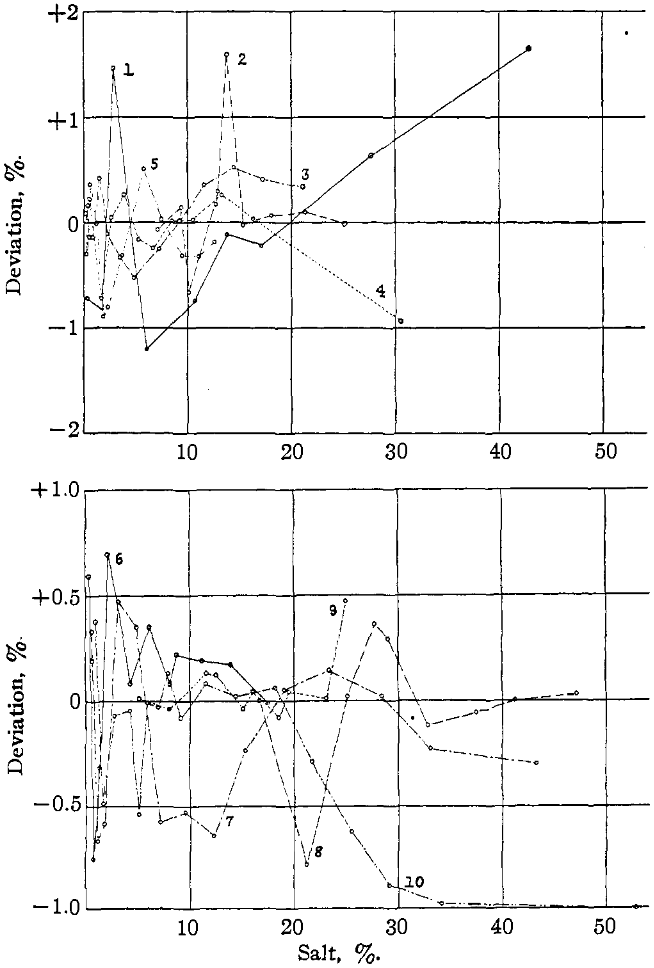
Notes

Ternary Systems: Water, Pyridine and Salts at 25°

By P. M. Ginnings, Bailey Webb and Emi Hinohara

In a previous study of the ternary systems water, aliphatic alcohols and salts,[1] empirical equations were obtained representing with reasonable accuracy the solubilities of the salts in aqueous alcoholic solutions. For purposes of comparison, we have now made similar measurements and have derived corresponding equations for systems in which pyridine is



Deviation charts of experimental values of weight per cent. of pyridine from values calculated using the empirical equations.

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(1) Ginnings, Herring and Webb, This Journal, **55**, 875–878 (1933).

employed instead of the aliphatic alcohols. Pyridine resembles the aliphatic alcohols (namely, isopropanol and tertiary butanol) in its complete miscibility with water, but is very unlike them in its chemical properties.

The methods and experimental procedure were essentially identical with those used previously (1) and if details are desired, reference should be made to the previous paper. The authors feel that the results obtained are not in error more than one per cent. in any case; and that the results can be reproduced with less deviation than this by a person experienced in this type of work. Plait points and percentage deviations are given in the following table and charts. C. P. pyridine, d_4^{20} 0.9812, was used throughout this investigation, without purification.

Empirical equations were derived to fit these data. It was found that the exponential equation

$$\text{(A)} \quad y = a + b(10)^{-cx}$$

where y = weight percentage of pyridine, x = weight percentage of salt, and a, b and c are arbitrary constants, gave the best fit in practically all cases. However, in the salt-rich solutions of ammonium sulfate and sodium chloride, the power equation

$$\text{(B)} \quad y = a + bx^{-c}$$

gave a better fit.

The values of the constants and the limiting values of x are given in the accompanying table.

TABLE I

Dev. curve	Salt	Eq.	Pyridine-rich section			Limit for "x"	Eq.	Salt-rich section			"x" at plait point
			a	b	c			a	b	c	
6	Na_2SO_4	A	17.2	43.5	0.1754	4.8	A	1.20	64.4	0.0975	4.97
9	KCl	A	−24.0	102.6	.0238	13.5	A	0	175.8	.0626	11.77
4	KF	A	9.8	57.45	.1402	4.4	A	1.17	88.1	.1332	4.11
5	$MgSO_4$	A	46.95	37.0	2.060	0.6	A	0	51.9	.0687	5.31
8	$NaNO_3$	A	−45.9	153.6	.01234	35.8	A	1.62	45960	.1047	29.93
3	Na_2CO_3	A	23.90	38.10	.3365	3.0	A	0.20	57.2	.1126	3.22
7	$Na_2S_2O_3$	A	22.65	48.35	.1527	6.1	A	.80	79.4	.0744	5.76
10	K_2CO_3	A	8.0	50.7	.0974	4.2	A	1.31	68.9	.0983	4.92
1	$(NH_4)_2SO_4$	A	22.8	47.15	.1682	5.9	B	−4.35	251.6	1.176	5.90
2	NaCl	A	17.1	104.7	.0722	12.5	B	0	96380	3.220	12.46

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A New Relation between Viscosity, Vapor Pressure and Density

BY FRANK HOVORKA

In attempting to make some useful calculations between the viscosity and the vapor pressure of liquids, it was found that the empirical equation $S = \eta P^{1/4} d^{1/2}$, where η is the viscosity, P the vapor pressure, d the density, and S a constant characteristic of the substance under consideration, holds very closely for a great many organic liquids.

In Table I are represented at random a few of the substances of different homologous series for which the constant S was calculated. It may be noticed in Table I that the variation of constant S is very small, and falls probably in many cases within the experimental error of the determination of the three properties involved in the calculation. About the same variation was found in the case of thirty or more other substances for which the constant S was calculated. In taking the values of S for aliphatic esters from methyl formate to methyl isobutyrate it was found that the constant S is approaching a constant value characteristic of that series. The same is indicated for the saturated hydrocarbons. If the value of S, for instance, obtained for ethyl acetate is used for any higher ester in calculating the density, vapor pressure, or the viscosity, the error in most of the cases proved to be very small. These same effects have been noticed for other series which thus far have been calculated only approximately due to the lack of experimental data.

TABLE I

VALUES OF CONSTANT S AT DIFFERENT PRESSURES

V. p., mm.	$CHCl_3$	$(C_2H_5)_2O$	n-C_5H_{12}	n-C_7H_{16}	$(CH_3)_2CO$	$CH_3COOC_3H_7$	$C_3H_7COOCH_3$
100	0.0244	0.0934	0.00868	0.00855	0.0108	0.0124	0.0124
200	.0244	.0936	.00870	.00857	.0108	.0124	.0124
400	.0244	.0938	.00871	.00859	.0109	.0124	.0123
600	.0243	.0939	.00870	.00859	.0110	.0123	.0123

An attempt is being made to evaluate the constant S independently.

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A Quantitative Study of the Lanthanum–Neodymium Separation

BY P. W. SELWOOD

The writer had occasion for another investigation to prepare a considerable quantity of a lanthanum–neodymium mixture and, during recovery of this material, opportunity has been taken to make quantitative measurements on eight separation procedures including all standard methods available for the cerium group. The fractions were analyzed by means of their magnetic susceptibilities. The original mixture contained 29.6% Nd. Six-gram samples of the mixed oxides were taken in each case.

While the above results have not necessarily been obtained through the optimum conditions for all or any one of the separations, yet Prandtl's basic ammonia separation is shown to be definitely the most efficient of the methods as described in the literature. In actual practice it is frequently found that a reversal of the solubility order facilitates rapid purification. The oxalate method, which is the most efficient of the solubility

TABLE I

SUMMARY ON LANTHANUM-NEODYMIUM SEPARATIONS

Method	Ppt. (g. oxide)	% Nd in ppt.	% Nd in in filtrate	More soluble element
Sulfate[1]	2.9	24	35	Nd
Oxalate[1]	3.1	43	16	La
Alkali carbonate[1]	5.3	25	62	Nd
NH_4 double nitrate[1]	3.5	20	44	Nd
Basic magnesia[1]	1.2	61	22	La
Basic ammonia[2]	2.3	59	11	La
Basic urea[3]	1.9	43	23	La
Basic electrolytic[4]	1.0	60	24	La

procedures, has unfortunately the same serial solubility order as the basic precipitations. The ammonium double nitrate seems to be the next best choice.

(1) Procedure as in Little, "Textbook of Inorganic Chemistry" (Friend), Griffin, London, 1917.

(2) This is Prandtl's modification, using $Cd(NO_3)_2 + NH_4NO_3$, of the straight ammonium hydroxide basic separation [Prandtl and Hüttner, *Z. anorg. allgem. Chem.*, **136**, 289 (1924)].

(3) Six grams of mixed oxides was converted to nitrates, almost neutralized with ammonium hydroxide and diluted to 1 liter. Ten grams of urea was added and the mixture was kept at the boiling point for four hours. The precipitate formed was quite granular. The writer is indebted to Professor H. H. Willard of the University of Michigan for suggesting this method. He understands that Professor Willard has made an exhaustive study of the use of urea as an analytical reagent for group three elements.

(4) Dennis and co-workers, THIS JOURNAL, **37**, 131, 1963 (1915); **40**, 174 (1918). Neckers and Kremers, *ibid.*, **50**, 950 (1928).

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A Mercury Seal for Stirrers

BY D. T. ROGERS

In the past mercury seals for stirrers used in this Laboratory were made from Pyrex glass. They frequently broke because of improper annealing and careless handling.

To overcome these difficulties seals have been made from steel which have proved very satisfactory. The seals made from Allegheny metal No. 22 have remained unattacked after six months of service. Those made from soft steel and covered with a coat of paint have also proved quite satisfactory. The seals weigh about 200 g. and can be used at speeds up to 1000 r. p. m. The upper part of the seal is not shown in the diagram. It consists of either a thin-walled glass or steel cylinder which is fitted to the stirrer shaft with any ordinary rubber stopper. Dimensions are such that stoppers can be changed without dismantling the seals.

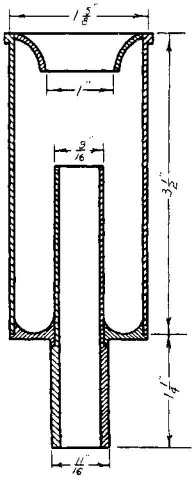

Fig. 1.

The seals were made by A. Bigelman, 1314 Third Avenue, Watervliet, N. Y.

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The Pyrolysis of Hydrocarbons. Further Studies on the Butanes[1]

BY CHARLES D. HURD[2] AND FORREST D. PILGRIM[3]

Recent work on the pyrolysis of the butanes[4-10] has elucidated much of the problem but such questions as the following seemed important for further study: (1) the reaction products at incipient decomposition, (2) the importance of the contact time, (3) the relationship of temperature and contact time, (4) the influence of metal reaction tubes. These items, among others, have been considered in the present paper.

The Reaction Products at Incipient Decomposition.—There are two approaches to this problem. One is to extrapolate the quantities of products formed at real conditions to their value at zero decomposition.[8] This method has been considered in the present paper. The other, which will be taken up in the following paper, is to carry out the pyrolysis at a very low decomposition temperature.[10]

The set-up for the pyrolysis experiments was essentially the same as that of Hurd and Spence.[4] The gas was forced through the reaction tube by a head of water. The customary flowmeters, manometer, drying towers and collecting bottles were in the train. Various size reaction tubes and furnaces were used. The gases were analyzed either by the absorption and combustion method[4] or by precision fractional distillation in a column of the type described by Oberfell and Alden[11] and Podbielniak,[12] or by a combination of these methods. The *n*-butane for this work was generously furnished by F. E. Frey of the Phillips Petroleum Company. Distillation analysis confirmed its purity. Less than 1% of low boiling material and

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(1) A part of this investigation was financed from funds donated to the American Petroleum Institute by the Universal Oil Products Co. The investigation was listed as Project No. 18.

(2) Director, Project No. 18.

(3) American Petroleum Institute Research Fellow.

(4) Hurd and Spence, THIS JOURNAL, **51**, 3353 (1929).

(5) Pease, *ibid.*, **50**, 1779 (1928); Pease and Durgan, *ibid.*, **52**, 1262 (1930).

(6) Hague and Wheeler, *J. Chem. Soc.*, 378 (1929).

(7) Frolich, Simard and White, *Ind. Eng. Chem.*, **22**, 240 (1930).

(8) Schneider and Frolich, *ibid.*, **23**, 1405 (1931); Neuhaus and Marek, *ibid.*, **24**, 400 (1932).

(9) Frey and Huppke, *ibid.*, **25**, 54 (1933).

(10) Norris and Thomson, THIS JOURNAL, **53**, 3108 (1931); Norris, *J. Chem. Educ.*, **9**, 1890 (1932); Norris and Standley, paper before the Organic Division, A. C. S. meeting at New Orleans, April, 1932.

(11) Oberfell and Alden, *Oil Gas J.*, **27**, 142 (1928).

(12) Podbielniak, *ibid.*, **28**, 58 (1929); **29**, 235 (1930).