

# Electrical Conductance of Aqueous Solutions of KCl Solutions at Pressures up to 2000 atm

F. H. Fisher<sup>1</sup> and A. P. Fox<sup>1</sup>

Received December 18, 1978; revised March 26, 1979

---

*Electrical conductance measurements are reported for aqueous KCl solutions at 25°C as a function of concentration up to 0.02 M and pressure up to 2000 atm. The data from 103 runs were analyzed with the Fuoss-Hsia-Fernandez-Prini (FHFP) equation. The standard error of fit  $\sigma_{\Delta}$  varies from 0.018 at 1 atm to 0.12 at 2000 atm. The increase of  $\sigma_{\Delta}$  with pressure arises from increasing nonrandomness in the distribution of errors about the FHFP equation, suggesting that modifications in the theory are necessary. Departures from the Walden product for KCl as a function of pressure are compared with  $MgSO_4$  and  $CaSO_4$  in aqueous solutions.*

---

**KEY WORDS:** Conductance; conductance theory; KCl; pressure dependence.

## 1. INTRODUCTION

In the course of making measurements of electrical conductance as a function of pressure for various classes of electrolytes, 1-2, 2-1, 3-2, and 2-2 salts,<sup>(1-4)</sup> we have used KCl solutions to monitor our conductivity cells. As a consequence we have a large amount of data (over 800 points at elevated pressures) on the effect of pressure on aqueous solutions of KCl. These data have been analyzed with the Fuoss-Hsia-Fernandez-Prini<sup>(5,6)</sup> equation.

The most significant result from this work is that, for this simple salt, we see a progressive increase in nonrandomness of differences between theory and experiment as pressure increases. This suggests that modifications to theory are necessary for a more precise representation of conductance data at elevated pressures.

---

<sup>1</sup> University of California, San Diego, Marine Physical Laboratory, Scripps Institution of Oceanography, San Diego, California 92152.

## 2. EXPERIMENTAL

The pressure cells are similar to those described recently<sup>(4)</sup> and consist of a cylindrical glass tube of approximately 30 ml volume immersed in a mineral oil bath. The cell is divided into two chambers by a cupped glass partition so that any oil that might leak in at high pressure past the Teflon plug or Viton diaphragm is prevented from entering the conductance section. Platinum discs are separated by a Pyrex spacer and connected to platinum wires of 0.81 mm diameter for the electrical connections.

Stock solutions were prepared from Alfa Ultrapure KCl and the samples were weighed in a temperature-controlled room using either a Mettler BSC1000 or M5 balance depending upon sample size.

The water used was prepared using a Culligan deionizing system and had a specific resistance greater than  $18 \times 10^6$  ohm-cm at delivery and about  $5 \times 10^6$  ohm-cm in the cells.

The solutions were weighed on a Mettler P1200 balance and all preparation of solutions was done in a glove box under nitrogen atmosphere to prevent CO<sub>2</sub> contamination.

Water conductance corrections were obtained from repeated runs in the various cells. Lead resistance was small and was accounted for along with the water conductance correction in determining the ratio of the conductance at elevated pressure to that at atmospheric pressure. The pressure ratios thus obtained were then converted to equivalent conductances by normalizing to the atmospheric pressure conductance data of other workers.<sup>(7,8)</sup> Pressure measurements were made with temperature-compensated Heise pressure gauges accurate to 2 atm. For water we used the density data of Kell and Whalley,<sup>(9)</sup> the dielectric constant data of Srinivasen and Kay,<sup>(10)</sup> and the viscosity data of Bett and Cappi.<sup>(11)</sup>

## 3. RESULTS

The experimental equivalent conductances are given in Table I. These data represent average values at the concentrations shown. The data were analyzed with the FHFP<sup>(6,6)</sup> conductance equation in the form

$$\Lambda = \Lambda^\circ - S\sqrt{c} + Ec \log c + J_1c - J_2c^{3/2} \quad (1)$$

by allowing  $\Lambda^\circ$  and the distance parameter  $d$  to vary to produce the coefficients shown in Table I. The data were analyzed using new values for the dielectric constant obtained from Srinivasen and Kay.<sup>(10)</sup> These values are shown in Table II, as well as the free-fit values obtained for  $d$ . If instead  $d$  is permitted to vary with pressure as given in Eq. (2) constrained fit (Table II), a least-squares fit gave new values for  $\lambda^\circ$ ,  $S$ ,  $E$ ,  $J_1$ , and  $J_2$  given by Eqs. (3–7).

**Table I.** Molar Conductances for KCl Aqueous Solutions at 25°C as a Function of Pressure

Concentration (moles-liter <sup>-1</sup> × 10 <sup>4a</sup> ) and coefficients	P (atm)									
	N <sup>c</sup>	1	250	500	750	1000	1250	1500	1750	2000
0.0000 <sup>b</sup>		[149.92]	[151.08]	[151.77]	[152.09]	[152.04]	[151.72]	[151.15]	[150.39]	[149.52]
2.000	1	148.60	149.78	150.40	150.77	150.64	150.34	149.74	148.98	148.14
3.000	1	148.28	149.45	150.20	150.47	150.46	150.14	149.53	148.85	148.06
4.000	3	148.05	149.18(1) <sup>d</sup>	149.86(4)	150.18(4)	150.17(7)	149.88(9)	149.36(10)	148.64(12)	147.72(17)
5.000	12	147.81	148.99(7)	149.62(7)	149.93(10)	149.89(10)	149.58(11)	149.02(12)	148.03(14)	147.41(19)
10.000	13	146.95	148.07(5)	148.84(9)	149.18(12)	149.16(11)	148.85(14)	148.31(19)	147.57(23)	146.67(28)
20.000	16	145.78	146.91(2)	147.63(6)	148.00(5)	148.02(5)	147.75(7)	147.24(8)	146.54(10)	145.69(10)
50.000	21	143.55	144.74(2)	145.46(2)	145.87(8)	145.92(5)	145.67(4)	145.20(4)	144.54(6)	143.80(8)
100.00	20	141.27	142.47(4)	143.20(4)	143.56(2)	143.63(3)	143.43(2)	142.97(3)	142.32(4)	141.52(4)
200.00	16	138.34	139.52(3)	140.24(1)	140.63(2)	140.68(2)	140.51(3)	140.11(4)	139.45(3)	138.70(2)
S		94.74	94.44	93.83	92.96	91.88	90.67	89.37	88.04	86.74
E		58.97	57.18	55.37	53.59	51.79	50.04	48.33	46.63	45.00
J <sub>1</sub>		221.09	222.15	217.63	215.40	214.58	211.75	210.70	204.36	199.56
J <sub>2</sub>		221.39	227.94	222.99	223.34	227.16	226.73	230.44	222.05	217.01
σ <sub>A</sub>		0.018	0.03	0.04	0.04	0.07	0.07	0.08	0.10	0.12

<sup>a</sup> Concentrations are given for atmospheric pressure.

<sup>b</sup> Calculated values.

<sup>c</sup> Number of runs at specified concentration.

<sup>d</sup> Standard deviations (× 10<sup>4</sup>) are given in parentheses.

**Table II.** Dielectric Constant and Comparison of Free Fit and Constrained-Distance Parameters vs. Pressure for KCl, 25°C

$P$ (atm)	Dielectric constant	Free-fit $d$ (Å)	Constrained fit $d$ (Å)
1	78.45	3.42	3.44
250	79.37	3.50	3.47
500	80.26	3.49	3.51
750	81.13	3.53	3.55
1000	81.98	3.60	3.58
1250	82.81	3.63	3.62
1500	83.61	3.70	3.65
1750	84.40	3.68	3.69
2000	85.17	3.69	3.73

However, the standard error of fit  $\sigma_\Lambda$  is essentially the same for the constrained fit as for the free fit (Table I).

$$d(P) = 3.437 + 1.446 \times 10^{-4}(P - 1) \pm 0.03 \quad (2)$$

$$\Lambda^\circ(P) = 149.922 + 5.628 \times 10^{-3}(P - 1) - 4.066 \times 10^{-6}(P - 1)^2 + 5.756 \times 10^{-10}(P - 1)^3 \pm 0.02 \quad (3)$$

$$S(P) = 94.6878 - 3.763 \times 10^{-4}(P - 1) - 2.951 \times 10^{-6}(P - 1)^2 + 5.209 \times 10^{-10}(P - 1)^3 \pm 0.07 \quad (4)$$

$$E(P) = 58.9873 - 7.216 \times 10^{-3}(P - 1) - 9.988 \times 10^{-8}(P - 1)^2 + 1.178 \times 10^{-10}(P - 1)^3 \pm 0.02 \quad (5)$$

$$I_1(P) = 222.112 - 4.330 \times 10^{-3}(P - 1) - 4.885 \times 10^{-6}(P - 1)^2 + 9.101 \times 10^{-10}(P - 1)^3 \pm 0.09 \quad (6)$$

$$J_2(P) = 223.596 + 6.790 \times 10^{-3}(P - 1) - 5.898 \times 10^{-6}(P - 1)^2 + 9.526 \times 10^{-10}(P - 1)^3 \pm 0.14 \quad (7)$$

In using these equations, we note that the molar concentration  $c$  increases at elevated pressures with the solvent density.

As seen in Fig. 1, the distribution of errors as a function of concentration is not random. While they are small at 1 atm, they are nevertheless not randomly distributed. Until the distribution of errors ( $\delta_\Lambda$ ) was plotted as a function of concentration, we first thought the increase of  $\sigma_\Lambda$  with pressure was due to experimental error. However, the steady increase in nonrandomness of  $\delta_\Lambda$  with increasing pressure makes it seem that some changes in theory are necessary.

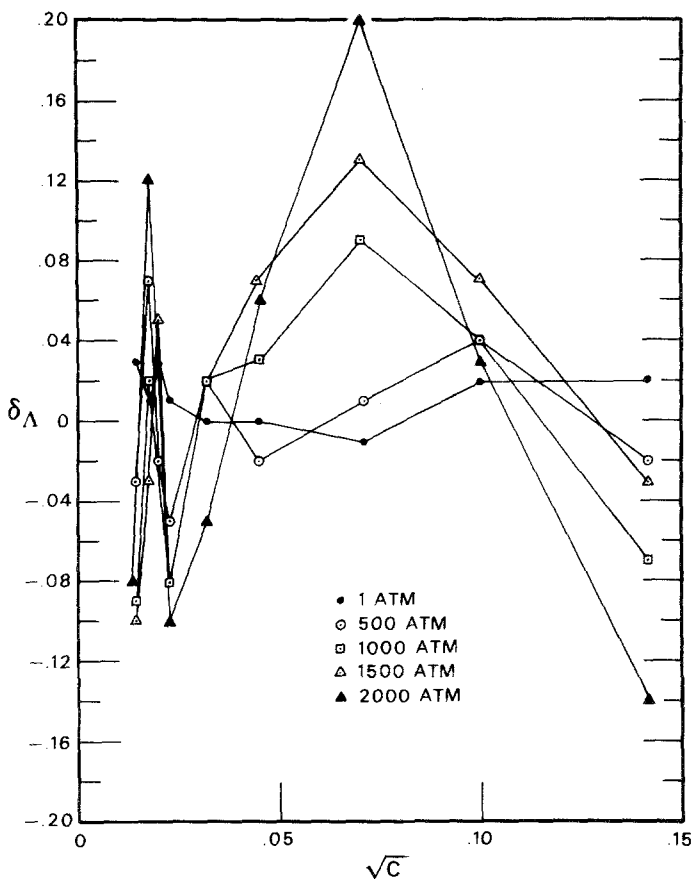


Fig. 1. Difference  $\delta\Lambda = \Lambda_{\text{exp}} - \Lambda_{\text{theor}}$  as a function of concentration at various pressures for aqueous solutions of KCl at 25°C.

Outside of possible errors in our low-concentration data due to the use of an averaged water correction, we are confident our work at elevated pressures is accurate. For example, as an internal check on our work we have made measurements on the effect of pressure on the conductance of standard seawater and find our results agree within 0.01% of those of Bradshaw and Schleicher.<sup>(12)</sup> From such agreement we conclude that we have no cell distortion or pressure-gauge problems to introduce significant errors.

In Table III we show a comparison of our value of  $\Lambda^\circ$  with those recently summarized by Hamann.<sup>(13)</sup> Our data for  $\Lambda^\circ$  agree most closely with those of Gancy and Brummer.<sup>(17)</sup> On the basis of this agreement with Gancy and Brummer who made extensive and careful investigations of the conductance

**Table III.** The Limiting Molar Conductivity  $\Lambda^\circ$  of KCl up to 2000 bars at 25°C

Reference	Pressure (bars)				
	1	500	1000	1500	2000
Buchanan and Hamann (1953)	149.9	—	152.7	—	149.9
Ellis (1959)	149.9	151.5	152.0	—	149.9
Fisher (1962)	149.9	152.3	152.6	151.4	149.4
Ovendon (1965)	149.9	151.7	152.5	151.8	150.1
Gancy and Brummer (1971)	149.9	151.8	152.2	151.4	149.7
Nakahara <i>et al.</i> (1972)	149.9	152.6	153.4	152.9	151.7
This work	149.9	151.8	152.1	151.2	149.6

of several electrolyte systems at elevated pressure, we feel that our water corrections are not in serious error.

At 1 atm our equation for  $\Lambda$ ,

$$\Lambda = 149.922 - 94.69c^{1/2} + 58.99c \log c + 222.1c - 223.6c^{3/2} \pm 0.015 \quad (8)$$

is in good agreement with that of Chiu and Fuoss<sup>(7)</sup>:

$$\Lambda = 149.93 - 94.88c^{1/2} + 58.67c \log c - 221.0c - 229c^{3/2} \pm 0.016 \quad (9)$$

#### 4. WALDEN PRODUCT

Since KCl is the conductance standard at atmospheric pressure, it is the appropriate solute to use to examine the conductance of other salts at elevated pressures. In particular we wish to examine the departures from the Walden product of KCl as a function of pressure. Kay<sup>(19)</sup> has recently discussed the subject at length for both aqueous and mixed solvents.

The ratio of the Walden product at pressure  $P$  to that at 1 atm,  $(\Lambda_p^\circ \eta_p / \Lambda_1^\circ \eta_1)$ , is shown in Fig. 2 for KCl. For purposes of comparison we include data for  $\text{MgSO}_4^{(4)}$  and  $\text{CaSO}_4^{(4)}$  reported recently. If Stokes' law is valid, then the ratio of the Walden products would remain at unity. The departures from unity of the Walden-product ratios are a measure of the effects of the ions on the solvent in the ionic cosphere.<sup>(19)</sup>

#### 5. SUMMARY

Our analysis of equivalent conductance in KCl solutions at elevated pressures has revealed nonrandom errors between experiment and the FHP

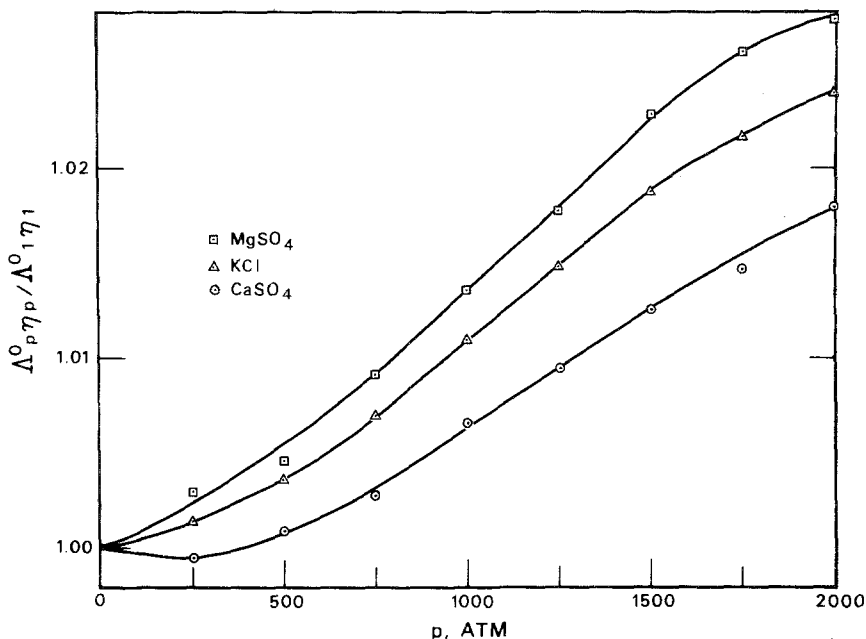


Fig. 2. Walden product as a function of pressure for aqueous solutions of KCl, MgSO<sub>4</sub>, and CaSO<sub>4</sub> at 25°C.

equations. From our agreement with the Gancy and Brummer data for  $\Delta^\circ$  as a function of pressure and from the agreement of our seawater (unpublished) data with those of Bradshaw and Schleicher, we conclude that some modifications are required in the FHFP conductance equations. Other equations will be incorporated into the analysis of our pressure data in the future.

A series of equations giving the pressure coefficients for all the parameters in the FHFP equation provides a good representation of conductance of KCl at 25 up to 2000 atm for concentrations up to 0.02 *M*. Since the theoretical basis for the FHFP equation gives rise to nonrandom errors, the equations for KCl must be regarded as a first attempt to provide an analytic representation of the equivalent conductance as a function of pressure. As discussed earlier, we expect that with a theoretical equation yielding random error distribution, a more accurate analytic representation can be achieved at elevated pressures.

## ACKNOWLEDGMENTS

This work was supported by the National Science Foundation Grants NSF OCE 76-02253 and NSF OCE 78-08488.

## REFERENCES

1. F. H. Fisher and A. P. Fox, *J. Solution Chem.* **6**, 641 (1977).
2. F. H. Fisher and A. P. Fox, *J. Solution Chem.* **7**, 561 (1978).
3. F. H. Fisher and D. F. Davis, *J. Phys. Chem.* **71**, 819 (1967).
4. F. H. Fisher and A. P. Fox, *J. Solution Chem.*, **8**, 309 (1979).
5. R. M. Fuoss and K. L. Hsia, *Proc. Nat. Acad. Sci. U.S.A.* **57**, 1550 (1967).
6. R. Fernandez-Prini, *Trans. Faraday Soc.* **65**, 3311 (1969).
7. Y-C Chiu and R. M. Fuoss, *J. Phys. Chem.* **72**, 4123 (1968).
8. T. Shedlovsky, A. S. Brown, and D. A. MacInnes, *Trans. Electrochem. Soc.* **66**, 165 (1934).
9. G. Kell and E. Whalley, *Philos. Trans. R. Soc. (London), Ser. A* **258**, 565 (1965).
10. K. R. Srinivasen and R. L. Kay, *J. Chem. Phys.* **60**, 3645 (1974).
11. K. E. Bett and J. B. Cappi, *Nature* **207**, 620 (1965); J. B. Cappi, Thesis, Imperial College, University of London (1964).
12. A. Bradshaw and K. E. Schleicher, *Deep-Sea Res.* **12**, 551 (1965).
13. S. D. Hamann, Electrolyte Solution at High Pressure, in *Modern Aspects of Electrochemistry*, Vol. 9, B. E. Conway and J. O'M. Bockris, eds. (Plenum Press), New York, 1974), p. 47.
14. J. Buchanan and S. D. Hamann, *Trans. Faraday Soc.* **49**, 1425 (1953).
15. A. J. Ellis, *J. Chem. Soc. London*, 3689 (1959).
16. G. J. Hills and P. J. Ovenden, Electrochemistry at High Pressures, in *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 4, P. Delahay, ed. (Interscience, New York, 1966), p. 225.
17. A. B. Gancy and S. B. Brummer, *J. Phys. Chem.* **73**, 2429 (1969); *J. Chem. Eng. Data* **16**, 385 (1971).
18. M. Nakahara, K. Shimizu, and J. Osugi, *Rev. Phys. Chem. Jpn.* **42**, 12 (1972).
19. R. L. Kay, in *Water: A Comprehensive Treatise*, Vol. 3, Felix Franks, ed. (Plenum Press, New York, 1973), pp. 173-209.