

amic acid (at 25°), ammonium sulfamate (at 20, 25, 35°), potassium sulfamate (at 20, 25, 35°) and sodium sulfamate monohydrate (at 25°).

3. The system ammonium sulfamate-sulfamic acid-water was studied at 25°; it forms

neither solid solution nor double compounds, and is marked by the very small effect of high concentrations of the salt on the solubility of the acid.

NEW YORK, N. Y.

RECEIVED NOVEMBER 27, 1946

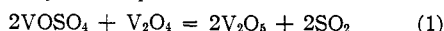
[CONTRIBUTION FROM INSTITUTT FOR UORGANISK KJEMI, NORGES TEKNISKE HØGSKOLE]

Investigations on the Equilibria in the System V_2O_4 , V_2O_5 , $VOSO_4$, SO_2 , SO_3

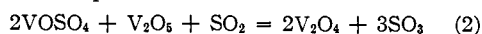
BY H. FLOOD AND O. J. KLEPPA

Introduction

In the presence of three solid phases the system V_2O_4 , V_2O_5 , $VOSO_4$, SO_2 , SO_3 is univariant. To each temperature corresponds a pressure of SO_2 , determined by the equilibrium



From the equilibrium



it is seen that p_{SO_3} is also determined.

When two solid phases are present, the system provides 1 univariant and 2 bivariant equilibria

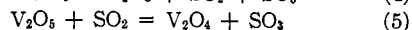
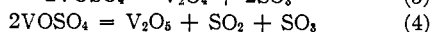
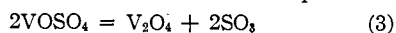


Figure 1 illustrates the conditions which at a given temperature allow for the existence of the three solid phases as functions of the partial pressure of SO_2 and SO_3 in the gas phase.

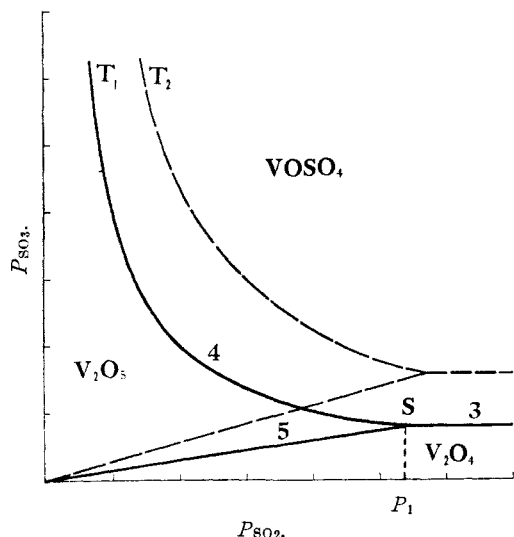


Fig. 1.—Conditions of existence of V_2O_4 , V_2O_5 and $VOSO_4$ as functions of the partial pressure of SO_2 and SO_3 .

The curves 3, 4 and 5 indicate the coexistence of two solid phases

$$p_{SO_2} = K_3 \text{ (curve 3)}$$

$$p_{SO_2} \cdot p_{SO_3} = K_4 \text{ (curve 4)}$$

$$p_{SO_2} \cdot p_{SO_3} = K_5 \text{ (curve 5)}$$

When $VOSO_4$ is heated in air it normally decomposes into V_2O_5 , SO_2 and SO_3 according to equation 4. Only when the partial pressure of SO_2 exceeds a certain limit (p_1 , see Fig. 1) will the decomposition proceed according to 3.

It will be seen that the intersection of the three curves (S) corresponds with the coexistence of all three solid phases.

The only information previously available on these equilibria refers to reaction 4. B. Neumann and A. Sonntag¹ measured K_4 using a static method. A. Ditte² has shown qualitatively that SO_2 at 500–600° reduces V_2O_5 to V_2O_4 .

Under the present investigation all three equilibria have been measured by a flow method. A current of SO_2 was led through a plug consisting of mixtures of V_2O_4 - $VOSO_4$, V_2O_5 - $VOSO_4$ or V_2O_4 - V_2O_5 , respectively. After having passed the contact the content of SO_3 was determined and the corresponding equilibrium constants for 3, 4 and 5 were calculated. The results of these investigations are given below.

Experimental

Preliminary investigations and calculations on these equilibria showed that at 500–600° a partial pressure of sulfur trioxide of 1–2% should be expected. The apparatus was constructed in accordance with this assumption.

From the bottle of sulfur dioxide (liquid) a slow current of gas was led at a constant rate through the two-phase-contact. Fig. 2a illustrates the arrangement of the contact. The gas is pressed from above through the contact-plug which is placed in a quartz tube. The temperature was measured by an iron-constantan thermoelement, checked at the melting points of tin, zinc and aluminum (99.99%). The temperature along the contact zone was within the limits of $\pm 1^\circ$, even before the contact proper was introduced. A constant temperature was secured by a lamp bank in the usual way.

Having passed the contact the gas mixture was led down through an Ahlintube, where the content of sulfur trioxide was adsorbed on asbestos as described by K. Schiel and H. Sieber³ (Fig. 2b). The adsorbed sulfur trioxide was removed by repeated washing with hot, boiled, distilled water. Afterwards sulfur dioxide was boiled out in a current of carbon dioxide, and the content of sulfur trioxide determined by titration with sodium hydroxide. The amount of sodium hydroxide was empirically corrected for the oxidation of sulfur dioxide to sulfur trioxide during the analytical procedure. This correction represented a con-

(1) B. Neumann and A. Sonntag, *Z. Elektrochem.*, **39**, 799 (1933).

(2) A. Ditte, *Compt. rend.*, **101**, 1487 (1885).

(3) R. Schepp and K. Schiel, *Papier-Fabr.*, **29**, 761 (1931); H. Sieber, *ibid.*, **23**, 209 (1925).

start reduction which varied within the limits 3-10% of the total amount of sodium hydroxide.

Before it entered the reaction tube the sulfur dioxide gas was dried by calcium chloride and phosphorus pentoxide, respectively. By using phosphorus pentoxide the rate of reaction seemed to be somewhat reduced, but apart from this no effect on the results was observed. Before entering the Ahl tube, part of the sulfur trioxide combined with moisture (from the asbestos), and formed a drop of oleum at the lower end of the quartz tube. This drop was carefully washed away with distilled water and the solution added to the rest of the sulfuric acid (sulfur trioxide, see above). The amount of sulfur dioxide, corresponding to the sulfur trioxide, was calculated from the known rate of gas flow, measured by a flow meter. The limits of error of this measurement were 1-2% depending on the flow of gas.

Stress was laid on finding the amount of sulfur trioxide in the gas mixture under quite stationary conditions, for instance: that the inner surface of the quartz tube was in adsorption equilibrium with the gas phase. The flow of sulfur dioxide gas was reduced as required in order to obtain a constant percentage of sulfur trioxide. This established the lower temperature limit to about 560°. The upper was approximately 650°, the sintering temperature of V_2O_5 .

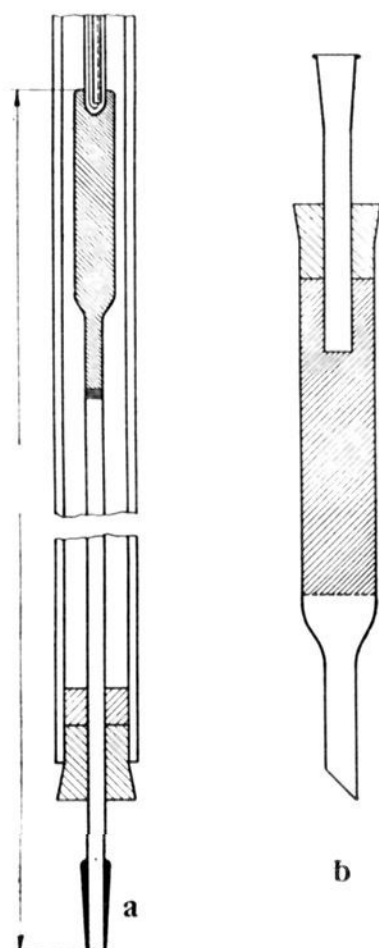
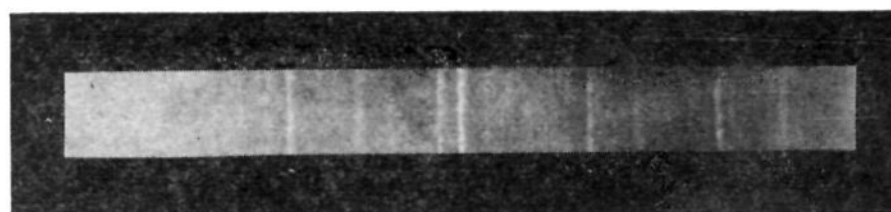


Fig. 2.—Arrangement of the contact-plug (a) and absorption tube (b).

The contact plug was prepared from V_2O_5 and $VOSO_4$, respectively, mixed with small pieces of quartz. Two different preparations of V_2O_5 were used, namely, purum and puriss, from Merck, Darmstadt. Consistent results were obtained with the two preparations, the only difference being that purum sintered at a somewhat lower temperature. $VOSO_4$ was prepared from $VOSO_4 \cdot 2H_2O$ (Merck). The water was removed by careful heating to about 300° in platinum crucible. By further heating to about 500° in an atmosphere of sulfur dioxide the last traces of water were lost, and the tendency again to take up water then seemed to disappear ("dead burning"). V_2O_4 was



(a) V_2O_4 (rutile)



(b) V_2O_4 (unknown)

Fig. 3.—X-Rays powder diagrams of: (a) V_2O_4 , rutile; (b), V_2O_4 , unknown.

prepared in the apparatus proper by reduction of V_2O_5 by sulfur dioxide. During a series of experiments a considerable part of the V_2O_5 might be reduced. In such cases the plug was reoxidized by sucking air through the apparatus for a short time. The difference in color between V_2O_5 (red-yellow) and V_2O_4 (blue-black) made easy a decision as to when reoxidation was required.

The composition of the solid phases was controlled by chemical analysis. The phases were identified and the modifications controlled by X-rays (powder-diagrams). During these investigations it was found that V_2O_4 formed by the reduction of V_2O_5 at temperatures below about 615° is not the well known tetragonal modification (rutile-lattice), but a modification not previously known to be described (Fig. 3).⁴ At temperatures above 615° mixtures which hold increasing amounts of the tetragonal modification were obtained.

Some experiments were carried out in order to ascertain the stability of the new modification. A complete transition into the rutile type lattice was easily attained by heating for a short period of time at 800° (inactive atmosphere). However, when heated for fourteen days at

(4) The editor of the Journal has brought to our notice the investigations of E. Hoschek and W. Klemm [*Z. anorg. allgem. Chem.*, **242**, 63 (1939)] on the system V_2O_4 - V_2O_5 . The authors prepared X-ray powder diagrams for different atomic ratios within this system. They found for pure VO_2 the lines of rutile lattice only (α -phase), while $VO_{2.08}$ showed a number of new lines as well as the α -lines.

"Ob es in dem Gebiet VO_2 bis $VO_{2.2}$ noch eine neue Verbindung existiert oder ob es sich um ein verzerrtes VO_2 -Gitter handelt, . . . kann erst durch weitere Untersuchungen durch thermische Analyse entschieden werden. Um diese Unklarheit anzudeuten bezeichnen wir vorläufig das Gebiet VO_2 - $VO_{2.2}$ als α' -Gebiet." ("Whether in the region from VO_2 to $VO_{2.2}$ there exists still another compound or whether there exists here a distorted VO_2 lattice. . . can only be decided by further investigation, utilizing a thermal analysis. In order to call attention to this uncertainty, we designate the region VO_2 to $VO_{2.2}$ as the α' region.")

By comparison of the lines of our V_2O_4 (unknown) with the characteristic lines of the " α' -region," we find that the lines are identical. There is the important difference, however, that our diagram shows the new modification with only quite negligible traces of the rutile modification, while the $VO_{2.08}$ of Hoschek and Klemm shows the lines of the rutile lattice with great intensity. In addition our product gives by chemical analysis VO_2 within the limits of analytical error.

This proves in the first place that the α' -phase is not a rutile lattice distorted by addition of more oxygen atoms and, secondly, it excludes the possibility of a new compound $VO_{2.1}$.

The problem needs further investigation, but it seems most likely to us that the existence of the α' -phase is a consequence of better conditions for the formation of the new VO_2 modification in presence of V_2O_5 .

605° neither modification showed any definite signs of change, judging by powder diagrams. The question of the stability is therefore still open.

Results

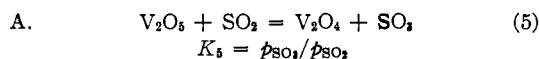


TABLE I

Limits of error for $\log K_5(\text{exp.}) = \pm 0.01$.

Temp., °C.	Temp., °K.	$-\log K_5(\text{exp.})$	$-\log K_5(\text{calcd.})$	V_2O_4 modification
654	927	1.656	1.665	Rutile
645	918	1.668	1.667	Rutile
643	916	1.682	1.681	Rutile
639	912	1.695	1.686	Rutile
633	906	1.699	1.695	Rutile
633	906	1.708	1.695	Rutile
633	906	1.695	1.695	Rutile
625	898	1.712	1.708	Rutile
618	891	1.723	1.717	Unknown
609	882	1.706	1.732	Unknown
605	878	1.740	1.738	Unknown
605	877	1.733	1.739	Unknown
590	863	1.801	1.762	Unknown
590	863	1.801	1.762	Unknown
589	862	1.759	1.764	Unknown
584	857	1.770	1.772	Unknown
576	849	1.777	1.785	Unknown
574	847	1.815	1.789	Unknown
570	843	1.801	1.795	Unknown
562	835	1.824	1.810	Unknown
558	831	1.813	1.816	Unknown

The values of $\log K_5(\text{calcd.})$ are calculated from the equation

$$-\log K_5 = \frac{1,216}{T} + 0.353$$

($T = 830\text{--}930^\circ\text{K.}$)

As two different modifications of V_2O_4 are involved, a change of direction of the curve for $\log K_5$ at a transition point might be expected. However, the experiments gave no definite evidence to this effect. This should perhaps indicate that the reaction V_2O_3 (unknown) \rightarrow V_2O_4 (rutile) will show only a minor change in enthalpy.

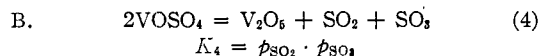


TABLE II

Limits of error for $\log K_4(\text{exp.}) = \pm 0.05$.

Temp., °C.	Temp., °K.	$-\log K_4(\text{exp.})$	$-\log K_4(\text{calcd.})$
599	872	1.32	1.31
598	871	1.34	1.33
591	864	1.51	1.50
590	863	1.52	1.53
582	855	1.72	1.70
581	854	1.76	1.76

The values of $\log K_4(\text{calcd.})$ are calculated from the equation

$$-\log K_4 = \frac{18,600}{T} - 20.01$$

($T = 854\text{--}872^\circ\text{K.}$)

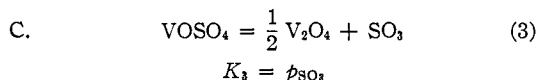


TABLE III

Limits of error for $\log K_3(\text{exp.}) = \pm 0.05$.

Temp., °C.	Temp., °K.	$-\log K_3(\text{exp.})$	$-\log K_3(\text{calcd.})$
570	843	1.90	1.90
558	831	2.07	2.08
539	812	2.32	2.37
537	810	2.38	2.39
527	800	2.51	2.55
526	799	2.57	2.57
525	798	2.64	2.58
524	797	2.64	2.59
523	796	2.72	2.60

The values of $\log K_3(\text{calcd.})$ are calculated from the equation

$$-\log K_3 = \frac{9,900}{T} - 9.84 \quad (T = 796\text{--}843^\circ\text{K.})$$

The three equilibria III, IV and V are interdependent according to the equation

$$2 \log K_3 = \log K_4 + \log K_5$$

This condition is fulfilled by the equations given above. If three solid phases are present, p_{SO_2} and p_{SO_3} will be determined through the equations

$$p_{SO_3} = K_3$$

$$p_{SO_2} \cdot p_{SO_3} = K_4$$

$$p_{SO_3}/p_{SO_2} = K_5$$

For $p_{SO_2} = 1$, $p_{SO_2} \gg p_{SO_3}$ and accordingly

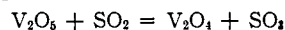
$$K_3 = K_4 = K_5$$

The three curves for K_p therefore will intersect at a single point, corresponding with the partial pressures

$$p_{SO_2} = \sim 1 \quad p_{SO_3} = \sim 0.02$$

From Fig. 3 it will be seen that this condition is also fulfilled by the experimental results. When $p_{SO_2} = \sim 1$ atm., the three solid phases are coexistent at $T = 854^\circ\text{K.}$ ($\pm 2^\circ$).

For the equilibrium



it was found that

$$-\log K_5 = \frac{1,216}{T} + 0.353$$

If it is assumed that the specific heat of the system is little changed by the reaction (complete data not available), we find

$$\Delta G_T^\circ = -RT \ln K_p = 5560 + 1.61 T$$

whence

$$\Delta G_{298}^\circ = 6040$$

$$\Delta H_{298}^\circ = 5560$$

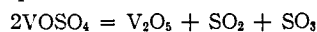
$$\Delta S_{298}^\circ = -1.6 [V_2O_4 (\text{unknown})].$$

(G = free enthalpy, thermodynamic potential, H = enthalpy, S = entropy). For reaction 5 a calculation of ΔS° from the generally accepted values for V_2O_5 , V_2O_4 (rutile) and SO_2 , combined

with the value for SO₃ (g) calculated by W. H. Stockmayer, G. M. Kavanagh and H. S. Mickley⁵

$$\Delta S_{298}^{\circ} = -4.8 \pm 1.1$$

For the equilibrium



the equation

$$-\log K_4 = \frac{18,600}{T} - 20.03$$

was found valid in the temperature interval 580–600°. This equation may be used to determine an approximate value for S₂₉₈^o (VOSO₄). If C_{p,SO₃} is set to 11, C_{p,SO₂} to 14, and applying Neumann-Kopp's rule for the specific heat of the solid, ΔC_{p,4} is calculated to -6. Accordingly we find

$$\Delta H_4 = 90,000 - 6T \text{ and}$$

$$\Delta G_4^{\circ} = 90,000 + 13.82 \log T - 137.91 T$$

The coefficient (137.91) is the average calculated from six experimental values varying within the limits 0.04.

Thus

$$\Delta G_{298}^{\circ} = 59,100$$

$$\Delta H_{298}^{\circ} = 88,200$$

$$\Delta S_{298}^{\circ} = 97.6$$

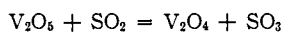
and

$$S_{298}^{\circ}(\text{VOSO}_4) = \frac{1}{2}(S_{298}^{\circ}(\text{V}_2\text{O}_5) + S_{298}^{\circ}(\text{SO}_3) + S_{298}^{\circ}(\text{SO}_2)) - \Delta S_{298}^{\circ} = 27.1$$

The aforementioned values for K₄ do not confirm those previously found by B. Neumann and A. Sonntag.¹ This is evident from Fig. 4, which gives log K = f(1/T) for the equilibrium in question, and where the values given by B. Neumann and A. Sonntag are also plotted. However, the temperature coefficient to a certain extent agrees with that of our own, but there is a difference in temperature of about 40°.

The values of B. Neumann and A. Sonntag¹ were measured by a static method where either phosphoric acid or "paraffin oil" was used as the manometric liquid. We are of the opinion that this procedure may give inaccurate results in view of the solubility in the liquid of the sulfur oxides. Since the sum of the partial pressures of two different gases is measured, a difference in solubility of the gases might also have influenced the results.

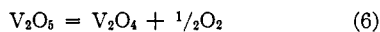
Other Reduction Oxidation Equilibria between V₂O₅-V₂O₄.—Combination of the two equilibria



and



gives the equilibrium



(5) W. H. Stockmayer, G. M. Kavanagh and H. S. Mickley, *J. Chem. Phys.*, **12**, 408 (1944).

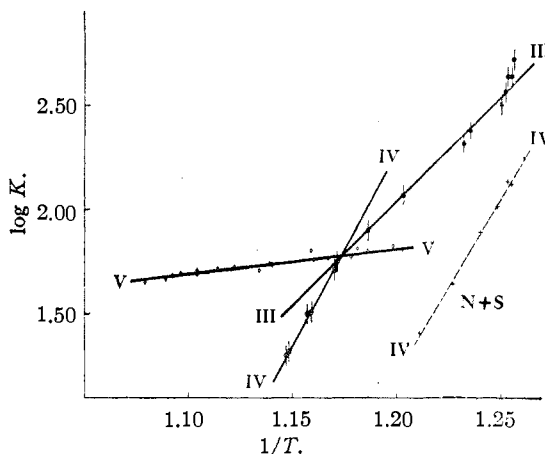


Fig. 4.—log K = f(1/T): (III) VOSO₄ = V₂O₄ + 2SO₃; (IV) VOSO₄ = V₂O₅ + SO₂ + SO₃; (V) V₂O₅ + SO₂ = V₂O₄ + SO₃; solid lines are own values; broken lines are B. Neumann and A. Sonntag's values.

For the SO₃-SO₂-O₂ equilibrium W. H. Stockmayer, G. M. Kavanagh and H. S. Mickley⁵ calculated

$$\Delta H_{298} = 23,490$$

$$\Delta G_{298}^{\circ} = 16,770$$

Hence, for the equilibrium V₂O₅-V₂O₄-O₂ we obtain

$$\Delta H_{298} = 29,050$$

$$\Delta G_{298} = 22,810$$

By combination of the experimental data for the SO₃-SO₂-O₂ equilibrium (M. Bodenstein and W. Pohl⁶ with our own data for the equilibrium V₂O₅-V₂O₄-SO₃-SO₂, the oxygen tension according to the reaction (in solid state)



is calculated to

t, °C.	p _{O₂} , atm.
400	2.5 × 10 ⁻¹⁰
500	4.5 × 10 ⁻⁸
600	3.5 × 10 ⁻⁶

These values are in satisfactory agreement with calorimetric data. For ΔH, W. G. Mixer⁷ gives 23,200 while H. Siemonsen and H. Ulich⁸ find 30,600 ± 600. The V₂O₄ phase presumably here is the rutile modification.

K. Iwasé and N. Nasu⁹ claim to have measured the oxygen tension over V₂O₅-V₂O₄ by manometer. They give the following data

$$\Delta G_{298(9)}^{\circ} = 7,900$$

$$\Delta H_{298(9)} = 14,300$$

$$\Delta S_{298(9)}^{\circ} = 15.6$$

These values completely disagree with our own, and give far too high oxygen tensions. It is

(6) M. Bodenstein and W. Pohl, *Z. Elektrochem.*, **11**, 373 (1905).

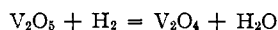
(7) W. G. Mixer, *Z. anorg. allgem. Chem.*, **78**, 222 (1912).

(8) H. Siemonsen and H. Ulich, *Z. Elektrochem.*, **46**, 141 (1940).

(9) K. Iwasé and N. Nasu, *Tôhoku Imp. Univ., Honda Anniversary*, 1936, p. 476.

easy to point out errors in the calculations of K. Iwasé and N. Nasu, but this will not greatly change the order of the figures.

Lastly may be mentioned that H. Müller¹⁰ claims to have measured the equilibrium

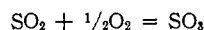


He finds

$$K_p = p_{\text{H}_2\text{O}}/p_{\text{H}_2} = 7.6, 21.2, 23.3$$

at 496, 530 and 600°, respectively. If $\log K_p$ is plotted against $1/T$ in the usual way, it will be evident that the values for K_p do not refer to an equilibrium.

VOSO₄ and Contact Process for Sulfuric Acid. B. Neumann, H. Panzner and E. Goebel,¹¹ have shown that a V₂O₅-catalyst for the reaction



showed a maximum catalytic effect at a certain temperature. The position of the maximum is shifted by a change in the rate of gas flow, but at moderate rates it is around 500–550°. They try to explain this by assuming that the maximum catalytic effect is related to the coexistence of the three phases V₂O₅, V₂O₄ and VOSO₄. This explanation is obviously incorrect (since three solid phases are coexistent at one temperature only). Our data, however, indicate that the maximum catalytic effect is obtained near the decomposition temperature of VOSO₄, accord-

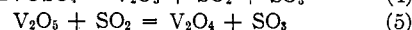
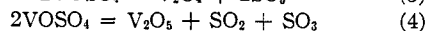
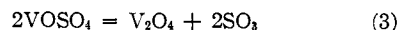
(10) H. Müller in W. Biltz's "Festschrift Hannover" (1927) (quoted by J. W. Mellor, Vol. IV, p. 744).

(11) B. Neumann, H. Panzner and E. Goebel, *Z. Elektrochem.*, **34**, 696 (1928).

ing to reaction 4. For the working conditions of B. Neumann, H. Panzner and E. Goebel, this temperature has been calculated to about 530°.

Summary

The equilibria



have been investigated by a flow method. The equations given below reproduce the results with good approximation

$$-\log K_3 = \frac{9,900}{T} - 9.84 \quad (520 - 581^\circ)$$

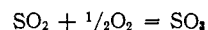
$$-\log K_4 = \frac{18,600}{T} - 20.01 \quad (581 - 600^\circ)$$

$$-\log K_5 = \frac{1,216}{T} + 0.353 \quad (550-650^\circ)$$

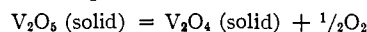
By V₂O₅ reduction, (VOSO₄) a modification of V₂O₄ not previously described,¹² is found at temperatures below 615°.

From the data for reaction 4 $S_{298}^{\circ}(\text{VOSO}_4)$ has been calculated to 27.1.

By combination of the data for reaction 3 (above) with those for the reaction



data for the equilibrium



has been calculated.

(12) Compare ref. 4.

TRONDHEIM, NORWAY

RECEIVED SEPTEMBER 28, 1946

[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT, MONSANTO CHEMICAL COMPANY]

Isomerization of Alkyl Phosphites. VI. Reactions with Chlorides of Singular Structure

BY GENNADY M. KOSOLAPOFF

The synthesis of phosphonic acids and their derivatives by the interaction of esters of phosphorous acid with alkyl halides is generally practicable only in the case of primary halides. The only recorded instance of a successful reaction involving non-primary halides is that of Arbuzov's synthesis of dialkyl triphenylmethanephosphonates from triphenylhalomethanes.

It was felt that it should be possible to effect the phosphonation reaction, with alkyl phosphite derivatives, with carbon tetrachloride, which in a number of instances displays a certain degree of reactivity of at least one chlorine atom. This expectation was realized and good yields of esters of trichloromethanephosphonic acid were obtained by the reaction of an excess of carbon tetrachloride

(1) A. E. and B. A. Arbuzov, *J. Russ. Phys.-Chem. Soc.*, **61**, 217 (1929).

with triethyl phosphite and tributyl phosphite. However, the reaction of carbon tetrachloride with an excess of the trialkyl phosphite, which was attempted with the expectation of poly-phosphonation, led to elimination of but two equivalents of alkyl chloride from the reaction mixture, which could not be resolved into definite products. Similarly, attempts to isolate definite products of poly-phosphonation from reaction mixtures of carbon tetrachloride with an excess of either sodium diethylphosphite or sodium dibutylphosphite were unsuccessful. In the first instance there was isolated only an undistillable gelatinous product which was chlorine free, as well as small amounts of diethyl phosphite and triethyl phosphate. In the second instance, a small amount of an unstable product, which was essentially chlorine free and which contained 25.5% phosphorus, was obtained.