Standard Potentials of Ag–AgX (X = Cl or Br) Electrodes in Glycolic Solvents at Different Temperatures and Related Thermodynamic Quantities

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The standard potentials of (*a*) the Ag–AgBr electrode in ethylene glycol and (*b*) the Ag–AgCl electrode in propylene glycol have been determined at nine temperatures (*t*) ranging from 5° to 45° C., by using a cell of the type: Pt/H_2 (g., 1 atm.), HX (*m*), solvent/AgX–Ag. The values can be fitted in the form of equations, obtained by using the least squares method:

$$\text{For (a), } E_m^\circ = -0.1007 - 1.16 \times 10^{-3}(t - 25) - 9.02 \times 10^{-7}(t - 25)^2$$

$$\text{For (b), } E_m^\circ = -0.0323 - 1.58 \times 10^{-3}(t - 25) - 8.96 \times 10^{-7}(t - 25)^2$$

These values have been utilized to determine the activity coefficients of HBr in ethylene glycol and HCl in propylene glycol at 5°, 25°, and 45° C. Utilizing the resulting temperature coefficients of activity coefficients, the relative partial molal heat contents, $\bar{L}_2$, were also evaluated for HCl and HBr in the respective solvents at 25° C. for round concentrations below 0.05 molal.

Ethylene and propylene glycols alone or with suitable hydrocarbon cosolvents have been widely used as media for nonaqueous acid-base titration (*7*). But the quantitative aspects of the subject were not extensively studied until recent years. A series of previous communications reported preliminary results on the standard potentials of Ag–AgCl and Ag–AgBr electrodes (*6*) as well as the dissociation constants of some acids and bases (*5*) in ethylene and propylene glycols. But these studies were restricted to one temperature only. To understand more clearly the proton transfer equilibria as well as ionic processes in general in any solvent, evaluation of the energetics involved should be of prime importance. The authors have undertaken to determine the standard potentials of silver–silver halide electrodes in glycolic solvents at different temperatures. In earlier communications, the findings were reported for the E_s° of Ag–AgBr (*2*) and Ag–AgCl (*8*) in several ethylene glycol-water mixtures (10 to 90%) and the Ag–AgCl electrode in pure ethylene glycol at temperatures ranging from 5° to 45° C. The standard potentials of the Ag–AgBr electrode in pure ethylene glycol and of the Ag–AgCl electrode in pure propylene glycol at nine temperatures ranging from 5° to 45° C. are now reported. The related thermodynamic quantities computed from the results are included. A cell of the following type was used for the purpose:

$$\text{Pt/H}_2\text{ (g., 1 atm.), HX}(m)\text{, glycol/AgX}-\text{Ag}$$

where X = Cl or Br.

EXPERIMENTAL

Ethylene glycol (Merck) and propylene glycol (L.R., British Drug House) were purified by the method described earlier (*6*). The characteristic properties of the solvents are:

	B.P. (1 atm.),	$d_o^{30°C.}$	$n_D^{30°C.}$
Ethylene glycol	196 to 197	1.1064	1.4289
Propylene glycol	185 to 186	1.0289	1.4294

These solvents, used for all the work, were considered pure, although the presence of traces of moisture cannot be ruled out, because of the hygroscopic nature of glycols. Care was taken during all the operations to avoid exposure of the solvents and solutions to the atmosphere as far as practicable.

The experimental procedures for preparing dry hydrobromic acid gas, dry hydrochloric acid gas, the cell solutions, the Ag–AgCl and Ag–AgBr electrodes, the hydrogen gas electrode, and hydrogen gas were the same as previously described (*6*). In the preparation of stock solutions of both types of acid solutions, care was taken to keep the vessel containing the solvent in a freezing mixture, to arrest the rise in temperature of the resulting solutions due to the heat evolved on dissolution of HCl and HBr gases in the solvents. It was expected that this would slow the rate of probable side reactions such as the formation of halohydrins, especially at appreciably higher concentrations.

E.m.f. measurements were made at nine temperatures in the range of 5° to 45° C., at intervals of 5° C., with a Leeds & Northrup K-type potentiometer and a moving coil galvanometer. Measurements below 25° C. were performed with a low temperature thermostat and those at higher temperatures with an ordinary thermostat, both capable of maintaining the temperature to ± 0.1° C.

Portions of the same acid solution were placed in two cells, each fitted with a platinum-foil hydrogen electrode, two Ag–AgX electrodes, and a train of presaturators containing solvent and cell solutions. Both cells were first placed in the same thermostat, set at 25° C. Equilibrium was established 3 to 4 hours after passage of hydrogen gas began, and was assumed to have been attained when the e.m.f. remained constant for an hour with an average variation of 0.2 mv. Individual readings in both cells for the same solution also agreed within 0.2 mv. Then one of the cells, with the respective train of presaturators, was transferred to the low temperature thermostat set at 5° C. After readings for 5° C. had been taken, the bath was successively adjusted to 10°, 15°, and 20° C. and the corresponding e.m.f. values of the cell were recorded, after attainment of equilibrium in each case. Meanwhile, readings for the second cell at the higher temperatures were similarly taken, using the other bath which was successively adjusted to 30°, 35°, 40°, and 45° C. Equilibrium at the lower temperatures was reached within one hour, while at higher temperatures it usually took 30 to 40 minutes. Constant e.m.f. values of 0.1 mv. for 15 minutes were taken as the criterion for the attainment of equilibrium.

With HBr solutions in ethylene glycol (particularly those of a concentration of 0.06*M* or greater), the e.m.f. readings at 45° C. changed perceptibly with time even after the usual period for achieving equilibrium had passed. Similar but smaller drifts were observed at 40° and 35° C., but began at higher concentrations. The rate of drift was higher for higher concentrations, and below a concentration of 0.05 molal, the rate of drift was usually imperceptibly small. This drift and drift rate generally decreased with decreasing concentrations of HBr and with decreasing temperature. The e.m.f. values at lower concentrations are expected, therefore, to involve comparatively little error from this source, affecting the extrapolated values ($E_m°$) to a negligible extent.

In the case of HCl solutions in propylene glycol, no drift of any perceptible extent was observed at higher temperatures, or at concentrations above 0.05 molal. Because of the increased viscosity of the solvent and consequent increase in electrical resistance, however, the sensitivity of the results, especially at concentrations of HCl below 0.005 molal, is low. The limitations are inherent in the results presented for ethylene glycol and propylene glycol, and the $E°$ values obtained are presumably correct within ±0.0005 volt for both glycols.

Densities of both solvents at different temperatures were measured with a pycnometer of 5-ml. capacity having a neck 10 cm. long calibrated in 0.1-cm. divisions. The diameter of the capillary tube was 1 mm. Vapor pressures of propylene glycol lie within 1 mm. of Hg even at the highest temperature, as can be seen from Table I, compiled from Curme and Johnston's monograph (*3*). Similar data for ethylene glycol are not available, but can reasonably be assumed to be still smaller, in view of its higher boiling point.

RESULTS AND DISCUSSION

Standard Potentials. Assuming that both HCl and HBr are completely dissociated in the respective solvents, the e.m.f. of the cell, E (corrected to 760 mm. H_2 pressure), at a given molal concentration (m) of HX solution is given by:

$$E = E_m° - 2k \log m + \frac{2k\, s_f\, c^{\frac{1}{2}}}{1 + a_o B c^{\frac{1}{2}}} + 2k \log (1 + 0.002\, Mm) + f(m) \qquad (1)$$

where $E_m°$ is the standard potential of the cell on the molal scale, s_f and B are the Debye-Hückel constants for the solvents at the respective temperatures, c is the molarity of HX, a_o is the ion-size parameter, $k = 2.3026\ RT/F$, M is the molecular weight of the solvent, and $f(m)$ is a function of m. If the function $E°'$ is defined (*4*) as

$$E°' = E + 2k \log m - \frac{2k\, s_f\, c^{\frac{1}{2}}}{1 + a_o B c^{\frac{1}{2}}} - 2k \log (1 + 0.002\, Mm)$$

we have $E°' = E_m° + f(m)$ (2)

Table I gives the values of s_f, B, D_s, the dielectric constants (*1*), and d_o, the densities of both the solvents at different temperatures, which were needed for the calculation of $E°'$.

Table II gives the observed e.m.f. values of the cell at different temperatures for different concentrations of HBr for ethylene glycol. Corresponding results with

Table I. Parameters for Evaluation of $E°'$ in Glycols at Different Temperatures

	5° C.	10° C.	15° C.	20° C.	25° C.	30° C.	35° C.	40° C.	45° C.
				Ethylene Glycol (M = 62.04)					
D_s	41.77	40.70	39.67	38.66	37.67	36.71	35.78	34.86	33.98
Density (d_o), g./cc.	1.1238	1.1203	1.1168	1.1134	1.1099	1.1064	1.1029	1.0093	1.096
s_f	1.456	1.474	1.492	1.511	1.532	1.553	1.574	1.599	1.623
B	0.4667	0.4685	0.4703	0.4724	0.4745	0.4767	0.4789	0.4813	0.4838
				Propylene Glycol (M = 76.10)					
D_s	35.17	34.07	33.02	32.00	31.00	30.04	29.12	28.21	27.33
V.p. (p), mm. of Hg	0.02	0.03	0.05	0.08	0.13	0.20	0.31	0.46	0.67
Density (d_o), g./cc.	1.0472	1.0435	1.0399	1.0363	1.0326	1.0289	1.0253	1.0217	1.0181
s_f	1.887	1.925	1.965	2.007	2.052	2.099	2.146	2.198	2.250
B	0.5087	0.5121	0.5156	0.5193	0.5231	0.5271	0.5310	0.5352	0.5394

HCl for propylene glycol are given in Table III. Since the vapor pressures of the glycols are small even at the highest temperature, the correction factors for converting the observed e.m.f. values to 1-atm. hydrogen pressure are negligible.

The values of $E^{\circ\prime}$ were plotted against the molalities of HX and the resulting straight-line plots were extrapolated to $m = 0$ to obtain the value of E_m° of the Ag–AgX electrode. The extrapolations at five temperatures are illustrated in Figures 1 and 2. The value of the ion size parameter (a_o) has been taken to equal 5 for both the glycols at different temperatures. Reasonable alterations in the value of a_o result in different slopes of the plots but have no significant influence on the values of E_m°, as obtained by extrapolations. The extrapolated values of E_m° at different temperatures in both the solvents are tabulated in Table IV, along with the corresponding values of the standard potentials on the molar and mole fraction scales, E_c° and E_N°, respectively. These have been computed with the help of the equations

$$E_c^\circ = E_m^\circ + 2k \log d_o \qquad (3)$$

$$E_N^\circ = E_m^\circ - 2k \log \frac{1000}{M} \qquad (4)$$

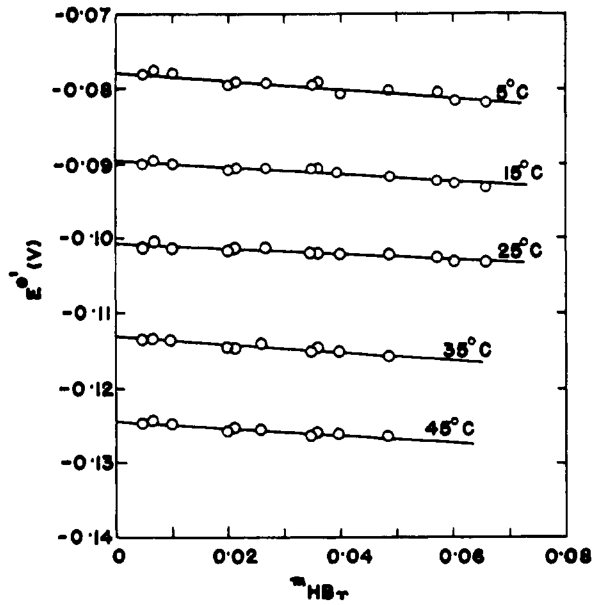

Figure 1. Extrapolation of e.m.f. data to give E_m° for Ag–AgBr electrode in ethylene glycol at different temperatures

Table II. Electromotive Force of Cell in Volts

Pt, H_2 (1 atm.)/HBr(m), ethylene glycol/AgBr–Ag from 5° to 45° C.

m_{HBr}	5° C.	10° C.	15° C.	20° C.	25° C.	30° C.	35° C.	40° C.	45° C.
0.00440	0.19065	0.19010	0.18950	0.18860	0.1878	0.1871	0.1862	0.1856	0.1850
0.00663	0.1724	0.1722	0.1719	0.1712	0.1705	0.1696	0.1684	0.1668	0.1654
0.00951	0.1574	0.1564	0.1544	0.1537	0.1530	0.1511	0.1495	0.1485	0.1460
0.01978	0.1264	0.1243	0.1228	0.1213	0.1198	0.1178	0.1148	0.1137	0.1116
0.02052	0.1250	0.1233	0.1216	0.1196	0.1186	0.1158	0.1131	0.1121	0.1101
0.02633	0.1149	0.1131	0.1110	0.1092	0.1079	0.1053	0.1031	0.1014	0.0995
0.03509	0.1031	0.1004	0.0991	0.0965	0.0941	0.0921	0.0888	0.0872	0.0846
0.03574	0.1030	0.0998	0.0985	0.0960	0.0940	0.0912	0.0884	0.0864	0.0843
0.03980	0.0967	0.0945	0.0930	0.0903	0.0881	0.0860	0.0840	0.0817	0.0795
0.04857	0.0893	0.0870	0.0853	0.0823	0.0811	0.0773	0.0739	0.0722	0.0699
0.05902	0.0812	0.0784	0.0760	0.0741	0.0721	0.0688	...	...	...
0.06020	0.0793	0.0767	0.0746	0.0722	0.0702	0.0674	...	...	...
0.06582	0.0753	0.0731	0.0705	0.0685	0.0666	0.0631	...	...	...
0.07336	0.0711	0.0688	0.0668	0.0638	0.0623	...	...	...	...
0.07683	0.0694	0.0669	0.0643	0.0618	0.0597	...	...	...	...
0.08264	0.0654	0.0634	0.0610	0.0584	0.0561	...	...	...	...
0.09294	0.0612	0.0590	0.0565	0.0537	0.0529	...	...	...	...
0.09319	0.0602	0.0582	0.0551	0.0529	0.0510	...	...	...	...

Table III. Electromotive Force of Cell in Volts

Pt, H_2 (1 atm.)/HCl(m), propylene glycol/AgCl–Ag from 5° to 45° C.

m_{HCl}	5° C.	10° C.	15° C.	20° C.	25° C.	30° C.	35° C.	40° C.	45° C.
0.00188	0.3085	0.3064	0.3043	0.3023	0.3003	0.2981	0.2962	0.2939	0.2916
0.00349	0.2815	0.2791	0.2768	0.2741	0.2714	0.2691	0.2666	0.2641	0.2618
0.00505	0.2663	0.2636	0.2608	0.2580	0.2553	0.2525	0.2492	0.2469	0.2442
0.00684	0.2527	0.2499	0.2472	0.2444	0.2417	0.2389	0.2355	0.2333	0.2309
0.00906	0.2414	0.2385	0.2358	0.2328	0.2300	0.2270	0.2237	0.2211	0.2183
0.01023	0.2371	0.2341	0.2310	0.2279	0.2250	0.2217	0.2185	0.2154	0.2120
0.01518	0.2210	0.2179	0.2148	0.2117	0.2084	0.2055	0.2025	0.1990	0.1958
0.02009	0.2109	0.2075	0.2041	0.2007	0.1973	0.1940	0.1904	0.1870	0.1839
0.02896	0.1972	0.1936	0.1900	0.1863	0.1827	0.1791	0.1751	0.1720	0.1686
0.04175	0.1814	0.1778	0.1740	0.1705	0.1675	0.1634	0.1598	0.1562	0.1527
0.05184	0.1734	0.1697	0.1663	0.1626	0.1592	0.1557	0.1523	0.1487	0.1453
0.05777	0.1704	0.1666	0.1630	0.1591	0.1552	0.1518	0.1482	0.1444	0.1406
0.06839	0.1637	0.1597	0.1560	0.1519	0.1480	0.1443	0.1409	...	...
0.08179	0.1573	0.1532	0.1490	0.1450	0.1411	0.1370	0.1331	...	...
0.09087	0.1518	0.1480	0.1441	0.1400	0.1362	0.1330	0.1295	...	...

where d_0 is the density of the solvent at the particular temperature.

The values of $E_m°$ at different temperatures can be expressed as a function of temperature ($t°$ C.) by equations obtained by the method of least squares. These are as follows for the two solvents:

For the Ag–AgBr electrode in ethylene glycol,

$$E_m° = -0.1007 - 1.16 \times 10^{-3}(t - 25) - 9.02 \times 10^{-7}(t - 25)^2 \quad (5)$$

For the Ag–AgCl electrode in propylene glycol,

$$E_m° = -0.0323 - 1.58 \times 10^{-3}(t - 25) - 8.96 \times 10^{-7}(t - 25)^2 \quad (6)$$

The standard deviation in $E_m°$, calculated from the differences between the extrapolated value of $E_m°$ at any temperature and the corresponding value obtained from Equation 5 or 6, comes out as ±0.4 mv.

Although $E_m°$ for the Ag–AgBr electrode in ethylene glycol at 30° C. exhibits only a 3-mv. discrepancy over the corresponding data of a previous study (*6*), the corresponding value for Ag–AgCl in propylene glycol at 30° C. is appreciably greater, being 11 mv. more negative. The more negative values of $E_m°$ in both cases of the present study indicate that the samples of the solvents used in previous studies were not dry enough, though they had similar treatment for purification. The physical properties noted by us did not, however, register the subtle differences in the moisture contents of the solvents.

$E°$ of the Ag–AgCl electrode for propylene glycol at 25° C. has subsequently been redetermined by Amrita Lal De in this laboratory, using a different sample of the solvent purified by the same method. The value of $E_m°$ obtained by him is −0.0315, which is in agreement with what is reported in the present paper. The $E°'$ values obtained by De are also plotted in Figure 2 for comparison.

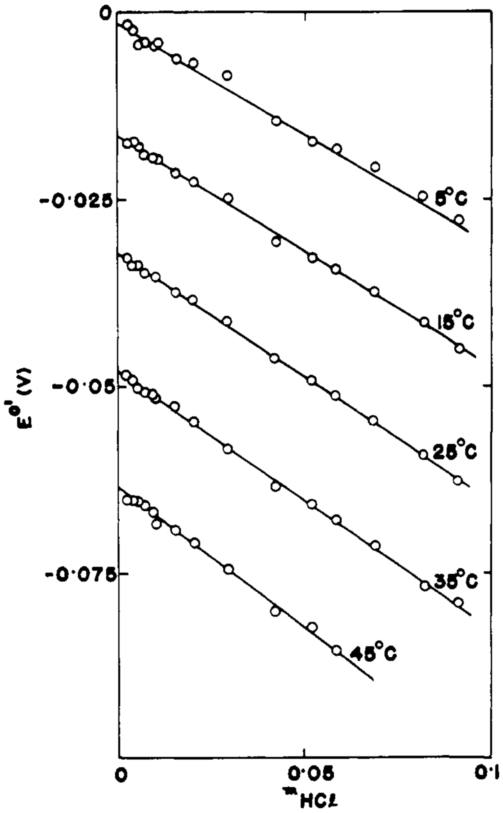

Figure 2. Extrapolation of e.m.f. data to give $E_m°$ for Ag–AgCl electrode in propylene glycol at different temperatures

ACTIVITY COEFFICIENTS OF HBr IN ETHYLENE GLYCOL AND HCl IN PROPYLENE GLYCOL

Activity coefficients of HBr in ethylene glycol and HCl in propylene glycol at 5°, 25°, and 45° C. for different molalities were computed from the equation

Table IV. Standard Potentials of Ag–AgX Electrodes in Glycols at Different Temperatures

	5° C.	10° C.	15° C.	20° C.	25° C.	30° C.	35° C.	40° C.	45° C.
				X = Br in Ethylene Glycol					
$E_m°$, v.	−0.0780	−0.0840	−0.0895	−0.0952	−0.1007	−0.1068	−0.1130	−0.1187	−0.1245
$E_N°$, v.	−0.2113	−0.2197	−0.2276	−0.2357	−0.2436	−0.2521	−0.2606	−0.2687	−0.2769
$E_c°$, v.	−0.0724	−0.0785	−0.0840	−0.0898	−0.0953	−0.1015	−0.1078	−0.1136	−0.1195
				X = Cl in Propylene Glycol					
$E_m°$, v.	−0.0015	−0.0089	−0.0166	−0.0244	−0.0323	−0.0402	−0.0483	−0.0561	−0.0638
$E_N°$, v.	−0.1250	−0.1346	−0.1444	−0.1545	−0.1646	−0.1748	−0.1851	−0.1951	−0.2050
$E_c°$, v.	+0.0007	−0.0068	−0.0147	−0.0226	−0.0307	−0.0387	−0.0470	−0.0549	−0.0628

Table V. Activity Coefficients $\left({}^s_s\gamma\right)$ of HX at 5°, 25°, and 45° C. and Relative Partial Molal Heat Content of HX ($\bar{L}_2$ in Cal./Mole) at 25° C. in Glycols

	X = Br in Ethylene Glycol					X = Cl in Propylene Glycol			
m_{HBr}	5° C.	25° C.	45° C.	$\bar{L}_2$	m_{HCl}	5° C.	25° C.	45° C.	$\bar{L}_2$
0.005	0.824	0.795	0.783	447	0.005	0.755	0.738	0.718	447
0.01	0.767	0.740	0.727	468	0.01	0.698	0.675	0.653	589
0.02	0.703	0.679	0.665	488	0.02	0.607	0.583	0.560	677
0.03	0.663	0.643	0.627	497	0.03	0.565	0.535	0.511	895
0.04	0.638	0.617	0.602	506	0.05	0.499	0.470	0.440	1119
0.05	0.625	0.602	...	...	0.07	0.462	0.428	...	...
0.07	0.605	0.582	...	...	0.10	0.445	0.410	...	...
0.10	0.590	0.557	...	...					

$$\log {}^s_s(\gamma) = \frac{E_m^\circ - E}{2k} - \log m \qquad (7)$$

using the respective values of E_m° evaluated above. The activity coefficients $\left({}^s_s\gamma\right)$ are referred to at a value of unity for infinitely dilute solutions in the respective solvents. The values of $\left({}^s_s\gamma\right)$ were plotted against molality on a large scale and from the plots the activity coefficients at round values of molalities were tabulated for HBr in ethylene glycol and HCl in propylene glycol (Table V). Values of relative partial molal heat content, $\bar{L}_2$, of HX were calculated from the temperature coefficients of $\left(\log {}^s_s\gamma\right)$ using the relation

$$\bar{L}_2 = -2 \times 2.303\, RT^2 \left[\frac{d \log({}^s_s\gamma)}{dT}\right]_P \qquad (8)$$

where T denotes temperature on the Kelvin scale.

Table V also includes $\bar{L}_2$ values for HX in the two solvents.

Since there is an average uncertainty of ±0.0005 volt in e.m.f. values, the activity coefficients $\left({}^s_s\gamma\right)$ in a logarithmic scale may involve an average error of nearly ±0.004 unit and, consequently, the average uncertainty in $\bar{L}_2$ is roughly ±90 cal. per mole.

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Received for review July 15, 1968. Accepted August 8, 1969. Work done under a project financed by the National Bureau of Standards.

Vapor-Liquid Equilibrium Data for the Ternary System: Methyl Acetate–Carbon Tetrachloride–Benzene

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Equilibrium data for the title ternary system are reported at 1 atm. Experimental values are in good agreement with vapor compositions and temperatures calculated from the Wilson equation.

THREE related sets of isobaric binary data have been published: methyl acetate-carbon tetrachloride (*8*), methyl acetate–benzene (*6*), and carbon tetrachloride–benzene (*2*). This work presents vapor-liquid equilibrium data for the ternary methyl acetate-carbon tetrachloride–benzene system at 1 atm. The Wilson equation, expressing activity coefficients as a function of liquid compositions and temperature, is used to correlate the observed results.

EXPERIMENTAL

All C.P. chemicals were used after purification. Methyl acetate was purified in accordance with the method of Hurd and Strong (*4*). Carbon tetrachloride was refluxed with sodium hydrate, washed with water, dried with anhydrous potassium carbonate, and distilled. Repeated recrystallization gave benzene of good quality. Table I shows the properties of the chemicals used. A Jones vapor-recirculation equilibrium still, designed by Jones, Schoenborn, and Colburn (*3*), was used to obtain the vapor-liquid equilibrium data. Temperatures of boiling mixtures were measured using a Yokogawa P-7 potentiometer and a copper-constantan thermocouple, which was calibrated against a standard mercury thermometer. The temperature measurements are believed to be accurate within ±0.05° C. The atmospheric pressure variation was recorded for each experimental run with a mercury barometer. The appropriate corrections to barometric reading were added to the measured pressures (*3*). The maximum deviations of the observed pressures from 1 atm. were −13.2 and