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A Reference Solution for Electrical Conductance Measurements to 800° and 12,000 Bars. Aqueous 0.01 Demal Potassium Chloride

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In recent years there has been much interest in the behavior of aqueous electrolyte solutions at high temperatures and pressures.[2] Experimental investigations of the properties of water and aqueous solutions have been greatly facilitated by the availability of new alloys that retain excellent mechanical strength at temperatures to 800° and above. Consequently, many measurements have been made on aqueous systems at supercritical temperatures and pressures. Since one of the simplest and most direct methods of investigating the behavior of ions in solution is the measurement of the electrical conductances of the solutions, several of these researches have been concerned with the measurement of this property. In view of the interest in conductance measurements at high temperatures and pressures, it seems desirable to establish a "reference" solution to permit direct comparison of the results obtained in different laboratories. Establishing reliable conductivity values for such a solution at these high temperatures and pressures would also allow direct experimental determination of cell constants under these conditions.

A 0.01 demal KCl solution (defined as 0.745263 g KCl/1000 g solution[3]) appears to be an appropriate choice as the reference solution for conductance measurements at high temperatures and pressures. This solution has been used for many years as a standard solution for cell constant determinations near 25° and atmospheric pressure.[3] Since aqueous KCl is both stable and a relatively strong electrolyte at supercritical temperatures and pressures, this solution would also appear to be suitable for use as a reference solution at these high temperatures and pressures. In recent years many conductance measurements have been made on either 0.01 demal or 0.01 *m* KCl solutions at temperatures to 1000° and at pressures to 12,000 bars. These measurements have been performed in the authors' laboratories over a period of years using several different designs of conductance cells and pressure vessels. Table I summarizes the ranges of temperature and pressure for the different sets of measurements from our laboratories. The literature references are included; these also contain descriptions of the conductance cells and experimental techniques.

Table I: Summary of Electrical Conductance Measurements on 0.01 Demal (or 0.01 Molal) Aqueous KCl Solutions at Elevated Temperatures and Pressures

Investigators	Temp range, °C	Max pressure, bars
Franck[a]	250–750	2,500
Hensel and Franck[b]	45–130	8,000
Franck, Hartmann, and Hensel[c]	45–220	8,000
Ritzert and Franck[d]	200–750	6,000
Mangold and Franck[e]	300–1000	12,000
Renkert[f]	200–350	8,000
von Osten[g]	200–400	8,000
Quist and Marshall[h]	0–800	4,000

[a] E. U. Franck, *Z. Phys. Chem.* (Frankfurt am Main), **8,** 92 (1956). [b] F. Hensel and E. U. Franck, *Z. Naturforsch.*, **19a,** 127 (1963). [c] E. U. Franck, D. Hartmann, and F. Hensel, *Discuss. Faraday Soc.*, **39,** 200 (1965). [d] G. Ritzert and E. U. Franck, *Ber. Bunsenges. Phys. Chem.*, **72,** 798 (1968). [e] K. Mangold and E. U. Franck, *ibid.*, **73,** 21 (1969). [f] H. Renkert, Diplomarbeit, Karlsruhe, 1965. [g] W. von Osten, Diplomarbeit, Karlsruhe, 1966. [h] A. S. Quist and W. L. Marshall, *J. Phys. Chem.*, **73,** 978 (1969), plus additional unreported measurements totaling 55 separate runs.

The experimental measurements were generally made at many different pressures at a constant temperature. Values of specific conductances at integral pressures, at the experimental temperatures, were obtained by interpolation. Some of the studies listed in Table I were carried out using 0.01 *m* rather than 0.01 demal solutions. However, minor corrections were applied so that the specific conductances could be correlated as based on 0.01 demal KCl solutions.

The measurements on KCl solutions from the sources listed in Table I were combined by plotting isobaric specific conductances *vs.* temperature and drawing a smooth curve through these data points.[4] Smoothed values for the specific conductances of 0.01 demal KCl solutions are presented in Table II at pressures from

(1) Operated by Union Carbide Corp. under contract with the U. S. Atomic Energy Commission.

(2) See, for example (*a*) E. U. Franck, *Endeavour*, **27,** 55 (1968); (b) J. W. Cobble, *Science*, **152,** 1479 (1966); (c) W. L. Marshall, *Rev. Pure Appl. Chem.*, **18,** 167 (1968).

(3) G. Jones and B. C. Bradshaw, *J. Amer. Chem. Soc.*, **55,** 1780 (1933).

(4) The earliest values of Franck (Table I, reference *a*) were omitted in this comparison because the uncertainty in these reported values was significantly larger than for those in the other references listed in Table I.

Table II: Specific Conductances (ohm^{-1} cm^{-1}) × 10^5 of 0.01 Demal KCl Solution at Integral Temperatures and Pressures

Pressure, bars	Temp, °C										
	100	150	200	250	300	350	400	450	500	600	700	800
1,000	368	498	599	663	689	685	650	578	460	125	...	...
2,000	364	491	593	659	698	707	701	679	643	516	336	116
3,000	358	483	585	651	695	715	718	709	689	625	528	405
4,000	351	481	574	640	687	712	723	724	714	670	610	526
6,000	338	466	555	617	665	699	722	733	732	707	672	628
8,000	326	446	536	598	645	679	703	716	721	711	692	664
10,000	...	...	...	...	625	665	690	707	711	709	694	675
12,000	...	...	...	...	601	644	674	694	704	703	688	673

1000 to 12,000 bars and at temperatures from 100 to 800°. These data are presented in graphical form in Figure 1, where specific conductances are plotted as a function of temperature at pressures from 1000 to 12,000 bars.

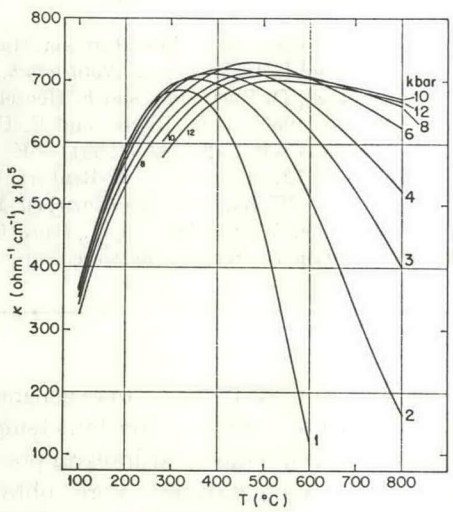

Figure 1. Specific conductances of 0.01 demal KCl solutions at integral temperatures and pressures.

In general, the results from Oak Ridge and Karlsruhe were in excellent agreement. Up to temperatures of 300° the scatter of the two sets of data about a smooth curve drawn through the combined results was generally less than 1%. Above 500° there was somewhat more scatter, but even so the differences in the two sets of data were usually less than 1% except at low pressures where the absolute values of the conductance had decreased considerably. The greatest differences between the Oak Ridge and Karlsruhe values were at temperatures near 400° at 1000 bars. Under these conditions the Oak Ridge data were up to 5% higher than the Karlsruhe results. The difference decreased with increasing pressure until at 4000 bars at 400° it was only about 1.5%.

Estimated uncertainties associated with the specific conductances reported in Table II tend to increase with increasing pressure and temperature. The probable uncertainty of about 0.5% at 100° and 1000 bars increased to approximately 1% at 8000 bars at this temperature. At higher temperatures the uncertainty was estimated to be near 1–1.5% at low pressures but in the region 10,000 to 12,000 bars it had increased to 3–4% at 800°. The uncertainty was greatest under conditions of temperature and pressure where the absolute value of the conductance was relatively low. For example, at 800° and 2000 bars the uncertainty may be as large as 5%.

Table III: Specific Conductances of Aqueous 0.01 *m* KCl Solutions at Saturation Vapor Pressures at Temperatures to 306°

Temp, °C	Pressure, bars	Specific conductance, ohm^{-1} cm^{-1} × 10^5	Temp, °C	Pressure, bars	Specific conductance, ohm^{-1} cm^{-1} × 10^5
25	1	140.9[a]	200	15.6	603[b]
					605[d]
50	1	212[b]			
			218	22.3	630[c]
100	1	358[b]			
		362[c]	225	25.5	635[b]
					637[d]
150	4.8	496[b]			
		496[d]	281	65.2	668[c]
156	5.6	512[c]	306	93.4	654[c]

[a] Calculated from the equation of J. E. Lind, Jr., J. J. Zwolenik, and R. M. Fuoss, *J. Amer. Chem. Soc.*, **81**, 1557 (1959). [b] A. J. Ellis, *J. Chem. Soc.*, 2299 (1963). [c] A. A. Noyes, *et al.*, "The Electrical Conductivity of Aqueous Solutions," Publication No. 63, Carnegie Institution of Washington, Washington, D. C., 1907; A. A. Noyes, *et al.*, *J. Amer. Chem. Soc.*, **30**, 335 (1908). [d] Interpolated by Ellis[b] from Noyes' data.[c]

In general, the apparatus at our laboratories were not designed to give conductances along the liquid–vapor curve which were as accurate as those previously reported by other investigators. Thus the values reported in Table III for specific conductances of 0.01

m KCl to 306° at saturation vapor pressures are those of earlier researchers but have been included here for completeness.

These specific conductances of KCl presented in Tables II and III are believed to represent the best values presently available for high temperatures and pressures. It is hoped that they will be useful in establishing the reliability of other conductance apparatus and in obtaining cell constants at high temperatures and pressures.