

[CONTRIBUTION FROM THE DIVISION OF CHEMICAL DEVELOPMENT, TENNESSEE VALLEY AUTHORITY¹]**Heat of Solution of Monocalcium Phosphate Monohydrate**

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The heat of solution of monocalcium phosphate monohydrate(c) in phosphoric and hydrochloric acids was measured as a function of acid concentration at 25°. The hypothetical heat of solution at infinite dilution could not be fixed closer than within the range -3 to -4 kcal. mole⁻¹.

As part of a long-range study of the thermodynamic properties of the calcium phosphates, the heat of solution of monocalcium phosphate monohydrate in acid was measured as a function of the concentration of the solvent. The final value sought was the heat of solution at infinite dilution.

Two solvents, solutions of hydrochloric acid and of phosphoric acid, were used on the naive assumption that two independent extrapolations to zero concentration of acid thus could be obtained.

Materials and Apparatus.—The solution calorimeter and the method of preparing the monocalcium phosphate monohydrate have been described.²

The volume of acid solution was 850 ml. in each measurement. The acid was weighed from a special volumetric flask.

The samples of monocalcium phosphate monohydrate, 4 to 8 g., were suspended below the stirrer in thin-walled glass bulbs about 3.5 cm. in diameter that were sealed to a glass rod extending through the hollow stirrer shaft. The bulbs were broken against the bottom of the calorimeter flask at the beginning of the dissolution period. The calorimeter system was calibrated electrically immediately before and after the dissolution. The initial temperature was adjusted so that the dissolution ended within a few hundredths of a degree of 25°, and no temperature corrections were necessary. The ice point was taken as 273.16°K., and one defined calorie as 4.1840 abs. j. No trend of ΔH with change in weight of salt was observed.

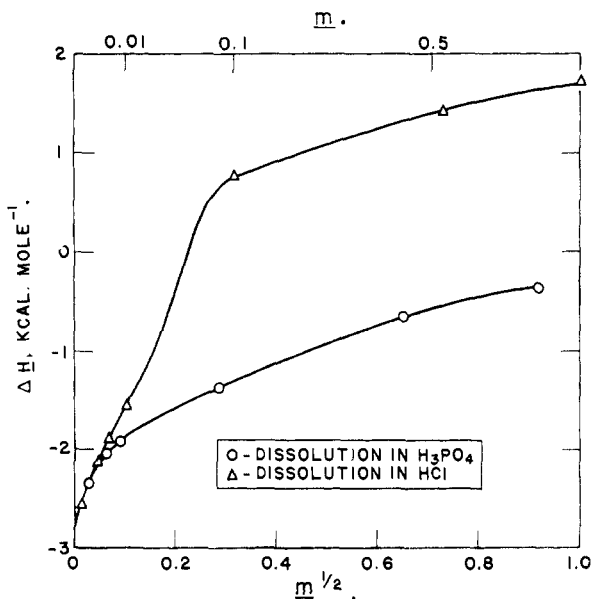
Observations.—The observed heats of solution are listed in Table I, and the average values at each concentration of acid are plotted in Fig. 1. The

curves in Fig. 1 do not follow the theoretical linear relation for low-valent electrolytes at high dilutions.³ Some of the necessary information is lacking for an extended Debye-Hückel extrapolation at low concentrations of solvent acid.

TABLE I

HEAT OF SOLUTION OF MONOCALCIUM PHOSPHATE MONOHYDRATE IN PHOSPHORIC AND HYDROCHLORIC ACIDS

Dissolution in H ₃ PO ₄			Dissolution in HCl		
Molality of acid	ΔH , cal. mole ⁻¹ Obsd.	Av.	Molality of acid	ΔH , cal. mole ⁻¹ Obsd.	Av.
0.0008	-2338	-2338	0.0002	-2543	-2543
.0040	-2033	-2035	.0022	-2121	-2121
	-2030				
	-2042		.0054	-1888	-1894
				-1899	
.0083	-1899	-1908			
	-1904		.0109	-1563	-1542
	-1921			-1521	
.079	-1391	-1387	.101	765	767
	-1398			769	
	-1372		.534	1410	1411
.429	-611	-665		1412	
	-678		1.038	1718	1708
	-705			1711	
.843	-351	-357		1696	
	-362				

Fig. 1.—Heat of solution of Ca(H₂PO₄)₂·H₂O(c).

(1) Article not copyrighted.

(2) E. P. Egan, Jr., Z. T. Wakefield and K. L. Elmore, *THIS JOURNAL*, **78**, 1811 (1956).

A power series equation expressing ΔH as a function of $m^{1/2}$ extrapolates to a value of -2750 cal. mole⁻¹ for ΔH at zero m . A plot of ΔH as a function of $m^{1/3}$ decreases the curvature of the lines, and a linear extrapolation through the ΔH values at the four lowest concentrations yields -2850 cal. mole⁻¹ for ΔH at zero m . The observed ΔH , extrapolated to infinite dilution, is taken as -2800 cal. mole⁻¹. Since the curves in Fig. 1 approach the axis rather steeply, an extrapolation to zero m probably represents a lower limit in absolute magnitude for the heat of solution at infinite dilution.

The difference between the heats of solution in the two acids at the same molality is approximately constant at 2000 cal. mole⁻¹ when the molality is greater than 0.1. The ΔH in solutions of hydrochloric acid is driven in the endothermic direction by an amount that apparently is equivalent to the endothermic heat of solution of calcium chloride. At molalities of less than 0.1, there is insufficient chloride ion in the solution of hydrochloric acid to

(3) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1943.

form calcium chloride with all the calcium, and the heats of solution approach those in solutions of phosphoric acid.

Substitution of the heats of formation, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}(\text{c})$, $-816,820$; $\text{Ca}^{++}(\text{aq})$,⁴ $-129,770$; $\text{H}_2\text{P}\text{O}_4^-(\text{aq})$,⁵ $-311,320$; and $\text{H}_2\text{O}(\text{liq})$,⁴ $-68,317$ cal. mole⁻¹ in the equation

(4) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Govt. Printing Office, Washington, D. C., 1952.

(5) Derived from the heat of formation of $\text{H}_3\text{PO}_4(\text{aq})$, $-309,440$ cal. mole⁻¹, and the heat of the first ionization of H_3PO_4 , -1880 cal. mole⁻¹, as reported by T. D. Farr, Tennessee Valley Authority, *Chem. Eng. Rept.* No. 8 (1950).

$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}(\text{c}) + (\text{aq}) = \text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}(\text{aq}) = \text{Ca}^{++}(\text{aq}) + 2\text{H}_2\text{PO}_4^-(\text{aq}) + \text{H}_2\text{O}(\text{liq})$ yields a value of -3910 cal. mole⁻¹ for the heat of solution of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}(\text{c})$ at infinite dilution. This value represents the difference between large numbers; also, one of the values used in its derivation—the heat of formation of $\text{H}_2\text{PO}_4^-(\text{aq})$ —is uncertain. With the uncertainty involved in the extrapolation of the observed heats of solution to infinite dilution, the hypothetical heat of solution of $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}(\text{c})$ at infinite dilution can be fixed no closer than within the range -3 to -4 kcal. mole⁻¹.

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Electrochemical Behavior of Aromatic N-Nitrosohydroxylamines

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The electrochemical behavior of three aromatic N-nitrosohydroxylamines was studied: N-nitrosophenylhydroxylamine, N-nitroso- α -naphthylhydroxylamine and N-nitroso-*p*-xenylhydroxylamine, whose ammonium salts are known as cupferron, neocupferron and *p*-phenylcupferron, respectively; the last is a new compound. Three well-defined polarographic waves can occur in the *pH* region from -0.4 to 12 . The first wave split (change from wave I to II) results from a tautomeric equilibrium between the nitroso hydroxy and amine oxide forms; the second wave split (change from wave II to III) is due to a typical acid-anion equilibrium. Coulometric studies, and isolation and identification of major reduction products by macroscale electrolysis at controlled potential indicate that the reduction in acidic solution (waves I and II) proceeds by a process, or processes, involving a total of 6 electrons to the aromatic hydrazine. In alkaline solution (wave III) only 4 electrons are involved with the final product being the aromatic hydrocarbon; the mechanism proposed has been substantiated by following the change in *pH* of the solution with electrolysis of the nitrosohydroxylamine. The apparent discrepancies in previous work have been elucidated.

A systematic study of the polarographic and coulometric behavior of N-nitrosophenylhydroxylamine,¹ N-nitroso- α -naphthylhydroxylamine (neocupferron) and a new compound, N-nitroso-*p*-xenylhydroxylamine (*p*-phenylcupferron), usually added as the ammonium salts, was undertaken to elucidate the reduction pattern and to resolve apparent differences in the literature.^{2,3} Such an investigation also served as background for the development of analytical methods including amperometric titration methods employing cupferron as titrant.

Previous polarographic study² of N-nitrosophenylhydroxylamine indicated two waves in the *pH* range from 1.1 to 12.5 . A similar study³ of N-nitroso- α -naphthylhydroxylamine, the abstract of which appeared after the present investigation was underway, described four polarographic waves in the same *pH* region; the apparent differences in behavior between the two closely related structures was not too convincingly explained; even so, the explanations involved selective emphasis. Attempted coulometric studies were unsatisfactory and the results were not given.³

(1) The ammonium salt which is the form in which the compound is usually used, is called cupferron; for convenience, this name will henceforth be used to designate both the compound and its ammonium salt. The names, neocupferron and *p*-phenylcupferron, apply and will be used in the same sense.

(2) I. M. Kolthoff and A. Liberti, *THIS JOURNAL*, **70**, 1885 (1948).

(3) C. Calzolari and A. Donda, *Ann. Chim. (Rome)*, **43**, 753 (1953).

Polarographic Behavior⁴

Figures 1 and 2 and Table I summarize the variations of half-wave potential, $E_{1/2}$, and of limiting

TABLE I
DIFFUSION CURRENT CONSTANTS OF AROMATIC N-NITROSOHYDROXYLAMINES²

<i>pH</i>	$I = i_d/Cm^2/2t^{1/2}$		
	Cupferron	Neocupferron	<i>p</i> -Phenylcupferron
10% H_2SO_4	10.5	9.38	6.47
1.02	10.8	8.84	6.71
1.99	10.2	9.10	6.19
2.80	10.1	9.39	6.19
3.78	10.1	9.56	5.66

^a These were measured on oxygen-free solutions, about 10 min. after mixing. The values, although reproducible, may be in slight error due to acid decomposition.

TABLE II
COMPOSITION OF MACILVAINE BUFFERS, IONIC STRENGTH =

$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, g./l.	$\text{H}_3\text{Cit} \cdot \text{H}_2\text{O}$, g./l.	KCl, g./l.	<i>pH</i>
1.4	20.6	74.5	1.99
14.7	16.7	68.7	2.80
27.6	12.9	62.8	3.78
36.9	10.2	55.5	4.72
45.2	7.7	48.9	5.69
58.9	3.7	40.4	6.76
69.6	0.6	32.9	7.58

(4) Detailed tables of experimental data can be secured from the authors.