[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

A Study of Heterogeneous Equilibria in Aqueous Solutions of the Sodium Salts of the Vanadic Acids at 30°

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Introduction

In the vast number of research reports that have been published covering various aspects of the chemistry of vanadium and its related applications, it is noteworthy to find that scant attention has been given during the past half-century to the alkali vanadates. Accordingly, little is known with certainty of the necessary conditions for their formation or of their stability in solution.

During a period of years near 1870, Roscoe[2] published extensive and comprehensive researches on the chemistry of the vanadium compounds the results of which constitute a large part of our present knowledge of the vanadates. Three kinds of vanadates were recognized by him; "orthovanadates" Na_3VO_4, "pyrovanadates" $Na_4V_2O_7$, and "metavanadates" $NaVO_3$ in which he thought there was a complete analogy with the phosphates. However, he mentioned[3] as a "remarkable reaction" the decomposition of orthovanadate in water with the formation of a strongly alkaline solution according to the equation

$$2Na_3VO_4 + H_2O = Na_4V_2O_7 + 2NaOH$$

from which sodium pyrovanadate could be crystallized; the anhydrous vanadates were prepared by fusing together the proper molecular ratios of vanadium pentoxide and sodium carbonate. The hydrates $Na_3VO_4 \cdot 16H_2O$ and $Na_4V_2O_7 \cdot 18H_2O$ were crystallized from aqueous solution by the addition of alcohol.

Since his work an unusually large number of hydrates,[4] the existence and identity of some of which might be doubted because of the lack of information as to conditions of preparation, analysis of compounds and conditions of stability, have been reported.

The state of the vanadate ions in solution has been the subject of the more recent researches. Probably all three types of ions exist together in rapidly established equilibria for, depending upon the solubility, it is possible to precipitate a pyrovanadate from a solution of an orthovanadate.[5] Also, a drop of acid to a colorless solution of a vanadate produces a deep yellow color possibly due to more highly associated or hydrated vanadate ions which persist for some time in the cold, even though the yellow substance or substances are unstable in the alkaline solution; the formation of the acid compound is instantaneous while the reverse reaction is comparatively slow. Düllberg[6] attacked the problem by conductometric titration and reported the existence of $VO_4^{\equiv}$, $V_2O_7^{=\,=}$, VO_3^-, and the yellow ion $V_6O_{17}^{=\,=}$ or $HV_6O_{17}^{\equiv}$. Rosenheim and Yang[7] attempted the determination of sodium orthovanadate by a sulfuric acid titration. Britton and Robinson[8] repeated Düllberg's work and attempted some potentiometric titrations which proved to be but partially successful: with the hydrogen electrode a blue color was evidence of reduction in the more acid solutions; the oxygen electrode yielded hardly more than qualitative results, while the behavior of the quinhydrone electrode was very erratic. From this work the conclusion was drawn that the yellow color was due to a complex of high V_2O_5:Na_2O ratio existing in large polymerized molecules, bordering between the state of a true solute and a colloidal micelle.

M. M. Parks[9] has demonstrated that when cobaltammine ion was added to a vanadate solution, the composition of the resulting precipitate was controlled by the acidity of the solution. Thus, the precipitates were: with alkaline solutions, the pyrovanadate, $(Co(NH_3)_6)_4(V_2O_7)_3$; with neutral solutions, the metavanadate, $Co(NH_3)_6(VO_3)_3$; and with slightly acidic solutions, the hexavanadate, $(Co(NH_3)_6)_4(V_6O_{17})_3$.

Consequently from the foregoing background it seemed probable that a study of the three-component system V_2O_5–Na_2O–H_2O from the viewpoint of the phase rule would yield valuable data.

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(1) Dr. Manfredo died August 24, 1936.

(2) H. E. Roscoe, *J. Chem. Soc.*, **21**, 322 (1868); **23**, 344 (1870); **24**, 23 (1871); *Trans. Roy. Soc.*, **158**, 1 (1868); **159**, 679 (1869); **160**, 317 (1870).

(3) H. E. Roscoe, *J. Chem. Soc.*, **24**, 30 (1871).

(4) Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. IX, Longmans, London, pp. 757 *et seq.*

(5) Carnot, *Compt. rend.*, **104**, 1844 (1887).

(6) Düllberg, *Z. physik. Chem.*, **45**, 129 (1903).

(7) Rosenheim and Yang, *Z. anorg. allgem. Chem.*, **129**, 181 (1923).

(8) Britton and Robinson, *J. Chem. Soc.*, 1261 (1930).

(9) M. M. Parks, "A Quantitative Method for the Determination of Vanadium," Dissertation, Columbia University, 1930; also W G. Parks and Prebluda, THIS JOURNAL, **57**, 1676 (1935).

Preparation and Analysis of Materials

Vanadium Pentoxide.—The material used for this investigation was in the form of a fine, orange-yellow powder. Analyses of this material showed a vanadium pentoxide content of 99.50% and a loss on gentle ignition of 0.48%. It was, within experimental error, free from the lower oxides. Qualitative tests gave negative results for barium, tungsten, silicon dioxide, elements precipitable by hydrogen sulfide in acid and alkaline solution, phosphates, and the alkali metals.

The pentoxide dissolving sparingly in water formed a yellow, dark, turbid solution from which the suspended matter settled with difficulty. A liquid, which did not "spurt" on cooling, was formed by fusion—a phenomenon attributed by Norblad[10] to evolution of oxygen from the tetroxide considered present and by Hautefeuille[11] to the presence of alkali. When the fused material cools to below the point of redness, the phenomenon of "calorescence" discovered by Berzelius[12] appears; a glowing ring forms at the circumference of the fused mass and moves toward the center. The final crystals, in the appearance of an open fan, varied in color from light brown and transparent in sufficiently thin layers, to a dark steel-gray with metallic luster in thicker layers.

Sodium Hydroxide.—The component sodium oxide was introduced and employed in the form of a 50% aqueous solution of the best sodium hydroxide obtainable; saturated solutions were prepared and filtered by suction through a Jena sintered glass filter of porosity grade 3 to eliminate carbonates. Solutions were handled in an atmosphere free from carbon dioxide.

Mercurous Nitrate.—The highest grade of $HgNO_3 \cdot 2H_2O$ obtainable was used. The non-volatile residue after ignition was not greater than 0.004%.

Other Reagents.—All chemicals although of the purest grade obtainable were tested before use for the presence of impurities which would be detrimental to the particular work intended.

Containers.—The experimental solutions covered the range from saturated sodium hydroxide to slightly acid. For the latter, "Pyrex" glass bottles were used; for the alkaline solutions, however, glass could not be employed because of contamination during the necessary time of contact. Containers (Fig. 1) of pure silver No. 20 (B. & S. gage), constructed in the form of tall, covered beakers with the rim reinforced for strength, the upper 1.5 cm. of which was slightly flared to take a correspondingly-shaped hollow silver stopper ground to fit, were used. The containers were rotated in a bath maintained at 30 ± 0.02°.

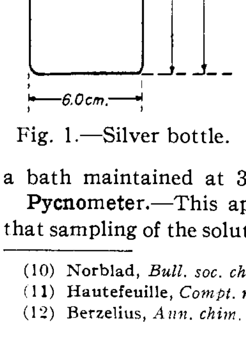

Fig. 1.—Silver bottle.

Pycnometer.—This apparatus (Fig. 2) was devised so that sampling of the solution, determination of density, and weighing out of samples could be performed conveniently with a minimum of transfer. Constructed throughout of Pyrex glass, it was essentially a weighing pipet with a 12-cc. capacity and a stem of such bore that a 0.5-cc. volume occupied a length of about 4.5 cm. The stem was graduated and calibrated from 0 to 0.5, with subdivisions of 0.01 cc., so that the estimation between graduations to 0.001 cc. was possible. The upper end of the stem was provided with a cap ground to fit. The bulb could be emptied through a glass stopcock at the bottom carrying a small nozzle of capillary bore, ground on the outside to fit either a base or a light glass sampling tube. The over-all length was 15 cm. and the total weight 35 g. The sampling tube, besides a ground joint to fit the pycnometer nozzle, had immediately below it a small enlargement into which could be placed glass wool as a filtering medium; the remainder was a simple tube 16 cm. long and 6 mm. in internal diameter. The pycnometer was calibrated at 30° with distilled water. The true volumes in milliliters with brass and other corrections[13] were determined.

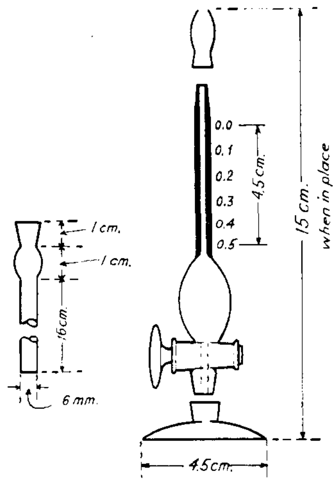

Fig. 2.—Sampler and pycnometer.

Analytical Apparatus.—Weights, burets, pipets, and volumetric flasks of the usual type were calibrated and checked with Bureau of Standards standards.

Method of Procedure

Method of Analysis.—Methods were considered with reference to the particular problem presented, the determination of vanadium pentoxide, sodium oxide, and water, in a system of these three components only. But two of these components need be determined directly; the third, water, may be calculated by difference for reasons of convenience.

There is a wide choice in methods for determining vanadium. A review of these need not be given in view of the fact that excellent reviews may be found in a dissertation by Parks,[9] in a publication of the Bureau of Mines,[14] and elsewhere.[15] The more recent method of Parks, which is a gravimetric method depending upon the formation of insoluble compounds between the hexammine cobaltic ion and the vanadate ions, and the volumetric method of Walden, Hammett, and Edmonds[16] in which a vanadic acid solution in 5 molar sulfuric acid is titrated with ferrous

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(10) Norblad, *Bull. soc. chim.*, [2] **23**, 64 (1875).

(11) Hautefeuille, *Compt. rend.*, **90**, 744 (1880).

(12) Berzelius, *Ann. chim. phys.*, [2] **47**, 337 (1831).

(13) U. S. Bureau of Standards, Circ. No. 19, Table No. 35, (1924).

(14) U. S. Bureau of Mines, Bulletin 212, part VII, 1921.

(15) Brearley, *Chem. News*, **83**, 163 (1901); Holverscheidt, *Chem. Zentr.*, **61**, I, 977 (1890); Von Klecki, "Analytische Chemie des Vanadins," Hamburg, 1894; Beard, *Ann. chim. anal. appl.*, **10**, 41 (1905).

(16) Walden, Hammett and Edmonds, This Journal, **56**, 95 (1934).

sulfate, with ferrous phenanthroline complex as an indicator, should be mentioned.

For the determination of sodium, the choice was restricted to the usual sulfate[17] method, the uranyl zinc acetate method in both its gravimetric[18] and volumetric[19] modifications, and to the uranyl magnesium acetate method.[20]

A determination of vanadium and sodium in the same solution had to be made. The ideal method would be a rapid and accurate volumetric analysis without separation of which there are several for vanadium. But in the case of sodium there are none. A separation therefore is imperative. A reagent had to be used such that the vanadium may be separated in a form ready for ignition and weighing, while the excess of reagent would cause no interference in the determination of sodium. The literature offered three possibilities: (1) the cupferron method recommended by Baudisch[21] and investigated by Turner[22] and likewise by Lundell and Knowles,[23] (2) the ammonium chloride method of Berzelius and Hauer,[24] (studied by Gooch and Gilbert[25] and Campagne[26]); and (3) the seldom used mercurous nitrate method of Rose.[27,28] In each of these methods the vanadium can be separated in a form which may be ignited and weighed as vanadium pentoxide while the excess of precipitant remaining in solution with the sodium may be removed during the process of evaporation with sulfuric acid.

These methods were tested in a series of experiments to determine the one most convenient, adaptable and precise for use in the present work. For comparison, Roscoe's lead acetate method, which is recommended in the literature for its accuracy, was followed. All the methods named except the one which required mercurous nitrate as the precipitant were found to be either impracticable or less precise and trustworthy.

The Mercurous Nitrate Method.—Since this method was adopted for use throughout this investigation, the procedure will be described in detail. The reagent contains 20 g. of mercurous nitrate and 1 cc. of nitric acid per 100 cc. in the presence of free mercury. The volume of the sample contained in a 150-cc. beaker should be not much more than 100 cc. as the filtrate and washings (which contain the sodium) must be collected in a platinum dish of convenient size to facilitate subsequent evaporation, fuming, ignition and weighing. The platinum dishes of 200-cc. capacity weighed 50 g., were 8.5 cm. in diameter, with vertical walls 4 cm. high. The solution to be analyzed should be either neutral or slightly alkaline. This is important because if too alkaline, the reagent will be consumed by the precipitation of black mercury compounds which are voluminous and cause unnecessary bulk which must be filtered, washed and expelled. They also interfere in the determination of the end-point in the precipitation. On the other hand, precipitation of the vanadium will not be quantitatively complete if the solution is too acid, even though a clean-looking, yellow-, quickly-settling mercurous vanadate is obtained. The color of the solution is a sufficient guide. When acid is added to a slightly alkaline solution of a vanadate, a yellow color is produced which soon fades if the solution is boiling. If the solution is acidified, the yellow color persists. Therefore, before precipitation, nitric acid is added dropwise to the boiling solution until a faint permanent yellow color is produced. The addition of a single drop of ammonium hydroxide then causes it to disappear. The mercurous nitrate reagent, usually about 10 cc., is added to this solution, dropwise, with stirring, to complete precipitation. The color of the precipitate may vary from almost black to yellowish gray. After stirring and heating the precipitate soon settles. The solution is always acid at this point, and it is again necessary to neutralize with ammonium hydroxide to litmus. The alkali is added drop by drop to a slight alkalinity, during which the excess of reagent precipitates as a gray cloud. More reagent is added dropwise at this point to ensure complete precipitation of mercurous vanadate. After short gentle boiling and settling, the precipitate is filtered on paper and washed with a warm 0.1% mercurous nitrate solution. The filtrate and washings are collected in a weighed platinum dish. Hydrogen peroxide may be added to the first few cc. in the dish as a test for complete precipitation of vanadium; if the precipitation has been properly conducted, no color will be seen.

The paper and residue are placed in a platinum crucible and carefully dried and charred, after which the heat may be increased to consume the carbon and volatilize the mercury in an adequately ventilated hood. Oxidizing conditions should be maintained at all times, but the temperature must be kept below a faint red heat. When all carbon and mercury compounds are expelled from the crucible two or three evaporations with concentrated nitric acid usually suffice to bring the reduced vanadium pentoxide to the fully oxidized condition and constant weight. It is advisable, after each evaporation, to heat the vanadium pentoxide to fusion and by a rotatory motion of the crucible to expose fresh surfaces of the solid to the next oxidizing treatment.

The filtrate and washings from the vanadium separation contain the sodium of the sample, excess mercurous nitrate, and ammonium nitrate. Excess sulfuric acid is added, the solution is evaporated to dryness, and then is heated cautiously under a hood until all but the sodium sulfate is volatilized. Removal of the last traces of sulfuric acid is aided by a few fragments of ammonium carbonate. After constant weight is obtained, the weight of sodium oxide is calculated. The sodium sulfate is perfectly white and free from vanadium.

Ignition of Vanadium Pentoxide.—In the ignition of vanadium pentoxide it is essential to prevent reduction that a low red heat be not exceeded. There are two reasons for the reduction of vanadium pentoxide during the ignition incidental to analysis: first, the filter paper

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(17) Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley & Sons, Inc., New York, 1929.

(18) Barber and Kolthoff, THIS JOURNAL, **50**, 1625 (1928).

(19) Dobbins and Byrd, *ibid.*, **53**, 3288 (1931).

(20) Caley and co-workers, *ibid.*, **51**, 1664 (1929); **52**, 1349 (1930); **52**, 4247 (1930).

(21) Baudisch, *Chem. Ztg.*, **33**, 1298 (1909).

(22) Turner, *Am. J. Sci.*, **41**, April, 1916.

(23) Lundell and Knowles, *Ind. Eng. Chem.*, **12**, 344 (1920).

(24) Berzelius and Hauer, *J. prakt. Chem.*, **69**, 388 (1856).

(25) Gooch and Gilbert, *Am. J. Sci.*, [4] **14**, 205 (1902).

(26) Campagne, *Ber.*, **36**, 3164 (1903).

(27) H. Rose, "Ausführliches Handbuch der analytischen Chemie," Braunschweig, Vol. II, 1851, p. 364.

(28) Carnot, *Compt. rend.*, **105**, 121 (1887).

being charred produces some reduction; second, according to a study by Milan[29] vanadium pentoxide dissociates appreciably into V_2O_4 and O_2 at temperatures only slightly above its melting point. The extent of error from these sources and the effect of nitric acid as a subsequent reoxidant were determined by experiment. Platinum crucibles containing vanadium pentoxide which had been brought to constant weight during an analysis were used to determine the effect of (1) heating at a temperature just above the fusion point; (2) heating to a bright red heat; (3) re-oxidation by concentrated nitric acid. When the temperature of molten vanadium pentoxide rises sufficiently, there is visible within the mass a rapid motion, probably due to convection currents but strongly resembling a state of incipient ebullition. This is the phenomenon described as "bubbling." When still higher temperatures are reached, the visible evolution of gas indicates that decomposition is taking place. The reduction may be kept to a minimum by observing the proper temperature during the ignition. Also repeated treatment with nitric acid is adequate for restoring the vanadium pentoxide which may be reduced in the initial heating and charring.

Experimental Procedure.—Much preliminary and semiquantitative information was gained from a series of small scale (test-tube) experiments made without shaking and at approximately regulated temperature. The mixtures contained thirty ratios of the components Na_2O/V_2O_5, ranging from 30/1 to 1/30, mixed with varying proportions of water. These experiments yielded an orientation on the general character of the problem; some knowledge of the nature of the solid phases to be encountered, *i. e.*, appearance, ease of settling, etc.; information as to the solutions, *i. e.*, color, viscosity, reaction toward litmus; an idea of the length of time necessary for equilibrium; together with such experimental details as to method of mixing the components, and the best procedure in sampling and analysis. With this information, the proportions of the complexes were so chosen as to give a total volume of about 100 cc. with sufficient solid phase at equilibrium. These complexes were put in the containers which were rotated in the bath. After equilibrium had been established samples were taken by means of the sampling tube into the weighed pycnometer. In the alkaline solutions, the solution both in the containers and pycnometer was protected from carbon dioxide.

The end of the sampling tube Fig. 2 extended below the liquid surface. By applying suction at the upper end of the pycnometer sufficient of the liquid phase was drawn upward to bring the level opposite the scale. The scale reading was taken immediately. After cleaning the capillary tip of the pycnometer the base and the cap were applied and the pycnometer with contents was weighed. The weight of solution was corrected "*in vacuo*" and the density calculated on the basis of water at 4°. Usually the solution showed no crystallization in the pycnometer due to cooling and a weighed portion for analysis could be taken without difficulty. If, however, the solution in the pycnometer did not remain clear the whole of the solution was washed into a volumetric flask from which aliquot portions for analysis were withdrawn with a pipet.

For sampling the solid phase, a small scoop made of nickel wire mesh fused into the end of a glass rod was employed. After drainage for a few seconds the moist solid was transferred to a weighed glass-stoppered weighing bottle for weighing and analysis. Simultaneously, and always, a small amount of the solid was placed on a microscope slide and covered with a cover-slip. During the operation of the sampling, exposure of the uncovered bottle to the air amounted to perhaps a minute.

The composition of the equilibrium solid was determined according to Schreinemakers'[30] residue method and confirmed by analysis after separation whenever possible in a pure state by the method of Hill.[31] The algebraic method of Schreinemakers was used when the graphic methods were subject to too large an error due to the small scale.

Equilibrium was approached from higher temperatures because the formation of stable phases was favored. In order to check the attainment of equilibria, however, some experiments with the same results were performed in which the approach was made from lower temperatures.

Whether equilibrium was reached or not was determined by three criteria: (1) two analyses of the liquid phase separated by a period of several days to several weeks (depending on the individual case) agreed within experimental error, if the system was in a state of equilibrium; (2) densities determined previously to the analyses also agreed; and (3) microscopic examination of the solid phase showed no change in the form of the crystals. Density determinations, being simple to perform, were used as preliminary indications. No analyses were made until successive density determinations showed agreement. Although no further use was made of the density data obtained, the density, reduced to "*in vacuo*," of each liquid phase is recorded, inasmuch as it may serve a useful purpose in converting the solubility, here expressed as mole percentages, subsequently to a volume basis.

The time required for the attainment of equilibrium varied from less than one week in the case of the larger well-formed crystals whose saturated solutions were not too viscous to a month or more in the alkaline region where $Na_3VO_4\cdot7H_2O$ and $Na_3VO_4\cdot2.5H_2O$ were involved.

Experimental Results

The experimental results for the isotherm at 30° only are expressed as mole percentages in Table I. Each value for the liquid phase is the mean of two consecutive analyses which agree within experimental error; values for the moist solid phases are also means of two determinations which theoretically fall on the same tie line, although there apparently might be a wide divergence between the individual results, owing to the varying proportions of liquid included in the sample of solid phase residue taken for analysis.

The data in Table I are converted to weight percentages and are plotted in Fig. 3 because the tie lines are shown more advantageously.

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[29] Milan, *J. Phys. Chem.*, **33**, 498 (1929).

[30] Schreinemakers, *Z. physik. Chem.*, **11**, 81 (1893).

[31] Hill, THIS JOURNAL, **52**, 3823 (1930).

TABLE I

EXPERIMENTAL RESULTS EXPRESSED AS MOLE PERCENTAGES

Point no.	Density at 30°	Liquid phase V_2O_5 Mole percentage	Liquid phase Na_2O Mole percentage	Moist solid phase V_2O_5 Mole percentage	Moist solid phase Na_2O Mole percentage	Solid phase	Point in Fig. 3
1	0.996	0.010	....	9.84	..	$V_2O_5 \cdot xH_2O$	A
2	.9957	.009	0.002	0.87	0.14	$V_2O_5 \cdot xH_2O \cdot xyH_2O$	
3	.9955	.004	.002	.60	.18	$V_2O_5 \cdot xH_2O \cdot xyH_2O$	
4	.9959	.013	.009	.58	.21	$V_2O_5 \cdot xH_2O \cdot xyH_2O$	
5	.9979	.030	.026	.57	.22	$V_2O_5 \cdot xH_2O \cdot xyH_2O$	
6	1.039	.46	.24	.77	.36	$V_2O_5 \cdot xH_2O \cdot xyH_2O$	
7	1.038	.44	.22	1.05	.43	$V_2O_5 \cdot xH_2O \cdot xyH_2O$	
8	1.163	1.73	1.30	2.60	1.82	$V_2O_5 \cdot xH_2O \cdot xyH_2O$	
9	1.224	2.43	1.46	3.61	1.95	$V_2O_5 \cdot xH_2O \cdot xyH_2O$	
10	1.236	2.54	1.55	..	..	$V_2O_5 + Na_4VO_6O_{17} \cdot 12H_2O$	B
11	1.219	2.34	1.58	6.75	4.10	$Na_4V_6O_{17} \cdot 12H_2O$	
12	1.215	2.26	1.59	9.55	5.89	$Na_4V_6O_{17} \cdot 12H_2O$	
13	1.224	2.40	1.57	17.89	10.82	$Na_4V_6O_{17} \cdot 12H_2O$	
14	1.208	2.22	1.68	..	..	$Na_4V_6O_{17} \cdot 12H_2O + NaVO_3 \cdot 2H_2O$	C
15	1.187	1.95	1.53	6.76	6.43	$NaVO_3 \cdot 2H_2O$	
16	1.167	1.76	1.45	6.61	6.36	$NaVO_3 \cdot 2H_2O$	
17	1.148	1.57	1.37	4.43	4.23	$NaVO_3 \cdot 2H_2O$	
18	1.130	1.35	1.29	4.34	4.27	$NaVO_3 \cdot 2H_2O$	
19	1.110	1.21	1.23	..	..	$NaVO_3 \cdot 2H_2O$	
20	1.124	1.31	1.42	..	..	$NaVO_3 \cdot 2H_2O$	
21	1.151	1.50	1.69	3.54	3.80	$NaVO_3 \cdot 2H_2O$	
22	1.265	2.36	3.19	5.64	6.27	$NaVO_3 \cdot 2H_2O$	
23	1.418	3.60	5.50	4.64	6.34	$NaVO_3 \cdot 2H_2O$	
24	1.536	4.57	7.55	..	..	$NaVO_2 \cdot 2H_2O + Na_4V_2O_7 \cdot 18H_2O$	D
25	1.460	3.76	6.47	4.17	7.66	$Na_4V_2O_7 \cdot 18H_2O$	
26	1.363	2.56	4.93	3.09	6.01	$Na_4V_2O_7 \cdot 18H_2O$	
27	1.352	2.32	4.46	..	..	$Na_4V_2O_7 \cdot 18H_2O$	
28	1.367	2.31	5.08	3.03	6.37	$Na_4V_2O_7 \cdot 18H_2O$	
29	1.379	2.42	5.60	..	..	$Na_4V_2O_7 \cdot 18H_2O + Na_3VO_4 \cdot 12H_2O$	E
30	1.278	1.55	4.19	2.15	6.38	$Na_3VO_4\ 12H_2O$	
31	1.239	1.28	3.79	..	..	$Na_3VO_4\ 12H_2O$	
32	1.228	1.12	3.54	2.00	6.48	$Na_3VO_4\ 12H_2O$	
33	1.200	0.91	3.26	1.72	5.82	$Na_3VO_4 \cdot 12H_2O$	
34	1.172	.67	2.97	1.39	5.04	$Na_3VO_4 \cdot 12H_2O$	
35	1.162	.55	2.93	1.86	6.73	$Na_3VO_4 \cdot 12H_2O$	
36	1.151	.40	2.87	2.07	7.51	$Na_3VO_4 \cdot 12H_2O$	
37	1.152	.22	3.19	1.33	5.91	$Na_3VO_4 \cdot 12H_2O$	
38	1.153	2.21	3.26	..	..	$Na_3VO_4 \cdot 12H_2O$	
39	1.169	0.14	3.72	0.92	5.45	$Na_3VO_4 \cdot 12H_2O$	
40	1.165	.14	3.66	..	..	$Na_3VO_4 \cdot 12H_2O$	
41	1.183	.11	4.04	0.84	5.64	$Na_3VO_4 \cdot 12H_2O$	
42	1.198	.09	4.50	..	..	$Na_3VO_4 \cdot 12H_2O$	
43	1.192	.09	4.38	0.72	5.64	$Na_3VO_4 \cdot 12H_2O$	
44	1.208	.08	4.76	..	..	$Na_3VO_4 \cdot 12H_2O$	
45	1.230	.07	5.40	0.67	6.46	$Na_3VO_4 \cdot 12H_2O$	
46	1.245	.06	5.70	.63	6.48	$Na_3VO_4 \cdot 12H_2O$	
47	1.312	.06	7.55	..	..	$Na_3VO_4 \cdot 12H_2O + Na_3VO_4 \cdot 7H_2O$	F
48	1.337	.04	8.39	1.99	11.33	$Na_3VO_4 \cdot 7H_2O$	
49	1.369	.03	9.34	1.60	11.42	$Na_3VO_4 \cdot 7H_2O$	
50	1.411	.03	10.94	1.57	12.54	$Na_3VO_4 \cdot 7H_2O$	
51	1.478	.06	13.39	1.56	14.36	$Na_3VO_4 \cdot 7H_2O$	
52	1.477	.07	13.33	1.64	15.82	($Na_3VO_4 \cdot 2.5H_2O$ meta-stable)	
53	1.472	.08	13.99	..	..	$Na_3VO_4 \cdot 7H_2O + Na_3VO_4 \cdot 2.5H_2O$	G
54	1.512	.12	14.77	1.48	15.20	($Na_3VO_4 \cdot 7H_2O$ meta-stable)	
55	1.504	.08	14.53	2.96	19.10	$Na_3VO_4 \cdot 2.5H_2O$	
56	1.519	.08	15.23	2.04	18.20	$Na_3VO_4 \cdot 2.5H_2O$	
57	1.538	.08	15.82	1.27	17.58	$Na_3VO_4 \cdot 2.5H_2O$	
58	1.543	.08	16.34	2.15	19.29	$Na_3VO_4 \cdot 2.5H_2O$	

Table I (*Concluded*)

Point no.	Density at 30°	Liquid phase V_2O_5 Mole percentage	Liquid phase Na_2O Mole percentage	Moist solid phase V_2O_5 Mole percentage	Moist solid phase Na_2O Mole percentage	Solid phase	Point in Fig. 3
59	1.557	0.08	16.96	..	..	$Na_3VO_4 \cdot 2.5H_2O + NaOH \cdot H_2O$	H
60	1.552	.02	16.79	0.02	19.19	$NaOH \cdot H_2O$	
61	1.549	..	16.81	..	18.43	$NaOH \cdot H_2O$	I

Errors

Analytical.—A study of the method of analysis disclosed that results for vanadium pentoxide are on the average low by 2 parts per 1000, and those for sodium oxide high by 2 parts per 1000.

Precision and Accuracy of the Results of Extrapolation.—The values for the compositions of the solid phases as finally found are burdened with all of the errors accumulating in the course of the work from all sources. They were determined and are as follows:

	$\%V_2O_5$	$\%Na_2O$	$\%H_2O$
$Na_3VO_4 \cdot 2.5H_2O$			
Mean extrapolated composition	40.43 ± 1.45	39.43 ± 0.02	20.14 ± 1.44
Theoretical composition	39.72	40.61	19.67
Deviation from theoretical	+0.71	−1.18	+0.47
$Na_3VO_4 \cdot 7H_2O$			
Mean extrapolated composition	29.87 ± 0.97	30.00 ± 0.16	40.14 ± 1.06
Theoretical composition	29.34	29.98	40.68
Deviation from theoretical	+0.52	+0.02	−0.54
$Na_3VO_7 \cdot 12H_2O$			
Mean extrapolated composition	21.72 ± 0.53	24.18 ± 0.61	54.09 ± 1.14
Theoretical composition	22.73	23.24	54.03
Deviation from theoretical	−1.01	+0.94	+0.06
$Na_4V_2O_7 \cdot 18H_2O$			
Mean extrapolated composition	28.81 ± 0.34	19.37 ± 0.40	51.82 ± 0.70
Theoretical composition	28.87	19.67	51.46
Deviation from theoretical	−0.06	−0.30	+0.36
$NaVO_3 \cdot 2H_2O$			
Mean extrapolated composition	58.22 ± 0.39	19.59 ± 0.12	22.19 ± 0.52
Theoretical composition	57.57	19.62	22.81
Deviation from theoretical	+0.65	−0.03	−0.62

The following results, not obtained by extrapolation but by isolation and direct analysis of the solid phase, are included for comparison.

	$\%V_2O_5$	$\%Na_2O$	$\%H_2O$
$Na_4V_6O_{17} \cdot 12H_2O$			
Mean composition by analysis	62.46 ± 0.51	12.88 ± 0.14	24.66 ± 0.60
Theoretical composition	61.60	14.00	24.40
Deviation from theoretical	+0.86	−1.12	+0.26

Discussion of Results

In the isothermal diagrams there are shown eight branches representing the range of liquid phase univariance. The theoretical and experimental compositions of the corresponding equilibrium solids are also plotted. A sufficient number of experimental points was determined to fix exactly the course of the isotherm; where maxima appear, they are very nearly the true maxima; the seven isothermally invariant points were fixed by actual experimental values and represent the mean of at least two results agreeing within experimental error. In the region of high sodium oxide content, in which equilibrium was attained comparatively slowly, it was possible to follow two metastable curves for a short distance.

The Vanadium Pentoxide Branch (Curve AB).—When vanadium pentoxide is shaken with water, a slimy and brownish-yellow solid settles very slowly, leaving a slightly turbid, yellow-colored solution which cannot be clarified by ordinary filtration. By analysis, these contained respectively, 0.104 and 52.42% of vanadium pentoxide by weight (Point No. 1). The addition of the third component, sodium oxide, even in very small amount caused a marked change. After shaking in the rotating apparatus the solution assumed a turbid deep-orange color and the insoluble substance became a brownish-red and swelled to a very voluminous, flocculent mass. It was evident that the addition of sodium ion furnished a peptizing electrolyte for the formation of a hydrosol and that the solid assumed the state of a gel. If colloidal phenomena were here encountered, then the validity of the application of the phase rule is questionable. True reversible equilibria did not occur, and the phases were not true phases for they were not homogeneous, physically distinct, and mechanically separable. The experimental results for this branch of the curve (points numbered from 1 to 9) bear out this viewpoint inasmuch as the tie lines do not intersect at a common point. There is no single solid phase which may be considered to be in equilibrium with the solutions in this region and because the solid phases (although they were much alike in appearance) could not be characterized as chemical individuals, they are referred to simply as $V_2O_5 \cdot xH_2O \cdot yNa_2O$. Nevertheless, repeated analysis of the solutions in this region fixed fairly definitely the course of the solubility curve.

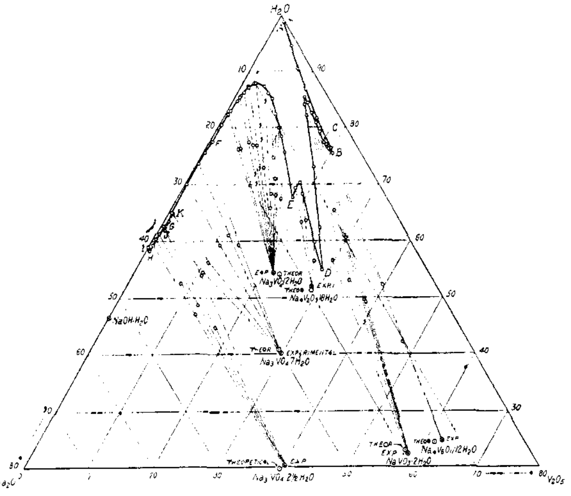

Fig. 3.—System Na_2O–V_2O_5–H_2O, 30° isotherm.

The Hexavanadate Branch (Curve BC).—This branch of the isotherm covering a concentration range of only 2.23% of vanadium pentoxide and 0.24% of sodium oxide, by weight, is very short. Within these narrow limits it is experimentally quite difficult to obtain equilibrium solutions other than those of the compositions corresponding to the isothermally invariant points which terminate this branch. During the work in this region, the persistent occurrence of these two points indicated the existence of this short though appreciable curve. Further work, therefore, resulted in the fixation of its course by three points besides those on the ends. The solutions were all of a deep orange color, were acid toward litmus paper, and changed when boiled with the separation of red-brown hydrated vanadic acid.

The residue method was of little aid in deciding the composition of the equilibrium solid. In this narrow area the tie lines are so nearly parallel that the intersection of their prolongations is attended with a considerable degree of uncertainty which can be removed only by an unattainable precision of analysis. Therefore this method was used only in a confirmatory way and the final decision rested on separation and direct analysis of the solid. By drying the wet crystals over partially dehydrated crystals of the same phase the analysis was corrected for the mother liquor contained in the crystals by Hill's method.[31] With appropriate corrections applied on this basis, the mean results of five analyses were

	Mean results, %	Theoretical for $Na_4V_6O_{17} \cdot 12H_2O$, %	Deviation from theoretical, %
V_2O_5	62.46 ± 0.51	61.60	+0.86
Na_2O	12.88 ± 0.14	14.00	−1.12
H_2O	24.66 ± 0.60	24.40	+0.26

The crystals obtained were transparent deep orange-red in color. When examined under the microscope they exhibited several crystal habits, owing to variations in the relative development of the faces. Six- or eight-sided plates occurred most frequently and six-sided prisms more rarely.

It may be stated as a result of the present work that the previously unreported sodium hexavanadate dodecahydrate, $Na_4V_6O_{17} \cdot 12H_2O$, is stable in contact with a short range of solutions at 30° and has a congruent solubility at 30° of 29.65 g. per 100 g. of water. In contact with solutions at temperatures somewhat higher than 30°, its stability decreases.

The Metavanadate Branch (Curve CD).—At the isothermally invariant point C the solutions represented by this branch of the isotherm were colored yellow and were acid in reaction; there was a gradual change in properties until at point D they were colorless and alkaline toward litmus.

The solid phase in equilibrium with these solutions was sodium metavanadate dihydrate, $NaVO_3 \cdot 2H_2O$, the composition of which was established both by algebraic computation of the tie lines and by direct analysis of the separated crystals. The solid phase was colorless and in the form of minute transparent needles. The saturated solution at 30° contained 18.55 g. of sodium metavanadate per 100 g. of water with the equilibrium solid the dihydrate. Norblad obtained a hydrate of this composition by treating a sodium vanadate solution with alcohol.

The Pyrovanadate Branch (Curve DE).—Solutions represented by this curve were colorless and alkaline. The crystals in equilibrium therewith were very thin six-sided plates with beveled edges; some were perfect hexagons in outline; others showed varying degrees of distortion.

The composition of the solid was determined to be $Na_4V_2O_7 \cdot 18H_2O$ by algebraic tie line computation and by direct analysis. At 30° the saturated solution contains 42.35 g. of $Na_4V_2O_7$ per 100 g. of water. The solid phase was the octadecahydrate, $Na_4V_2O_7 \cdot 18H_2O$.

A sodium pyrovanadate of this degree of hydration, made by treating an aqueous solution of the orthovanadate with alcohol and crystallizing the resulting oily liquid layer, has been reported by Roscoe, by Norblad and by Rammelsberg.

The Orthovanadate Dodecahydrate Branch (Curve EF).—The extensive curve EF represents a series of colorless, alkaline solutions in equilibrium with solid sodium orthovanadate dodecahydrate, $Na_3VO_4 \cdot 12H_2O$. The solid phase occurred as transparent hexagonal rods, the surfaces of which bore numerous striations running parallel to the long edges. On standing in contact with the solution they tended to group themselves into a columnar structure and became attached with the long axes parallel. This structure rather than the individual crystal was observed more commonly. The composition of the solid phase was established indirectly by algebraic calculation and directly by analysis. At 30° the saturated solution of the dodecahydrate contains 27.31 g. of the anhydrous salt per 100 g. of water. Baker obtained an orthovanadate of this composition by adding excess of sodium hydroxide to a solution of pyrovanadate and crystallizing.

The Orthovanadate Heptahydrate Branch (Curve FG).—In this region the solutions were colorless, strongly alkaline, and viscous. Perhaps because of the viscosity of the solutions, equilibrium was but slowly attained. The time required was a matter of weeks under the conditions of the experiments.

The solid phase was colorless and had the form of flat plates, trapezoidal in outline, usually distinctly developed. Another form was of the same general shape, but prismatic rather than flat. As may be seen from the isotherm, this hydrate is incongruently soluble in water. The composition of the solid phase was fixed by algebraic tie-line computation and confirmed by direct analysis. Analyses of the solid phases were made immediately after they were separated from the solution by a fritted glass filter and dried by pressing between filter paper.

A heptahydrate of sodium orthovanadate, first erroneously termed by Baker an octahydrate, was described by Hall as occurring in 4- or 8-sided plates.

The Orthovanadate Hemipentahydrate Branch (Curve GH).—On the isothermal diagram, the curve from G to H represents solutions in equilibrium with the incongruently soluble solid phase $Na_3VO_4 \cdot 2.5H_2O$, which has not been reported hitherto in the literature. The solution is colorless, very caustic, and quite viscous; the crystals are minute and settle very slowly. These facts caused some experimental difficulty. The time necessary for equilibrium extended over several weeks. Further time was consumed in allowing the solid to settle before removing a sample of clear solution because any filter soon became clogged.

The crystals, though small, were usually definitely shaped. One form observed consisted of triangular prisms with plane base and with a cap formed by an intersecting tetrahedron. A more common habit was one in which the prism was capped at both ends, and, most commonly, the prismatic portion was very short or even entirely lost, giving the appearance of more or less distorted polyhedra.

No direct isolation and analysis of these crystals were successful. Besides being in contact with a viscous, alkaline, and not easily separable mother liquor, the hydrate itself was extremely hygroscopic, so that the point of greatest interest—the proportion of water of hydration—presented the greatest analytical difficulty. For this reason tie-line extrapolation by graphical and algebraic means was relied upon to fix the composition of the solid phase. Under the experimental circumstances it was not easy to be absolutely sure about half a molecule of water, more or less, in the molecule of this hydrate. Error is summed up in the indirectly determined water content, and is enhanced by the quite large extrapolation and by the smaller molecular weight of water as compared with the other components of the system.

Algebraic computation yielded mean extrapolated composition 40.43 ± 1.45% V_2O_5; 39.43 ± 0.02% Na_2O; 20.14 ± 1.44% H_2O. Graphical extrapolation showed the composition to lie between the dihydrate and the trihydrate. Therefore the mean composition as calculated was compared with the theoretical composition of the hydrates containing 3, 2.5, and 2 molecules of water, as follows

	V_2O_5,%	Na_2O,%	H_2O,%	Av.
Theoretical composition, $Na_3VO_4{\cdot}3H_2O$	38.22	39.07	22.71	
Deviation of extrapolated composition	+2.21	+0.36	−2.51	1.71
Theoretical composition, $Na_3VO_4{\cdot}2.5H_2O$	39.72	40.61	19.67	
Deviation of extrapolated composition	+0.71	−1.18	+0.47	0.78
Theoretical composition, $Na_3VO_4{\cdot}2H_2O$	42.27	41.35	16.38	
Deviation of extrapolated composition	−1.84	−0.92	+3.76	2.17

Averaged over the three components, the deviation of extrapolated from theoretical composition is least in the case of the hemipentahydrate, confirming the composition of the solid phase for this region of the isotherm as $Na_3VO_4{\cdot}2.5H_2O$.

Metastable Curves.—Evidence of a metastable condition was noticed in the course of the experiments only in the vicinity of the isothermally invariant point G. Here, after the mixing of the phase complex, a metastable condition sometimes occurred before the more slowly attained stable state was reached. The results of analyses made at such times appear in the diagram as slight prolongations of the isotherms for $Na_3VO_4{\cdot}7H_2O$ (G to J) and $Na_3VO_4{\cdot}2.5H_2O$ (G to K).

The Sodium Hydroxide Branch (Curve HI).—This is the short curve extending from H to I on the isothermal diagram. The saturated solution in water was found to contain 41.00% of sodium oxide at 30° and had a density of 1.549. The solid phase appeared as very large thin, transparent plates having six or eight sides and of a very soft consistency.

Points on this curve were determined as shown in the diagram and table, but extrapolation to the solid phase failed to give definite results, because of the slight separation of the points. It was not attempted to isolate the solid phase in sufficient purity for analysis. From the work of Pickering[32] it is known to be the monohydrate, $NaOH{\cdot}H_2O$ and to be in equilibrium at 30° with a solution containing 54.1% of sodium hydroxide.

The results recorded and discussed in the foregoing paragraphs were obtained for one temperature, 30°, only and this work does not necessarily disprove the existence (metastable or stable) and correctness of the great variety of other compounds for the system over a wide range of temperature and conditions.

Summary

1. The solubility relations in the ternary system V_2O_5–Na_2O–H_2O at 30° only have been determined and a complete isotherm constructed.

2. Rose's method in the quantitative separation and determination of vanadium in a solution of a sodium vanadate was used because on the basis of accuracy and general suitability it was found by comparison to be superior for this purpose to several other methods.

3. The eight solid phases of this system having stable existence in contact with solution at 30° have been described, namely, sodium hydroxide monohydrate, $NaOH{\cdot}H_2O$; sodium orthovanadate hemipentahydrate, $Na_3VO_4{\cdot}2.5H_2O$; sodium orthovanadate heptahydrate, $Na_3VO_4.7H_2O$; sodium orthovanadate dodecahydrate, $Na_3VO_4{\cdot}12H_2O$; sodium pyrovanadate octadecahydrate, $Na_4V_2O_5{\cdot}18H_2O$; sodium metavanadate dihydrate, $NaVO_3.2H_2O$; sodium hexavanadate dodecahydrate, $Na_4V_6O_{17}{\cdot}12H_2O$; and V_2O_5 in a hydrated gel-like form.

4. Of these compounds, two have not been reported previously, namely, $Na_3VO_4{\cdot}2.5H_2O$ and $Na_4V_6O_{17}{\cdot}12H_2O$.

5. An apparatus has been described whereby the operations of sampling of a liquid phase and determination of its density may be performed conveniently.

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[32] Pickering, *J. Chem. Soc.*, **63**, 890 (1893).