlled by a minicomputer, which also handles the switching of the power and the logging of the data. The measurement of thermal conductivity for a single point is accomplishment by balancing the bridge as close to null as is practical at the cell or reference temperature. The lead resistance, the hot wire resistances, and the ballast resistors are read first; then the power supply is set to the desired power and the voltage developed across the bridge as a function of time is read and