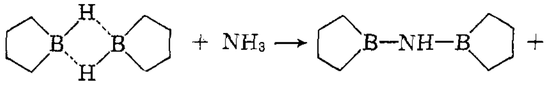
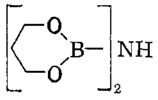
obtained by Koester and Iwasaki[8] through the reaction of bisborolanes with ammonia or primary amines



(7)

and Lappert[9] reported the preparation of $[(RHN)_2B]_2$-NH (R = *t*-butyl) by the interaction of bis(*t*-butylamino)chloroborane with *t*-butylamine. Finally, the formation of a material as illustrated (IV) has been mentioned.[10]

III now illustrates the existence of a new type of bisborylamine which is the intermediate between those compounds reported by Nöth and those reported by Lappert. Their potential for utilization in the synthesis of B- and N-containing heterocycles and linear B–N compounds is obvious and will be investigated.



IV

In the infrared spectrum of III, the NH absorption was recorded as a weak band near 3390 cm.$^{-1}$. Two extremely strong absorptions near 1300 and 1400 cm.$^{-1}$, respectively, might be assigned to B–N stretching.

III disproportionates easily to trisaminoborane and B-trisaminoborazine. Analogous observations have been made in our laboratory with bisborylamines of the type $(R_2B)_2NH$, which readily yield triorganoboranes and B-triorganoborazines.

---

[8] R. Koester and K. Iwasaki, Preprints of Papers, International Symposium on Boron–Nitrogen Chemistry, Durham, N. C., April, 1963, p. 123.

[9] M. F. Lappert and co-workers, ref. 8, p. 152.

[10] A. Finch, P. J. Gardner, J. C. Lockhart, and E. J. Pearn, *J. Chem. Soc.*, 1428 (1962).

---

CONTRIBUTION FROM UNION CARBIDE CORPORATION,
NUCLEAR DIVISION, TUXEDO, NEW YORK

# A Study of the Chemistry of the Polyvanadates Using Salt Cryoscopy

BY A. W. NAUMANN AND C. J. HALLADA

*Received January 3, 1963*

Glauber's salt cryoscopy and pH measurements have been made on sodium vanadate solutions in the pH range 2.5 to 7. Vanadium was found to exist in neutral solutions as a tetramer of $VO_3^-$. At lower pH values, confirmation was found for the equilibria

$$V_{10}O_{28}^{-6} \xrightleftharpoons{H^+} HV_{10}O_{28}^{-5} \xrightleftharpoons{H^+} H_2V_{10}O_{28}^{-4} \xrightleftharpoons{H^+} VO_2^+$$

No evidence was found for a hexavanadate in the pH range studied. The formation of a heteropolyanion between vanadium and phosphorus was indicated. The heteropolyanion forms from $H_2V_{10}O_{28}^{-4}$, but not from the other anionic polyvanadates.

## Introduction

Despite the efforts of numerous investigators, the nature of the anionic vanadium(V) species in neutral and acidic solutions remains in doubt. The degree of aggregation, $\bar{n}$, of the metavanadate ion, *i.e.*, the anion present in neutral solutions, is variously reported as being 3 or 4.[1-3] Similarly, degrees of aggregation ranging from 2 to 10 have been reported for the species existing in acidic solutions.[4-9]

Rossotti and Rossotti,[9] whose potentiometric titrations probably represent the most definitive work that has been done on acidic vanadium solutions, found the species and equilibria that best fit their results were as shown below.

$$V_{10}O_{28}^{-6} \rightleftharpoons HV_{10}O_{28}^{-5} \rightleftharpoons H_2V_{10}O_{28}^{-4} \rightleftharpoons VO_2^+$$

Since the Rossottis' work, a number of others[10-16] have re-examined the vanadium system using a variety of methods. In many cases these newer data have supported the Rossottis' findings, but often only by being consistent with them, rather than by being unambiguous verifications. On the other hand, support for a hexavanadate has continued to appear,[17,18] and there has been disagreement as to whether an $\bar{n}$ of 10 or an $\bar{n}$ of 6, and multiples thereof, best fits the Rossottis' data.[19,20]

In addition to isopolyanions, vanadium forms heteropolyanions with phosphorus. Both octavanadate[21] and hexavanadate[22] have been proposed as the basic

---

[1] N. Ingri and F. Brito, *Acta Chem. Scand.*, **13**, 1971 (1959).

[2] K. F. Jahr and L. Schoepp, *Z. Naturforsch.*, **14b**, 467 (1959).

[3] K. Schiller and E. Thilo, *Z. anorg. allgem. Chem.*, **310**, 261 (1961).

[4] L. P. Ducret, *Ann. chim.* (Paris), **6**, 705 (1951).

[5] H. T. S. Britton and G. Welford, *J. Chem. Soc.*, 764 (1940).

[6] G. Jander and K. Jahr, *Z. anorg. allgem. Chem.*, **212**, 1 (1933).

[7] P. Souchay and G. Carpeni, *Bull. Soc. Chim. France*, 160 (1946).

[8] J. F. Hazel, W. M. McNabb, and R. Santini, *J. Phys. Chem.*, **57**, 681 (1953).

[9] F. J. C. Rossotti and H. Rossotti, *Acta Chem. Scand.*, **10**, 957 (1956).

[10] K. F. Jahr and L. Schoepp, *Z. Naturforsch.*, **14b**, 468 (1959).

[11] P. Souchay and F. Chauveau, *Compt. rend.*, **244**, 1923 (1957).

[12] J. Meier and G. Schwarzenbach, *Chimia*, **12**, 328 (1958).

[13] O. Glemser and E. Preisler, *Z. anorg. allgem. Chem.*, **303**, 303 (1960).

[14] L. Newman and K. P. Quinlan, *J. Am. Chem. Soc.*, **81**, 547 (1959).

[15] J. Magee and E. Richardson, *J. Inorg. Nucl. Chem.*, **15**, 272 (1960).

[16] A. Morette and N. Strupler, *Bull. Soc. Chim. France*, 154 (1961).

[17] A. K. Sen Gupta, *Z. anorg. allgem. Chem.*, **304**, 328 (1960).

[18] R. U. Russell and J. E. Salmon, *J. Chem. Soc.*, 4708 (1958).

[19] B. S. Jensen, *Acta Chem. Scand.*, **15**, 487 (1961); **16**, 1049 (1962).

[20] L. G. Sillén, *ibid.*, **15**, 1421 (1961); **16**, 1051 (1962).

[21] G. Jander, K. F. Jahr, and H. Witzman, *Z. anorg. allgem. Chem.*, **217**, 65 (1934).

[22] P. Souchay and S. Dubois, *Ann. Chim.* (Paris), **3**, 88 (1948).

structural unit, but more consistent with the Rossottis' findings, Russell, Salmon, and Tietze[23] found evidence for two heteropolyanions, $H_2PV_{10}O_{30}^{-3}$ and $HPV_{10}O_{30}^{-4}$.

In principle, salt cryoscopy should be useful for finding degrees of aggregation of vanadium-containing ions, since with this method the number of foreign ions in solution is directly related to a readily determined transition temperature depression. Also of pertinence, cryoscopy measurements on sodium vanadate systems would begin on neutral solutions and be extended toward lower pH values. The converse was true for the potentiometric titrations of Rossotti and Rossotti, thereby making their low pH data the more accurate, and the high pH data more open to question. The salt cryoscopy and potentiometric methods, therefore, complement one another, both with respect to the use of fundamentally differing principles of measurement and by the relative magnitude of the accuracy of the measurement in opposite pH ranges.

Thermodynamic considerations and the characteristics of Glauber's salt cryoscopy have been given elsewhere.[24,25] The essential feature of the method is that the transition temperature of the following reaction, which normally occurs at 32.384°, is lowered by foreign ions.

$$Na_2SO_4\cdot 10H_2O\ (\text{solid}) \rightleftharpoons Na_2SO_4\ (\text{solid}) + Na_2SO_4\ (\text{saturated solution})$$

For polymeric solutes at concentrations small compared to the total salt content, degree of aggregation and transition temperature depression are related by the expression

$$\bar{n} = KC/\Delta T$$

where $\bar{n}$ is the number of solute atoms per aggregate ion for a monodisperse system and is a number average of solute atoms for a polydisperse system, $K$ is the molal transition point depression constant for Glauber's salt, and $\Delta T$ is the transition point depression at a concentration of $C$ moles of solute per kilogram of $Na_2SO_4\cdot 10H_2O$. It should be emphasized that the measured $\Delta T$ is a result of all foreign ions. When sodium metavanadate and sulfuric acid are used, hydrogen ions and bisulfate ions are foreign ions as well as the vanadium species. To find $\bar{n}$ for vanadium alone, the total hydrogen ion plus bisulfate ion concentration must be known.

The Glauber's salt method has previously been applied to acidic vanadium systems by Souchay and Carpeni,[7] by Schwarzenbach and Parissakis,[24,25] and by Jahr and Schoepp.[2] Based on measurements that were not described in detail, Souchay and Carpeni concluded that metavanadate anions contain three vanadium atoms, and polyvanadates, six. More recently, Schwarzenbach and Parissakis obtained apparent degrees of aggregation of 3.4 for metavanadate and 8.1 for polyvanadate (at an $H^+/NaVO_3$ ratio of 0.4). These workers made measurements on a number of salts in addition to the vanadates, and on the basis of the variations and behavior observed for other materials, they concluded that the true degree of aggregation of meta- and polyvanadate should be 4 and 10, respectively. Jahr and Schoepp have questioned the elaborate experimental set-up used by Schwarzenbach and Parissakis, but agree with their conclusions.

TABLE I
RESULTS OF pH EXPERIMENTS

| $H^+/NaVO_3$ | pH | Free acid concn., $h$ |
|---|---|---|
| 0.40 | 5.40 | $<1 \times 10^{-5}$ |
| 0.50 | 4.21 | $6.60 \times 10^{-4}$ |
| 0.55 | 3.50 | $2.35 \times 10^{-3}$ |
| 0.60 | 3.20 | $5.50 \times 10^{-3}$ |
| 0.65 | 3.02 | $8.70 \times 10^{-3}$ |
| 0.70 | 2.85 | $1.38 \times 10^{-2}$ |
| 0.75 | 2.70 | $1.74 \times 10^{-2}$ |
| 0.80 | 2.65 | $1.91 \times 10^{-2}$ |
| 0.85 | 2.60 | $2.14 \times 10^{-2}$ |
| 0.90 | 2.55 | $2.40 \times 10^{-2}$ |

Recently, Tobias[26] has pointed out certain limitations of the salt cryoscopy method. When cryoscopy data were compared to results by other procedures, it appeared that the method was of limited value for the study of polynuclear complexes containing more than three or four metal atoms. Thus, the cryoscopy method has been used only sparingly on polyvanadates (*i.e.*, at only a few polyvanadate compositions), and then only with questionable results. In the present investigation, an improved Glauber's salt procedure was used to obtain measurements on the polyvanadate system at close intervals from pH 2.5 to 7.

## Experimental

**The Cryoscopy Cell.**—The cryoscopy cell consisted of a 500-ml. strip-silvered dewar flask with a brass top. Strip silvering made it possible to observe the contents of the cell so that measurements could be stopped if precipitation occurred. Extending into the cell were a Beckmann thermometer, a stirrer, and a U-tube for use either in heating or cooling the system with water. There were also ports for the introduction of liquid and solid materials. The cell was submerged in a water bath maintained at 32.5°.

**Materials.**—Vanadium stock solutions were prepared from purified $V_2O_5$ by stirring with appropriate amounts of standardized NaOH solutions at 60°. After dissolution was complete, the solutions were cooled and filtered. The required amounts of sulfuric acid to give the desired $H^+/NaVO_3$ ratios were added and dilutions to the desired final volumes were made. The stock solutions were prepared either directly by weight, or else by volume with subsequent density determinations to convert concentrations to a weight basis.

The $V_2O_5$ used in preparing the $NaVO_3$ stock solutions was purified by preparing ammonium metavanadate from already very pure $V_2O_5$, then calcining. This cycle was repeated until spectrographic analysis showed less than 0.01% of any impurity. These were principally silicon and alkali and alkaline earth elements.

Glauber's salt for use as seed was prepared by crystallizing $Na_2SO_4\cdot 10H_2O$ at 33° from a saturated aqueous solution of sodium sulfate. All other materials were reagent grade chemicals.

---

[23] R. U. Russell, J. E. Salmon, and H. R. Tietze, *J. Chem. Soc.*, 3211 (1961).

[24] G. Parissakis and G. Schwarzenbach, *Helv. Chim. Acta*, **41**, 2042 (1958).

[25] G. Schwarzenbach and G. Parissakis, *ibid.*, **41**, 2425 (1958).

[26] R. S. Tobias, *J. Inorg. Nucl. Chem.*, **19**, 348 (1961).

TABLE II

SUMMARY OF GLAUBER'S SALT CRYOSCOPY DATA[a]

| | $10^3C$ | $10^3\Delta T$ | $\Delta T/C$ |
|---|---|---|---|
| NaCl (A) | 13.3 | 37 | |
| | 25.4 | 79 | |
| | 30.6 | 93 | |
| | 43.7 | 137 | |
| | 53.9 | 168 | 3.14 |
| | 75.3 | 238 | |
| | 78.7 | 251 | |
| | 113.3 | 362 | |
| | 138.8 | 443 | |
| NaCl (B) | 55.7 | 182 | |
| | 57.0 | 177 | |
| | 93.6 | 303 | |
| | 95.9 | 310 | 3.22 |
| | 122.2 | 402 | |
| | 224.9 | 717 | |
| $NaH_2PO_4$ | 43.1 | 127 | |
| | 86.5 | 267 | |
| | 120.4 | 364 | |
| | 124.8 | 380 | 3.06 |
| | 156.0 | 481 | |
| | 159.0 | 492 | |
| $H_2SO_4$ | 17.9 | 64 | |
| | 34.3 | 113 | |
| | 80.1 | 259 | |
| | 96.6 | 318 | 3.28 |
| | 132.3 | 433 | |
| | 141.6 | 472 | |
| $NaVO_3$ (A) | 55.3 | 44 | |
| | 78.9 | 65 | 0.83 |
| | 91.9 | 72 | |
| | 98.5 | 75 | |
| | 109.5 | 86 | |
| $NaVO_3$ (B) | 48.5 | 39 | |
| | 71.1 | 59 | 0.83 |
| | 84.3 | 68 | |
| $NaVO_3$ (C) | 27.1 | 24 | |
| | 60.5 | 47 | |
| | 68.7 | 57 | |
| | 72.8 | 56 | |
| | 94.4 | 76 | 0.78 |
| | 106.4 | 85 | |
| | 120.1 | 88 | |
| | 121.5 | 94 | |
| | 148.1 | 108 | |
| | 195.2 | 144 | |
| $NaVO_3$ (D) | 61.7 | 46 | |
| | 80.2 | 62 | |
| | 110.1 | 86 | 0.74 |
| | 125.4 | 95 | |
| | 136.7 | 106 | |
| | 152.2 | 115 | |
| $NaVO_3 \cdot 0.10H^+$ | 66.7 | 50 | 0.71 |
| | 140.6 | 95 | |
| $NaVO_3 \cdot 0.20H^+$ | 73.4 | 38 | |
| | 110.9 | 67 | 0.58 |
| | 115.5 | 70 | |
| | 140.9 | 82 | |
| $NaVO_3 \cdot 0.294H^+$ | 60.0 | 29 | |
| | 101.7 | 44 | |
| | 130.6 | 65 | 0.46 |
| | 205.8 | 95 | |
| | 311.6 | 142 | |
| $NaVO_3 \cdot 0.300H^+$ | 51.5 | 23 | |
| | 137.1 | 62 | |
| | 143.9 | 62 | 0.45 |
| | 212.2 | 94 | |
| | 219.7 | 98 | |
| | 270.1 | 121 | |
| $NaVO_3 \cdot 0.400H^+$ | 39.8 | 14 | |
| | 75.8 | 26 | |
| | 76.0 | 27 | 0.35 |
| | 103.5 | 37 | |
| | 110.5 | 39 | |
| | 133.8 | 47 | |
| $NaVO_3 \cdot 0.400H^+$ | 25.0 | 7 | |
| | 47.4 | 15 | |
| | 71.9 | 20 | |
| | 84.1 | 23 | 0.29 |
| | 107.4 | 32 | |
| | 114.2 | 33 | |
| $NaVO_3 \cdot 0.440H^+$ (A) | 42.3 | 14 | |
| | 48.8 | 14 | |
| | 70.6 | 20 | |
| | 86.5 | 25 | |
| | 102.5 | 33 | 0.31 |
| | 118.1 | 36 | |
| | 118.2 | 34 | |
| | 149.4 | 45 | |
| | 150.5 | 45 | |
| $NaVO_3 \cdot 0.440H^+$ (B) | 58.4 | 16 | |
| | 89.1 | 26 | 0.29 |
| | 89.8 | 25 | |
| | 118.5 | 36 | |
| $NaVO_3 \cdot 0.470H^+$ | 58.3 | 19 | |
| | 98.1 | 35 | |
| | 154.2 | 58 | 0.34 |
| | 238.8 | 72 | |
| | 312.4 | 104 | |
| $NaVO_3 \cdot 0.475H^+$ (A) | 71.4 | 24 | |
| | 107.2 | 35 | |
| | 117.4 | 43 | 0.34 |
| | 146.6 | 51 | |
| | 157.0 | 52 | |
| $NaVO_3 \cdot 0.475H^+$ (B) | 48.9 | 19 | |
| | 68.6 | 24 | |
| | 87.3 | 32 | |
| | 103.5 | 34 | 0.34 |
| | 116.6 | 39 | |
| | 138.2 | 47 | |
| $NaVO_3 \cdot 0.490H^+$ | 100.0 | 34 | 0.31 |
| | 203.4 | 60 | |
| $NaVO_3 \cdot 0.510H^+$ | 26.6 | 10 | |
| | 64.4 | 20 | |
| | 65.1 | 24 | 0.36 |
| | 130.7 | 47 | |
| $NaVO_3 \cdot 0.526H^+$ (A) | 31.5 | 10 | |
| | 67.6 | 27 | |
| | 90.4 | 38 | 0.39 |
| | 104.3 | 38 | |
| | 126.8 | 49 | |
| | 144.0 | 54 | |
| $NaVO_3 \cdot 0.526H^+$ (B) | 24.6 | 9 | |
| | 60.9 | 25 | |
| | 64.2 | 25 | 0.38 |
| | 97.0 | 36 | |
| | 116.9 | 46 | |
| $NaVO_3 \cdot 0.540H^+$ | 60.3 | 18 | |
| | 100.7 | 30 | |
| | 140.8 | 49 | 0.32 |
| | 182.8 | 56 | |
| | 219.8 | 74 | |
| | 285.6 | 94 | |
| $NaVO_3 \cdot 0.560H^+$ (A) | 21.9 | 9 | |
| | 32.7 | 15 | |
| | 46.8 | 17 | |
| | 56.8 | 24 | |

TABLE II (*Continued*)

| | $10^3C$ | $10^3\Delta T$ | $\Delta T/C$ |
|---|---|---|---|
| $NaVO_3 \cdot 0.560H^+$ (A) (*Contd.*) | 75.4 | 34 | 0.49 |
| | 92.0 | 39 | |
| | 103.3 | 42 | |
| | 118.9 | 51 | |
| $NaVO_3 \cdot 0.560H^+$ (B) | 23.1 | 11 | |
| | 40.4 | 21 | |
| | 58.6 | 27 | 0.48 |
| | 71.7 | 34 | |
| | 96.6 | 48 | |
| $NaVO_3 \cdot 0.560H^+$ (C) | 32.9 | 15 | |
| | 56.0 | 25 | |
| | 82.0 | 35 | 0.45 |
| | 107.0 | 52 | |
| | 142.1 | 63 | |
| $NaVO_3 \cdot 0.560H^+$ (D) | 67.5 | 32 | |
| | 112.5 | 51 | 0.42 |
| | 181.4 | 81 | |
| | 239.1 | 111 | |
| $NaVO_3 \cdot 0.580H^+$ | 32.9 | 6 | |
| | 58.1 | 29 | |
| | 89.6 | 35 | |
| | 137.8 | 58 | 0.46 |
| | 285.2 | 115 | |
| $NaVO_3 \cdot 0.580H^+$ | 101.4 | 48 | |
| | 204.3 | 84 | 0.40 |
| | 313.6 | 129 | |
| $NaVO_3 \cdot 0.603H^+$ (A) | 29.7 | 12 | |
| | 66.3 | 34 | |
| | 77.7 | 42 | |
| | 89.9 | 44 | 0.51 |
| | 104.4 | 52 | |
| | 127.2 | 63 | |
| $NaVO_3 \cdot 0.603H^+$ (B) | 36.9 | 20 | |
| | 68.1 | 35 | |
| | 73.2 | 40 | 0.50 |
| | 94.4 | 48 | |
| | 114.4 | 58 | |
| $NaVO_3 \cdot 0.630H^+$ | 133.4 | 80 | |
| | 210.6 | 120 | 0.58 |
| | 284.6 | 148 | |
| $NaVO_3 \cdot 0.704H^+$ (A) | 41.9 | 26 | |
| | 60.5 | 49 | 0.83 |
| | 84.3 | 57 | |
| $NaVO_3 \cdot 0.704H^+$ (B) | 38.4 | 30 | |
| | 55.8 | 40 | |
| | 73.6 | 56 | 0.74 |
| | 75.2 | 54 | |
| | 92.5 | 70 | |
| $NaVO_3 \cdot 0.704H^+$ (C) | 16.5 | 13 | |
| | 27.8 | 26 | |
| | 39.6 | 29 | |
| | 48.6 | 40 | 0.71 |
| | 51.6 | 46 | |
| | 64.9 | 53 | |
| $NaVO_3 \cdot 0.800H^+$ | 27.1 | 26 | |
| | 45.6 | 42 | |
| | 52.9 | 47 | |
| | 72.3 | 64 | 0.92 |
| | 92.1 | 86 | |
| | 105.7 | 92 | |
| $NaVO_3 \cdot 0.990H^+$ (A) | 14.1 | 22 | |
| | 24.5 | 32 | |
| | 31.4 | 42 | |
| | 33.6 | 48 | 1.56 |
| | 42.0 | 57 | |
| | 55.6 | 87 | |
| | 62.5 | 87 | |
| | 82.6 | 115 | |
| $NaVO_3 \cdot 0.990H^+$ (B) | 14.3 | 23 | |
| | 19.6 | 31 | |
| | 25.8 | 37 | |
| | 29.0 | 43 | |
| | 29.1 | 45 | 1.42 |
| | 31.4 | 46 | |
| | 35.5 | 55 | |
| | 37.0 | 65 | |
| | 49.8 | 76 | |

[a] The concentration, $C$, is in moles per kilogram of Glauber's salt, and $\Delta T$ is in degrees centigrade.

**pH Measurements.**—The pH measurements were made with a Beckman Model G pH meter, on solutions saturated with sodium sulfate and equilibrated in a bath at 33°. A standard curve of pH *vs.* equivalents of acid was determined using standard sulfuric acid solutions. From this curve, the free sulfuric acid content of each vanadium-containing Glauber's salt melt was determined.

**Cryoscopy Measurements.**—The solutions on which measurements were made were prepared in the cryoscopy cell. By successive additions of stock solution and/or water, two to four temperature depressions could be found in a day. The experimental procedure found to give the most reproducible results was: (1) Weighed amounts of water and stock solution were introduced into the cell and, while water at 32.5° was passed through the U-tube, an excess of anhydrous sodium sulfate was added with stirring. (2) The salt mixture was stirred several minutes at a temperature above the Glauber's salt transition temperature to ensure that the solution was saturated and that all the undissolved salt was present as anhydrous sodium sulfate. Cool water was then passed through the U-tube until the system was slightly below the transition temperature. (3) A small, weighed amount of Glauber's salt seed was added to the supercooled mixture. The temperature at first rose quickly, then leveled off and slowly approached the equilibrium temperature. (4) The temperature was read every 5–10 min. until it did not change for 30–60 min. (5) The cycle was then repeated, being sure to heat the system above the transition temperature for several minutes after adding more stock or water and, if necessary, anhydrous sodium sulfate.

Some of the difficulties encountered must also be acknowledged. The usable concentration range for vanadium solutions was rather limited. At high concentrations, especially at higher $H^+/NaVO_3$ ratios, precipitation occurred readily. On the other hand, with very dilute solutions, errors in determining the transition temperature were a large percentage of the observed $\Delta T$. The concentration range found most convenient for this work was between 0.02 and 0.2 mole of vanadium per kilogram of Glauber's salt.

## Results and Discussion

**pH Measurements.**—The data of Table I relate free acid concentration, $h$, to the $H^+/NaVO_3$ ratio. These data were obtained for 0.1 $m$ vanadium solutions saturated with respect to sodium sulfate at 33°.

The free acidity term, $h$, does not correspond exactly to hydrogen ion concentration, but differs from hydrogen ion concentration by a multiplicative constant. It has been shown[27] that the dissociation of bisulfate is enchanced in a high sulfate medium, but the possible presence of some bisulfate in acidic solutions must be allowed for following the relation

$$K_{\text{assoc}} = \frac{[HSO_4^-]}{[H^+]\,[SO_4^{-2}]} \frac{\gamma_{HSO_4^-}}{\gamma_{H^+}\gamma_{SO_4^{-2}}} \equiv K_c K_\gamma$$

---

(27) N. R. Rao, *Indian J. Phys.*, **17**, 283 (1943).

Values for the activity terms needed to correct for bisulfate concentration are not available. It can be assumed, however, that in saturated sodium sulfate both $K_\gamma$ and sulfate concentration will remain constant so that

$$\frac{[\mathrm{HSO_4^-}]}{[\mathrm{H^+}]} = \text{constant} = K''$$

and

$$h = [\mathrm{H^+}]\left(1 + \frac{[\mathrm{HSO_4^-}]}{[\mathrm{H^+}]}\right) = K'[\mathrm{H^+}]$$

In the discussions that follow, expressions will be derived to describe the formation of the various acidic vanadium species. These expressions will involve constants that are not equilibrium constants in a thermodynamic sense, but, rather, are "concentration product" constants. This, like the bisulfate considerations, is an expediency made necessary by a lack of activity coefficients for the ionic species involved. Again like the bisulfate case, the use of concentration products is justified because Glauber's salt measurements are carried out in the presence of a high, fixed concentration of supporting electrolyte.

While concentration product constants are nonthermodynamic, they present data in a convenient form for conversion as the appropriate activity data become available. Consistent with this aim, the concentration products of the present study were derived using the free acidity terms, $h$, in place of estimated hydrogen ion concentrations.

**Cryoscopy Standards.**—The changes in transition temperature of Glauber's salt due to sodium chloride, sulfuric acid, and sodium dihydrogen phosphate were determined to check on experimental techniques and to establish the validity of the method. Each of these reagents adds only one equivalent of foreign ion per equivalent of solute to a Glauber's salt melt and should give the same value for the molal freezing point depression constant, $K$. The complete data are given in Table II. The table gives $\Delta T$ in degrees centigrade and concentration of foreign ions, *i.e.*, $Cl^-$, $h(H^+ + HSO_4^-)$, or $H_2PO_4^-$, in moles per kilogram of Glauber's salt. The data for all three substances agree well and fall on a straight line. A least-squares slope of 3.20 was obtained. This is very close to the theoretical value, 3.16, calculated from the latent heat of melting of Glauber's salt.[28]

The good agreement with the theoretical $K$ and general consistency of results indicates that the assumptions inherent in salt cryoscopy are valid, and that the method can be used to determine the degree of aggregation of polymeric ions in solution. Much of the success of the present investigation is no doubt due to the fact that with the equipment used, temperature measurements were extended over relatively long periods of time. This made it possible to follow individual Glauber's salt melts until equilibrium was reached, as evidenced by the temperature remaining constant for 0.5 hr. or more. Previous workers have relied on much shorter temperature plateaus and, based on the experience of the present investigation, it is suspected that in many cases the systems studied were not in true equilibrium.

**Cryoscopy of Acidic Vanadium Solutions.**—The results obtained on acidic vanadium solutions are given in Table II. These data, when plotted, point out a general characteristic of all the vanadium–acid data, namely, their linearity. This permitted the use of a simple least-squares treatment to find $\Delta T/C$. More data points were found for some of the stock solutions than for others, so a least-squares treatment was used for each individual stock to avoid introducing a bias toward any one of them.

It should be pointed out that one would expect some curvature in a $\Delta T$ *vs.* $C$ plot when an equilibrium of the type

$$H_2V_{10}O_{28}^{-4} + 14H^+ \rightleftharpoons 10VO_2^+ + 8H_2O$$

applies. This is because the vanadium species dealt with enter the equilibrium expression to different powers, and, because of this, the average degree of aggregation will vary somewhat with total vanadium concentration. Over the concentration range covered by the Glauber's salt measurements, this effect was negligibly small and was hidden by the general scatter of the data.

The cryoscopy results obtained with the individual stock solutions are summarized in Fig. 1. The amount of acid consumed by the formation of polyvanadate species, as determined by a combination of cryoscopy and pH data, is given as a function of $H^+/NaVO_3$ ratio in Table III.

**Species for $H^+/NaVO_3$ 0.0 to 0.8.**—At an $H^+/NaVO_3$ ratio of zero, $(\Delta T/C)_V$ was approximately 0.80. This corresponds to an $\bar{n}$ of 4, indicating that the metavanadate anion is a tetramer. The $\Delta T/C$ values drop to a value corresponding to an $\bar{n}$ of 10 at $0.4H^+/NaVO_3$

TABLE III

CRYOSCOPY DATA AND DERIVED QUANTITIES[a]

| $\left[\frac{H^+}{NaVO_3}\right]$ | $\left[\frac{\Delta T}{C}\right]_{\text{exptl}}$ | $\left[\frac{\Delta T}{C}\right]_h$ | $\left[\frac{\Delta T}{C}\right]_V$ | $\left[\frac{H^+}{NaVO_3}\right]_{\text{consumed}}$ |
|---|---|---|---|---|
| 0.00 | 0.80 | $\approx 0.00$ | 0.80 | . . |
| 0.10 | 0.71 | $<0.01$ | 0.71 | 0.10 |
| 0.20 | 0.58 | $<0.01$ | 0.58 | 0.20 |
| 0.30 | 0.45 | $<0.01$ | 0.45 | 0.30 |
| 0.40 | 0.32 | $<0.01$ | 0.32 | 0.40 |
| 0.45 | 0.32 | $<0.01$ | 0.32 | 0.45 |
| 0.50 | 0.34 | 0.02 | 0.32 | 0.49 |
| 0.55 | 0.41 | 0.08 | 0.33 | 0.53 |
| 0.60 | 0.50 | 0.18 | 0.32 | 0.54 |
| 0.65 | 0.62 | 0.28 | 0.34 | 0.56 |
| 0.70 | 0.75 | 0.44 | 0.31 | 0.56 |
| 0.75 | 0.88 | 0.56 | 0.32 | 0.58 |
| 0.80 | 1.01 | 0.61 | 0.40 | 0.61 |
| 0.85 | 1.14 | 0.68 | 0.46 | 0.64 |
| 0.90 | 1.26 | 0.77 | 0.49 | 0.66 |

[a] $[H^+/NaVO_3]$ is the total acid added per mole of $NaVO_3$, $[\Delta T/C]_{\text{exptl}}$ is the observed change in transition temperature with change in vanadium concentration, $[\Delta T/C]_h$ is the contribution of free acid to $(\Delta T/C)_{\text{exptl}}$, $[\Delta T/C]_V$ is the contribution of vanadium species to $(\Delta T/C)_{\text{exptl}}$, and $[H^+/NaVO_3]_{\text{consumed}}$ is the amount of acid per mole of vanadium consumed in the formation of polyvanadate species.

---

(28) G. Brodale and W. F. Giauque, *J. Am. Chem. Soc.*, **80**, 2042 (1958).

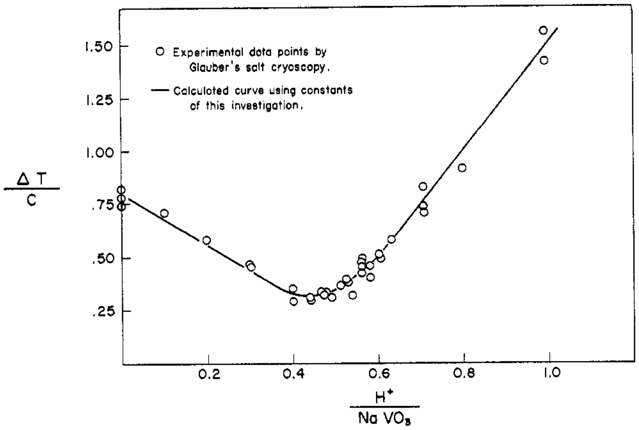


Fig. 1.—Summary of Glauber's salt measurements.

and retain this value up to an $H^+/NaVO_3$ ratio of 0.5.

Up to approximately 0.5, essentially all of the acid was consumed in the formation of polyvanadates. The $(\Delta T/C)_V$ values correspond to the equation

$$5V_4O_{12}^{-4} + 8H^+ \rightarrow 2V_{10}O_{28}^{-6} + 4H_2O$$

for $H^+/NaVO_3 = 0$ to 0.4, and to

$$V_{10}O_{28}^{-6} + H^+ \rightarrow HV_{10}O_{28}^{-5}$$

for $H^+/NaVO_3 = 0.4$ to 0.5.

The $(\Delta T/C)_V$ values remain at approximately 0.32 up to an $H^+/NaVO_3$ ratio of 0.75, indicating the existence of a decavanadate up to this point. The $(H^+/NaVO_3)_{\text{consumed}}$ at 0.75 was 0.6, which corresponds to the formation of $H_2V_{10}O_{28}^{-4}$ from $NaVO_3$. Therefore, in this decavanadate region the species found are in agreement with those found by Rossotti and Rossotti, and the equilibria up to an $H^+/NaVO_3$ ratio of about 0.8 can be expressed as

$$V_4O_{12}^{-4} \underset{(A)}{\overset{H^+}{\rightleftharpoons}} V_{10}O_{28}^{-6} \underset{(B)}{\overset{H+}{\rightleftharpoons}} HV_{10}O_{28}^{-5} \underset{(C)}{\overset{H+}{\rightleftharpoons}} H_2V_{10}O_{28}^{-4}$$

Actually, neither the Rossottis' data nor the present results give an indication of the detailed structure or composition of the ionic vanadate species. Possibly formulas reflecting higher degrees of hydration would give a truer picture of the ions. The formulas given are merely the simplest representations consistent with the data.

The equilibrium constants for reactions A and B above are large, for as mentioned previously, essentially all of the acid added up to an $H^+/NaVO_3$ ratio of 0.5 was consumed by polyvanadate formation.

This was not the case for reaction C, which is

$$HV_{10}O_{28}^{-5} + H^+ \rightleftharpoons H_2V_{10}O_{28}^{-4}$$

The equilibrium constant for this reaction was determined using the equations

$$H_T = h + 5[HV_{10}O_{28}^{-5}] + 6[H_2V_{10}O_{28}^{-4}] \qquad (1)$$

$$V_T = 10[HV_{10}O_{28}^{-5}] + 10[H_2V_{10}O_{28}^{-4}] = 0.1 \qquad (2)$$

$$\log K = \log [H_2V_{10}O_{28}^{-4}] - \log [HV_{10}O_{28}^{-4}] - \log h \qquad (3)$$

where $H_T$ is the total equivalents of acid added per kilogram of Glauber's salt, $h$ is the free acid concentration (moles/kg.), and $V_T$ is the total vanadium concentration (moles/kg.). Equations 1 and 2 are material balance expressions; eq. 3 is the equilibrium expression in log form.

$V_T$ was taken as 0.1 *m*. This was an average concentration for the cryoscopy determinations and was the vanadium concentration used for the pH measurements. For each point, values for $H_T$, $h$, and $V_T$ were known. Values for $[HV_{10}O_{28}^{-5}]$ and $[H_2V_{10}O_{28}^{-4}]$ were obtained by solving (1) and (2) as simultaneous equations. These, in turn, were used to calculate log $K$ and $n$, the sum of hydrogen and vanadium ion concentrations. Table IV presents the results of these calculations along with $(\Delta T/C)$ values derived from the calculated $n$ values and the experimental $(\Delta T/C)$ values.

The calculated and experimental $(\Delta T/C)$ values were in good agreement. Also the log $K$ values were quite constant, an average value of 2.19 ± 0.07 being obtained. It must be kept in mind, however, that this constant may be considerably different from the thermodynamic constant since neither the free $H^+$ ion concentration nor the activity coefficient of the vanadium species is known.

For completeness, it was of interest to attempt to fit the equilibrium

$$3HV_{10}O_{28}^{-5} + 5H^+ \rightleftharpoons 5V_6O_{16}^{-2} + 4H_2O$$

to our data, even though the $(\Delta T/C)_V$ values indicate that a hexavanadate is not present in the region up to an $H^+/NaVO_3$ of 0.8. The equations used for this purpose were

$$H_T = h + 5[HV_{10}O_{28}^{-5}] + 4[V_6O_{16}^{-2}] \qquad (4)$$

$$V_T = 10[HV_{10}O_{28}^{-5}] + 6[V_6O_{16}^{-2}] = 0.1 \qquad (5)$$

$$\log K = 5 \log [V_6O_{16}^{-2}] - 3 \log [HV_{10}O_{28}^{-4}] - \log h \qquad (6)$$

The results are given in Table V.

The values of log $K$ were fairly constant, but not as constant as those of Table V. Also, the $(\Delta T/C)$ values did not agree as well as for the $H_2V_{10}O_{28}^{-4}$ calculations. It does not appear that $V_6O_{16}^{-2}$ can be considered a major species in this region.

**Species beyond $H^+/NaVO_3$ = 0.8.**—Only two sets of data were obtained at $H^+/NaVO_3$ ratios higher than 0.8, because of the difficulty with precipitation noted previously. These points fell on a reasonable extrapolation of the data at lower $H^+/NaVO_3$ ratios, however, and such an extrapolation appears justified.

Attempts were made to fit values from the extrapolated curve to the equilibria

$$H_2V_{10}O_{28}^{-4} + 14H^+ \rightleftharpoons 10VO_2^+ + 8H_2O \qquad (7)$$

$$3H_2VO_{10}O_{28}^{-4} + 2H^+ \rightleftharpoons 5V_6O_{16}^{-2} + 4H_2O \qquad (8)$$

The best fit was obtained for both equilibria when a combination of $(\Delta T/C)_V$ and hydrogen ion concentration was used to find the equilibrium constants. For the first equilibrium, $H_2V_{10}O_{28}^{-4}$ and $VO_2^+$ were found from the relationships

$$[VO_2^+] + 10[H_2V_{10}O_{28}^{-4}] = V_T = 0.1 \qquad (9)$$

$$[VO_2^+] + [H_2V_{10}O_{28}^{-4}] = 0.1(\Delta T/C)_V/3.2 \qquad (10)$$

where

$$(\Delta T/C)_V = (\Delta T/C)_{\text{exptl}} - (\Delta T/C)_h$$

TABLE IV

SUMMARY OF CALCULATIONS ASSUMING A DECAVANADATE–DECAVANADATE EQUILIBRIUM

| $\frac{H^+}{NaVO_3}$ | $H_T$ | $h$ | $10^3[HV_{10}O_{28}^{-5}]$ | $10^3[H_2V_{10}O_{28}^{-4}]$ | log $K$ | $10^3n$ | $\left(\frac{\Delta T}{C}\right)_{calcd}$ | $\left(\frac{\Delta T}{C}\right)_{exptl}$ |
|---|---|---|---|---|---|---|---|---|
| 0.55 | 0.055 | $2.4 \times 10^{-3}$ | 7.4 | 2.6 | 2.17 | 12.4 | 0.40 | 0.41 |
| 0.60 | 0.060 | $5.5 \times 10^{-3}$ | 5.5 | 4.5 | 2.17 | 15.5 | 0.50 | 0.50 |
| 0.65 | 0.065 | $8.7 \times 10^{-3}$ | 3.7 | 6.3 | 2.29 | 18.7 | 0.60 | 0.62 |
| 0.70 | 0.070 | $1.38 \times 10^{-2}$ | 3.8 | 6.2 | 2.07 | 23.8 | 0.76 | 0.75 |
| 0.75 | 0.075 | $1.74 \times 10^{-2}$ | 2.4 | 7.6 | 2.26 | 27.4 | 0.88 | 0.88 |

TABLE V

SUMMARY OF CALCULATION ASSUMING A DECAVANADATE–HEXAVANADATE EQUILIBRIUM

| $\frac{H^+}{NaVO_3}$ | $10^3[V_6O_{16}^{-2}]$ | $10^3[HV_{10}O_{28}^{-5}]$ | log $K$ | $10^3n$ | $(\Delta T/C)_{calcd}$ | $(\Delta T/C)_{exptl}$ |
|---|---|---|---|---|---|---|
| 0.55 | 2.6 | 8.4 | 6.4 | 13.4 | 0.43 | 0.41 |
| 0.60 | 4.5 | 7.3 | 5.9 | 17.3 | 0.55 | 0.50 |
| 0.65 | 6.3 | 6.2 | 5.9 | 21.2 | 0.68 | 0.62 |
| 0.70 | 6.2 | 6.3 | 4.8 | 26.3 | 0.84 | 0.75 |
| 0.75 | 7.6 | 5.4 | 5.0 | 30.4 | 0.97 | 0.88 |

TABLE VI

SUMMARY OF CALCULATIONS FOR SPECIES BEYOND $H^+/NaVO_3 = 0.8$

$$H_2V_{10}O_{28}^{-4} + 14H^+ \rightleftharpoons 10VO_2^+ + 8H_2O$$

| $\frac{H^+}{NaVO_3}$ | $10^{-2}h$ | $(\Delta T/C)_V$ | $10^3[H_2V_{10}O_{28}^{-4}]$ | $10^3[VO_2^+]$ | log $K$ | $10^3n$ | $(\Delta T/C)_{calcd}$ | $(\Delta T/C)_{exptl}$ |
|---|---|---|---|---|---|---|---|---|
| 0.85 | 2.14 | 0.46 | 9.5 | 4.9 | 2.3 | 35.8 | 1.15 | 1.14 |
| 0.90 | 2.40 | 0.49 | 9.4 | 5.9 | 2.4 | 39.3 | 1.26 | 1.26 |
| 0.95 | 2.69 | 0.52 | 9.4 | 6.8 | 2.3 | 43.1 | 1.38 | 1.38 |
| 1.00 | 2.95 | 0.56 | 9.2 | 8.3 | 2.6 | 47.0 | 1.50 | 1.50 |

$$H_2V_{10}O_{28}^{-4} + 2H^+ \rightleftharpoons 5V_6O_{16}^{-2} + 4H_2O$$

| $\frac{H^+}{NaVO_3}$ | $10^{-2}h$ | $(\Delta T/C)_V$ | $10^3[H_2V_{10}O_{28}^{-4}]$ | $10^3[V_6O_{16}^{-2}]$ | log $K$ | $10^3n$ | $(\Delta T/C)_{cacld}$ | $(\Delta T/C)_{exptl}$ |
|---|---|---|---|---|---|---|---|---|
| 0.85 | 2.14 | 0.46 | 3.3 | 10.4 | 0.7 | 35.1 | 1.12 | 1.14 |
| 0.90 | 2.40 | 0.49 | 2.0 | 13.3 | 1.9 | 39.3 | 1.26 | 1.26 |
| 0.95 | 2.69 | 0.52 | 0.6 | 15.7 | 3.8 | 43.2 | 1.38 | 1.38 |
| 1.00 | 2.95 | 0.56 | 0 | All V in this form | ... | ... | ... | ... |

As before, the factor 3.2 is the molal transition depression constant for Glauber's salt. The factor 0.1 enters since $(\Delta T/C)$ gives $\Delta T$ for 1 mole of V and $\Delta T$ for 0.1 mole is required.

For the second equilibrium $[H_2V_{10}O_{28}^{-4}]$ and $[V_6O_{16}^{-2}]$ were found from

$$6[V_6O_{16}^{-2}] + 10[H_2V_{10}O_{28}^{-4}] = 0.1 \qquad (11)$$

$$[V_6O_{16}^{-2}] + [H_2V_{10}O_{28}^{-4}] = 0.1(\Delta T/C)_V/3.2 \qquad (12)$$

The results of the calculations are given in Table VI.

The $(\Delta T/C)_{calcd}$ and $(\Delta T/C)_{exptl}$ agree closely for both equilibria; but the log $K$ values for the first were quite constant, whereas a constant log $K$ was not found for the second. Once again, it appears the hexavanadate is an unlikely species, and it must be concluded that the hexavanadate does not exist in the pH region studied.

In the region where the present work and the Rossottis' work overlap the same species have been found to exist. Only the roughest of comparisons can be made between the equilibrium constants, however, because of the difference in medium and $T$, and, more importantly, because in the present work the free $H^+$ concentration is only known to be some constant times the amount of $H^+$ not consumed by the vanadium. Although this does not affect the constancy of the $K$ values, the $K$ values determined may be different from the thermodynamic $K$ values by several orders of magnitude.

Figure 1 shows the experimental data points resulting from Glauber's salt cryoscopic measurements with a superimposed curve calculated assuming constants for the reactions

$$5V_4O_{12}^{-4} + 8H^+ \rightarrow 2V_{10}O_{28}^{-6} + H_2O$$

and

$$V_{10}O_{28}^{-6} + H^+ \rightarrow HV_{10}O_{28}^{-5}$$

so large that the reactions are essentially complete, and the observed constants for the reactions

$$HV_{10}O_{28}^{-5} + H^+ \rightleftharpoons H_2V_{10}O_{28}^{-4}; \; \log K = 2.19$$

and

$$H_2V_{10}O_{28}^{-4} + 14H^+ \rightleftharpoons 10VO_2^+ + 8H_2O; \; \log K = 2.4$$

**Heteropolyvanadate Formations.**—Cryoscopy measurements of a very preliminary nature were undertaken to determine whether the method would show evidence for heteropolyvanadate formation, and, if so, whether the method would be applicable to the study of these interactions in detail.

The solutions on which measurements were made had $H^+/NaVO_3$ ratios of 0.5, 0.6, and 0.7 and $H_2PO_4^-/NaVO_3$ ratios of 0.1, 0.2, and 0.3. The results are

TABLE VII

SUMMARY OF RESULTS FOR SODIUM VANADATE WITH SODIUM PHOSPHATE PRESENT

| $\frac{H_2PO_4^-}{NaVO_3}$ | $\frac{H^+}{NaVO_3} = 0.5$ | | $\frac{H^+}{NaVO_3} = 0.6$ | | $\frac{H^+}{NaVO_3} = 0.7$ | |
|---|---|---|---|---|---|---|
| | $(\Delta T/C)_{exptl}$ | $(\Delta T/C)_{apparent}$ | $(\Delta T/C)_{exptl}$ | $(\Delta T/C)_{apparent}$ | $(\Delta T/C)_{exptl}$ | $(\Delta T/C)_{apparent}$ |
| 0 | 0.34 | 0.34 | 0.50 | 0.50 | 0.75 | 0.75 |
| 0.1 | 0.64 | 0.32 | 0.72 | 0.40 | 0.72 | 0.40 |
| 0.2 | 0.96 | 0.32 | 1.07 | 0.43 | 0.88 | 0.24 |
| 0.3 | 1.30 | 0.34 | 1.23 | 0.27 | 1.06 | 0.10 |

summarized in Table VII. Presented are the experimental $(\Delta T/C)$ values, *i.e.*, the change in transition temperature with vanadium ions, and the $(\Delta T/C)_{apparent}$ values due to the vanadium and acid after the contribution to be expected for $H_2PO_4^-$ (*i.e.*, $H_2PO_4^-/NaVO_3 \times 3.20$) was subtracted. This is, of course, only a convenient way of looking at deviations from a simple additivity of $(\Delta T/C)$ values.

At an $H^+/NaVO_3$ ratio of 0.5, $(\Delta T/C)_{apparent}$ was the same with and without $H_2PO_4^-$. At an $H^+/NaVO_3$ of 0.6, although there was some inconsistency, $(\Delta T/C)_{apparent}$ was less when $H_2PO_4^-$ was present than when it was not. Again, at $0.7H^+/NaVO_3$, $(\Delta T/C)_{apparent}$ was lowered by the presence of phosphate, and this time the lowering progressed in a regular manner with phosphate concentration. The two important trends which can be seen from this behavior are: (1) At an $H^+/NaVO_3$ of 0.7, $(\Delta T/C)_{apparent}$ decreased as $H_2PO_4^-/NaVO_3$ increased, and this general trend occurred at $0.6H^+/NaVO_3$ also. The $(\Delta T/C)_{apparent}$ values were too low to be accounted for on the basis of a protonation of $H_2PO_4^-$. The results can best be explained by the formation of a heteropolyanion between vanadium and phosphate. (2) At an $H^+/NaVO_3$ of 0.5, the vanadium and phosphate simply act additively on transition temperature depression, therefore no interaction takes place between the polyvanadate and phosphate. It seems reasonable to propose, therefore, that only the polyvanadate species that predominates at the higher $H^+/NaVO_3$ ratios, $H_2V_{10}O_{28}^{-4}$, forms the complex with $H_2PO_4^-$.

---

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OKLAHOMA STATE UNIVERSITY,
STILLWATER, OKLAHOMA, AND THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR
SCIENCE, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS

# A Computer Analysis of Static and Dynamic Models of the Hafnium Fluoride Complexes Extracted by Tri-*n*-octylphosphine Oxide

BY LOUIS P. VARGA AND DAVID N. HUME

*Received May 2, 1963*

Distribution measurements at 25° between fluoride-containing trace hafnium solutions in 3 *M* perchloric acid and 0.01 and 0.05 *M* tri-*n*-octylphosphine oxide (TOPO) in cyclohexane were interpreted in terms of both static and dynamic models of the hafnium-containing TOPO adducts extracted into the organic phase. The static model which best fits the experimental data assumed the extraction of four species: $Hf(ClO_4)_4 \cdot TOPO$, $Hf(ClO_4)_4 \cdot 2TOPO$, $HfF_2(ClO_4)_2 \cdot TOPO$, and $HfF_2(ClO_4)_2 \cdot 2TOPO$. The dynamic model assumed a labile solvate equilibrium between the hafnium species and TOPO to give average compositions for two extracting species of $Hf(ClO_4)_4 \cdot 1.5TOPO$ and $HfF_2(ClO_4)_2 \cdot 1.5TOPO$. This model concedes the inability and lack of necessity of the equilibrium measurements to distinguish between labile solvate species and treats data in a practical fashion by assuming only the two extractable species. This was the most satisfactory model both from the standpoint of the number of parameters required to explain the data and the goodness of fit. The distribution coefficients for all assumed species were determined and these were used to calculate the over-all formation constants of the hafnium fluoride system.

The solvent extraction behavior of organophosphorus compounds toward a variety of metal species has been described by several workers[1] and in a recent solvent extraction symposium[2] several studies on extraction mechanisms and the extractable metal species were reported. In the case of the monoacidic phosphates and phosphonates nonintegral extractant dependencies have been noted[3] in the extraction of Ca(II) but discrete extracting species were nevertheless postulated. Burger[4] described the mechanism of extraction for metals using neutral organophosphorus compounds, such as the phosphine oxides, as solvation for metal salts, and this mechanism was assumed in this paper.

(1) (a) C. A. Blake, K. B. Brown, and C. F. Coleman, U. S. Atomic Energy Commission ORNL-1964, Nov. 17, 1955; (b) L. L. Burger, *J. Phys. Chem.*, **62**, 590 (1958); (c) J. P. Young and J. C. White, *Anal. Chem.*, **31**, 393 (1959); (d) W. J. Ross and J. C. White, *ibid.*, **31**, 1847 (1959); (e) W. J. Maeck, G. L. Booman, M. C. Elliott, and J. E. Rein, *ibid.*, **32**, 922 (1960); (f) J. C. White and W. J. Ross, "Separations by Solvent Extraction with Tri-*n*-octylphosphine Oxide," U. S. Atomic Energy Commission, NAS-NS 3102, February 8, 1961.

(2) Solvent Extraction Chemistry Symposium, U. S. Atomic Energy Commission, Gatlinburg, Tenn., Oct. 23–26, 1962.

(3) D. F. Peppard and G. W. Mason, ref. 2, paper No. 1.

(4) L. L. Burger, ref. 2, paper No. 8.