

# Conductivity Measurements of Dilute Aqueous HCl Solutions to High Temperatures and Pressures Using a Flow-Through Cell

Patience C. Ho,\* Donald A. Palmer, and Mirosław S. Gruszkiewicz

Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831-6110

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The limiting molar conductance  $\Lambda_0$  and molal ion association constant  $K_A(m)$  of dilute ( $10^{-5}$  to  $10^{-3}$  mol·kg $^{-1}$ ) aqueous HCl solutions were determined using a flow-through conductance cell at temperatures from 100 to 410 °C and densities from 0.96 to 0.27 g·cm $^{-3}$ . The flow-through cell is designed to measure molar conductances of dilute aqueous electrolytes with a high degree of accuracy at high temperatures and low densities. The resulting  $\Lambda_0$  values are in general agreement with those reported by Noyes (1907), Wright et al. (1961), Pearson et al. (1963), and Lukashov et al. (1975) for densities that range from 0.7 to 0.4 g·cm $^{-3}$  at comparable conditions. However, when compared to values reported by Frantz and Marshall (1984), the new results are in agreement at densities ( $\rho$ ) > 0.5 g·cm $^{-3}$ , but from 0.5 to ca. 0.4 g·cm $^{-3}$ , their calculated results are 5–11% higher. Below 0.4 g·cm $^{-3}$  where the experimental uncertainties are large, the weighted values from the new study are approximately 14–35% lower. Within experimental uncertainties, the new  $K_A(m)$  values are in good agreement with the reported values from Franck (1956), Wright et al. (1961), Pearson et al. (1963), and Lukashov et al. (1975) at densities from 0.7 to 0.3 g·cm $^{-3}$  but are only in fair agreement with the Frantz and Marshall values at densities above 0.5 g·cm $^{-3}$ . Below 0.5 g·cm $^{-3}$ , the latter values are 0.5–2.5 log units higher than the new results.

## 1. Introduction

In aqueous solutions, hydrochloric acid behaves similarly to other electrolytes but exhibits a stronger tendency to associate at high temperatures and at low solution densities. Knowledge of the association constants of HCl is important in interpreting the thermodynamics of ion–ion and ion–water interactions in solutions from sub- to supercritical conditions where the thermodynamic properties of electrolytes such as HCl undergo dramatic changes. Conductance data not only provide a basic understanding of the behavior of electrolytes under extreme conditions but also yield information relevant to geochemical systems, the chemistry occurring in water/steam cycles in power plants, nuclear waste disposal, and supercritical water degradation of organic wastes.

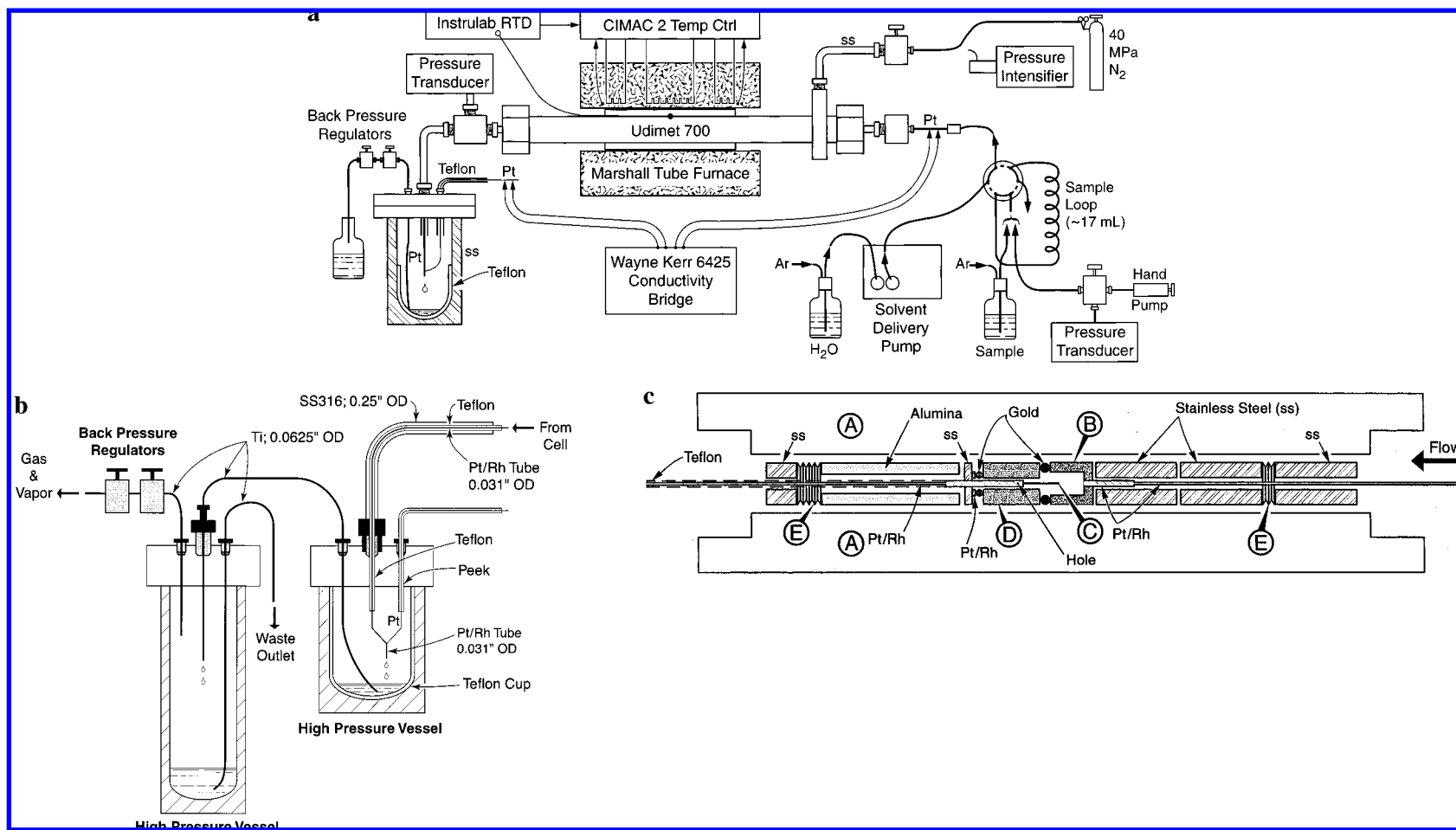
The electrical conductance of dilute aqueous HCl solutions at high temperatures and pressures has been measured at saturated vapor pressure by Noyes<sup>1</sup> and Wright et al.<sup>2</sup> In 1956 Franck<sup>3</sup> measured the electrical conductance of a 0.01 mol·kg $^{-1}$  HCl solution at temperatures from 200 to 700 °C and at pressures up to 250 MPa and computed the ionization constants. However, due to corrosion the experiments were then considered to be suspect. In 1963 and 1975 Pearson et al.<sup>4</sup> and Lukashov et al.<sup>5</sup> measured the conductances of HCl solutions at 300–383 °C and 306–373 °C, respectively, but it was not until 1984 that Frantz and Marshall<sup>6</sup> used the original static-cell setup<sup>7</sup> at Oak Ridge National Laboratory to perform measurements of HCl (aq) over wider ranges of temperatures (to 800 °C) and pressures (to 400 MPa). Because of the inherent physical limitations of the static cell as well as corrosion problems, the data obtained by this technique were quite scattered. Therefore,

before these measurements could be repeated effectively, corrosion-free conditions had to be achieved and much lower concentrations needed to be investigated.

In two recent studies,<sup>8,9</sup> a flow-through cell was used to measure the conductances of dilute alkali chloride and hydroxide solutions in the concentration range of  $10^{-5}$  to  $10^{-3}$  mol·kg $^{-1}$ , at densities as low as 0.3 g·cm $^{-3}$  with a high degree of accuracy. In this report, the results of measurements with this cell of HCl-(aq) are presented from 100 to 410 °C and at pressures up to 32 MPa.

## 2. Experimental Section

The design of the flow-through conductance cell has been described in detail in previous papers.<sup>8,9</sup> The configuration of the cell incorporating a coaxial electrode arrangement is shown schematically in Figure 1a. However, as shown in Figure 1b, a minor modification was made by adding a second low-temperature, high-pressure vessel (High Pressure Equipment) downstream of the conductance cell for waste collection. In this setup, only gas and vapor were allowed to vent through the two back-pressure regulators in order to prevent corrosion of the regulators. Figure 1c presents a cross-sectional view of the tubular conductance cell, which consists of a 60.96 cm long (2.54 cm o.d.) Udimet high-pressure vessel<sup>7</sup> housing platinum (90%)-rhodium (10%) (Pt/Rh) alloy tubing, gold gaskets, and a rutile insulator. The input flow to the cell was routed through a series of Pt/Rh tubes gold-welded together: initially a 0.159 cm o.d. (60 cm long and 0.073 cm i.d.) tube, then a larger tube,



**Figure 1.** (a) Schematic diagram of the flow-through conductance measurement system. (b) Schematic diagram of the partial downstream section of the flow-through cell apparatus. (c) Cross-sectional view of the tubular, flow-through conductance cell: (A) high pressure vessel (Udimet 700); (B) Pt/Rh cell chamber; (C) Pt/Rh inner electrode; (D) sapphire or rutile insulator; (E) Belleville washer springs.

0.318 cm o.d. (10 cm long and 0.159 cm i.d.), and finally, the Pt/Rh cup (1.98 cm long, 0.635 cm o.d. and 0.318 cm i.d.). The cup, which was in electrical contact with the Udimet vessel wall and served as the outer electrode, was coated on the inside with platinum black to maintain a reasonably small frequency dependence. The outflow from the cell was routed directly through a slit cut near the base of the inner electrode, which was made from a 0.079 cm o.d. Pt/Rh tube sealed at one end with gold. The outer surface of the electrode was coated with platinum black. Flow continued through another series of gold-welded Pt/Rh tubes: first a 0.318 cm o.d. tube (15 cm long and 0.159 cm i.d.) and, then, a 0.159 cm o.d. tube (ca. 54 cm long and 0.079 cm i.d.). The inner electrode protruded from a rutile insulation disk (1.27 cm long, 0.625 cm o.d., and 0.165 cm i.d.) and extended about 1 cm into the cup. One annealed gold washer was placed on the rim of the cup to create the seal between the sample chamber and the rutile insulator. Another annealed gold washer was backed by Pt/Rh and stainless steel disks and was located on the downstream side of the rutile to provide support and cushion for the rutile. In addition to the Pt/Rh cell body, the tubing was fabricated from titanium metal, which is highly resistant to corrosion by dilute acid and base solutions. The conductivity of dilute aqueous HCl solutions was measured using a commercial titanium metal injector valve, pump, and tubing that were rated to 50, 69, and 104 MPa, respectively.

The experimental procedures employed here were similar to those described in previous papers.<sup>8,9</sup> To eliminate problems due to small contributions from adsorption of ionic species on the metal oxide surfaces,<sup>9</sup> at temperatures  $\leq 350$  °C, the initial flow rate was set at 0.4 mL·min<sup>-1</sup> for 20 min and then reduced to 0.15 mL·min<sup>-1</sup> for another 30 min before the resistance measurement was taken. Above 350 °C, this initial flushing of this cell was reduced to ca. 5 min before being reduced to 0.18–0.2 mL·min<sup>-1</sup> and resistance was measured after 40–50 min. Generally, 20 min after the sample solution was injected, the resistance reading reached a constant value for the next 30 min. After the resistance of the conductance of water (solvent) was measured, the injector valve was returned to the load position with a flow rate of 0.2 mL·min<sup>-1</sup> until the next solution was ready for injection. Each sample solution was prepared by adding an aliquot of stock solution from a weighed polyethylene syringe into a bottle containing a weighed quantity of degassed water under helium. The empty syringe was then reweighed to determine the amount of stock solution delivered. After mixing, the sample solution was forced into the sample loop with the valve set on load, then injected in the same manner described.

For each sample series, the resistance of the solvent water was measured prior to measuring the sample solutions at frequencies from 0.5 to 10 kHz. The frequency dependence was extrapolated (resistance versus the reciprocal square root of frequency) to infinite frequency by means of a simple linear regression.

**2.1 Solutions.** The stock solutions of HCl were obtained by diluting a standardized 1.4646 mol·kg<sup>-1</sup> HCl solution (standardized by weight against NaOH and Na<sub>2</sub>CO<sub>3</sub> solutions, contains 94.9305% H<sub>2</sub>O) with conductivity water<sup>8</sup> to achieve the desired concentrations. The concentrated stock solutions were stored in polyethylene bottles under helium. Dilute solutions were prepared by adding aliquots of the concentrated stock solution from polyethylene syringes to “confirmed” conductivity-grade water under helium. A series of sample solutions in the

concentration range of 10<sup>-5</sup> to 10<sup>-3</sup> mol·kg<sup>-1</sup> was prepared by consecutively adding stock solution to the most dilute sample solution.

**2.2 Cell Constant.** The cell constant at 25 °C was approximately 0.2 cm<sup>-1</sup> as determined by measuring the resistance of 10<sup>-4</sup> to 10<sup>-3</sup> mol·kg<sup>-1</sup> KCl solutions and calculated according to equations given by Justice<sup>10</sup> adjusted to the ITS90 scale. The exact value of cell constant is dependent upon the specific dimensions of the electrode assembly. Note that molality was converted to molarity using density data for KCl at 25 °C calculated from the partial molar volumes of KCl at 25 °C.<sup>11</sup> Cell constants obtained at 25 °C from seven sample solutions generally agree to within  $\pm 0.2\%$ . The cell was then heated to 400 °C (30 MPa) and allowed to cool to 25 °C, whereupon the cell constant was generally observed to change less than 0.3%. The cell constant was calculated at high temperatures by correcting for the thermal expansion of rutile and platinum. The correction is less than 0.1% at 400 °C.

### 3. Results and Discussion

The HCl solution concentrations ranged from 10<sup>-5</sup> to 10<sup>-3</sup> mol·kg<sup>-1</sup> at 100–410 °C and pressures up to 32 MPa. Table 1 gives the experimental values for the molar conductances ( $\Lambda_{\text{exp}}$ ) of HCl(aq) and the average percentage relative deviations ( $\delta\Lambda$ ) from values ( $\Lambda_{\text{calcd.}}$ ) calculated by the FHFP (Fuoss–Hsia–Fernández–Prini) equation<sup>12</sup>

$$\Lambda = \alpha(\Lambda_0 - S(\alpha c)^{1/2} + E\alpha c \ln(\alpha c) - J_1\alpha c + J_2(\alpha c)^{3/2}) \quad (1)$$

where  $\alpha$  is the degree of dissociation calculated from the mass action equation with the mean activity coefficient  $\gamma_{\pm}$  of the free ions calculated based on the Debye–Hückel limiting law.

$$K_A(M) = \rho K_A(m) = (1 - \alpha)/(\alpha^2 c \gamma_{\pm}^2) \quad (2)$$

$$\ln \gamma_{\pm} = -\kappa q \alpha^{1/2} / (1 + \kappa a \alpha^{1/2}) \quad (3)$$

The constants  $S$ ,  $E$ ,  $J_1$  and  $J_2$  in eq 1 carry the same definitions and are calculated according to equations given in ref 12. In eqs 2 and 3,  $K_A(M)$  and  $K_A(m)$  are the molar and molal association constants, respectively,  $\rho$  is the solvent density,  $\kappa$  is the reciprocal radius of the ionic atmosphere,  $q$  is the Bjerrum distance, and  $a$  is the distance of the closest approach set equal to  $q$  according to the recommendation of Justice.<sup>10</sup> The values of dielectric constant ( $\epsilon$ ) and viscosity ( $\eta$ ) used for calculating constants  $S$  and  $E$  in eq 1 are obtained from Archer and Wang,<sup>13</sup> Uematsu and Franck,<sup>14</sup> Watson et al.<sup>15</sup> and the NBS/NRC Steam Tables.<sup>16</sup>

The solution densities are computed from the partial molar volumes of HCl(aq) at temperatures up to 350 °C<sup>17,18</sup> and using water densities<sup>19</sup> at the experimental temperatures and pressures. At temperatures  $> 350$  °C the partial molar volumes of 1–1 electrolytes are not too different from one another and, therefore, the partial molar volumes of HCl(aq) are calculated on the basis of measured values for NaCl.<sup>20,21</sup>

Figure 2 presents examples of experimental  $\Lambda$  values of HCl(aq) at temperatures from 380 to 410 °C and densities from 0.5 to 0.27 g·cm<sup>-3</sup> as a function of the square roots of the molar concentration (mol·dm<sup>-3</sup>). It can be seen that  $\Lambda$  decreases sharply with increasing temperature and decreasing density, indicating strong ion association in these HCl solutions, particularly at low densities. Above 390 °C the experimental data deviated considerably from the calculated values from eq 1, and the degree of deviation ( $\delta\Lambda$ ) increased with decreasing

**TABLE 1: Experimental Value of  $\Lambda$  of HCl Solutions and Percent Average Relative Errors ( $\delta\Lambda$ ) from Value Calculated by Eq 1**

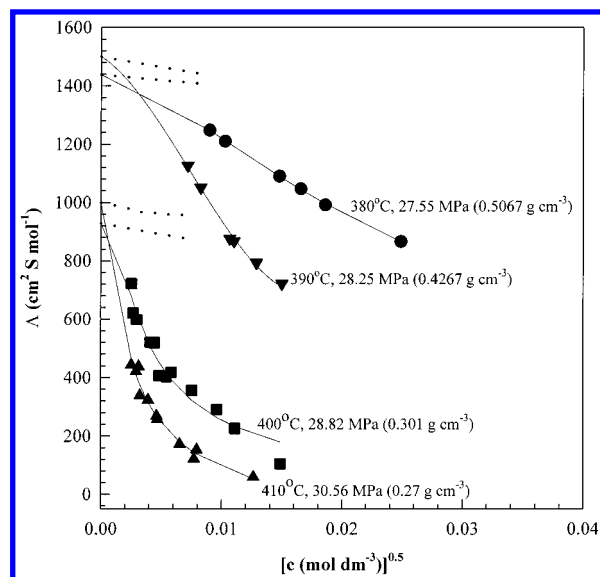
| $T, ^\circ\text{C}$ | $P, \text{MPa}$ | $10^7\chi_s^a$<br>$\text{S}\cdot\text{cm}^{-1}$ | $10^5m$ ,<br>$\text{mol}\cdot\text{kg}^{-1}$ | $10^5c$ ,<br>$\text{mol}\cdot\text{dm}^{-3}$ | $\Lambda, \text{S}\cdot\text{cm}^2\cdot$<br>$\text{mol}^{-1}$ | $\delta\Lambda, \%$ | $T, ^\circ\text{C}$ | $P, \text{MPa}$ | $10^7\chi_s^a$<br>$\text{S}\cdot\text{cm}^{-1}$ | $10^5m$ ,<br>$\text{mol}\cdot\text{kg}^{-1}$ | $10^5c$ ,<br>$\text{mol}\cdot\text{dm}^{-3}$ | $\Lambda, \text{S}\cdot\text{cm}^2\cdot$<br>$\text{mol}^{-1}$ | $\delta\Lambda, \%$ |
|---------------------|-----------------|---|--|--|---|---------------------|---------------------|-----------------|---|--|--|---|---------------------|
| 100.00              | 9.81            | 30.95   | 19.534                                       | 18.811                                       | 831.8   | -0.01               | 380.00              | 27.59           | 5.77  | 20.787                                       | 10.547                                       | 1210.5  | -0.11               |
|                     | 9.9             |   | 41.643                                       | 40.099                                       | 829.02  | 0.02                |                     | 27.59           |   | 43.097                                       | 21.871                                       | 1090.7  | 0.1                 |
|                     | 9.79            |   | 67.619                                       | 65.107                                       | 826.21  | 0.003               |                     | 27.55           |   | 68.258                                       | 34.616                                       | 992.19  | -0.4                |
|                     | 9.88            | 22.67   | 30.610                                       | 29.475                                       | 830.32  | 0.01                |                     | 27.61           |   | 122.09                                       | 62.048                                       | 867.04  | 0.08                |
|                     | 9.9             |   | 55.357                                       | 53.304                                       | 827.23  | -0.02               | 390.00              | 27.23           | 4.62  | 29.727                                       | 11.274                                       | 850.68  | 1.04                |
| 200.00              | 10.04           | 48.75   | 23.626                                       | 20.579                                       | 1186.9  | -0.16               |                     | 27.23           |   | 66.353                                       | 25.176                                       | 680.26  | 1.24                |
|                     | 9.98            |   | 42.222                                       | 36.775                                       | 1183.8  | -0.01               |                     | 27.23           |   | 94.915                                       | 36.026                                       | 553.92  | 8.17                |
|                     | 10.04           |   | 73.063                                       | 63.64  | 1178  | 0.03                |                     | 27.28           |   | 130.82                                       | 49.6   | 494.55  | -8.73               |
|                     | 10.05           |   | 116.39                                       | 101.38                                       | 1170.6  | -0.02               |                     | 27.22           |   | 17.821                                       | 6.7502                                       | 987.39  | 4.06                |
|                     | 10.01           |   | 175.21                                       | 152.61                                       | 1161.7  | -0.13               | 390.00              | 28.26           | 4.2   | 12.123                                       | 5.1777                                       | 1126.8  | 0.11                |
|                     | 9.99            |   | 22.348                                       | 19.465                                       | 1188.5  | -0.05               |                     | 28.25           |   | 28.597                                       | 12.207                                       | 868.06  | -0.96               |
|                     | 10.02           |   | 46.189                                       | 40.231                                       | 1184.1  | 0.1                 |                     | 28.26           |   | 52.884                                       | 22.597                                       | 721.2   | 1.72                |
|                     | 10.05           |   | 94.162                                       | 82.019                                       | 1177  | 0.24                |                     | 28.24           |   | 16.084                                       | 6.8611                                       | 1051.9  | 0.81                |
| 300.00              | 10.19           | 31.85   | 39.99  | 28.630                                       | 1395.5  | 0.03                |                     | 28.23           |   | 26.868                                       | 11.45  | 876.84  | -2                  |
|                     | 10.19           |   | 55.666                                       | 39.854                                       | 1388.9  | 0.03                |                     | 28.23           |   | 39.121                                       | 16.674                                       | 793.79  | 0.6                 |
|                     | 10.2            |   | 81.363                                       | 58.256                                       | 1378.9  | -0.06               | 390.00              | 30.45           | 5.89  | 3.0848                                       | 1.468  | 1464.7  | 4.12                |
|                     | 10.14           |   | 120.05                                       | 85.942                                       | 1367.7  | -0.06               |                     | 30.46           |   | 9.8666                                       | 4.6974                                       | 1201.7  | -5.26               |
|                     | 10.14           |   | 182.4  | 130.58                                       | 1354.7  | 0.05                |                     | 30.46           |   | 17.663                                       | 8.4096                                       | 1158  | -0.0001             |
| 300.00              | 10.17           | 30.76   | 23.663                                       | 16.94  | 1404  | -0.24               |                     | 30.48           |   | 34.233                                       | 16.313                                       | 1012.5  | 0.08                |
|                     | 10.27           |   | 42.645                                       | 30.538                                       | 1399.5  | 0.06                |                     | 30.43           |   | 59.934                                       | 28.518                                       | 871.54  | -0.68               |
|                     | 10.27           |   | 65.293                                       | 46.757                                       | 1392.3  | 0.12                | 400.00              | 28.8            | 2.83  | 2.142  | 0.6439                                       | 721.93  | 7.78                |
|                     | 10.3            |   | 108.47                                       | 77.688                                       | 1381  | 0.16                |                     | 28.81           |   | 6.5431                                       | 1.9637                                       | 519.32  | 4.97                |
|                     | 10.27           |   | 219.65                                       | 157.31                                       | 1355.4  | -0.12               |                     | 28.82           | 2.12  | 2.3682                                       | 0.7119                                       | 620.34  | -5.04               |
| 350.00              | 26.11           | 20.06   | 31.404                                       | 19.79  | 1410.8  | -0.02               |                     | 28.83           |   | 5.5573                                       | 1.6736                                       | 520.84  | 0.19                |
|                     | 26.1            |   | 53.953                                       | 33.997                                       | 1390.7  | -0.02               |                     | 28.80           |   | 11.26  | 3.3738                                       | 417.78  | 2.85                |
|                     | 26.13           |   | 81.51  | 51.373                                       | 1371.1  | 0.06                |                     | 28.84           |   | 2.9346                                       | 0.8837                                       | 598.28  | -3.65               |
|                     | 26              |   | 113.48                                       | 71.467                                       | 1350.3  | 0.03                |                     | 28.85           |   | 7.6965                                       | 2.3179                                       | 406.53  | -14.9               |
|                     | 26.18           |   | 147.7  | 93.127                                       | 1329.9  | -0.05               |                     | 28.81           | 3.05  | 9.7764                                       | 2.9343                                       | 403.1   | -6.28               |
| 350.00              | 27.82           | 20.88   | 9.8963                                       | 6.3001                                       | 1459.6  | -0.04               |                     | 28.81           |   | 18.91  | 5.6764                                       | 355.98  | 8.7                 |
|                     | 27.8            |   | 20.618                                       | 13.124                                       | 1447.3  | -0.03               |                     | 28.81           |   | 30.678                                       | 9.2107                                       | 291.33  | 12.8                |
|                     | 27.79           |   | 28.179                                       | 17.936                                       | 1440.8  | 0.03                |                     | 28.81           |   | 41.032                                       | 12.322                                       | 226.04  | 5.36                |
|                     | 27.79           |   | 50.303                                       | 32.02  | 1422.3  | -0.02               |                     | 28.81           | 2.5   | 3.3003                                       | 0.9932                                       | 599.78  | 1.73                |
|                     | 27.79           | 20.97   | 14.503                                       | 9.2315                                       | 1455.3  | 0.06                |                     | 28.81           |   | 27.848                                       | 8.3828                                       | 271.42  | -6.53               |
| 370.00              | 28.89           | 11.75   | 1.4609                                       | 0.8362                                       | 1477.1  | -0.03               |                     | 28.82           |   | 73.387                                       | 22.097                                       | 105.39  | -31.3               |
|                     | 28.89           |   | 9.6413                                       | 5.5188                                       | 1442.2  | 0.03                | 400.00              | 29.55           | 4.5   | 11.343                                       | 3.8279                                       | 669.48  | 3                   |
|                     | 28.9            |   | 3.9318                                       | 2.2508                                       | 1464.8  | 0.01                |                     | 29.55           |   | 22.461                                       | 7.581  | 499.61  | -7.49               |
|                     | 28.89           |   | 8.5582                                       | 4.8882                                       | 1446.9  | 0.08                |                     | 29.56           |   | 37.707                                       | 12.747                                       | 396.95  | -14.5               |
|                     | 28.89           |   | 13.812                                       | 7.9065                                       | 1426.6  | -0.1                |                     | 29.52           | 3.19  | 7.3613                                       | 2.4738                                       | 769.49  | 6.58                |
|                     | 28.9            |   | 26.993                                       | 15.456                                       | 1392.6  | 0.02                |                     | 29.54           | 2.96  | 7.1536                                       | 2.4107                                       | 784.01  | 7.8                 |
| 370.00              | 27.81           | 10.48   | 14.503                                       | 8.1953                                       | 1401.7  | -0.21               |                     | 29.54           |   | 14.09  | 4.7485                                       | 574.2   | -6.94               |
|                     | 27.79           |   | 24.242                                       | 13.696                                       | 1355.7  | -0.08               |                     | 29.55           | 3.5   | 3.6026                                       | 1.2157                                       | 807.11  | -1.46               |
|                     | 27.82           |   | 12.083                                       | 6.8286                                       | 1421.3  | 0.14                |                     | 29.55           |   | 1.4609                                       | 0.493  | 897.15  | -1.58               |
|                     | 27.84           |   | 25.863                                       | 14.622                                       | 1347.6  | 0.004               | 400.00              | 30.75           | 2.35  | 3.1175                                       | 1.2073                                       | 803.02  | -2.61               |
|                     | 27.83           |   | 42.841                                       | 24.221                                       | 1285.8  | -0.02               |                     | 30.76           |   | 6.9044                                       | 2.6762                                       | 610.94  | 1.99                |
| 380.00              | 31.14           | 9.29  | 2.2931                                       | 1.2476                                       | 1380.2  | 0.01                |                     | 30.76           |   | 14.697                                       | 5.6935                                       | 325.73  | -1.8                |
|                     | 31.14           |   | 5.2558                                       | 2.8597                                       | 1334.7  | -0.01               |                     | 30.76           | 2.65  | 2.521  | 0.9771                                       | 869.07  | -0.45               |
|                     | 31.17           |   | 11.059                                       | 6.0201                                       | 1263.1  | -0.01               |                     | 30.75           |   | 4.6739                                       | 1.81   | 742.75  | 3.43                |
|                     | 31.15           | 8.59  | 1.4681                                       | 0.7989                                       | 1394.7  | 0.02                |                     | 30.76           |   | 1.6113                                       | 0.6245                                       | 977.62  | 1.73                |
|                     | 31.15           |   | 3.7582                                       | 2.0451                                       | 1355.7  | -0.07               |                     | 30.76           |   | 3.3204                                       | 1.287  | 784.63  | -3.03               |
|                     | 31.14           |   | 6.1643                                       | 3.3543                                       | 1323.2  | 0.01                | 410.00              | 30.52           | 2.43  | 3.6253                                       | 0.9729                                       | 438.01  | 11.6                |
| 380.00              | 28.6            | 7.93  | 6.206  | 3.2274                                       | 1337.5  | -0.18               |                     | 30.57           |   | 7.9034                                       | 2.1354                                       | 268.81  | 0.51                |
|                     | 28.59           |   | 14.247                                       | 7.4071                                       | 1247.8  | 0.05                |                     | 30.56           |   | 15.779                                       | 4.2571                                       | 172.18  | -4.8                |
|                     | 28.6            |   | 22.758                                       | 11.837                                       | 1169.1  | -0.32               |                     | 30.57           |   | 23.273                                       | 6.2894                                       | 153.43  | 9.91                |
|                     | 28.59           |   | 29.122                                       | 15.143                                       | 1129.1  | 0.17                |                     | 30.56           |   | 2.3581                                       | 0.6361                                       | 443.53  | -4.25               |
|                     | 28.59           |   | 8.0119                                       | 4.1652                                       | 1319.1  | 0.21                |                     | 30.55           |   | 5.6587                                       | 1.5245                                       | 323.54  | 2.37                |
|                     | 28.58           |   | 17.258                                       | 8.9719                                       | 1219.5  | 0.06                |                     | 30.57           |   | 3.8752                                       | 1.0467                                       | 338.17  | -11.1               |
| 380.00              | 27.58           | 8.82  | 15.931                                       | 8.0806                                       | 1248  | 0.04                |                     | 30.57           |   | 8.0756                                       | 2.1819                                       | 257.39  | -2.75               |
|                     | 27.45           |   | 54.226                                       | 27.415                                       | 1047.3  | 0.29                |                     | 30.53           | 1.86  | 3.1547                                       | 0.8474                                       | 421.29  | 2.51                |
|                     |                 |   |  |  |   |                     |                     | 30.56           |   | 22.024                                       | 5.9424                                       | 122.28  | -17.8               |
|                     |                 |   |  |  |   |                     |                     | 30.54           |   | 59.151                                       | 15.927                                       | 59.726  | 11.5                |

<sup>a</sup> Specific conductance of solvent.

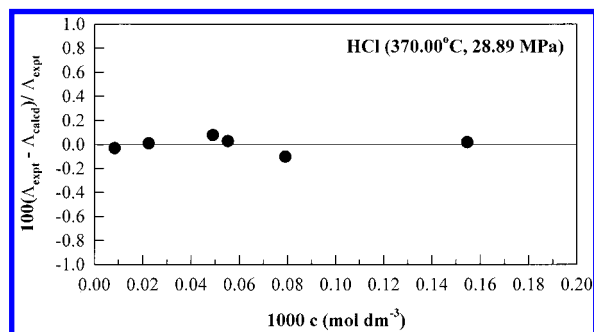
density. Therefore, large  $\delta\Lambda$  values were obtained at temperatures  $>390^\circ\text{C}$  and  $\rho < 0.5 \text{ g}\cdot\text{cm}^{-3}$ . The deviations between  $\Lambda_{\text{expt}}$  and  $\Lambda_{\text{calcd}}$  using the best fit of each data set with eq 1 are in most cases less than 0.2% at temperatures  $<380^\circ\text{C}$  and increase to greater than 10% in several cases above  $400^\circ\text{C}$  (see Table 1). Figure 3 illustrates an example of percentage average errors ( $\delta\Lambda$ ) of HCl(aq) at  $370^\circ\text{C}$  and 28.89 MPa as a function of the molar concentration.

Compared to the results measured with the static cell at concentrations at 0.002, 0.005, and  $0.01 \text{ mol}\cdot\text{kg}^{-1}$ ,<sup>6</sup> the new results show an improvement of more than an order of magnitude in the precision, especially at low densities, and the lowest solute concentration that can be measured, is lower by 3 orders of magnitude. Therefore, the new results are very valuable in correlation with the previously reported values, especially at low densities.





**Figure 2.** Molar conductance of HCl(aq) as a function of square roots of molarity at 380 (●), 390 (▼), 400 (■), and 410 (▲) and Debye-Hückel-Onsager slopes (····). The solid lines were calculated by eq 1.



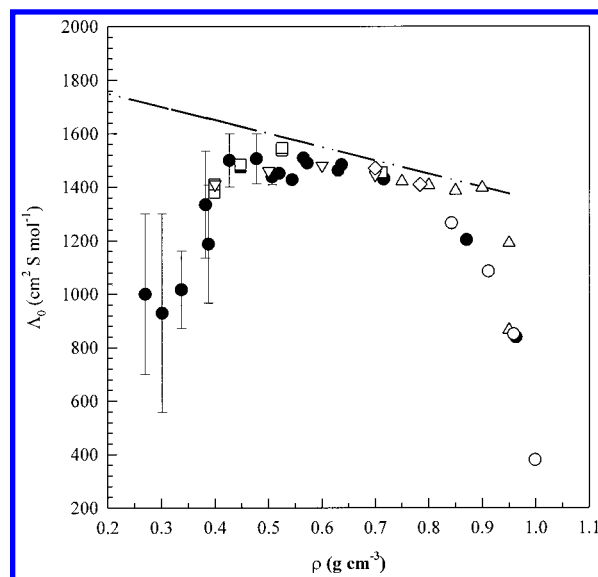
**Figure 3.** Deviations of experimental and fit values of molar conductance of HCl(aq) at 370 °C and 28.89 MPa as a function of molarity.

**TABLE 2: Limiting Molar Conductances ( $\Lambda_0$ ),  $\log K_A(m)$ , and  $\sigma$  of Aqueous HCl Solutions**

| <i>T</i> , K | <i>P</i> , MPa | $\rho$ , g·cm <sup>-3</sup> | $\Lambda_0$ , S·cm <sup>2</sup> ·mol <sup>-1</sup> | $\log K_A$              | $\sigma$ , S·cm <sup>2</sup> ·mol <sup>-1</sup> |
|--------------|----------------|-----------------------------|--|-------------------------|---|
| 373.15       | 9.87           | 0.9629                      | 838.14 ± 0.17                                      |                         | 0.1   |
| 473.15       | 10.02          | 0.871                       | 1202.8 ± 1.1                                       | 0.43 ± 0.23             | 1.6   |
| 573.15       | 10.17          | 0.7159                      | 1429.1 ± 0.9                                       | 0.97 ± 0.05             | 0.8   |
| 573.15       | 10.26          | 0.7161                      | 1432.2 ± 2.2                                       | 0.68 ± 0.23             | 2.7   |
| 623.15       | 27.8           | 0.6365                      | 1484.1 ± 0.7                                       | 1.68 ± 0.014            | 0.8   |
| 623.15       | 26.16          | 0.6301                      | 1462.4 ± 0.7                                       | 1.83 ± 0.003            | 0.7   |
| 643.15       | 28.89          | 0.5724                      | 1489.7 ± 2.5                                       | 2.29 ± 0.03             | 1.3   |
| 643.15       | 27.82          | 0.5651                      | 1508.8 ± 14.7                                      | 2.64 ± 0.06             | 3   |
| 653.15       | 31.15          | 0.5441                      | 1427.2 ± 4.3                                       | 3.07 ± 0.06             | 0.7   |
| 653.15       | 28.59          | 0.5198                      | 1451.1 ± 11.5                                      | 3.10 ± 0.03             | 2.9   |
| 653.15       | 27.55          | 0.5067                      | 1437.9 ± 29.2                                      | 3.00 ± 0.05             | 7.2   |
| 663.15       | 30.46          | 0.4772                      | 1505.9 ± 94  | 3.42 ± 0.24             | 45  |
| 663.15       | 28.25          | 0.4267                      | 1500 ± 100   | 3.87 ± 0.15             | 43.2  |
| 663.15       | 27.24          | 0.3823                      | 1334.6 ± 200                                       | 3.94 ± 0.25             | 40  |
| 673.15       | 30.76          | 0.3876                      | 1187.4 ± 220.6                                     | 4.15 ± 0.31             | 23.1  |
| 673.15       | 29.55          | 0.3373                      | 1016.7 ± 145                                       | 4.38 ± 0.22             | 47.2  |
| 673.15       | 28.82          | 0.301                       | 928.87 ± 371                                       | 4.97 ± 0.2              | 40  |
| 683.15       | 30.56          | 0.27                        | 1000 ± 300 <sup>a</sup>                            | 5.12 ± 0.4 <sup>a</sup> | 36.6  |

<sup>a</sup> These values were not estimated from the least-squares fit which would not determine accurate values for both  $\Lambda_0$  and  $\log K_A(m)$ . Instead we estimated  $\Lambda_0 = 1000 \pm 300$  by extrapolation from higher densities and then calculated  $K_A$  and its error bars by least squares with  $\Lambda_0$  equal to its extreme values. See text.

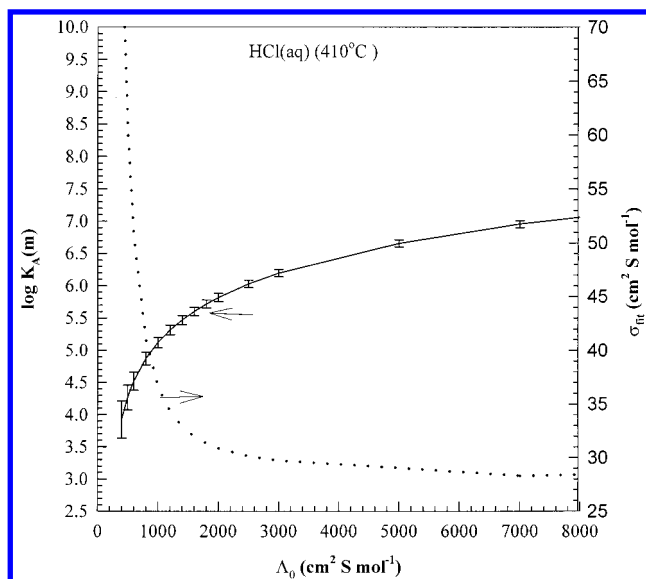
Table 2 gives the values of  $\Lambda_0$  and  $K_A(m)$  of HCl(aq) calculated by eqs 1–3. Figure 4 is a plot of  $\Lambda_0$  values for HCl-



**Figure 4.** Comparison of  $\Lambda_0$  of HCl(aq) as a function of density at 100–410 °C with those reported by Noyes<sup>1</sup> (○), Wright et al.<sup>2</sup> (◇), Pearson et al.<sup>4</sup> (□), Lukashov et al.<sup>5</sup> (▽), Frantz and Marshall<sup>6</sup> (Δ, expt, 100, 200 °C,  $\rho = 0.95$ , 300 °C,  $\rho = 0.85$ –0.75 and 350 °C,  $\rho = 0.9$  g·cm<sup>-3</sup>; ---, calcd), and this study (●) at corresponding conditions.

(aq) as a function of density, illustrating that  $\Lambda_0(\text{HCl})$  increases with increasing temperatures to 300 °C and increases linearly with decreasing density. Above 300 °C,  $\Lambda_0(\text{HCl})$  is nearly independent of temperature, but increases virtually linearly with decreasing density between 0.7 and 0.5 g·cm<sup>-3</sup>, and subsequently decreases with decreasing density. At  $\rho < 0.5$  g·cm<sup>-3</sup> considerable uncertainties were observed in the results obtained from eq 1, probably due to the drastic decrease of free ion concentrations with decreasing density. Nevertheless, this behavior is similar to that reported previously for alkali hydroxide solutions.<sup>22–24</sup>

Note that in several cases at  $\rho < 0.5$  g·cm<sup>-3</sup>, particularly at 410 °C and 0.27 g·cm<sup>-3</sup> nonlinear regression of the experimental results using eq 1 yields unreasonable  $\Lambda_0$  values due to the significant association of HCl(aq) at concentrations well below the ranges studied. Because the slope of  $\Lambda$  versus concentration is very steep (see Figure 2),  $\Lambda_0$  cannot be determined accurately and large uncertainties result in the calculated  $K_A(m)$  values. A simultaneous fit of  $\Lambda_0$  and  $K_A(m)$  at low solvent densities requires either very precise experimental data that extend to extremely low concentrations, where the  $\Lambda_0$  value can be determined independently or results that extend to high concentrations in conjunction with suitable models for both the conductance and activity coefficients of ions, that constrain the  $K_A(m)$  values. The present results do not cover concentration ranges wide enough to determine accurately both  $\Lambda_0$  and  $K_A(m)$  concurrently at densities below 0.45 g·cm<sup>-3</sup>. On the other hand, as shown by the example in Figure 5, once the  $\Lambda_0$  value is set, the corresponding value of  $K_A(m)$  can be calculated with good accuracy from the existing experimental results. The initial value of  $\Lambda_0$  can be estimated by extrapolating the experimental  $\Lambda_0$  values at densities between 0.45 and 0.55 g·cm<sup>-3</sup> where  $\Lambda_0(\text{HCl})$  reaches the maximum and subsequently decreases with decreasing density (see Figure 4). Given appropriate  $\Lambda_0$  values with acceptable  $\sigma$  values (the standard deviation of experimental data from eq 1),  $K_A(m)$  values can be determined with uncertainties better than  $\pm 0.5$ . Considering this, we estimated that  $\Lambda_0$  value at 410 °C and 0.27 g·cm<sup>-3</sup> is  $1000 \pm 300$  cm<sup>2</sup>·S·mol<sup>-1</sup> (see Figure 5) and the calculated  $\log K_A(m)$  is  $5.12 \pm 0.4$ .



**Figure 5.** Molal association constant of HCl(aq) as a function of limiting molar conductance and standard deviation of experimental data from eq 1 at 410 °C, 0.27 g·cm<sup>-3</sup>: (solid line) log  $K_A(m)$  vs  $\Lambda_0$ ; (dotted line)  $\sigma$  vs  $\Lambda_0$ .

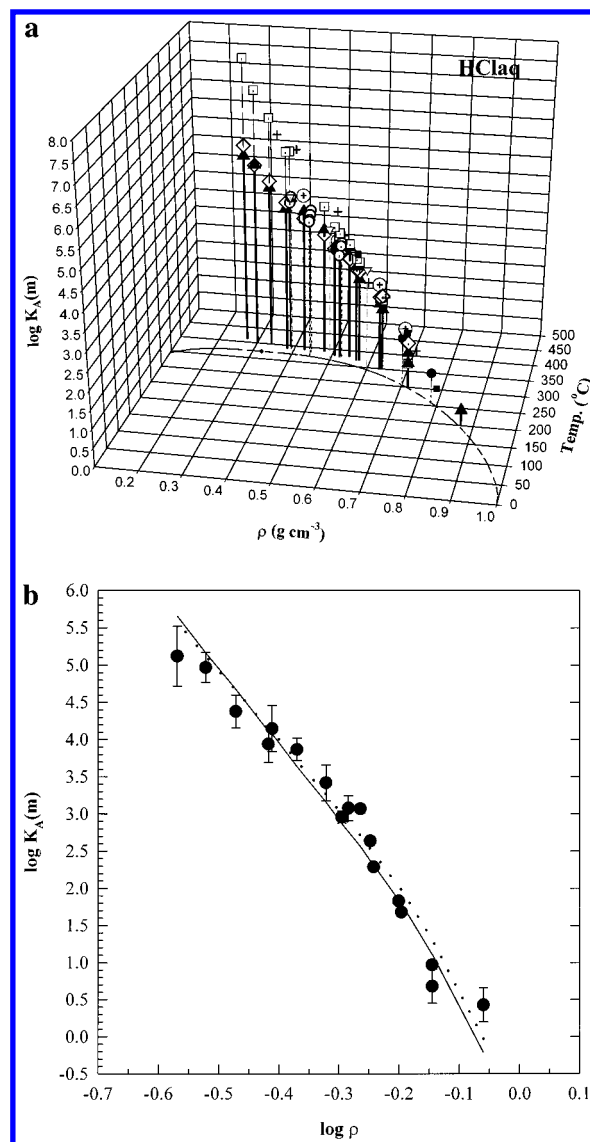
Figure 4 illustrates good agreement with the  $\Lambda_0$  values reported by Noyes,<sup>1</sup> Wright et al.,<sup>2</sup> Pearson et al.,<sup>4</sup> and Lukashov et al.<sup>5</sup> However, these results are only in agreement with those reported (experimental and calculated) by Frantz and Marshall<sup>6</sup> at  $\rho > 0.5$  g·cm<sup>-3</sup>. For densities 0.5 and 0.4 g·cm<sup>-3</sup> their values range from 5 to 11% higher, whereas below 0.4 g·cm<sup>-3</sup>, the weighted values of this study are approximately 14–35% lower, but large uncertainties exist in these data.

Figure 6a illustrates the dependence of log  $K_A(m)$  on densities and temperatures at 200–410 °C. Moreover, Figure 6a presents the comparison of  $K_A(m)$  from this study with the reported values<sup>2–6,25–27</sup> at analogous conditions. It can be seen that our results are in good agreement with those reported by Franck,<sup>3</sup> Wright et al.,<sup>2</sup> and Pearson et al.<sup>4</sup> at 0.86–0.3 g·cm<sup>-3</sup> and those from Lukashov et al.<sup>5</sup> at 0.7 and 0.4 g·cm<sup>-3</sup> within the combined experimental uncertainties. It is interesting to note that reported  $K_A(m)$  values derived from solubility measurements at 25–350 °C, saturation vapor pressure by Ruaya and Seward<sup>25</sup> and 350–500 °C, 50–250 MPa by Tagirov et al.<sup>26</sup> are in good agreement with this study, whereas values computed with the computer program “SUPCRT92,”<sup>27</sup> are only in agreement at  $\rho > 0.5$  g·cm<sup>-3</sup>. Again our results only agree with the reported values of Frantz and Marshall<sup>6</sup> at  $\rho > 0.5$  g·cm<sup>-3</sup> (presumably the SUPCRT92 estimations are based on the Frantz and Marshall data), while at densities below 0.5 g·cm<sup>-3</sup> their values are 0.5–2.5 log units higher.

The ion association constant  $K_A(m)$  of HCl(aq) can be described by eq 4 as functions of temperature ( $T$  in Kelvin) and density, based on the best weighted-least-squares fits of the experimental data from 200 to 410 °C. In view of the good agreement with the reported data of Wright et al.<sup>2</sup> (260 and 306 °C and saturation vapor pressure) and Franck<sup>4</sup> (400–600 °C at 0.8–0.4 g·cm<sup>-3</sup>) (see Figure 6b), eq 5 is derived by combining the data of this study with these reported values.

$$\log K_A(m) = 1.95 - 1303.3/T - 9.876 \log \rho (200-410\text{ }^\circ\text{C}) \quad (4)$$

$$\log K_A(m) = 2.638 - 1518.8/T - 9.078 \log \rho (200-600\text{ }^\circ\text{C}) \quad (5)$$

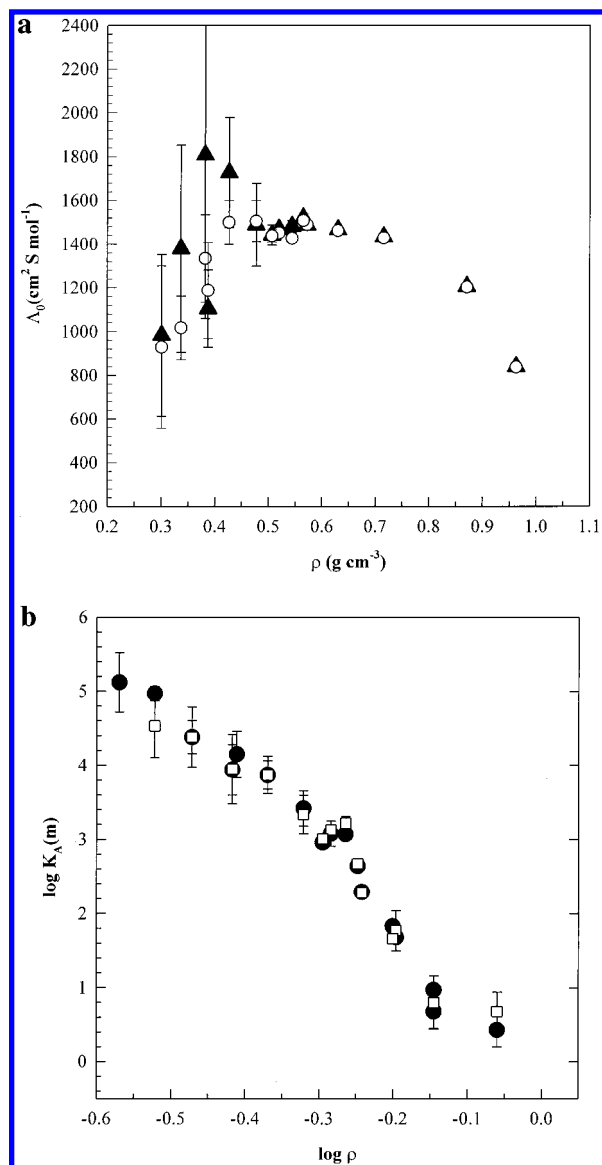


**Figure 6.** (a) Comparison of log  $K_A(m)$  of HCl(aq) as a function of density and temperature with those reported by Franck<sup>3</sup> (◇), Wright et al.<sup>2</sup> (●), Pearson et al.<sup>4</sup> (○), Lukashov et al.<sup>5</sup> (▽), Frantz and Marshall<sup>6</sup> (□), Ruaya and Seward<sup>25</sup> (■), Tagirov et al.<sup>26</sup> (⊗), Johnson et al.<sup>27</sup> (+), and this study (▲) at corresponding conditions. (b) log  $K_A(m)$  of HCl(aq) as a function of log  $\rho$  at 200–410 °C (●) (solid line and dotted lines are from eqs 4 and 5, respectively).

In addition to utilizing eq 1, values of  $\Lambda_0$  and  $K_A(m)$  were computed using a computer program developed by Sharygin et al.<sup>28</sup> for the conductivity of ionic mixtures at high temperatures using either eq 1 or the TBBK equation.<sup>29</sup> Compared to the results in Table 2, the two set values of  $\Lambda_0$  (at  $\rho > 0.5$  g·cm<sup>-3</sup>) and log  $K_A(m)$  are in reasonable agreement within experimental uncertainties (see Figure 7a,b).

#### 4. Conclusion

Values of ionic and molar conductances and association constants of HCl solutions at temperatures of 100–410 °C and pressures up to 32 MPa have been calculated with the FHFP equation. Within experimental uncertainties, the resulting  $\Lambda_0$  and  $K_A(m)$  values are generally in agreement with the results of measurements by Noyes,<sup>1</sup> Wright et al.,<sup>2</sup> Franck,<sup>3</sup> Pearson et al.,<sup>4</sup> Lukashov et al.,<sup>5</sup> Ruaya and Seward,<sup>25</sup> and Tagirov et al.<sup>26</sup> under analogous conditions. However, these values are only in agreement with those reported by Frantz and Marshall<sup>6</sup> and calculated with “SUPCRT92” program<sup>27</sup> at densities  $> 0.5$  g·cm<sup>-3</sup>.



**Figure 7.** (a) Comparison of  $\Lambda_0$  of HCl(aq) as a function of density at 100–400 °C with this study (○) and those calculated with computer program of Sharygin et al.<sup>28</sup> (▲) at corresponding conditions. (b) Comparison of  $\log K_A(m)$  of HCl(aq) calculated by eq 1 (●) and computer program of Sharygin et al.<sup>28</sup> (□) as a function of  $\log \rho$  at 100 to 400 °C.

Finally, the plan is to extend the measurements of HCl(aq) to temperatures of 600 °C and pressures up to 300 MPa by completing the modification of the flow-through cell as discussed previously.<sup>8</sup>

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