plete at temperatures as low as 100°. All other ratios tried gave products more difficult to oxidize.

Mechanism of the Action of the Catalyst.—Summing up, the over-all mechanism is

$$V_2O_5 + K_2S_2O_7 + 2SO_2 \longrightarrow 2KV(SO_4)_2$$

$$2KV(SO_4)_2 + 2SiO_2 \longrightarrow K_2S_2O_7 + V_2Si_2O_7 + 2SO_3$$

$$V_2Si_2O_7 + O_2 \longrightarrow V_2O_5 + 2SiO_2$$

Experimental

Preparation of the Catalyst.—The catalyst used in this investigation was made according to example 2 of the Slama and Wolf patent.[10]

Potassium Vanadium Sulfate ($KV(SO_4)_2$).—This sulfate was made by melting potassium pyrosulfate in a round-bottomed flask and adding 10% potassium vanadate with stirring. Sulfur dioxide was then bubbled in until the melt had a bright green color. The melt was poured on an enameled iron slab. When cool, the mixture was broken up and placed in a beaker of water. It was filtered rapidly and washed free of excess pyrosulfate. $KV(SO_4)_2$ when dry was a yellowish green powder.

Acknowledgments.—The authors are indebted to Professor J. C. W. Frazer of the Johns Hopkins University for permission to use part of the investigation that was carried out under his direction. The authors also express their gratitude to the officers of the John Hopkins University for granting permission to use their laboratory facilities during the summer of 1936.

Summary

A new mechanism for the action of the vanadium pentoxide–silica–alkali pyrosulfate is proposed. The assumption, formerly accepted, that tetravalent vanadium is an intermediate is shown to be untenable. Evidence for the existence of trivalent vanadium as an intermediate is presented. The roles of alkali pyrosulfate and silica are explained.

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[10] Slama and Wolf, U. S. Reissue Patent No. 19,282.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

A Study of Heterogeneous Equilibria in Aqueous Solutions of the Sulfates of Pentavalent Vanadium at 30°

BY OSCAR E. LANFORD AND SAMUEL J. KIEHL

Introduction

Although vanadium pentoxide is known to be chiefly acid-forming in water systems, crystalline compounds containing vanadium pentoxide, sulfur trioxide, and water only were prepared long ago. Substances believed to be $V_2O_5 \cdot 2SO_3$, $V_2O_5 \cdot 3SO_3$ and $V_2O_5 \cdot 3SO_3 \cdot 3H_2O$ were reported and discussed by Berzelius, Gerland, Ditte and Munzing.

Moreover the only data available on the solubility of vanadium pentoxide in solutions of sulfuric acid, are those of Meyer and Aulich.[1] But these data are not entirely satisfactory because evidence of the attainment of equilibrium is lacking, no sulfate determinations were made, and, in addition, the only indication given of the sulfuric acid concentration of such solutions is the initial concentration of the sulfuric acid with which each solution was started. The authors conclude that, both at 25 and at 100°, the solubility curve shows two maxima, "between which lies presumably a region of colloidal solution." No information was given regarding the nature of the solid phase in contact with these vanadium pentoxide–sulfuric acid solutions.

In view of the fact that the compounds prepared by Berzelius represent more or less arbitrary stopping-points in the decomposition by heat of vanadium pentoxide–sulfuric acid solutions, a consideration of the three-component system $V_2O_5–SO_3–H_2O$ seems likely to add significantly to the existing knowledge.

Accordingly, a study was made at 30° (and at ordinary atmospheric pressure). The effect of changes in atmospheric pressure on the solubility in such systems is negligible.

Preparation and Analysis of Material

Vanadium Pentoxide.—The starting material was a fine yellow powder, analysis of which showed a vanadium pentoxide content of 99.75% and a weight loss of 0.19% on gentle ignition. Ten-gram portions of this product

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[1] Meyer and Aulich, *Z. anorg. Chem.*, **194**, 278 (1930).

showed negative qualitative tests for barium, tungsten, silica, and elements precipitated by hydrogen sulfide in acid or in alkaline solution. Within the limit of experimental error, the material was free from lower oxides of vanadium.

Freshly precipitated vanadium pentoxide was prepared conveniently by dissolving 15 to 20 g. of ammonium metavanadate in water and diluting to 1200 ml. approximately. This solution was heated to boiling and 3 *N* sulfuric acid added until the solution assumed a deep orange color. If, on continued boiling, the color of the solution faded, more sulfuric acid was added. (The solution should be neutral or slightly acid to litmus at this point.) After an incubation period of thirty minutes, golden crystals appeared. Boiling was continued, sulfuric acid added from time to time as the color faded, until precipitation was complete and the solution remained almost colorless even after the addition of acid.

This precipitate, settling quickly and easily filterable, was washed 12 to 15 times with water on a Büchner funnel. It was then air-dried either at room temperature or at 100° without undergoing change. The composition of the material prepared by this method at different times varied slightly, but approximated the following analysis: V_2O_5, 91.25%; loss on ignition (= $H_2O + NH_3$), 8.78%; $SO_4^=$, none. It was not found practicable to remove the last traces of ammonia by washing. An examination under the microscope revealed uniform lemon-colored, diamond-shaped, anisotropic crystals. Moreover, whatever the nature of this particular compound, it gave up the last traces of ammonia when warmed on a steam-bath with a sulfuric acid solution containing up to 30% sulfur trioxide. The final product was a red, freshly precipitated vanadium pentoxide, from which the ammonium ion was removed readily by washing with dilute sulfuric acid.

The advantage of this method over the simple decomposition of an alkali vanadate with acid is that less washing of the red, easily dispersed vanadium pentoxide is required, since most of the ammonium ion is removed prior to the formation of this difficultly filterable material.

Sulfuric Acid.—Sulfuric acid of the highest purity obtainable was used without further purification. By gravimetric analysis, the sulfur trioxide content was 77.51 ± 0.05%. By acidimetric titration against sodium hydroxide which had previously been standardized with potassium acid phthalate supplied by the Bureau of Standards, the sulfur trioxide content was 77.46 ± 0.06%, assuming all acid present to be sulfuric. It was within experimental error free from reducing substances and other substances which would interfere with the subsequent determinations of vanadium and sulfate.

Potassium Permanganate.—The potassium permanganate solutions were prepared according to the usual analytical procedure and standardized against sodium oxalate obtained from the Bureau of Standards by the procedure outlined in the certificate which accompanied it.

Sulfur Dioxide.—The sulfur dioxide for reduction was found (by performing blank vanadium determinations) to contain no substance which would affect the results of the analyses.

Barium Chloride.—For the sulfate determinations, barium chloride of the highest grade obtainable was employed.

Apparatus.—All apparatus for temperature control, stirring, containers and analytical work has been described previously.[2]

Experimental Procedure

Analytical Determinations. (a) **Sulfate.**—For the determination of sulfur trioxide the standard gravimetric method for sulfate was used. The barium chloride solution (0.05 *M*) was added dropwise to a hot solution agitated by an electrical stirrer. The precipitate was filtered into a porous-bottom Gooch type crucible, ignited to constant weight (in a muffle furnace at about 750°), and weighed as barium sulfate.

Experiments to ascertain whether the presence of pentavalent vanadium would affect the results of the sulfur trioxide determination were performed by the following procedure and a maximum ratio was established: a small amount of sulfuric acid was diluted to volume in a 1000-ml. volumetric flask, and 100-ml. portions taken for analysis; to these solutions were added, respectively, varying weights of ammonium metavanadate, and the sulfate content of each aliquot portion determined by the usual method. A summary of results of such determinations is given below.

Ratio of V_2O_5 to SO_3	Weight of $BaSO_4$, g.	Deviation caused by V_2O_5
No V_2O_5 present	0.5003	None
1:2	.5004	+0.0001
1:1	.5007	+ .0004
2:1	.5030	+ .0030

In all the experiments to establish the ratio the same amount of sample was used and the analytical precision covered by the first three cases was plus or minus two parts per thousand.

From the results of such determinations we were assured that the precision of the usual procedure for the determination of sulfate is not significantly affected by the presence of pentavalent vanadium in the samples provided the weight ratio of vanadium pentoxide to sulfur trioxide is not greater than one to one. The removal of the vanadium before the sulfate determination was therefore deemed unnecessary.

(b) **Vanadium Pentoxide.**—In view of the fact that the solutions contained no substances which interfere with the volumetric determination by the method described by Hillebrand and Lundell[3] this method was adopted. For the introduction of sulfur dioxide and later for the introduction of nitrogen to remove the sulfur dioxide, Folin ammonia tubes were used.

As a standard for vanadium pentoxide, ammonium metavanadate which had been recrystallized three times from water was taken. Aliquot portions of a solution prepared from it were reduced with sulfur dioxide and the vanadium determined by titration with (approximately 0.1 *N*) potassium permanganate. These values were checked with those obtained by the evaporation and ignition to vanadium pentoxide of similar portions of the solutions. The results were in good agreement. The average values with their deviations are: by permanganate titration, 0.4971 ±

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[2] Kiehl and Manfredo, THIS JOURNAL, **59**, 2118 (1937).

[3] Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929, p. 359.

0.0003 g. V_2O_5; by evaporation and ignition, 0.4969 ± 0.0005 g. V_2O_5.

(c) Water.—The third component, water, was determined by difference.

Attainment of Equilibrium.—In the attainment and recognition of equilibrium several criteria were employed: *first,* the composition of the solution remained constant over a period of at least a week, this being confirmed by the agreement of two analyses separated by this interval of time, and as a rule it being found profitable to perform density determinations as a preliminary criterion before making the first analysis. *Second,* the composition of the solution at equilibrium was approached from a lower and from a higher temperature; this was accomplished by preparing the complex containing the components in the desired ratio and stirring the mixture at 30° until the solution gave the other indications of having reached equilibrium; the mixture was then divided into two portions, one of which was held at 20° for one hour and the other, at 40° for the same length of time; each portion was then agitated at 30° until the same equilibrium point was reëstablished. *Third,* microscopic examination showed no change in the crystal form of the stable solid phase. In all difficult cases duplicate experiments were performed.

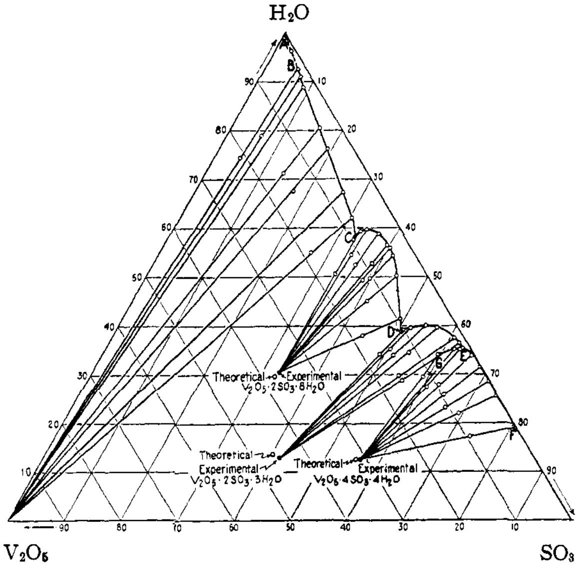

Fig. 1.—System V_2O_5–SO_3–H_2O, 30° isotherm, data in weight percentage.

The minimum length of time necessary to establish equilibrium in each particular region is not known exactly, since in most cases the bottles containing the complexes were allowed to remain in the thermostat for two or three weeks before any preliminary examination was made.

Preparation of Solutions and Experimental Technique.—The complexes consisting of the three components in the desired ratio were prepared, placed in the thermostat, and stirring by rotation started. After the proper interval, the rotation was stopped and the solid phase allowed to settle while the bottles remained in the thermostat. Samples of the solution for trial were drawn directly into the pycnometer[2] from time to time through a sampling tube[2] the bottom end of which was filled with glass wool to prevent the accidental introduction of solid phase. The solution was not exposed to the atmosphere for more than a few seconds. After the criteria of equilibrium had been satisfied, a portion of the solid phase was withdrawn by means of a Mohr pipet and transferred quickly to a previously weighed porous-bottom crucible supported in a suction flask to which a pump was connected. After a portion of the solution was removed by suction the crucible with contents was placed in a weighing bottle and the weight of the sample determined. The entire contents of the crucible were dissolved in water into a volumetric flask and aliquot portions taken for analysis. In no case was the solid exposed to the atmosphere for more than a few seconds prior to weighing.

Experimental Results

The experimental results for the isotherm at 30° are expressed as mole percentages in Table I. Each value for the liquid phase and for the moist solid is the mean of at least two determinations which agreed within the experimental error. The mole percentage of water, by difference, is omitted from Table I.

The data are plotted as percentages by weight on triangular coördinates in Fig. 1 because the tie-lines may be drawn more advantageously.

Discussion of Errors. Exposure to the Atmospheric Moisture.—Although many of the solutions and all of the solid phases, with the exception of vanadium pentoxide, appeared to be hygroscopic, they were not in any case exposed to the atmosphere for more than a few seconds. The longest exposure was in the sampling of the solid phase. Since such samples were normally several grams in weight, it is not likely that any appreciable error was thereby introduced.

Analytical Errors.—In every case, tests before analysis showed the solutions to be free of vanadium of a valence lower than five, as well as free of any other substances capable of reducing permanganate. On the basis of experimental confirmation of the methods for both vanadium and sulfate as described above, it may safely be said that the analytical results are not burdened with an error greater than three parts per thousand in the case of sulfate and two parts per thousand in the case of vanadium.

Precision and Accuracy of Results of Extrapolation.—In determining the point of intersection of the tie-lines by direct graphical methods it is impossible to attain a precision approaching the precision of the analytical work.[4] For that

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[4] Manfredo, "A Study of Heterogeneous Equilibria in Aqueous Solutions of the Vanadic Acids at 30°C.," Dissertation, Columbia University, 1936.

TABLE I

EXPERIMENTAL RESULTS EXPRESSED AS MOLE PERCENTAGES

Density at 30°	Solution, mole percentage		Moist solid phase, mole percentage		Solid phase	Point on curve, Fig. 1
	V_2O_5	SO_3	V_2O_5	SO_3		
0.996	0.011	0.000	2.42	0.00	....	
1.030	.094	.684	1.34[a]	.73[a]	....	
1.066	.172	1.428	2.63[a]	1.28[a]	V_2O_5	
1.070	.212	1.742	1.82[a]	1.71[a]	V_2O_5	
1.091	.270	2.150	..	...	V_2O_5	
1.178	.459	4.232	1.96[a]	4.02[a]	V_2O_5	
1.219	.587	5.341	2.03[a]	5.33[a]	V_2O_5	
1.319	.850	8.04	..	...	V_2O_5	
1.370	1.051	9.81	2.88	9.52	V_2O_5	
1.440	1.388	11.26	2.95	12.21	V_2O_5 + $V_2O_5 \cdot 2SO_3 \cdot 8H_2O$	C
1.418	1.060	11.11	2.68	12.55	$V_2O_5 \cdot 2SO_3 \cdot 8H_2O$	
...	0.870	11.32	1.75	12.97	$V_2O_5 \cdot 2SO_3 \cdot 8H_2O$	
...	.646	12.24	1.88	13.07	$V_2O_5 \cdot 2SO_3 \cdot 8H_2O$	
...	.600	13.53	1.36	13.96	$V_2O_5 \cdot 2SO_3 \cdot 8H_2O$	
1.443	.578	13.75	2.01	14.63	$V_2O_5 \cdot 2SO_3 \cdot 8H_2O$	
1.466	.620	14.58	1.74	15.01	$V_2O_5 \cdot 2SO_3 \cdot 8H_2O$	
1.519	.898	16.46	2.40	16.72	$V_2O_5 \cdot 2SO_3 \cdot 8H_2O$	
1.661	1.690	20.73	3.49	20.08	$V_2O_5 \cdot 2SO_3 \cdot 8H_2O$	
1.734	2.030	22.33	3.42	22.72	$V_2O_5 \cdot 2SO_3 \cdot 8H_2O$ + $V_2O_5 \cdot 2SO_3 \cdot 3H_2O$	D
1.717	1.920	22.26	3.52	23.62	$V_2O_5 \cdot 2SO_3 \cdot 3H_2O$	
1.694	1.690	22.34	2.69	23.23	$V_2O_5 \cdot 2SO_3 \cdot 3H_2O$	
1.695	1.580	22.47	2.89	23.57	$V_2O_5 \cdot 2SO_3 \cdot 3H_2O$	
...	1.020	23.20	3.06	24.71	$V_2O_5 \cdot 2SO_3 \cdot 3H_2O$	
...	0.710	24.34	2.29	25.36	$V_2O_5 \cdot 2SO_3 \cdot 3H_2O$	
...	.306	26.72	3.48	28.12	$V_2O_5 \cdot 2SO_3 \cdot 3H_2O$	
...	.311	28.15	3.57	29.15	$V_2O_5 \cdot 2SO_3 \cdot 3H_2O$	
...	1.280	28.00	2.54	30.16	$V_2O_5 \cdot 4SO_3 \cdot 4H_2O$ (metastable)	G
1.739	0.601	28.23	3.79	33.48	$V_2O_5 \cdot 4SO_3 \cdot 4H_2O$ (metastable)	
1.731	.560	28.28	3.41	33.12	$V_2O_5 \cdot 4SO_3 \cdot 4H_2O$ (metastable)	
1.708	.360	28.61	2.74	32.36	$V_2O_5 \cdot 4SO_3 \cdot 4H_2O$ (metastable)	
1.727	.056	30.22	2.16	32.97	$V_2O_5 \cdot 4SO_3 \cdot 4H_2O$	
1.745	.019	32.78	2.20	35.17	$V_2O_5 \cdot 4SO_3 \cdot 4H_2O$	
1.790	.018	36.91	2.63	38.11	$V_2O_5 \cdot 4SO_3 \cdot 4H_2O$	
1.799	.015	39.43	2.26	40.48	$V_2O_5 \cdot 4SO_3 \cdot 4H_2O$	
1.817	.014	48.93	2.59	47.75	$V_2O_5 \cdot 4SO_3 \cdot 4H_2O$	
1.714	.300	28.68	2.37	26.67	$V_2O_5 \cdot 4SO_3 \cdot 4H_2O$ + $V_2O_5 \cdot 2SO_3 \cdot 3H_2O$	E

[a] Indicates composition of original complex rather than composition of moist solid phase.

reason, a method of algebraic extrapolation was used.

As a more objective and a more highly satisfactory procedure for the evaluation of the composition of the pure compounds by the algebraic method, the method of least squares was used, because it affords a comprehensive solution of all the equations for the tie-lines for each respective compound. For example, there were in one case seven equations which would give twenty-one possibly different intersections, representing twenty-one possibly different values for each of the components. By the use of the method of least squares the one most probable value for each of the components within the limits of the analytical results was obtained. The values listed below for each of the pure compounds were determined by the method of least squares.

The values for the composition of the pure compounds as finally determined are burdened with the errors accumulating from all sources in the course of the work. These values are given in Table II.

TABLE II

	% V_2O_5	% SO_3	% H_2O
	$V_2O_5 \cdot 2SO_3 \cdot 8H_2O$		
Most probable extrap. compn.	36.56 ±0.70	33.29 ±0.89	30.15 ±0.55
Theoret. compn.	37.43	32.93	29.64
Dev. from theoret.	−0.87	+0.36	+0.51
	$V_2O_5 \cdot 2SO_3 \cdot 3H_2O$		
Most probable extrap. compn.	44.94 ±1.09	41.62 ±1.30	13.44 ±0.71
Theoret. compn.	45.94	40.40	13.66
Dev. from theoret.	−1.00	+1.22	−0.22
	$V_2O_5 \cdot 4SO_3 \cdot 4H_2O$		
Most probable extrap. compn.	30.18 ±0.54	56.68 ±0.65	13.14 ±0.36
Theoret. compn.	31.70	55.76	12.54
Dev. from theoret.	−1.52	+0.92	−0.60

Attempts made to verify the above values by isolation and direct analysis were unsuccessful. In every case the introduction of a solvent to remove the excess sulfuric acid resulted in the decomposition of the compound.

Discussion of Results

There are five branches of the solubility curve in the isotherm representing the range of liquid phase variation from solutions containing no sulfuric acid to solutions containing 80.93% sulfur trioxide by weight. In Fig. 1, curve AB represents a region in which colloidal solutions are encountered; curve BC, the range of concentrations in which V_2O_5 is in equilibrium with the solution; and curves CD, DE, and EF, the composition of solutions with which the solid phases $V_2O_5 \cdot 2SO_3 \cdot 8H_2O$, $V_2O_5 \cdot 2SO_3 \cdot 3H_2O$, and $V_2O_5 \cdot 4SO_3 \cdot 4H_2O$, respectively, are in equilibrium. In each case, a sufficient number of experimental points was determined to fix nearly exactly the course of the isotherm. In addition, three isothermally invariant points, C, D, and E, were experimentally determined. It was found possible also to follow one metastable curve (EG, Fig. 1) for a short distance.

The Branch (AB).—Freshly precipitated vanadium pentoxide shaken with pure water produces a brownish-red solid of variable composition in apparent equilibrium at 30° with a solution containing 0.106% vanadium pentoxide. Likewise with sulfuric acid solutions containing less than 5.83% by weight sulfur trioxide, the composition of the solid phase, in apparent equilibrium, was not determined. In this region, the phase encountered is perhaps similar to that previously described.[2] In such cases, the exact composition of the solid phase could not be determined.

The Vanadium Pentoxide Branch (BC).—The solid phase at equilibrium with solutions containing from 5.83 to 33.03% by weight of sulfur trioxide is anhydrous vanadium pentoxide. The tie-lines all intersect at the point on the isotherm representing pure vanadium pentoxide. Moreover, on account of the nature of the solutions, all that may be said is that the lowest concentration of sulfuric acid with which vanadium pentoxide is in equilibrium is less than 5.83% by weight sulfur trioxide.

The $V_2O_5 \cdot 2SO_3 \cdot 8H_2O$ Branch (CD).—This compound is stable in contact with solutions of sulfuric acid in which the ratio by weight of sulfur trioxide to water varies from 1:1.747 to 1:0.768. Solutions in contact with it are red. In large masses the solid appears to be brownish-red and to consist of minute needle-like crystals. The polarizing microscope revealed groups of extremely fine acicular incipient crystals possessing parallel extinction. Owing to the small crystal size, no interference figure was obtainable.

The $V_2O_5 \cdot 2SO_3 \cdot 3H_2O$ Branch (DE).—The solutions in contact with this solid phase are a deeper red than those in contact with the solid $V_2O_5 \cdot 2SO_3 \cdot 8H_2O$. The solid phase in large masses is also red. It is stable in contact with solutions of sulfuric acid in which the ratio by weight of sulfur trioxide to water extends from 1:0.768 to 1:0.558. An examination of the solid phase with the polarizing microscope showed that it consisted of transparent dichroic crystals. The dichroism varied from colorless to orange with crystal lengths, respectively, parallel and perpendicular to the analyzer. The crystal form is prismatic with basal pinacoids. The crystals are anisotropic, length slow with parallel extinction. The small size of the crystals prevented the observation of an interference figure.

Moreover, in the present investigation, considerable difficulty was encountered in the crystallization of the solids $V_2O_5 \cdot 2SO_3 \cdot 8H_2O$ and $V_2O_5 \cdot 2SO_3 \cdot 3H_2O$. At first, the sulfuric acid of these concentrations seemed capable of dissolving a very large amount of vanadium pentoxide, the rate of solution simply becoming slower as the solution became more concentrated and more viscous. In some cases, solutions containing approximately 35% by weight of vanadium pentoxide remained in the thermostat for approximately two months before crystallization occurred. However, as soon as crystallization did occur in one solution in each of these ranges of concentration, no trouble was encountered in causing crystallization in the other solutions by seeding. During the later work in these regions even seeding proved unnecessary. It is presumably in this range of concentrations of sulfuric acid that Meyer and Aulich[1] conclude that there is a region of colloidal vanadium pentoxide.

The $V_2O_5 \cdot 4SO_3 \cdot 4H_2O$ Branch (EF).—This solid has been found to be stable in solutions of sulfuric acid in which the ratio by weight of sulfur trioxide to water varied from 1:0.235 to 1:0.558. The color of solutions in equilibrium with this solid varies from light yellow in the more concentrated sulfuric acid solutions to brownish-red as the concentration of water is increased. In large masses the solid is light yellow. An examination of the material under the polarizing microscope revealed a mass of incipient crystals with an occasional one well developed. Such crystals are anisotropic, transparent yellow, and not pleochroic. Due to small crystal size, no interference figure was obtained.

No difficulty was encountered in causing crystallization in this range of concentrations. For a short distance (EG) it was possible to follow the curve which represents the composition of solutions existing in metastable equilibrium with this solid phase.

No observations were made in solutions containing more sulfur trioxide than the former value, which corresponds to 99.2% sulfuric acid.

The authors wish to acknowledge their indebtedness to Messrs. Ralph J. Holmes and Russel N. Thatcher of the Department of Mineralogy, Columbia University, for their help in the optical examination of the crystals of the compounds herein described.

Summary

1. Solubility relationships in the aqueous region of the three component system V_2O_5–SO_3–H_2O have been studied and the isotherm at 30° constructed.

2. The five solid phases encountered in this system are $V_2O_5 \cdot 4SO_3 \cdot 4H_2O$, $V_2O_5 \cdot 2SO_3 \cdot 3H_2O$, $V_2O_5 \cdot 2SO_3 \cdot 8H_2O$, anhydrous V_2O_5, and hydrated V_2O_5 of variable composition. None of the above pentavalent vanadium sulfate compounds has been reported previously in the literature. No indication has been found for the existence, under the conditions of these experiments, of either of the compounds of Berzelius.

3. Some of the crystalline properties of these compounds have been described.

4. A method for the preparation of pure, freshly precipitated, vanadium pentoxide has been given.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

Influence of External Resistance in the Cell Circuit on the Maxima in Polarographic Current–Voltage Curves

BY JAMES J. LINGANE

About four years ago, Brdicka[1] made the interesting discovery that the prominent maximum on the c. v. curve of the reduction of mercurous ions at the dropping mercury electrode was greatly decreased by inserting a high resistance in series with the electrolysis cell.[2] Brdicka investigated only the reduction of mercurous ions, and no studies of this effect have heretofore been reported in other cases. Since the reduction of mercurous ions is a unique case, involving as it does the ions of the electrode, we investigated various other cases to determine whether the resistance effect was a general phenomenon, or was peculiar to the discharge of mercurous ions.

Experimental

The c. v. curves (polarograms) were recorded photographically in the usual way with a Heyrovsky–Shikata type polarograph.[2,3] The ordinary style of cell was used, with a stationary layer of mercury on the bottom of the cell serving as the anode. Except when the maximum of oxygen itself was being studied (Fig. 2), air was displaced from the cell solution with nitrogen. Care was taken to exclude from the solutions accidental impurities which might have influenced the maxima.[2,4]

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[1] R. Brdicka, *Collection Czechoslov. Chem. Commun.*, **8**, 419 (1936).

[2] For a review of the fundamental theory and technique of the polarographic method, see I. M. Kolthoff and J. J. Lingane, *Chem. Rev.*, **24**, 1–94 (1939).

[3] J. Heyrovsky and M. Shikata, *Rec. trav. chim.*, **44**, 496 (1925).

[4] J. Heyrovsky, "Polarographie," in W. Böttger's "Die physikalischen Methoden der chemischen Analyse." Akademische Verlagsgesellschaft, Leipzig, Vol. 2, 1936, pp. 260–322.