exhibited in the kinetic processes of acid–base catalysis.[9,10]

Summary

The Walden constant = $\Lambda_0\eta$ increases (linearly) by 1.93% on passing from H_2O to D_2O for both potassium acetate and potassium chloride. With this equation and the rule

$$[\Lambda_c/\Lambda_0]_{H_2O} = [\Lambda_c/\Lambda_0]_{D_2O}$$

which follows from the Onsager equation and the Walden rule, it is shown how the dissociation constants of weak acids in D_2O may be calculated with satisfactory accuracy from a limited amount of conductance data. K' (acetic acid) equals 0.55×10^{-5} in pure D_2O, and exhibits a marked negative deviation (10%) from linearity on passing from H_2O to D_2O.

NEW YORK, N. Y.

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

[10] La Mer and Greenspan, not yet published.

[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 inwater led Le Blanc and Noyes[1] to the explanation of double salt or complex ion formation in the liquid phase. Solubility determinations by Glasstone and Saunders[2] at temperatures between 25 and 100° gave no evidence of double salts as solid phase, and similar experiments by Ehret[3] at 0° gave likewise a negative result. The work of Glasstone and Saunders[2] with sodium nitrate as added salt showed a decrease in solubility of lead nitrate, also without 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 to cover a wider range of concentrations, is here reported.

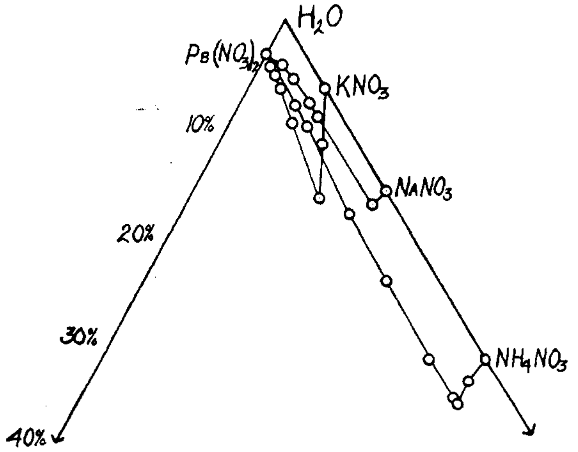

Fig. 1.—25° Isotherm, $Pb(NO_3)_2$–NH_4NO_3–H_2O, in mole per cent.

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 ± 0.03°. 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.

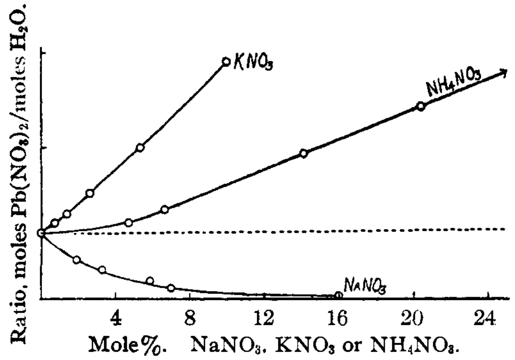

Fig. 2.—Effect of added nitrate on solubility of $Pb(NO_3)_2$ at 25°.

The solubility curves, plotted in molar percentages, are shown in Fig. 1. On the same diagram are shown the results of Glasstone and Saunders[2] 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

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[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).

TABLE I

SYSTEM: $Pb(NO_3)_2$–NH_4NO_3–H_2O AT 25°

Original complex Wt., % $Pb(NO_3)_2$	Original complex Wt., % NH_4NO_3	Saturated solution Wt., % $Pb(NO_3)_2$	Saturated solution Wt., % NH_4NO_3	Moles $Pb(NO_3)_2$ per mole H_2O	Solid phase
...	...	37.17[2]	0.00	0.0322	$Pb(NO_3)_2$
48.03	9.72	33.99	12.35	.0344	$Pb(NO_3)_2$
59.64	10.04	34.02	16.28	.0372	$Pb(NO_3)_2$
38.39	26.74	33.65	28.75	.0487	$Pb(NO_2)_2$
41.87	31.90	32.61	36.92	.0581	$Pb(NO_3)_2$
35.91	41.39	30.79	44.58	.0680	$Pb(NO_3)_2$
39.06	42.03	29.63	48.47	.0735	$Pb(NO_3)_2$
32.36	54.54	29.44	49.00	.0743	$Pb(NO_3)_2$ + NH_4NO_3
27.84	55.22				
15.37	62.65	18.04	56.15		NH_4NO_3
...	...	0.00	68.17		NH_4NO_3

of saturated solution and original complex pass through the compositions of the two simple salts with average deviation of 1.1%.

From the molar ratio of lead nitrate to water, shown in column 5, it is apparent that addition of ammonium nitrate increases the solubility of the salt markedly. A plot of the change in solubility, as thus defined, is shown in Fig. 2, in which are shown also curves for potassium nitrate and sodium nitrate calculated from the work of Glasstone and Saunders.

Summary

The solubilities in the system $Pb(NO_2)_2$–NH_4NO_3–H_2O at 25° have been determined. The solubility of lead nitrate is increased by ammonium nitrate, but to a smaller degree than by potassium nitrate. No double salts have been found as solid phases.

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Studies in the Mechanism of Decomposition. I. The Vapor Phase Photolysis of Acetic Acid

BY MILTON BURTON

In order to explain certain observations on the pyrolysis of acetic acid, Hurd[1] suggested the formation of ketene as an intermediate reaction product. F. O. Rice[2a] showed that such formation might be considered a logical consequence of a free radical chain mechanism. However, Franck and Rabinowitsch,[3] in discussing the photolysis of organic molecules by the intermediary of free radicals and atoms, pointed out that certain polyatomic molecules might decompose directly into stable molecules and that the work of L. Farkas and Wansbrough-Jones[4] indicated that acetic acid is an example of such a compound. That conclusion was based primarily upon an analysis of the ultimate products of the decomposition, which showed such a clear correspondence of yields among the products that the two reactions following appeared to be the only tenable ones in the gaseous state

$$CH_3COOH + h\nu \longrightarrow CH_4 + CO_2 \qquad (1)$$

$$(CH_3COOH)_2 + h\nu \longrightarrow C_2H_6 + CO + CO_2 + H_2O \qquad (2)$$

Although they reported a yield of approximately 1% by volume of hydrogen, Farkas and Wansbrough-Jones favored the idea that that substance, as well as traces of acetylene found, might be a product of some subsequent reaction of the resultant molecules.

This appears to be a clear-cut case in which to test whether decomposition takes place by rupture into free radicals or by rearrangement of a stable constellation of groups into stable constellations of ultimate molecules. The mirror methods developed by Paneth[5] and by F. O. Rice and his co-workers[6] and used by Pearson[7] in the study of the photochemical decomposition of aldehydes and ketones are well suited to the test. In a previous communication[8] the writer described a procedure for the detection of hydrogen atoms in the presence of free radicals and indicated evidence for the reactions

$$CH_3COOH + h\nu \longrightarrow CH_3 + COOH \qquad (3)$$

$$COOH \longrightarrow CO_2 + H \qquad (4)$$

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(1) Hurd, "Pyrolysis of Carbon Compounds," Chemical Catalog Co., New York, 1929, p. 334.

(2) Rice and Rice, "The Aliphatic Free Radicals," Johns Hopkins University Press, Baltimore, 1935, (a) p. 135, (b) p. 14, (c) p. 187.

(3) Franck and Rabinowitsch, *Trans. Faraday Soc.*, **30**, 120 (1934).

(4) L. Farkas and Wansbrough-Jones, *Z. physik. Chem.*, **18**, 124 (1932).

(5) Paneth and co-workers, *Ber.*, **62**, 1335 (1929); *Z. physik. Chem.*, **B7**, 155 (1930); *Nature*, **125**, 564 (1930); *Ber.*, **64**, 2702 (1931); **64**, 2708 (1931); *et seq.*

(6) Ref. 2 reviews this work thoroughly.

(7) Pearson, *J. Chem. Soc.*, 1718 (1934); Pearson and Purcell, *ibid.*, 1151 (1935).

(8) Burton, THIS JOURNAL, **58**, 692 (1936).