

all five hydrogens of pyrrole. At $pH > 1.5$, all the hydrogens do not exchange; at $pH < 1$, acid-induced decomposition of the pyrrole becomes serious. Pyrrole- d_5 was prepared by an exchange between pyrrole and heavy water at this optimum pH .

Adjusting the heavy water to pH 1 without contaminating it with light hydrogen required special methods. Deuterium chloride was made from heavy water and thionyl chloride, using the apparatus of Langseth and Klit.⁷ The deuterium chloride was bubbled into heavy water to which had been added a trace of dry methyl violet, until the color of the solution matched that of a comparison solution of ordinary hydrochloric acid whose pH had been adjusted to 1.0. Trials with ordinary water and hydrogen chloride showed that the pH could readily be adjusted in this manner to 1.0 ± 0.2 unit, which is sufficiently close. The procedure for exchange was similar to that for pyrrole- $N-d$. Because decomposition of the pyrrole resulted in the formation of a scum, and because the liquids did not separate as nicely as in the former case, the separatory funnels were rotated rather slowly in a large centrifuge to hasten the separation. The product was dried and distilled as before. About 1 ml. of pyrrole was lost during the exchange.

Symmetrical Pyrrole- d_4 .—This compound was prepared from pyrrole- d_5 by an exchange with neutral water. It has already been shown that under these conditions only the N-deuterium will be involved. The procedure for carrying out the exchange and purifying the product was identical with that for pyrrole- $N-d$. There was practically no loss of material.

(7) A. Langseth and A. Klit, *Kgl. Danske Videnskab Selskab, Math. fys. Medd.*, **15**, No. 13, p. 7 (1937).

Spectroscopic Results.—It is well known that C-H stretching frequencies in aromatic rings are in the 3000–3100 cm^{-1} region, while the corresponding C-D frequencies are found at 2200–2300 cm^{-1} . The N-H stretching frequency in liquid pyrrole occurs at 3400 cm^{-1} , and the N-D at 2530 cm^{-1} . Thus the vibrational spectrum offers a good criterion for the isotopic purity of the products. Each of the deuteropyrroles has been studied by the Raman effect.² In every case valence frequencies were found only in the expected regions: even on long exposure there was no trace of lines due to an improper isotope. This is thought to mean that the isotopic purity was at least 99%. It also offers convincing proof that exchange between pyrrole and water at pH 1 involves all five of the pyrrole hydrogens, but that at pH 7 only the N-hydrogen is involved.

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Summary

Simple and efficient methods of preparing pyrrole- $N-d$, *sym*-pyrrole- d_4 , and pyrrole- d_5 are described. It is confirmed that exchange between pyrrole and water at pH 1 involves all five of the pyrrole hydrogens. In neutral solution only the N-hydrogen exchanges.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YENCHING UNIVERSITY]

Conductivity Studies.¹ III. The Limiting Equivalent Conductances of Potassium Chloride in Water at Temperatures between 15 and 40°

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The determination of the electrical conductivity of electrolytes has been the subject of many investigations. A search of the recent extensive literature in this field shows that many investigators study conductivity as a function of concentration at some particular temperature or conduc-

tivity as a function of temperature at some particular concentrations, and only few study the variation of the limiting equivalent conductances with temperature.

Since aqueous solutions of potassium chloride have been used as standard solutions for determining cell constants, extensive conductivity studies on these are desirable. Recently Jones and Bradshaw⁴ and Bremner and Thompson⁵ studied the variation in conductance of "demal"

(1) Earlier papers in this series: Li and Fang, *J. Chinese Chem. Soc.*, **6**, 32–39, 44–50 (1938).

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(4) Jones and Bradshaw, *THIS JOURNAL*, **55**, 1780 (1933).

(5) Bremner and Thompson, *ibid.*, **59**, 2372 (1937).

potassium chloride solutions and Clews⁶ applied the Debye-Hückel-Onsager equation to data on 0.1, 0.01 and 0.001 *N* potassium chloride solutions at different temperatures. Except at 18 and 25°, however, there are no precise values of the limiting equivalent conductance, Λ_0 , of potassium chloride in water. It was the purpose of this investigation to study the electrical conductances of potassium chloride solutions over a wide range of concentrations and temperatures in order to determine the temperature coefficient of Λ_0 . In the paper following this one, certain transference data will be used together with the conductance data reported in this paper to calculate the limiting equivalent conductances of several univalent ions at different temperatures.

Experimental

The Wheatstone bridge and accessory apparatus used in conductivity determinations have been described.¹ The temperatures investigated were 15, 20, 22, 25, 30 and 40°. For each temperature the bath was adjusted and the temperature variation observed by a Beckmann thermometer which had been compared against a standard thermometer. The temperature variation was 0.005°. The standard solutions for the determination of cell constants were the 0.1 and 0.01 normal solutions defined and measured by Jones and Bradshaw⁴ at 0, 18 and 25°. The measured specific conductance was corrected in each case for the conductivity of the water used, amounting to about 1.2×10^{-6} at 25°. The potassium chloride was of Merck reagent quality and was further purified by repeated recrystallization from conductivity water, dried and fused. Solutions were prepared by direct weighing of both solute (or concentrated stock solution) and solvent, the balance used for weighing the dry salt being sensitive to 0.01 mg. with a 50-g. load and that for the solvent sensitive to 0.1 mg. The weights were carefully calibrated on each balance and all weighings were corrected to vacuum, taking the density of the air to be 0.0012 g./ml. and the density of potassium chloride to be 1.987.

Since the salt solutions were made up by weight and the concentrations used in the theory are on a volume basis (moles per liter, *C*), it was necessary to know the density of the solutions. It was found that the density of the aqueous solutions of potassium chloride was a linear function of the concen-

tration up to the highest concentration used, and obeyed the equation

$$d = d_0 + bf_{\text{KCl}} \quad (1)$$

where *d* is the density of a solution of f_{KCl} weight per cent. concentration in potassium chloride and d_0 is the density of pure water, both at the same temperature. The values of the density coefficients at 20, 22, 25, 30 and 40° were calculated from the density data in the "International Critical Tables." These were confirmed by the experimental determination of the density of the potassium chloride solutions at 25 and 30°. The density values for 15° are not given, but were calculated by the equation:

$$d = 1.00661 + 0.0000407t - 7.95 \times 10^{-6}t^2 + 4.83 \times 10^{-8}t^3$$

the equation obtained from an analysis of the data given in "I. C. T." for 1% potassium chloride solutions. The equations for density at different temperatures are listed

$$\begin{aligned} d_{15} &= 0.99913 + 0.00646f \\ d_{20} &= .99823 + .00640f \\ d_{22} &= .99780 + .00637f \\ d_{25} &= .99707 + .00635f \\ d_{30} &= .99567 + .00631f \\ d_{40} &= .99225 + .00622f \end{aligned}$$

The solutions were kept in seasoned and steamed Pyrex glass-stoppered bottles. In determining the resistance of a given solution, each cell was rinsed with four or five portions of the solution and allowed to stand, filled with the same solution, for fifteen to thirty minutes. The cell was then refilled with a fresh portion of the solution and immersed in the thermostat until temperature equilibrium was reached. The leads were placed in position and the bridge balanced. The leads were then shifted to the next cell and the bridge rebalanced.

Results

Table I gives the results of measurements on the potassium chloride solutions at different temperatures. The third column gives the equivalent conductances calculated from the Shedlovsky-Onsager equation

$$\Lambda_0 = \frac{\Lambda + \beta \sqrt{C}}{1 - \alpha \sqrt{C}} - BC$$

The fourth column lists the values of Λ'

$$\Lambda' = \frac{\Lambda + \beta \sqrt{C}}{1 - \alpha \sqrt{C}}$$

In order to calculate the theoretical coefficients α and β , we made use of the viscosity data given in "I. C. T." and the dielectric constant data of

(6) Clews, *Proc. Roy. Phys. Soc. (London)*, **46**, 764 (1934).

Drake, Pierce and Dow⁷ and substituted them in the equations⁸

$$\alpha = 8.147 \times 10^5 / (DT)^{3/2} \quad \beta = 81.86 / (DT)^{1/2} \eta \quad (2)$$

where D and η are the dielectric constant and viscosity of the medium at temperature T . These constants are collected in Table II for reference.

Graphs corresponding to the data in Table I for the various temperatures are shown in Fig. 1, where the values of Λ are plotted against \sqrt{C} and Λ'_0 plotted against C . The values of Λ_0 and B

TABLE I
EQUIVALENT CONDUCTANCES OF POTASSIUM CHLORIDE SOLUTIONS

$C \times 10^2$	$\Lambda_{obs.}$	$\Lambda_{calcd.}$	Λ'_0
15°			
0.22312	117.43	117.58	120.89
.30737	117.09	117.04	121.16
.57183	115.82	115.76	121.38
.62728	115.70	115.54	121.53
.99925	114.29	114.29	121.64
1.1657	113.83	113.81	121.77
1.2696	113.64	113.55	121.94
2.3693	111.25	111.32	122.61
4.7486	108.36	108.31	124.54
5.0481	108.09	108.03	124.77
9.9195	104.79	104.76	128.45
9.9209	104.73	104.76	128.39
20°			
0.07603	132.89	132.82	135.19
.15061	131.95	131.96	135.18
.15564	131.88	131.90	135.17
.28941	130.73	130.82	135.21
.30709	130.59	130.71	135.21
.31715	130.59	130.64	135.28
.58989	129.23	129.15	135.64
.64944	128.96	128.89	135.68
1.2035	126.93	126.92	136.09
1.2685	126.85	126.73	136.26
1.3220	126.66	126.59	136.27
2.4451	124.14	124.05	137.53
2.7090	123.74	123.67	137.54
9.9809	116.66	116.66	143.58
22°			
0.07599	138.71	138.62	141.12
.13626	137.64	137.82	140.88
.15558	137.65	137.62	141.10
.27833	136.66	136.60	141.35
.31702	136.46	136.32	141.39
.56759	134.93	134.87	141.53
.64919	134.59	134.40	141.65
1.1627	132.45	132.54	141.88
1.3215	132.12	132.06	142.20
2.3789	129.50	129.53	143.06
4.8709	125.85	125.81	144.36

25°			
0.03977	148.05	148.05	149.92
.06037	147.67	147.63	149.98
.08092	147.25	147.29	149.92
.12184	146.71	146.72	149.99
.16497	146.19	146.22	150.01
.33649	144.65	144.75	150.10
.49651	143.58	143.73	150.20
.68358	142.85	142.75	150.62
.99646	141.40	141.44	150.63
1.3802	140.01	140.14	151.06
1.3896	139.99	140.10	151.09
30°			
0.16040	160.64	160.59	164.45
.19252	160.14	160.22	164.74
.31781	159.05	159.04	164.96
.38429	158.49	158.51	165.00
.63086	156.92	156.95	165.25
.68514	156.67	156.65	165.55
.76056	156.21	156.26	165.37
1.2504	154.21	154.17	165.97
1.5025	153.23	153.28	166.12
2.4956	150.69	150.60	167.33
4.9813	146.23	146.17	169.89
5.9252	144.92	144.96	170.77
40°			
0.06189	191.10	191.08	194.29
.09635	190.31	190.33	194.28
.24763	188.14	188.11	194.51
.49164	185.79	185.80	194.77
.98778	182.65	182.64	195.40
1.9761	178.52	178.54	196.59
3.9341	173.50	173.43	199.12
7.7969	163.43	163.48	199.53

TABLE II
CONSTANTS PERTAINING TO EQUATION (2)

$t, ^\circ\text{C.}$	D_0	$\log \eta$	η	α	β
15	82.32	-1.9413	0.011447	0.2231	46.44
20	80.41	-1.9962	.010087	.2252	52.86
22	79.67	-2.0174	.009608	.2260	55.57
25	78.57	-2.0482	.008949	.2273	59.77
30	76.79	-2.0967	.008004	.2294	67.04
40	73.41	-2.1847	.006536	.2338	82.61

are obtained graphically from Fig. 1 and are listed in Table III.

TABLE III
LIMITING EQUIVALENT CONDUCTANCES AND SLOPES, B

$t, ^\circ\text{C.}$	Λ_0	B
15	120.88	75.9
18	129.4 ^a	80 ^a
20	135.06	85.3
22	140.96	89.4
25	149.84	94.9
30	164.62	104.5
40	194.18	123.7

The limiting conductance at 25° as obtained by Shedlovsky⁹ and recalculated by Krieger and Kil-

(^a) Data taken from Shedlovsky, THIS JOURNAL, 54, 1410 (1932).

(7) Drake, Pierce and Dow, *Phys. Rev.*, **35**, 613 (1930).
(8) MacInnes, "Principles of Electrochemistry," Reinhold Publishing Corp., New York, N. Y., 1939, Chapter 18.

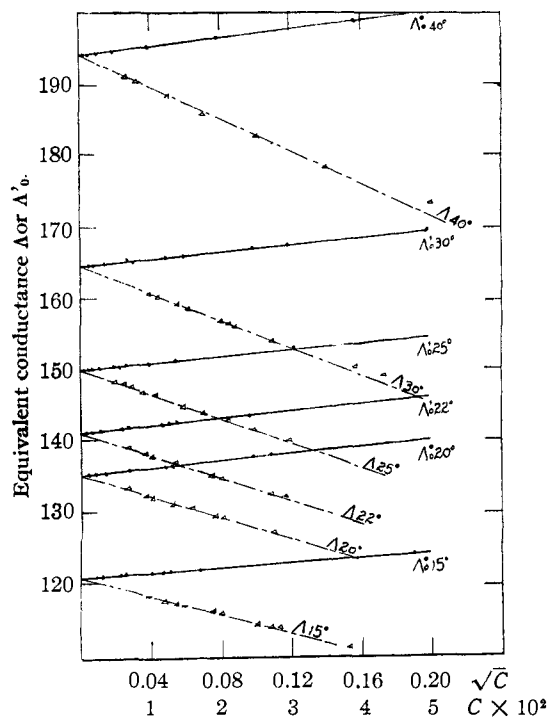


Fig. 1.—Variation of equivalent conductance with concentration.

patrick¹⁰ is 149.86, with which our value of 149.84 is in good agreement. Figure 2 brings out the relationship between Λ_0 and temperature.

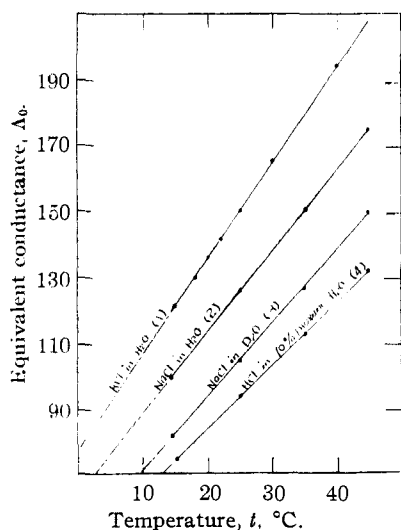


Fig. 2.—Variation of conductance at infinite dilution with temperature.

The relationship in Curve I can be expressed by the empirical equation $\Lambda_0 = 75.94 + 2.956 t$. It

(10) Krieger and Kilpatrick, *THIS JOURNAL*, **59**, 1881 (1937).

is also interesting to note that the relationship between B and temperature is linear and can be expressed by the equation $B = 46.9 + 1.92 t$.

Curves 2, 3 and 4 in Fig. 2 are plots taken from data by Brescia, LaMer and Nachod¹¹ and Owen and Waters¹² and the limiting conductances can be expressed by the equations

NaCl in H ₂ O	$\Lambda_0 = 64.08 + 2.462 t$
NaCl in D ₂ O	$50 + 2.2 t$
HCl in 70% dioxane	$45.9 + 1.91 t$

It was shown by Owen and Waters¹² that viscosity and equivalent conductance in a given solvent at various temperatures are simply related by an equation $\Lambda_0 \eta_0^s = r$. Figure 3 gives such a plot between $\log \Lambda_0$ and $\log \eta_0$ and the constants s and r are found to be 0.872 and 3.039, respectively.

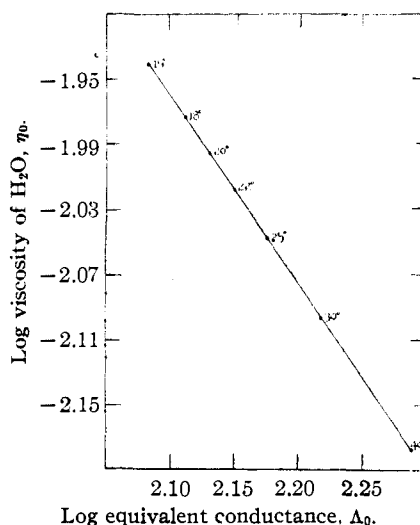


Fig. 3.—Variation of conductance at infinite dilution with viscosity of medium.

Summary

1. The equivalent conductances of potassium chloride solutions have been measured at 15, 20, 22, 25, 30 and 40° in the concentration range 0.0004 to 0.1 N . The experimental data follow closely the Onsager limiting slope at high dilutions. At other concentrations only one empirical constant B is needed.

2. The temperature dependence of the limiting conductance is linear between 15 and 40°. The variation with viscosity can be expressed by $\Lambda_0 \eta_0^s = r$, s being less than 1.

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(11) Brescia, LaMer and Nachod, *ibid.*, **62**, 615 (1940).

(12) Owen and Waters, *ibid.*, **60**, 2377 (1938).