

The rate of interdiffusion of the same acid and base in sodium chloride solution has been studied. It is shown that the diffusion coefficients are unchanged if sufficient sodium chloride is present initially; in the porous disk cell, the diffusion rates are, however, greatly increased since the concentration gradients become much

sharper because of the neutralization within the disk.

Some limitations of the porous disk diffusion cell are demonstrated. Adequate mixing must be maintained in the cell solutions either by natural convection or by auxiliary stirring.

NEW YORK, N. Y.

RECEIVED FEBRUARY 12, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

## The Conductance of Salts (Potassium Acetate) and the Dissociation Constant of Acetic Acid in Deuterium Oxide

BY VICTOR K. LA MER AND JAMES P. CHITTUM

The accurate calculation of the dissociation constant of a weak acid, like acetic acid, in deuterium oxide requires values of comparable accuracy of the limiting conductances  $\Lambda_0$ , of deuteriochloric acid, potassium chloride and potassium acetate. In ordinary water the problem is solved by measuring a series of conductance values at increasing dilutions and controlling the extrapolation to infinite dilution by the Onsager<sup>1</sup> equation.

The limited quantities of heavy water available do not permit execution of this tedious and experimentally difficult problem at this time. We are accordingly interested in establishing the validity of two approximate rules, which will permit the calculation of  $\Lambda_0$  for the deuterium ion and for the anion of the weak acid with sufficient precision for present purposes from a single measurement at an experimentally convenient concentration ( $C = 0.01$ ) in heavy water which is not necessarily 100%  $D_2O$ .

These rules are

$$[\Lambda_c/\Lambda_0]_{H_2O} = [\Lambda_c/\Lambda_0]_{D_2O} \quad (1)$$

valid for acids and salts in pure  $D_2O$ , but presumably accurate only for salts in intermediate mixtures of  $D_2O$ - $H_2O$ , owing to the complication of the exchange reactions which acids suffer in the mixed waters.<sup>2</sup>

$$\Lambda\eta = \text{Constant}; \quad \eta = \text{Viscosity} \quad (2)$$

valid for interpolation and for extrapolation to pure  $D_2O$  of the data obtained for the salts in  $H_2O$ - $D_2O$  mixtures.

- (1) Onsager, *Physik. Z.*, **27**, 288-292 (1926); **28**, 277-298 (1927).  
 (2) Baker and La Mer, *J. Chem. Phys.*, **3**, 406 (1935).

The justification of (1) follows from the Onsager equation<sup>3</sup>

$$\Lambda_0 = \Lambda_0 - [\alpha\Lambda_0 + 2\beta] \sqrt{C} \quad (3)$$

where

$$\alpha = \frac{8.173 \times 10^6}{(DT)^{3/2}} \quad \text{and} \quad \beta = \frac{41.7}{(DT)^{1/2}} \times \frac{1}{\eta} \quad (4)$$

Let  $\beta' = 2\beta\eta$ , then  $\alpha$  and  $\beta'$  differ in  $H_2O$  and  $D_2O$  only by the ratio of the dielectric constants of  $H_2O$  and  $D_2O$  which ratio appears to be almost unity.<sup>4,5</sup>

$$\Lambda_c/\Lambda_0 = 1 - [\alpha + \beta'/\Lambda_0\eta] \sqrt{C} \quad (5)$$

and

$$\frac{[\Lambda_c/\Lambda_0]_{H_2O}}{[\Lambda_c/\Lambda_0]_{D_2O}} = 1 + \frac{\beta' \sqrt{C} [1/(\Lambda_0\eta)_{H_2O} - 1/(\Lambda_0\eta)_{D_2O}]}{1 - [\alpha + \beta'/(\Lambda_0\eta)_{D_2O}]} \quad (6)$$

The experimental data on potassium chloride and on potassium acetate presented below show that  $(\Lambda_0\eta)_{H_2O}$  differs from  $(\Lambda_0\eta)_{D_2O}$  by only 1.93%. Hence equation (6) reduces without appreciable error to equation (1).<sup>6</sup>

The error in  $\Lambda_0(D_2O)$  calculated through equations (1) and (6) is thus less than 0.1% and less than our present experimental errors. The  $\Lambda_c$  vs.  $\sqrt{C}$  curves in  $D_2O$  are, therefore, sensibly parallel to those in  $H_2O$ , and the  $D_2O$  curve can be constructed from a measurement of  $\Lambda$  at a single low concentration.

Since the only difference in the limiting conductance of non-acid ions in  $D_2O$  and in  $H_2O$  appears to be resident in the change in  $\beta$ , the electrophoretic part of the Onsager equation, we expect

(3) MacInnes, Shedlovsky and Longworth, *Chem. Rev.*, **13**, 29 (1933), eq. (7).

(4) Horst Müller, *Physik. Z.*, **35**, 1009-1011 (1935).

(5) P. Abadie and G. Champetier, *Compt. rend.*, **200**, 1387 (1935).

(6)  $\eta$  does not change significantly on passing from  $C = 0.01$  to  $C = 0$ .

TABLE I

$\frac{\Delta S}{0.1079} = N_{D_2O}$	0.0	27.4	77.0	93.0	97.0	100.0
$10^5 K'$ acetic	1.84	1.352	0.741	0.608	0.575	( 0.555)
$\Lambda_0 KAc$	114.4	108.1	98.2	96.0	95.5	( 94.7)
$(\Lambda_0\eta) KAc$	114.4	115.0	115.8	116.4	116.5	(116.6)
$\Lambda_0\eta^{0.913} KAc$	114.4	114.4	114.1	114.5	114.5	
$\Lambda_0 (HAc-DAc)$	390.6	345.6	297.5	285.9	285.2	
$A$ (Eq. 8)	148.6	134.8	117.2	114.2	113.7	

that  $\Lambda_0(H_2O)/\Lambda_0(D_2O)$  is practically constant for all completely dissociated salts of the same valence type and equal to approximately  $\eta_{D_2O}/\eta_{H_2O}$ .

**Experimental.**—The measurements on potassium acetate have been made at 25°, using a Jones bridge and the semi-micro method described previously,<sup>2</sup> at approximately 0.015 *N* at different mixtures of H<sub>2</sub>O–D<sub>2</sub>O.  $\Lambda_0$  obtained by linear extrapolation from 93 and 97% D<sub>2</sub>O is 94.8 Kohlrausch units (K. U.), a decrease of 17.1% from the H<sub>2</sub>O value. The corresponding decrease for potassium chloride is 17.2%. Table I shows that the empirical equation

$$\Lambda_0\eta^{0.913} = \text{Constant} \quad (7)$$

shown in the previous paper to be valid for potassium chloride, applies equally well to potassium acetate. The value of  $\Lambda_0(KAc)$  at 100% D<sub>2</sub>O calculated either from equation (1) or (7) is 94.7 K. U.

**Dissociation Constant of Acetic Acid.**

—The stoichiometric constant for approximately 0.02 *N* acetic acid, has been calculated using the MacInnes–Shedlovsky<sup>7</sup> method for each H<sub>2</sub>O–D<sub>2</sub>O mixture (Table I), by omitting the last (empirical) term in the equation

$$\Lambda_e(HAc) = \Lambda_0 - A\sqrt{C_i} + Bc(1 - \alpha\sqrt{C}) \quad (8)$$

$\Lambda_0$  (HCl) and  $\Lambda_0$  (KCl) were calculated by means of equation (1). A short series of approximations gives  $\Lambda_e$  and hence  $C_i$  from  $(1000 \bar{L})/\Lambda_e$ . ( $\bar{L}$  = specific conductance of solution.)

The stoichiometric constant  $K'$  is defined as  $C_i^2/(C - C_i)$ , where  $C$  is the stoichiometric concentration of the acid. Linear extrapolation from 93 to 97% D<sub>2</sub>O (Fig. 1, curve 1), gives  $K' = 0.555 \times 10^{-5}$  for deutoacetic acid, which compares favorably with Lewis and Schutz' estimate of  $0.59 \times 10^{-5}$  obtained on less than one cc. of solution. Our value proves to be in excellent

(7) MacInnes and Shedlovsky, *THIS JOURNAL*, **54**, 1429 (1932). We did not attempt the precautions taken by these authors, namely, of adding traces of HAc to KAc solutions because of the small volumes of D<sub>2</sub>O available.

agreement with the value of  $0.55 \times 10^{-5}$  obtained by Korman and La Mer<sup>8</sup> from the e. m. f. of quinhydrone–silver chloride, Ag cells without transference and a formula defined by them for extrapolating  $K$  to 100% D<sub>2</sub>O.

As was found previously for potassium chlo-

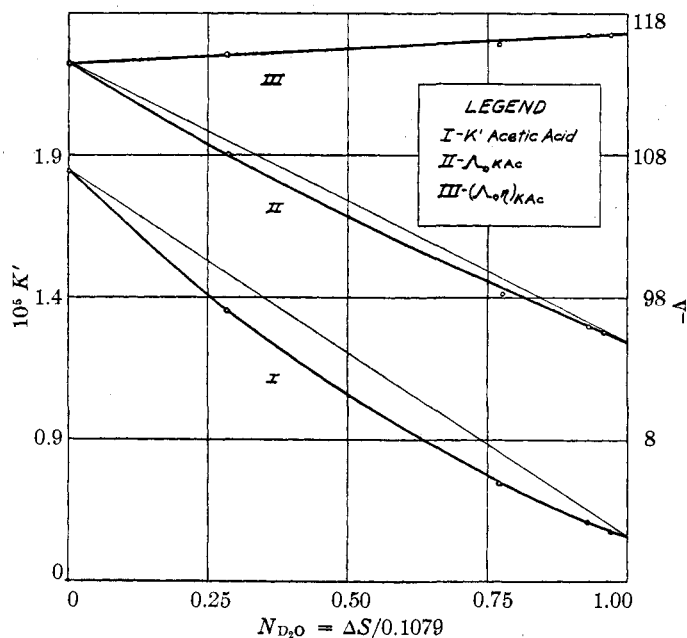


Fig. 1.

ride  $\Lambda_0$  for potassium acetate exhibits a small negative deviation of approximately 2% at  $N_{D_2O} = 0.5$ . On the other hand, the dissociation constant of hydrogen acetate exhibits a much larger negative deviation from linearity amounting to 10% at  $N_{D_2O} = 0.5$ . The non-linear behavior of the dissociation constant when plotted against the deuterium content of the solvent  $N_{D_2O} = \Delta S/0.1079$  arises from the complications of the proto- and deuterotropic exchanges in the mixtures as was suggested for the  $\Lambda$  hydrogen chloride curve, which exhibits a negative deviation of 6.5% at the midpoint. Similar deviations from linearity are uniformly

(8) Korman and La Mer, *THIS JOURNAL*, **58**, 1396 (1936); *Science*, N. S., **83**, 624 (1936).

exhibited in the kinetic processes of acid-base catalysis.<sup>9,10</sup>

### Summary

The Walden constant =  $\Lambda_0\eta$  increases (linearly) by 1.93% on passing from H<sub>2</sub>O to D<sub>2</sub>O for both potassium acetate and potassium chloride. With this equation and the rule

(9) Hamill and La Mer, *J. Chem. Phys.*, **2**, 891 (1934); **4**, 395 (1936).

(10) La Mer and Greenspan, not yet published.

$$[\Lambda_c/\Lambda_0]_{\text{H}_2\text{O}} = [\Lambda_c/\Lambda_0]_{\text{D}_2\text{O}}$$

which follows from the Onsager equation and the Walden rule, it is shown how the dissociation constants of weak acids in D<sub>2</sub>O may be calculated with satisfactory accuracy from a limited amount of conductance data.  $K'$  (acetic acid) equals  $0.55 \times 10^{-5}$  in pure D<sub>2</sub>O, and exhibits a marked negative deviation (10%) from linearity on passing from H<sub>2</sub>O to D<sub>2</sub>O.

NEW YORK, N. Y.

RECEIVED JULY 1, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

## Ternary Systems. XXI. Lead Nitrate, Ammonium Nitrate and Water at 25°

BY ARTHUR E. HILL AND NATHAN KAPLAN

The effect of potassium nitrate in increasing the solubility of lead nitrate in water led Le Blanc and Noyes<sup>1</sup> to the explanation of double salt or complex ion formation in the liquid phase. Solubility determinations by Glasstone and Saunders<sup>2</sup> at temperatures between 25 and 100° gave no evidence of double salts as solid phase, and similar experiments by Ehret<sup>3</sup> at 0° gave likewise a negative result. The work of Glasstone and Saunders<sup>2</sup> with sodium nitrate as added salt showed a decrease in solubility of lead nitrate, also without

to cover a wider range of concentrations, is here reported.

Pure recrystallized lead nitrate and ammonium nitrate were used in making up the complexes, which were rotated in closed tubes for several days at  $25 \pm 0.03^\circ$ . The solutions at equilibrium were analyzed by evaporation of a weighed sample to give total solids, and the determination of lead as lead sulfate by the standard method. The results are given in Table I.

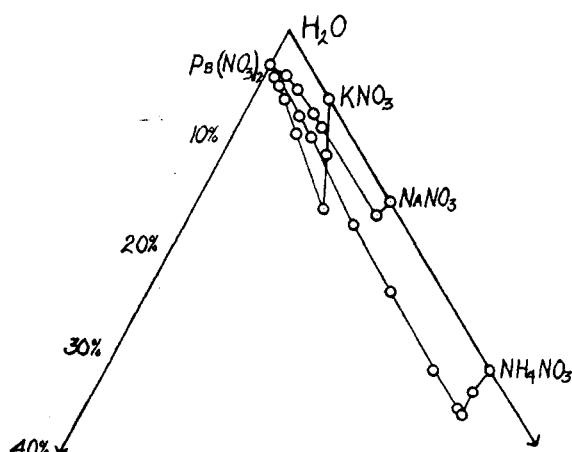


Fig. 1.—25° Isotherm,  $\text{Pb}(\text{NO}_3)_2\text{-NH}_4\text{NO}_3\text{-H}_2\text{O}$ , in mole per cent.

formation of double salt in the solid phase. The effect of ammonium nitrate, which has a much higher solubility than the corresponding sodium and potassium salts, permitting the investigation

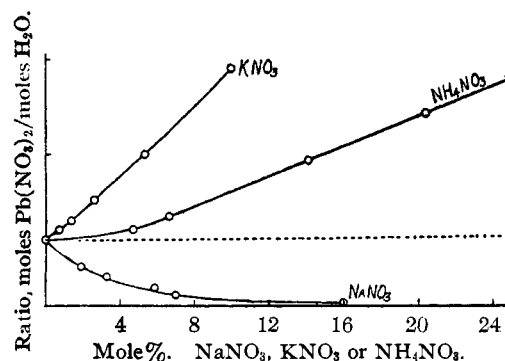


Fig. 2.—Effect of added nitrate on solubility of  $\text{Pb}(\text{NO}_3)_2$  at 25°.

The solubility curves, plotted in molar percentages, are shown in Fig. 1. On the same diagram are shown the results of Glasstone and Saunders<sup>2</sup> for potassium nitrate and sodium nitrate. It is apparent that the effect of ammonium nitrate upon the solubility of lead nitrate is intermediate between the effects of the potassium and sodium salts, at similar molar concentrations. There is no indication of double salt formation as solid phase; tie lines drawn through the compositions

(1) Le Blanc and Noyes, *Z. physik. Chem.*, **6**, 385 (1890).

(2) Glasstone and Saunders, *J. Chem. Soc.*, **123**, 2134 (1923).

(3) Ehret, *THIS JOURNAL*, **54**, 3126 (1932).