Aqueous Hydrochloric Acid Conductance from 0 to 100 °C

Laurence E. Strong

Chemistry Department, Earlham College, Richmond, Indiana 47374

Conductance measurements have been made for dilute aqueous hydrochloric acid from 0 to 100 °C at 5 °C intervals. The results are internally consistent to about 0.02%. They have been analyzed to provide limiting conductivities for HCl and for H^+. Between 0 and 55 °C the results agree closely with data already in the literature. Above 65 °C there are no data of similar precision in the literature.

In our studies (*1–3*) of the conductance behavior of various weak acids between 0 and 100 °C in water, an important property is the limiting conductivity of each acid as a function of temperature. It is helpful to compare the conductivity of these acids through calculation of the limiting anion conductivity of each. For this calculation the limiting conductivity of the hydrogen ion is needed. Thus far we have relied on the work of Owen and Sweeton (*4*) and Harned and Dreby (*5*) for the limiting conductivity of the hydrogen ion based on the conductances of HCl solutions as a function of temperature. The former workers measured conductances of HCl in solution from 5 to 65 °C at 10 °C intervals while the latter reported their measurements of the transference numbers for the ions in HCl solutions from 5 to 50 °C. These data were presented by Harned and Owen (*6*) as a cubic equation in Celsius temperature which described the limiting anion conductivity of aqueous hydrogen ion. The equation is

$$\lambda_0(H^+) = 349.85 + 4.81595(t - 25) - (1.0312 \times 10^{-2})(t - 25)^2 - (7.67 \times 10^{-5})(t - 25)^3 \quad (1)$$

Since we had no better source, we have used the Harned and Owen equation for temperatures from 0 to 100 °C. At 100 °C it gives $\Lambda_0 = 620.7$ cm^2 Ω^{-1} mol^{-1}. To reduce the uncertainty introduced by extrapolating from 65 to 100 °C, we modified the Harned and Owen equation so that it included a value for $\lambda_0(H^+) = 634$ cm^2 Ω^{-1} mol^{-1} at 100 °C reported by Quist and Marshall (*7*). This they based on conductance measurements for HCl at 100 °C by Noyes (*8*) and an estimate of the chloride ion limiting conductivities derived from transference number measurements on sodium chloride between 55 and 125 °C reported by Smith and Dismukes (*9*).

Hamer and DeWane (*10*) summarized the conductance data available for HCl in 1970. For dilute solutions (<0.01 M) the temperature range was 5–65 °C at 10 °C intervals plus one set of measurements by Cook and Stokes (*11*) at 50 °C. At 25 °C a number of studies have been reported. Hamer and DeWane concluded that the best results at 25 °C are those described by Murr and Shiner (*12*) and so they recalculated these data by using the conductance function recommended by Fuoss, Onsager, and Skinner (*13*). This led to a value of 426.06 cm^2 Ω^{-1} mol^{-1} for Λ_0 at 25 °C.

There remains then the problem as to how $\lambda_0(H^+)$ changes with temperature above 65 °C. Reported here is a new study of the conductance of HCl in dilute solution from 0 to 100 °C at 5 °C intervals for concentrations from about 1 to 0.1 mM and the derived Λ_0 values.

Experimental Section

Apparatus and measuring techniques were essentially the same as described by Strong, Kinney, and Fisher (*1*). Temperatures were held constant to ±0.002 °C and measured with a calibrated platinum resistance thermometer connected to a G-2 Mueller bridge.

Hydrochloric acid solutions were prepared for resistance measurements by diluting a specially purified preparation (GFS redistilled 6 M HCl) with water. All water used was purified by ion exchange in a recirculating system and had a specific conductivity of $(1–3) \times 10^{-7}$ cm^{-1} Ω^{-1}. Concentrations were calculated from cell resistance measurements at 25.00 °C by using the interpolation equation given by Hamer and DeWane (*10*) which they had fitted to the Murr and Shiner (*12*) data. No corrections were made for solvent conductivity.

Cell constants were corrected for dimension changes of the cells at temperatures other than 25 °C by the factor $[1 + 14(t - 25) \times 10^{-6}]$ on the basis of a discussion by Robinson and Stokes (*14*). Each cell electrode chamber was filled with mercury and the resistance of the leads determined in order to correct resistance readings for solutions. The two corrections together were less than 0.1% of the conductance at 100 °C.

Results

Molar conductivity values at the various temperatures are listed in Table I. Molar concentrations at 25.00 °C are given in the table and from these concentrations appropriate to the other temperatures can be calculated by using the density data for water published by Kell (*15*).

Limiting molar conductivities for HCl as a function of temperature are tabulated in Table II. These were calculated first with the conductance function proposed by Fuoss in 1975 (*16*) using a computer program developed by Pethybridge (*17*) which searched for that value of the distance parameter, *R*, that would give the best fit of the data to the function. However, the range of concentrations available did not include high enough concentrations to generate a minimum in the residuals of significant depth as the Gurney sphere diameter, *R*, was varied. Furthermore, trial calculations with the Murr and Shiner data (*12*) showed that it made an insignificant difference in Λ_0 whether *R* was selected to minimize the square of the residuals in the fitting equation or was simply chosen to be twice the Bjerrum radius. The latter choice was then the one that was used for the data reported here.

In Table II the third column labeled σ gives the standard deviation derived from differences between experimental Λ values and those calculated with the conductance function. The fourth column lists the standard deviation as a percentage of Λ_0. Except for the three highest temperatures σ% is less than 0.02% and averages 0.016% for all temperatures. Limiting conductivities assembled by Hamer and DeWane (*10*) are listed in the fifth column of Table II as Λ_0(NBS). Their reported standard deviations do not differ significantly from ours except at 65 °C although the percentage difference, Δ%, between the NBS data and ours averages 0.07%. The Λ_0 value of 845 cm^2 Ω^{-1} mol^{-1} calculated from the Noyes data (*8*) at 100 °C agrees with our Λ_0 of 847.67 cm^2 Ω^{-1} mol^{-1} within the precision of the data reported by Noyes, who determined conductances at only four different concentrations.

The conductance function also gives an apparent association constant with a value of about 0.3. However, since the theory assumes ions to move with a submarine-like motion while the hydrogen ion undoubtedly moves mostly by chain conduction

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Table I. Molar Conductivities, Concentrations, and Temperatures for Hydrochloric Acid Solutions

temp, °C	molar conductivities, cm^2 Ω^{-1} mol^{-1}									
0.00	262.752	262.944	263.099	262.954	263.488	263.461	263.855	264.058	264.314	264.618
5.00	294.302	294.511	294.680	294.933	295.119	295.097	295.544	295.783	296.077	296.440
10.00	326.067	326.292	326.489	326.827	327.006	327.020	327.438	327.705	328.058	328.471
15.00	357.931	358.081	358.286	358.731	358.942	358.906	359.436	359.719	360.101	360.578
20.00	389.624	389.803	390.026	390.404	390.724	390.775	391.317	391.625	392.047	392.591
25.00	421.096	421.298	421.554	422.008	422.390	422.366	422.937	423.291	423.786	424.365
30.00	452.413	452.513	452.769	453.253	453.655	453.757	454.320	454.715	455.235	455.906
35.00	483.150	483.355	483.637	484.191	484.561	484.733	485.343	485.764	486.359	487.073
40.00	513.660	513.803	514.045	514.679	515.085	515.298	515.950	516.367	517.044	517.838
45.00	543.574	543.706	544.047	544.669	545.204	545.360	545.990	546.525	547.252	548.085
50.00	573.035	573.170	573.522	574.180	574.686	574.965	575.686	576.203	576.993	577.882
55.00	601.852	602.074	602.420	603.166	603.697	603.950	604.751	605.323	606.168	607.126
60.00	630.263	630.434	630.798	631.608	632.182	632.405	633.282	633.862	634.799	635.814
65.00	658.029	658.137	658.555	659.435	660.172	660.307	661.227	661.844	662.848	663.919
70.00	685.201	685.293	685.770	686.692	687.359	687.579	688.523	689.244	690.285	691.427
75.00	711.859	711.831	712.387	713.383	714.227	714.339	715.254	716.019	717.152	718.323
80.00	737.865	737.928	738.340	739.457	740.172	740.419	741.457	742.194	743.418	744.594
85.00	763.146	763.297	763.781	764.881	765.625	765.937	766.962	767.767	769.072	770.175
90.00	787.875	787.937	788.520	789.707	790.385	790.848	791.766	792.711	794.149	795.083
95.00	812.015	812.042	812.737	814.031	814.624	815.127	815.980	817.039	818.578	819.315
100.00	835.528	835.443	836.254	837.646	838.136	838.791	839.411	840.638	842.378	842.656
$10^3 C$ at 25 °C	1.04850	0.98398	0.86410	0.69308	0.56677	0.56294	0.41010	0.30616	0.20190	0.11547

Table II. Hydrochloric Acid Limiting Conductivity Data in Water Solutions[a]

temp/°C	Λ_0/cm^2 Ω^{-1} mol^{-1}	σ	σ%	Λ_0(NBS)	Λ_0(NBS) − Λ_0	Δ%	σ(NBS)
0	265.487	0.040	0.015				
5	297.529	0.047	0.016	297.42	−0.11	−0.037	0.10
10	329.699	0.044	0.014				
15	361.986	0.083	0.023	362.05	0.06	0.017	0.12
20	394.117	0.036	0.009				
25	426.056	0.027	0.006	426.06	0.00	0.00	0.05
30	457.728	0.046	0.010				
35	489.084	0.050	0.010	488.91	−0.17	−0.035	0.07
40	519.984	0.078	0.015				
45	550.418	0.059	0.011	550.12	−0.29	−0.053	0.10
50	580.389	0.089	0.016	579.94	−0.46	−0.079	0.15
55	609.828	0.079	0.013	609.17	−0.66	−0.108	0.10
60	638.672	0.086	0.014				
65	666.999	0.089	0.014	665.55	−1.45	−0.218	0.09
70	694.673	0.093	0.014				
75	721.781	0.116	0.016				
80	748.245	0.128	0.017				
85	774.104	0.115	0.015				
90	799.320	0.168	0.021				
95	823.883	0.218	0.027				
100	847.665	0.357	0.043	845[b]			

[a] Data labeled NBS taken from ref 10. [b] Proposed by Quist and Marshall (*7*) based on a recent analysis of 1907 data by Noyes (*8*).

process involving the water molecules, it is therefore not feasible to attach any significance to an association constant in highly ionized acid systems like HCl in water.

Our Λ_0 values have been fitted to a polynomial in the Celsius temperature by weighted multiple linear regression to give

$$\Lambda_0 = 265.40 + 6.4128t + (3.90424 \times 10^{-3})t^2 - (1.48319 \times 10^{-4})t^3 + (5.06198 \times 10^{-7})t^4 \quad (2)$$

Weights were calculated as the reciprocal of the square of the standard deviation expressed as a percentage of Λ_0. The standard deviation of the fit was 0.42 cm^2 Ω^{-1} mol^{-1}.

Stokes (*18*) has proposed that conductance measurements are especially suitable for standardizing HCl solutions to a precision of about 0.01%. Our results show that the temperature coefficient of the conductance is about 1.5% per degree around 25 °C. Therefore it is necessary to establish the temperature and control it to a precision of better than 0.005 °C if one is to take advantage of the precision that is inherent in Stokes' data.

The results reported here have been fitted by a set of equations that make it possible to calculate the conductivity for any solution whose concentration is not more than about 1 mM for any temperature within the range of 0–100 °C. The equation set is

$$\Lambda = \Lambda_0 - Sc^{1/2} + Ec \log c + Ac \quad (3)$$

$$S = (8.20456 \times 10^5)\Lambda_0/(DT)^{3/2} + 82.4866/(\eta^2 DT)^{1/2} \quad (4)$$

$$E = (6.7750 \times 10^{12})\Lambda_0/(DT)^3 - (19.9518 \times 10^7)/\eta(DT)^2 \quad (5)$$

$$A = 571.8 + 1.3964t + 0.1886t^2 \quad (6)$$

$$\Lambda_0 = 265.40 + 6.4128t + (3.9042 \times 10^{-3})t^2 - (1.48319 \times 10^{-4})t^3 + (5.06198 \times 10^{-7})t^4 \quad (2)$$

$$D = \exp(4.47615 - (4.60128 \times 10^{-3})t + (2.6952 \times 10^{-7})t^2) \quad (7)$$

$$\log \eta = -1.999132 - (1.37023(t - 20) + (8.36 \times 10^{-4})(t - 20)^2)/(109 + t) \quad (8)$$

Λ is described in the first equation by two empirical constants, Λ_0 and A, and two theoretical constants, S and E (*19*). The equation for the dielectric constant, D, of water as a function of Celsius temperature is the one proposed by Owen et al. (*20*), and the equation for the viscosity, η, of water is taken from Coe and Godfrey (*21*). The equation for A is an empirical one produced by putting our experimental data into the equation for Λ using calculated values for S and E together with Λ_0 values calculated from the 1975 equation by Fuoss (*16*) applied to our experimental data. In this way an A value was obtained for each temperature. These A values were then fitted to a polynomial in the Celsius temperature.

A computer program was constructed with the set of seven equations so that a value of Λ could be calculated for any chosen values of concentration and temperature. In general each calculated Λ agreed within 0.02% or better with the experimental value. The most serious disagreements were found at temperatures above 90 °C where the experimental values have the greatest uncertainty.

Finally a set of cationic conductivity values for the hydrogen ion are desired. Unfortunately there is no single set of internally consistent, high-quality transference numbers available covering temperatures from 0 to 100 °C. Harned and Dreby (*5*) reported transference numbers for H^+ in HCl from 5 to 50 °C which appear to be of high quality while Macdonald and Owen (*22*) have reported transference numbers for H^+ in HCl from 60 to 200 °C. However, these two sets of data disagree by more than 2% in the region between 50 and 60 °C. Alternative data are those by Smith and Dismukes (*9*) who measured transference numbers for Cl^- in NaCl from 54 to 125 °C. To make use of these data, it is necessary to have limiting molar conductivities for NaCl so that limiting anionic conductivities can be calculated for Cl^-. Benson and Gordon (*24*) have published conductance data for NaCl from 15 to 45 °C at 10 °C intervals. These were reanalyzed by Kay (*23*) in 1960 and values added at 5 and 55 °C. However, there is no entirely satisfactory set of Λ_0 for NaCl in the temperature range from 55 to 100 °C. Quist and Marshall (*7*) have published data for NaCl at 200 and 300 °C. There is a set of measurements reported in 1898 by Schaller (*25*) although of somewhat doubtful reliablity, in part because only three concentrations were used at each temperature. These data have been recalculated by using the Fuoss conductance theory (*16*) to give Λ_0 values which were then combined with transference numbers for Cl^- ion to give $\lambda_0(Cl^-)$ from 25 to 100 °C at 10 °C intervals while the Benson and Gordon data (*24*) for Λ_0 of NaCl, as recalculated by Kay (*23*), were combined with transference numbers to give $\lambda_0(Cl^-)$ from 0 to 55 °C. These various data were fitted to polynomials in the Celsius temperature to give the equations

$$t_0(Cl^-) = 0.6122 - (3.704 \times 10^{-4})t + (6.75 \times 10^{-7})t^2 \qquad (9)$$

$$\Lambda_0(NaCl) = 65.928 + 2.2668t + (8.0705 \times 10^{-3})t^2 = (1.7403 \times 10^{-5})t^3 \qquad (10)$$

$$\lambda_0(H^+) = 225.04 + 5.0496t - (2.4646 \times 10^{-4})t^2 = (1.3623 \times 10^{-4})t^3 + (4.9616 \times 10^{-7})t^4 \qquad (11)$$

It is worth noting that the transference number for Cl^- is nearly a linear function of the temperature. The transference number equation (9) reproduces the data closely with a standard deviation of 5.88×10^{-7} and covers a range of temperatures from 5 to 125 °C. Equation 10 reproduces data for NaCl over a temperature range from 0 to 300 °C with a standard deviation of 7.3 $cm^2\ \Omega^{-1}\ mol^{-1}$. Equation 11 reproduces within about 0.17% the cationic conductivity for H^+ derived from the equation reported earlier by Harned and Owen up to 60 °C. It agrees within about 1% with the cationic conductivity at 100 °C reported by Quist and Marshall (*7*). Therefore this equation appears to be the best available representation of the limiting cationic conductivity of the hydrogen ion from 0 to 100 °C. It is to be hoped that better data will become available in the not too distant future.

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