

Fig. 1.—1, Absorption curve of the products of reaction of HCl and $(C_6H_5)_2NN(C_6H_5)_2$ in EPA at low temperature; 2, absorption curve of $(C_6H_5)_2N^+$. In both cases the vertical scale is arbitrary.

The difficulties encountered in establishing the presence of $(C_6H_5)_2N^+$ seem to be attributable not merely to its remarkable instability but also to the small contribution that it makes to the total absorption. This is not due to a small absorption coefficient; presumably this ion and the chloride ion are in equilibrium with diphenylchloramine according to the equation



the diphenylchloramine being ionized only to a small extent. The situation is quite analogous to that of triphenylchloromethane in such a solvent as chlorobenzene.

Summary

Of the many reactions that are ordinarily observed when acid is added to tetraphenylhydrazine, none is the initial reaction. The first process, which occurs rapidly even near the temperature of liquid air, is the formation of $(C_6H_5)_2N^+$, which we have identified by its absorption spectrum. If tetraphenylhydrazine is assumed to be in rapid equilibrium with the positive and negative diphenylnitrogen ions, the effect of an acid is to remove the negative ion and thus cause accumulation of the colored positive ion, a considerable part of which, however, presumably combines with chloride ion to form colorless diphenylchloramine. The chloramine and its positive ion are too unstable to be observable except at extremely low temperatures.

BERKELEY, CALIFORNIA

RECEIVED AUGUST 3, 1942

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

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

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Introduction

The hydrates of the sulfates of tetravalent vanadium reported in the literature by previous investigators are divided into two series by Mellor¹: the one, $VO_2 \cdot SO_3 \cdot xH_2O$ and the other $2VO_2 \cdot 3SO_3 \cdot xH_2O$. However, we believe that he entertains some doubt as to the number of hydrates in each, for he states: "... some of them may be mixtures representing arbitrary states in the process of dehydration." This uncertainty is more clearly substantiated if one considers the water ratio of each series. There are reported²⁻⁵ for the first series the following molecular ratios of H_2O/VO_2 :

SO_3 : 0, 1, 1.5, 2, 2.5, 3, 3.5, 5, 6.5, and for the second series, the molecular ratios of $H_2O/2VO_2 \cdot 3SO_3$: 0, 1, 1.5, 2, 3, 4, 6, 14 and 16.

Doubtless in many of the preparations, since the products depended upon drying at various temperatures up to 360°, it is quite possible that intermediate states of incomplete hydration were reached. For, at 360° insoluble $VO_2 \cdot SO_3$ is invariably precipitated from concentrated sulfuric acid. Then, too, Gerland³ dried the pentahydrate at 100° and reported not only $VO_2 \cdot SO_3 \cdot 2.5H_2O$, but also $VO_2 \cdot SO_3 \cdot 1.5H_2O$ by prolonged heating at that temperature.

By the same procedure Koppel and Behrendt⁵ reported $VO_2 \cdot SO_3 \cdot 2.5H_2O$ and $VO_2 \cdot SO_3 \cdot 2H_2O$. If, however, the heating was done at 125°, they obtained $VO_2 \cdot SO_3 \cdot 1.5H_2O$ and $VO_2 \cdot SO_3 \cdot H_2O$ at 150°. Moreover, by heating $2VO_2 \cdot 3SO_3 \cdot 4H_2O$ in the second series at from 140 to 160° they obtained

(1) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. IX, Longmans, Green and Company, New York, N. Y., 1929.

(2) J. J. Berzelius, *Phil. Mag.*, **10**, 321 (1831); **11**, 7 (1832).

(3) B. W. Gerland, *Chem. News*, **34**, 2 (1876); *Ber.*, **9**, 869 (1876); **10**, 2109 (1877); **11**, 104 (1878).

(4) J. W. Crow, *J. Chem. Soc.*, **30**, 453 (1876).

(5) I. Koppel and E. C. Behrendt, *Z. anorg. Chem.*, **35**, 154 (1903).

$2\text{VO}_2 \cdot 3\text{SO}_3 \cdot 3\text{H}_2\text{O}$; upon further heating, however, at 175° $2\text{VO}_2 \cdot 3\text{SO}_3 \cdot 1.5\text{H}_2\text{O}$ was obtained, which finally, by continued heating to 200° , changed to the anhydrous salt $2\text{VO}_2 \cdot 3\text{SO}_3$.

Furthermore, there is little information given as to the ratios of vanadium dioxide to sulfur trioxide or to water in the reported preparations of the salts. Other authors,³⁻⁵ besides, have reported failure in attempts to prepare hydrates by methods previously described.

From the above considerations and since nothing more than qualitative statements have been made as to the solubility of the various hydrates, it appears that a study of the system $\text{VO}_2\text{-SO}_3\text{-H}_2\text{O}$ would not only provide solubility data for the various hydrated sulfates of tetravalent vanadium, but also tend to clarify the available data. The results of such a study at 30° and under ordinary atmospheric pressure are given below.

Preparation of Materials

Vanadium Dioxide.—The vanadium dioxide was prepared from a very good commercial product which by analysis gave 99.92% of vanadium pentoxide and showed no measurable loss of weight upon ignition. The material was very finely divided and quite insoluble in water. However, a suspension of it was slowly reduced to a solution of tetravalent vanadium by sulfur dioxide, the excess of which was removed by heating the solution for about twenty-four hours on a water-bath while a stream of nitrogen passed through it. During this process a lilac or orchid precipitate was formed which Gain and Dritte⁶ identify as $\text{V}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. The expulsion of the sulfur dioxide by boiling, recommended in their procedure, was found to be impractical with more than a few grams of the vanadium pentoxide, because the very finely powdered oxide attached itself so firmly to the sides of the vessel that severe bumping approaching explosive violence at times, occurred. This difficulty was overcome by passing a stream of nitrogen through the solution while it was being heated on the water-bath.

The resulting precipitate was filtered on a fritted glass funnel and washed twenty times with hot water. In order to eliminate from our experiments any of the traces of soluble impurities which may have been in the anhydrous pentoxide, this washed precipitate only was used in preparing mixtures which were to be brought to equilibrium. By analysis this prepared dioxide was free from sulfur dioxide and was shown to have undergone no oxidation during exposure to the atmosphere in its preparation. The analysis, however, showed the compound to contain $1.3 \pm 0.7\%$ by weight of sulfur trioxide as an impurity which really was no impurity in the preparation of the vanadyl sulfates. In preparing the mixtures for solubility measurements of the solid phase $\text{VO}_2 \cdot \text{H}_2\text{O}$, however, it was an impurity. In this case the sulfur trioxide content was reduced to $0.3 \pm 0.2\%$ by agitating the finely ground ma-

terial in an atmosphere of nitrogen for one month in pure water which was changed twice each week. The dioxide was reground in a mortar each time the water was changed.

The sulfuric acid, the potassium permanganate and the barium chloride, have been discussed heretofore.⁷

Apparatus.—All apparatus and their standardizations for temperature control, for stirring, for analytical work and for other purposes have been described previously.^{8,9}

The containers were 250-ml. "non-sol" bottles tested for water tightness. The stoppers were sealed to the bottles with paraffin, as an added precaution, to prevent leakage while the samples were being agitated.

Analytical Determinations

Vanadium.—Since the vanadium to be determined was in the pure tetravalent state, the procedure was simple. The sample was dissolved and made up to a volume, aliquot portions of which were titrated directly with a standard solution of potassium permanganate in the presence of sulfuric acid. As an assurance that no oxidation had occurred, frequent checks were made by treating one of the aliquot parts with sulfur dioxide and titrating after removal of the excess. In no case was oxidation of the tetravalent vanadium observed.

In order to get the moist residue of the solid phase $\text{VO}_2 \cdot \text{H}_2\text{O}$, which is quite insoluble, into solution, the addition of an acid was necessary. Since the chloride ion did not interfere with the sulfate determinations, hydrochloric acid was used. Nevertheless, it was necessary to remove it from the aliquot by evaporation almost to dryness with sulfuric acid before titrating with permanganate. The sulfate thus formed, however, is the insoluble form of the normal vanadyl sulfate identified by Gerland⁸ as $\text{VO}_2 \cdot \text{SO}_4$ which is not to be confused with the $\text{VO}_2 \cdot \text{SO}_3$ discussed later in this investigation, a form quite soluble. This insoluble form was dissolved by boiling in a quite concentrated solution of sulfuric acid. The solutions so obtained were reduced with sulfur dioxide, prepared and titrated with a standard solution of potassium permanganate in the usual manner.

An alternate method for the analysis in the hydrochloric acid solution was used. In this procedure the tetravalent vanadium was oxidized to the pentavalent state with chlorine, and the determinations made, after the removal of the excess, according to a method developed by Walden, Hammett and Edmonds.¹⁰ The results obtained by the two methods were in close agreement.

Sulfate Determinations.—Sulfur trioxide determinations were made according to the standard method for sulfates.¹¹ Moreover, in our analytical procedure the removal of the vanadyl ion was deemed unnecessary because no serious interference due to coprecipitation occurred. This fact was confirmed by taking aliquot portions of a concentrated solution of the vanadyl ion and determining the sulfur trioxide content first in the presence of the ion and, second,

(7) O. E. Lanford and S. J. Kiehl, *THIS JOURNAL*, **62**, 1660 (1940).

(8) S. J. Kiehl and E. J. Manfredo, *ibid.*, **59**, 2118 (1937).

(9) E. J. Manfredo, "A Study of Heterogeneous Equilibria in Aqueous Solutions of the Sodium Salts of the Vanadic Acids at 30° , C.," Ph.D. Dissertation, Columbia University, 1936.

(10) G. H. Walden, L. P. Hammett and S. M. Edmonds, *THIS JOURNAL*, **56**, 57 (1934).

(11) H. A. Fales, "Inorganic Quantitative Analysis," Century Company, New York, N. Y., 1925.

(6) G. Gain and M. A. Dritte, *Compt. rend.*, **143**, 873 (1906).

after its removal from the aliquot portion by precipitation with ammonium hydroxide. The results from these experiments were in agreement within experimental error. The samples were filtered in a porous bottom Gooch type crucible, and dried in a muffle furnace at 600 to 700°.

Experimental Procedure

Individual mixtures were prepared by adding the moist vanadium dioxide monohydrate to solutions of water and sulfuric acid of definite ratio ranging from pure water to pure sulfuric acid. For mixtures with higher concentrations of sulfur trioxide, it was necessary to use fuming sulfuric acid. As a precautionary measure against oxidation all samples were placed under an atmosphere of nitrogen and hermetically sealed with paraffin. These mixtures were stirred by end over end rotation for a period of time which exceeded that necessary for the attainment of equilibrium.

In order to determine the time necessary for the attainment of equilibrium, duplicate samples were prepared by taking one of the mixtures, as prepared above, at apparent equilibrium, and dividing it into two parts: one of these was maintained at 0° for twenty-four hours with frequent stirring; the other was treated likewise at 70 to 100°; they were then agitated again at 30 ± 0.01° until equilibrium, with identical phases, was reached in both.

Three criteria were used to determine the establishment of equilibrium: first, the densities of the mother liquors remained constant at the same value for both of the duplicates; this served as preliminary criterion before analyses were made; second, the analyses of the mother liquors agreed within experimental error; third, microscopic examinations revealed a single identical solid phase of definite crystalline form in both samples.

The time necessary to establish equilibrium ranged from three days, approximately, with VO₂·SO₃·5H₂O, where the crystals grew rapidly in the less viscous solutions, to a year or more for the 2VO₂·3SO₃·4H₂O and VO₂·SO₃ in the highly viscous solutions of concentrated sulfuric acid.

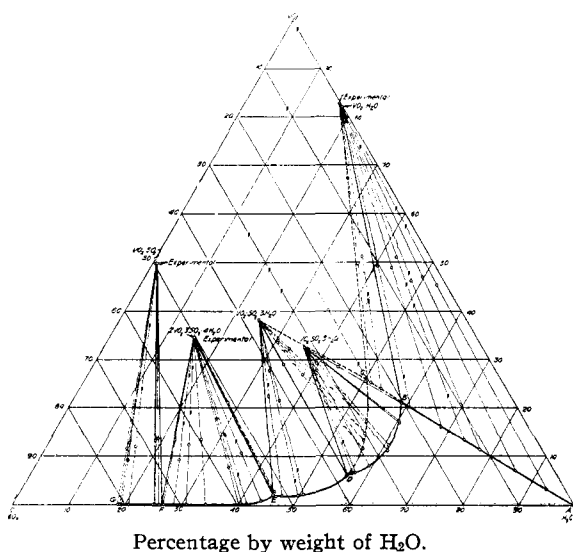


Fig. 1.—System VO₂·SO₃·H₂O, 30° isotherm, data in weight percentage.

The attainment of equilibrium by approach from both higher and lower temperatures was employed, because it afforded an opportunity for formation of all possible hydrates. While temperatures of 0 and 70° or above were not the most satisfactory for economy of time, they nevertheless gave further opportunity during a period of several weeks for the crystallization of any other possible hydrates from the various concentrated solutions. During this time, moreover, they were repeatedly subjected to alternate changes from high to low temperatures as well as to stirring. No matter what compound separated at lower temperatures or higher temperatures, the mixtures obtained finally at equilibrium by stirring at 30° were the hydrates represented in Fig. 1.

After equilibrium was attained, rotation of the solutions was halted, and the solid phase was allowed to settle. Samples for density determinations and for analyses of the mother liquor were taken by the use of the pycnometer and

TABLE I

Density	Liquid phase Percentages		Moist solid phase Percentages		Solid phase
	VO ₂	SO ₃	VO ₂	SO ₃	
0.996	0.0068				a
1.048	3.45	3.33	45.58	1.64	a
1.096	7.21	6.83	47.22	3.31	a
1.231	11.51	10.93	46.52	5.68	a
1.278	13.41	12.78	51.20	5.97	a
1.361	16.19	15.40	49.15	7.80	a
1.468	20.21	19.02	49.53	10.15	a
1.595	24.10	22.22	51.47	12.13	a m
1.639	25.41	23.38	49.92	13.36	a m
1.663	25.90	23.83	40.39	23.58	a m
1.508	21.14	20.09	28.67	27.58	b
1.473	17.24	22.35	29.08	29.27	b
1.461	17.28	22.50	29.84	29.88	b
1.427	12.40	26.77	29.48	30.70	b
1.422	11.24	27.40	29.40	31.12	b
1.416	8.11	32.35	27.85	31.82	b
1.436	6.70	35.44	29.05	32.16	b
1.441	6.52	36.11	28.51	32.37	b
1.535	17.35	28.09	32.51	34.32	c m
	17.36	28.09	34.43	35.25	c m
1.506	14.77	29.71	34.10	35.66	c m
1.496	13.52	30.72	33.77	35.78	c m
	11.73	31.64	28.96	34.67	c m
1.448	6.04	37.50	29.28	36.82	c
1.506	2.27	46.96	21.77	41.51	c
1.517	2.11	48.17	27.85	40.04	c
1.662	2.05	50.96	22.58	42.95	c
1.578	2.19	52.45	26.03	43.42	c
1.583	2.80	51.91	21.31	50.95	d m
1.589	2.51	52.27	17.82	51.49	d m
1.593	0.96	55.24	11.95	53.65	d m
1.622	.37	58.06	10.73	55.84	d
1.582	.275	58.89	17.87	54.60	d
1.717	.245	59.58	7.84	57.52	d
1.754	.072	65.52	13.61	59.59	d
1.783	.080	69.09	12.42	62.39	d
1.787	.080	71.16	9.40	65.52	d
1.795	.088	72.97	13.34	64.30	d
1.801	.097	73.67	13.84	66.89	e
1.844	.086	74.46	13.45	67.68	e
1.811	.081	74.56	12.27	68.40	e
1.827	.062	79.17	12.01	71.95	e
1.827	.041	80.18	9.16	74.52	e
1.835	.035	80.58	12.84	72.53	e
1.825	.036	81.02	11.73	73.59	e

a = VO₂·H₂O. b = VO₂·SO₃·5H₂O. c = VO₂·SO₃·3H₂O. d = 2VO₂·3SO₃·4H₂O. e = VO₂·SO₃. m = metastable.

TABLE II

	VO ₂	Percentage SO ₃	H ₂ O
VO ₂ ·H ₂ O			
Most probable calculated value	82.78±0.86	0.19 ±0.26	17.03±0.84
Value by analysis of purified compound	81.51	.30	18.2
Theoretical composition	82.16	.00	17.84
Deviation from the theoretical value	0.62	+ .19	-0.81
VO ₂ ·SO ₃ ·5H ₂ O			
Most probable calculated value	32.81±0.17	31.60±0.23	35.58±0.29
Value by analysis of purified compound	32.96	31.46	35.58
Theoretical composition	32.78	31.63	35.59
Deviation from the theoretical value	+0.03	-0.03	-0.01
VO ₂ ·SO ₃ ·3H ₂ O			
Most probable calculated value	38.25±0.20	36.83±0.14	24.92±0.24
Value by analysis of purified compound	38.41	36.67	24.92
Theoretical composition	38.22	36.88	24.90
Deviation from the theoretical value	+0.03	-0.05	+0.02
2VO ₂ ·3SO ₃ ·4H ₂ O			
Most probable calculated value	34.36±0.86	50.49±0.42	15.14±0.75
Value by analysis of purified compound	32.84	51.26	15.90
Theoretical composition	34.69	50.23	15.07
Deviation from the theoretical value	-0.33	+0.26	+0.07
VO ₂ ·SO ₃			
Most probable calculated value	49.81±2.80	49.28±2.37	0.91±1.50
Theoretical composition	50.89	49.11	0.00
Deviation from the theoretical value	-1.08	+0.17	+ .91

sampling tube described by Kiehl and Manfredo.⁸ The solid phase was sampled by placing some of the mixture at equilibrium in a glass porous bottom Gooch type crucible which permitted a rapid and more complete withdrawal of the mother liquor. Thus, in turn the accuracy of the extrapolation in the determination of the solid phase was increased. These samples of mother liquors and precipitates were in due course diluted and dissolved, respectively, with water in a volumetric flask and aliquot parts taken for the determinations of both vanadium dioxide and sulfur trioxide. The water was determined by difference.

Experimental Results

Table I gives the results of the analysis for the mother liquor and for the moist solid phase expressed in percentage by weight of vanadium dioxide, sulfur trioxide. The percentage of water may be obtained by difference. In order to be consistent throughout the paper, all reference to tables, solubility, etc., will, likewise, be expressed in percentage by weight of the respective components. The results plotted on triangular coordinate paper are shown in the accompanying figure.

Calculations

The composition of the solid phase at equilibrium was determined by the method of Schreinemakers.¹² But because the errors in plotting do not permit a sufficiently accurate determination of the composition of the pure solid phase, the

tie-lines were expressed by algebraic equations as described by Roozeboom.¹³

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 ten equations which would give forty-five possibly different intersections, representing forty-five 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 of the most probable compositions of the various compounds together with the deviation from theoretical composition are listed in Table II. Moreover, these values for the composition of the pure compound as finally determined are burdened with the errors which accumulated from all sources in the course of the work. The

(12) Schreinemakers, *Z. physik. Chem.*, **11**, 76 (1893).

(13) Bakhuis Roozeboom, "Die heterogene Gleichgewichte vom Standpunkte der Phasenlehre," 1911, Vol. 3, Part I, p. 149.

method of computation of the errors has been described.^{9,14}

There is more consistency in some of the most probable values for composition than the errors would indicate. For example, if one determines the deviation from the most probable value in each equation by substituting the value for one component (the one most probable value) and solving for the other, one obtains for the composition of $\text{VO}_2\cdot\text{SO}_3$: 49.81% \pm 0.99 vanadium dioxide, 49.28% \pm 0.96 sulfur trioxide, and 0.91% \pm 0.25 water. The larger deviations listed for this compound in the table are, of course, due to the acute angles of intersection of the tie-lines on the one hand and to the closely located points which represent the composition of the saturated solution and that of the moist solid phase, respectively, on the other.

Discussion of Results

The isothermal diagram Fig. 1 shows five solid phases: $\text{VO}_2\cdot\text{H}_2\text{O}$, $\text{VO}_2\cdot\text{SO}_3\cdot 5\text{H}_2\text{O}$, $\text{VO}_2\cdot\text{SO}_3\cdot 3\text{H}_2\text{O}$, $2\text{VO}_2\cdot 3\text{SO}_3\cdot 4\text{H}_2\text{O}$, and $\text{VO}_2\cdot\text{SO}_3$, at equilibrium, with their isothermally univariant liquid phase, respectively, in contact. Sufficient determinations were made to follow the course of the solubilities from pure water to 81.02% sulfur trioxide. No higher concentrations of sulfur trioxide were practicable since tetravalent vanadium was oxidized in the more concentrated solutions.

The Solubility Curve A-B-C for the Solid Phase $\text{VO}_2\cdot\text{H}_2\text{O}$.—The stable portion of the curve A-B has a range of solubility from 0.0068% of the unhydrated oxide in pure water to 21.2% VO_2 at 20.1% SO_3 , the invariant point B. This is the invariant point for the solid phases $\text{VO}_2\cdot\text{H}_2\text{O}$ and $\text{VO}_2\cdot\text{SO}_3\cdot 5\text{H}_2\text{O}$ in contact with the solution. It was determined by intersection. The portion B-C is a metastable range in which the solubility extends to a maximum value of 25.90% vanadium dioxide at the metastable invariant point C where the percentage of sulfur trioxide is 23.83. The invariant point C was established by direct analysis of the solution at equilibrium with the two solid phases $\text{VO}_2\cdot\text{H}_2\text{O}$ and $\text{VO}_2\cdot\text{SO}_3\cdot 3\text{H}_2\text{O}$. The solutions of this hydrate vary in color from an almost clear solution at point A to a solution which is so blue that it is almost opaque at the invariant point C. This hydrated oxide was described and identified by Gain and Dritte.⁶ A comparison of

the calculated value with one obtained by analyzing the purified compound as well as with the theoretical composition is given in Table II.

The Solubility Curve B-D for the Solid Phase $\text{VO}_2\cdot\text{SO}_3\cdot 5\text{H}_2\text{O}$.—The stable range of solubility for the solid $\text{VO}_2\cdot\text{SO}_3\cdot 5\text{H}_2\text{O}$ in this system is from invariant point B in Fig. 1 to the invariant point D. This point is the intersection of the two solubility curves B-D and C-D-E. At this point the percentage of vanadium dioxide is approximately 6.2 and that of sulfur trioxide about 37.3. No metastable equilibrium of this hydrate was observed. The color of the solutions of the compound in this region ranges from a very dark blue translucent solution at point B, 21.1% vanadium dioxide, to a blue of medium intensity at point D which contains about 6.2% vanadium dioxide.

Moreover, it was necessary to seed all the solutions in order to prepare this hydrate. After the crystals were once obtained, no difficulty was encountered in preparing the samples, as equilibrium was reached within three days or less after the seeding. The hydrate first appeared from a metastable saturated solution of the trihydrate which had been standing for a year or more.

On account of its stability, the slight viscosity of the solutions, and the larger size of the crystals, the removal of almost all of the mother liquor was accomplished quite easily. This made possible a much greater distance between the points representing the composition of mother liquor and that of the moist solid which determine the tie-lines on the diagram. For this reason the determination of the composition of this pure solid phase was made with greater precision.

In Table II a comparison of the most probable composition with the analytically determined composition and that of the theoretical will be found.

Gerland⁸ prepared the pentahydrate by heating the insoluble anhydrous $\text{VO}_2\cdot\text{SO}_3$ with a little water in a sealed tube to 150°. The resulting oily solution was boiled with alcohol to a gummy mass and dried over sulfuric acid. This remaining hard transparent mass when moistened with alcohol and left under a loose cover gradually assumed a crystalline form. The formula for it, he established by analysis. Koppel and Behrendt⁶ by allowing one of the lower hydrates to deliquesce on standing in air prepared small well-defined crystals from the resulting dark blue solution. These

(14) O. E. Lanford, "A Study of Heterogeneous Equilibria in Aqueous Solutions of the Sulfates of Pentavalent Vanadium at 30° C.," Ph.D. Dissertation, Columbia University, 1939.

crystals when washed with alcohol and ether gave analyses corresponding to $\text{VO}_2\cdot\text{SO}_3\cdot 5\text{H}_2\text{O}$.

The Solubility Curve C-D-E for the Solid Phase $\text{VO}_2\cdot\text{SO}_3\cdot 3\text{H}_2\text{O}$.—The solid phase $\text{VO}_2\cdot\text{SO}_3\cdot 3\text{H}_2\text{O}$ has a stable solubility range from the invariant point D to the invariant point E, 2.19% vanadium dioxide in 52.45% sulfur trioxide, in Fig. 1, which was established by direct analysis of a solution at equilibrium with the solid phases $\text{VO}_2\cdot\text{SO}_3\cdot 3\text{H}_2\text{O}$ and $2\text{VO}\cdot 3\text{SO}_3\cdot 4\text{H}_2\text{O}$. A metastable range extends from the invariant point D to the metastable invariant point C for this solid phase and vanadium dioxide monohydrate. It is of interest to note that there are two complete metastable solubility curves B-C and D-C above B-D, the curve for the pentahydrate in the diagram. The color of the saturated solutions of this solid varies from a very dark blue, almost opaque, solution at point C to a very clear, light blue solution at point E.

The trihydrate of the normal vanadyl sulfate may be isolated and purified without decomposition. It crystallizes readily into large, clear light blue crystals which permit removal of practically all of the mother liquor. A close agreement of the experimental with the theoretical value of the composition was therefore obtained, Table II.

In this study the hydrate was easily prepared at room temperature or slightly above by slowly adding concentrated sulfuric acid to the oxide suspended in a concentrated solution of vanadyl sulfate. These crystals of normal vanadyl sulfate trihydrate are reported by Koppel and Behrendt⁵ to appear when an acid solution is evaporated at 90°.

The Solubility Curve E-F for the Solid Phase $2\text{VO}_2\cdot 3\text{SO}_3\cdot 4\text{H}_2\text{O}$.—The solid phase of $2\text{VO}_2\cdot 3\text{SO}_3\cdot 4\text{H}_2\text{O}$ has a stable range of solubility from the invariant point E to the invariant point F. Invariant point F is somewhat indefinitely located at 0.10%, approximately, vanadium dioxide in about 73.0% sulfur trioxide. The difficulty in locating the percentage of sulfur trioxide for this point is apparent if one notes in Fig. 1 how nearly the curves E-F and G-F approach each other as an almost continuous line. However, in Table I it may be observed that there is a slight but definite tendency for increased solubility which would give an intersection at point F. A metastable range extends from point E to 2.80% vanadium dioxide in 51.91% sulfur trioxide.

The solutions of this solid phase vary in color from a very light blue in solutions of minimum sulfur trioxide to an almost clear solution in higher concentrations of sulfur trioxide.

Due to increased viscosity of the solutions and to the decreasing solubility of the solid phase, equilibrium was slowly attained. One to two months for the attainment of equilibrium was required in solutions of minimum sulfur trioxide while even longer times were required in the more concentrated solutions.

In Table II a comparison of the most probable calculated value with the analytical value and that of the theoretical value may be made.

While hydrates have been reported in this series carrying 16, 14, 6, 4, 3, 2, 1.5, and no molecules of water of hydration, the tetrahydrate alone appeared as a compound at equilibrium in this study. Throughout the course of this investigation it was found that if an insufficient time was permitted for attainment of equilibrium, intermediate stages were encountered. In these cases the tie-lines would fall at random between those for this solid phase and those for $\text{VO}_2\cdot\text{SO}_3$. This behavior would tend to support Mellor's¹ suggestion that some of the hydrates reported were intermediate stages in the process of dehydration.

The compound was found to be readily soluble in water and more slowly but quite soluble in absolute alcohol. Partial purification, nevertheless, was secured by first washing with ether-alcohol mixtures and finally with pure ether. It was reported by Gerland³ that this compound may be purified by washing with water or alcohol. Koppel and Behrendt⁵ also prepared it.

The Solubility Curve F-G for the Solid Phase $\text{VO}_2\cdot\text{SO}_3$.—The anhydrous vanadyl sulfate has a short range of stability in concentrated solutions of sulfur trioxide. In concentrations higher than about 83 or 84% sulfur trioxide, the tetravalent vanadium is oxidized to the pentavalent state. The solubility at 81.02% sulfur trioxide is 0.036%, expressed as vanadium dioxide, which increases to 0.097% in 73.67% sulfur trioxide. These solutions are almost clear.

The time necessary for attainment of equilibrium for this compound was not determined exactly, but a year or more was required. The samples described were agitated for several months and then allowed to stand for two years before consistent analytical results were obtained. The

crystals are white with a slight tint of blue. Direct analysis of the crystals was not successful since but a small amount was available. The crystals were very small and were contaminated always with the mother liquor of highly concentrated sulfur trioxide. They are very soluble in ether-alcohol or water solutions.

In Table II a comparison of the most probable calculated value with the theoretical value of the composition is shown.

Gerland³ identified an anhydrous normal vanadyl sulfate which he prepared by boiling the soluble hydrated sulfates in concentrated sulfuric acid. His resulting gray compound is very insoluble even in boiling water. While Gerland's insoluble compound was encountered in the course of this work, as previously mentioned, our anhydrous sulfate is quite soluble in water and dilute acid as well as in alcohol.

Summary

Solubility measurements are given for the ternary system $\text{VO}_2\text{-SO}_3\text{-H}_2\text{O}$ at 30° and an isothermal ternary diagram has been constructed.

Over the total range of solubilities these five compounds only, $\text{VO}_2\cdot\text{H}_2\text{O}$, $\text{VO}_2\cdot\text{SO}_3\cdot 5\text{H}_2\text{O}$, $\text{VO}_2\cdot\text{SO}_3\cdot 3\text{H}_2\text{O}$, $2\text{VO}_2\cdot 3\text{SO}_3\cdot 4\text{H}_2\text{O}$, and VO_2SO_3 , were found to exist as stable solid phases at equilibrium with the various solutions.

For purposes of inoculation, attempts were made to prepare other compounds prepared previously by methods described in the literature in order to establish equilibrium relationships for the other reported hydrates. But no evidence was found for their existence.

A soluble form of the anhydrous normal vanadyl sulfate found in our study has not previously been reported.

NEW YORK, N. Y.

RECEIVED AUGUST 13, 1942

[CONTRIBUTION OF THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Second Virial Coefficients of Gaseous Mixtures¹

BY A. E. EDWARDS^{1a} AND W. E. ROSEVEARE²

Introduction.—Accurate p - V - T data at low pressures are few for pure gases and are almost non-existent for gaseous mixtures. This paper reports on the theory and experimental techniques of an indirect method of determining the second virial coefficients of gaseous mixtures. The method consists of measuring the change in volume on mixing two different gases at constant temperature and pressure and does not require determinations of absolute densities of gaseous mixtures.

Theoretical.—In this paper the virial equation of state is used in the form³

$$PV = RT + BP + CP^2 + DP^3 + \dots \quad (1)$$

where B , C , D . . . are the second, third, fourth . . . virial coefficients. Pressures are expressed in mm. of mercury and volumes are expressed either in cc. or in Amagat units. The Amagat unit is considered to be 2.24×10^4 cc. for all gases used.

If two different gases are mixed at constant temperature and pressure, there is usually a change

(1) Original manuscript received February 25, 1942.

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(3) For a discussion of the various forms of the virial equation of state, see Hirschfelder, Ewell and Roebuck, *J. Chem. Phys.*, **6**, 205 (1938).

in total volume. The magnitude of this volume change depends upon the intermolecular forces between the molecular species making up the mixture and may be interpreted in terms of the virial coefficients of the pure gases and of the gaseous mixture in the following manner.

If n_1 moles of gas 1 and n_2 moles of gas 2, occupying volumes v_1 and v_2 , respectively, are mixed at constant pressure P and constant temperature T and if we neglect the effect of virial coefficients higher than the second,⁴ we may write

$$P(v_1/n_1) = RT + B_1P \quad (2)$$

$$P(v_2/n_2) = RT + B_2P \quad (3)$$

$$P(v_m(n_1 + n_2)) = RT + B_mP \quad (4)$$

where v_m is the volume occupied by the mixture and B_m is the second virial coefficient of the mixture. By combining these equations, we have for the volume change on mixing at constant temperature and pressure

$$\Delta v = v_m - (v_1 + v_2) = (n_1 + n_2)B_m - n_1B_1 - n_2B_2 \quad (5)$$

or in terms of the mole fractions in the mixture

$$\Delta v/n = B_m - N_1B_1 - N_2B_2 \quad (6)$$

(4) The contribution of virial coefficients higher than the second is very small at low pressures. It will be shown that no significant error is introduced in this work by neglecting these terms.