Conductivity Studies.   IV.   The Limiting Ionic Mobilities of Several Univalent Ions at Temperatures between 15 and 45°

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Conductance data on aqueous solutions of potassium chloride at several temperatures are given in a paper preceding this one.[1] Allgood, LeRoy and Gordon[2] describe the accurate determination by moving boundary method of the transference numbers of aqueous solutions of potassium chloride at 15, 25, 35 and 45°. With these data on conductances and transference numbers at hand, we can calculate the equivalent conductances of ion constituents and the limiting ionic mobilities at different temperatures, with an accuracy of a part in several thousand.

Table I contains the assembled data on the equivalent conductances, Λ, of potassium chloride solutions and the corresponding transference numbers of the chloride ion, t_{Cl}, for 15, 25, 35 and 45°. The values of Λ are calculated from the equation

$$\Lambda = \Lambda_0' \, (1 - \alpha\sqrt{C}) - \beta\sqrt{C}$$

in which the theoretical coefficients α and β are calculated in the same way as described by Li and Fang[1] and Λ_0' is given by the equation

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

The constants Λ_0 and B are either given in or interpolated from Table III of the preceding paper. The transference numbers as given by Allgood, LeRoy and Gordon are either the directly determined values or calculated by the equation

$$t_+{}^{0'} = t_+{}^0 + AC = \frac{t_+\Lambda + \frac{1}{2}\beta\sqrt{C}}{\Lambda + \beta\sqrt{C}} \qquad (1)$$

where A is a disposable constant and β is the same theoretical coefficient as before,   It is interesting to note that data on transference number and equivalent conductance can be treated in a similar way.

Column 4 of Table I gives the conductance of the chloride ion constituent $\lambda_{Cl} = \Lambda t_{Cl}$, and column 5 gives the values of λ_0' obtained by means of the equation

$$\lambda_0' = \lambda + \frac{1}{2}\beta\sqrt{C}/1 - \alpha\sqrt{C} = \lambda_0 + bC \qquad (2)$$

in which λ_0 is the limiting equivalent conductance of the ion species and b is an empirical constant.

(1) Li and Fang, THIS JOURNAL, **64**, 1544 (1942).
(2) Allgood, LeRoy and Gordon, J. Chem. Phys., **8**, 421 (1940).

TABLE I

Λ_{Cl} FOR POTASSIUM CHLORIDE SOLUTIONS OF DIFFERENT CONCENTRATIONS

C	Λ_{KCl}	t_{Cl}	λ_{Cl}	λ_0'
		15°		
0.005	116.07	0.5074	58.89	61.50
.01	114.29	.5075	58.00	61.70
.02	111.97	.5076	56.84	62.09
.05	108.08	.5077	54.87	63.21
.10	104.73	.5079	53.19	65.12
		25°		
0.005	143.67	0.5097	73.23	76.58
.01	141.38	.5098	72.08	76.82
.02	138.41	.5099	70.62	77.33
.05	133.36	.5100	68.02	78.71
.10	128.98	.5100	65.78	81.06
		35°		
0.005	171.74	0.5113	87.81	91.96
.01	168.89	.5114	86.37	92.24
.02	165.17	.5115	84.48	92.80
.05	158.83	.5115	81.24	94.48
		45°		
0.005	199.72	0.5131	102.48	107.48
.01	196.26	.5132	100.72	107.81
.02	191.73	.5132	98.40	108.44
.05	183.96	.5131	94.37	110.33

This equation was first given by MacInnes, Shedlovsky and Longsworth.[3] Fig. 1 shows values of λ plotted against $\sqrt{C}$ and λ_0' against C. The
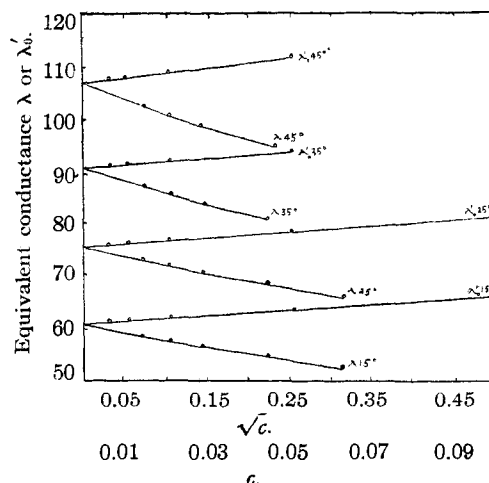

Fig. 1.—Variation of equivalent conductance with concentration.

(3) MacInnes, Shedlovsky and Longsworth, THIS JOURNAL, **54**, 2760 (1932).

values of λ_0 and b in Eq. 2 are obtained graphically and are listed in Table II.

TABLE II
LIMITING MOBILITIES OF THE CHLORIDE ION

t, °C.	b	λ_0 for Cl ion
15	40	61.30
25	48	76.34
35	56	91.68
45	64	107.16

The values of λ_{Cl}° can be calculated directly from the product of $\Lambda_{0\,KCl}$ and t°_{Cl}. Table III, columns 4 and 5 list the values of λ_0 for potassium and chloride ions, respectively, for 15, 25, 35 and 45°. The values of $\Lambda_{0\,KCl}$ are taken from Li and Fang[1] and $t^\circ_{+\,KCl}$ from Allgood, LeRoy and Gordon.[2]

TABLE III
LIMITING IONIC MOBILITIES

t, °C.	$\Lambda_{0\,KCl}$	$t^\circ_{+\,KCl}$	λ_K	λ_{Cl}°
15	120.88	0.4928	59.57	61.31
25	149.84	.4905	73.50	76.34
35	179.40	.4889	87.71	91.69
45	208.96	.4872	101.81	107.15

The values of λ_{Cl}° as seen agree very well with those listed in Table II and the very close agreements are somewhat surprising, since the transference numbers at very low concentrations are not known accurately. The relationship between λ° and temperature is linear so that the following equations can be applied

$$\lambda_{Cl}^\circ = 38.50 + 1.519t$$
$$\lambda_K^\circ = 38.44 + 1.407t$$

The value of λ_{Cl}° at 25° agrees with that given by MacInnes, Shedlovsky and Longsworth.[3]
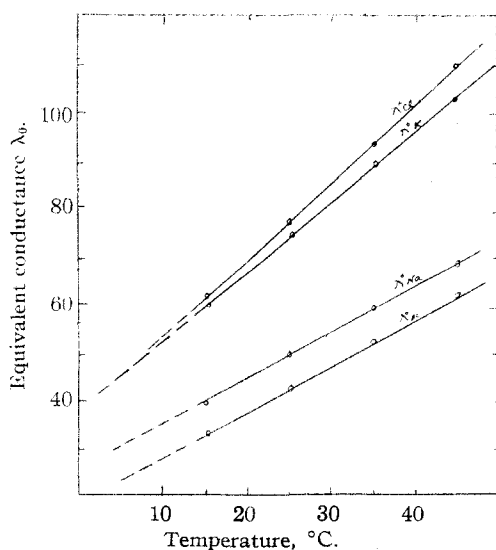

Fig. 2.—Variation of limiting ionic conductances with temperature.

From the values of λ_K° and λ_{Cl}° just given and the limiting conductances Λ_0 of sodium chloride and sodium acetate in water as given by Brescia, LaMer and Nachod,[4] the limiting ion conductances of sodium and acetate ions at different temperatures can be calculated from Kohlrausch's law of independent ion mobilities. The results obtained are shown in Table IV and in Fig. 2. The values for λ_{Na}° and λ_{Ac}° at 25° given by MacInnes, Shedlovsky and Longsworth[3] are 50.10 and 40.87, respectively, and differ considerably from the corresponding values given in Table IV, owing to the differences in the values of Λ_{NaCl}° and Λ_{NaAc}° used.

TABLE IV
LIMITING ION CONDUCTANCES AND LIMITING TRANSFERENCE NUMBERS

t, °C.	λ_{Na}°	λ_{Ac}°	t°_+ in NaCl	t°_+ in NaAc
15	39.70	32.80	0.3930	0.5476
25	49.29	42.07	.3923	.5395
35	58.57	51.65	.3898	.5314
45	67.72	61.36	.3872	.5256

The values of Λ_{NaCl}° and Λ_{NaAc}° given by Brescia, LaMer and Nachod,[5] however, are calculated from data in "International Critical Tables" and are not as accurate as the more recent values given by MacInnes, Shedlovsky and Longsworth. Using the equation

$$t_+^\circ = \frac{\lambda_+^\circ}{\lambda_+^\circ + \lambda_-^\circ} = \frac{\lambda_+^\circ}{\Lambda_0}$$

we have calculated the limiting transference numbers of aqueous solutions of sodium chloride and sodium acetate at the several temperatures and the results are shown in columns 3 and 4 of Table IV.

The cation transference numbers in aqueous solutions of sodium acetate are seen to decrease with rising temperature. This decrease is in accord with the well-known generalization that if the transference numbers are less than 0.5 they increase, and if greater than 0.5 they decrease with rise in temperature. The cation transference numbers in aqueous solutions of potassium and sodium chlorides, which are all less than 0.5, are seen to decrease with rising temperature and this is apparently contrary to the above generalization. Allgood, LeRoy and Gordon[2] have tentatively explained the anomaly of potassium chloride solutions as due to the hydration of the cation resulting in a different mechanism of transport for cation and anion. This difference may be-

(4) Brescia, LaMer and Nachod, THIS JOURNAL, 62, 615 (1940).

come prominent because the anion and cation of potassium chloride have approximately the same mobility, but it is not sufficient to explain the case of sodium chloride, in which the mobilities of anion and cation are quite different. We believe that the apparent decrease in cation transference numbers in sodium chloride solutions with rise in temperature is due to the inaccurate conductivity data given in "International Critical Tables." Thus if we use the more recent value, $\Lambda_0 = 126.42$, for sodium chloride at 25°, the calculated value of t^0_+ for aqueous solution of sodium chloride at 25° will be 0.3963 in agreement with the value found from direct transference data and in agreement with the above generalizations in that the limiting transference number at 25° is higher than at 15°. However, since the recent accurate conductivity data have been determined for 25° only, all the values given in Table IV for the four different temperatures are taken from the paper by Brescia, LaMer and Nachod which is based on the values given in "International Critical Tables." The older value

for $\Lambda_{0\,NaCl}$ at 25° is 125.63, which is only 0.79 unit different from the new value. This illustrates the immense importance and need of obtaining accurate conductivity data at different temperatures, in order to obtain limiting ionic mobilities and limiting transference numbers with a high degree of accuracy.

Summary

Tables are given of the limiting mobilities of potassium and chloride ions at 15, 25, 35 and 45°, based on conductance data given by Li and Fang and transference data given by Allgood, LeRoy and Gordon. Approximate values for the limiting ionic mobilities of sodium and acetate as well as the limiting transference numbers in aqueous solutions of sodium chloride and sodium acetate for these temperatures are also given. The transference numbers calculated for sodium chloride solutions illustrate the necessity of obtaining accurate conductivity data not at one temperature, 25°, only, but at different temperatures.

Studies of Lead Oxides.[1] VI. The Effect of Grinding on the X-Ray Diffraction Patterns of Mixtures Containing Lead Oxides

By George L. Clark and Stanley F. Kern

Of all the variables which are known to affect the nature of materials used in the lead storage battery, grinding, especially of mixtures, has been studied the least. Leblanc and Eberius[2] report, "A hard stroke with a spatula, leaving a brown-red trail in the yellow oxide, suffices for the conversion of Y-PbO (yellow, orthorhombic) into R-PbO (red, tetragonal), while the conversion of Pb_3O_4 (black) into Pb_3O_4 (red) proceeds only under the hardest grinding and crushing on the roughest surfaces." Clark and Rowan[3] have shown that the R-PbO obtained on grinding Y-PbO is different from the normal R-PbO in that it gives an X-ray diffraction pattern identical with a distorted R-PbO formed by the vacuum decomposition of lead carbonate, basic carbonate or white lead, or lead oxide hydrate, and in that

it exhibits an abnormal chemical activity toward hydrogen peroxide and an increased heat of solution in perchloric acid over that of the normal R-PbO.

It has been observed previously in this Laboratory that intense grinding of normal R-PbO caused a slight broadening of some lines on the X-ray diffraction pattern. This non-uniform broadening is indicative of distortion.

Brown, Cook and Warner[4] have reported the effect of grinding upon the apparent density of Pb_3O_4 samples obtained by oxidation of three different lead oxides.

Procedure

Seven binary mixtures involving the lead oxides were investigated using six to eight different percentage compositions of each. These mixtures were ground with a rubbing or shearing action and in identical manner in an agate mortar and samples reserved after various times of

(1) For the fifth paper of this series, see Clark and Rowan, This Journal, 63, 1305 (1941).

(2) M. Leblanc and E. Eberius, Z. physik. Chem., A160, 69 (1932); see also M. Petersen, This Journal, 63, 2617 (1941).

(3) Clark and Rowan, ibid., 63, 1302 (1941).

(4) O. W. Brown, S. V. Cook and J. C. Warner, J. Phys. Chem., 26, 477 (1922).