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The action of vanadium catalysts in the sulfur trioxide synthesis[☆]

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In this first article, an account is rendered of investigations carried out to determine the action of vanadium catalysts in the sulfuric acid contact process.

The catalyst examined was vanadium pentoxide–alkalipyrosulfate on kieselgur. It was proved that during the reaction the vanadium compounds of the catalyst were dissolved in a highly viscous melt which covers the carrier with a film.

Those alkaline metals which produce compounds with a higher sulfur trioxide content than pyrosulfates were shown to be the most suitable catalyst components. The metals concerned are K, Rb, Cs and among the heavier ones T1, whereas Na, Ba and Ag, which do not form compounds with higher sulfur trioxide content than pyrosulfates, make less active catalysts.

Some further investigations were made, as, for instance, measurements of the absorption of light in films of melt to determine the varying valences of vanadium, but as yet no uniform results have been obtained.

The oxidation of sulfur dioxide to sulfur trioxide, which is one of the most important processes in chemical industry, has been the object of extensive investigations and many catalysts have been developed for the process.

Among these, especially the oxides of nitrogen, and in the contact method platinum and vanadium compounds, have become technically important, but whereas the uncatalyzed process, as well as also the action of the platinum catalyst (in so far as the speed determining steps of reaction are known) especially are set out in the works of Bodenstein et al. [1–4], the vanadium contact reaction mechanism is still very disputable. For instance, as yet it is not established whether the vanadium contact operates by homogeneous or heterogeneous catalysis.

The process may roughly be divided into the following successive reactions:

(1) Diffusion of SO_2 and O_2 to the outer surface and when using a porous catalyst body through the pores to the inner surface.
(2) Diffusion in a possible microphase, eventually absorption.
(3) The chemical reaction.
(4) Desorption.
(5) Diffusion of SO_3 from the catalyst.

When using a platinum-catalyst the speed determining process according to Bodenstein is diffusion of the reactants through the microphase to the active centers. As to the vanadium contact, the process is as yet not entirely clear and may be complicated by the fact that the speed determining process does not remain the same in the entire temperature range.

Not even the question as to the successive steps through which the chemical reaction progresses has as yet been answered, and also as to the range of valences for the active vanadium compound, different opinions have been set forth. Neumann et al. have studied the action of a series of oxide contact materials, and for the vanadium contact process adopted a valence shift between 5 and 4 [5–7], whereas Frazer and Kirkpatrick [8] state that the oxidation of vanadium alternates between 5 and 3, and that tetravalent vanadium is not stable under normal reaction conditions.

On one point, however, the investigators seem to agree. The catalytic agent, when not yet activated, is alkaline and absorbs sulfur trioxide during the reaction. The theory relative to a sulfatizing of the catalyst has been set forth by Neumann for the active vanadium compounds and by Boreskov and Pliigunow [9] for the alkaline metals added as promotors. Frazer and Kirkpatrick state that V_2O_5 and alkali-pyrosulfate form a highly viscous film on the carrier. Finally, we have demonstrated that such alkaline metals, which are known to produce compounds with a higher SO_3 content than pyrosulfates are the best activators.

According to Weber [10], the metals concerned are K, Rb and Cs and among the heavier ones Tl, whereas Na and Ag do not form such compounds. Experimentally, we have

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demonstrated that K, Rb and Tl are far better activators than Na, Ba and Cu. V_2O_5 itself, though preferably appearing as acid anhydride, also combines with SO_3, forming, for instance, at 30 °C solid phases of the formulae $V_2O_5{\cdot}4SO_3{\cdot}4H_2O$ and $V_2O_5{\cdot}2SO_3{\cdot}3H_2O$ [11] and at temperatures up to several hundred degrees compounds of the type $V_2O_5{\cdot}3SO_3$ and $V_2O_5{\cdot}2SO_3$ [12].

According to our investigations, the chemical condition of the ordinary alkali promoted vanadium catalyst on kieselguhr, defined, for instance, in U.S.P. 1,371,004 [13] is as follows: on a skeleton, inactive as far as the chemical processes are concerned, the active catalyst is found as a highly viscous film of xK_2O, yV_2O_5, zSO_3. The sulfur trioxide content varies with the reaction conditions, as, for instance, temperature and partial pressure of sulfur trioxide in the gas. Therefore, it cannot be expected that the catalyst, after being allowed to cool, has the same sulfur trioxide content as during the reaction period, and the actual composition of the catalyst during the reaction period cannot be determined by simply weighing a sample taken from a converter.

By weighing portions of the catalyst before and subsequent to the activation we have, however, found weight increases equivalent to compounds with a SO_3 content essentially higher than that of pyrosulfate.

Subsequent to these investigations, we successfully tried to accomplish the reaction with a catalytic agent which was liquid at the temperature at which the reaction took place—400–600 °C, and the components of which were those chemicals – i.e. pyrosulfates and vanadium compounds – which form an active part of the above catalysts. Based hereon, we have developed an altogether new principle for the oxidation of sulfur dioxide. A description hereof will be given in a later article; here, we shall describe a series of investigations on vanadium catalysts of conventional type.

1. Apparatus

Our apparatus was very similar to the one described by Olsen and Maisner [14], the converter, however, being quite different.

The set-up roughly consisted of two purification systems, one for air and one for sulfur dioxide, a mixing bottle, converter and measuring aggregate as shown in Figs. 1 and 2.

The air comes from an ordinary air cylinder (1) containing either normal air or a special mixture 88% N_2–12% O_2 and is regulated by the reduction valve (2), passes the cleaning bottles (3) with glass wool and (4) with concentrated sulfuric acid, the pressure regulators (5) and (6) the calcium chloride tube (7), is measured in the flowmeter (8) and finally passes into the mixing bottle (14).

Sulfur dioxide is taken from the sulfur dioxide cylinder (9), is regulated by means of the needle valve (10), passes the scrubber with concentrated sulfuric acid (11), the pressure

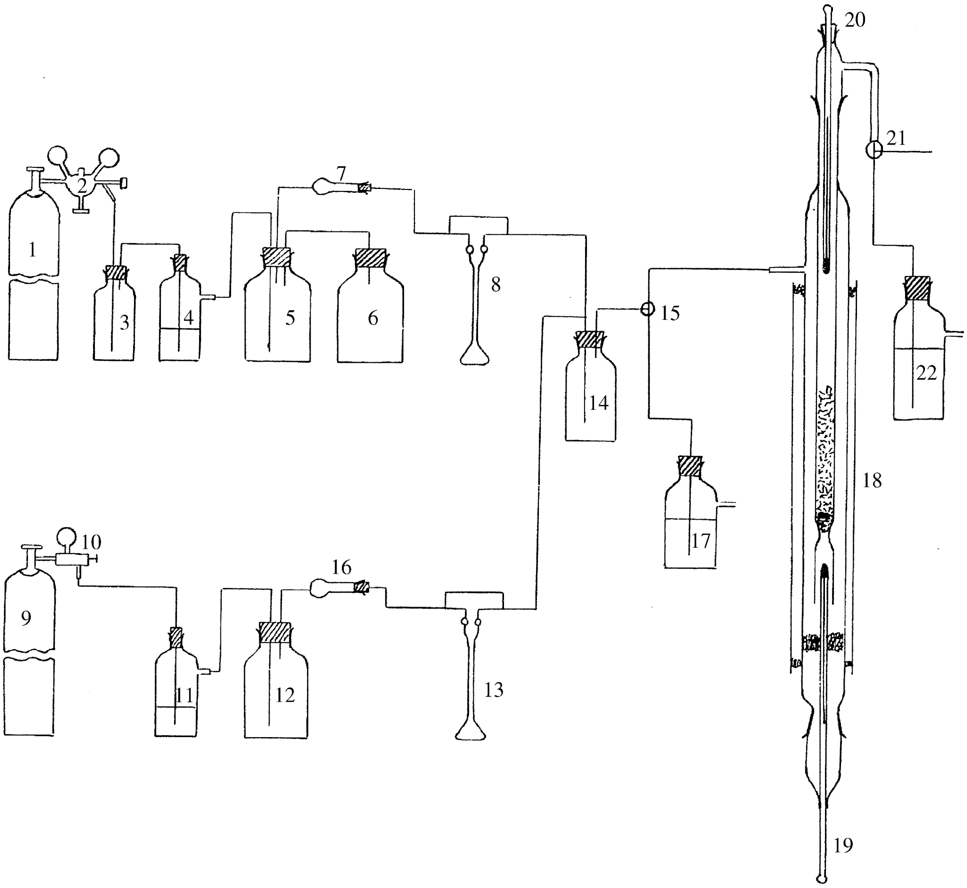


Fig. 1.

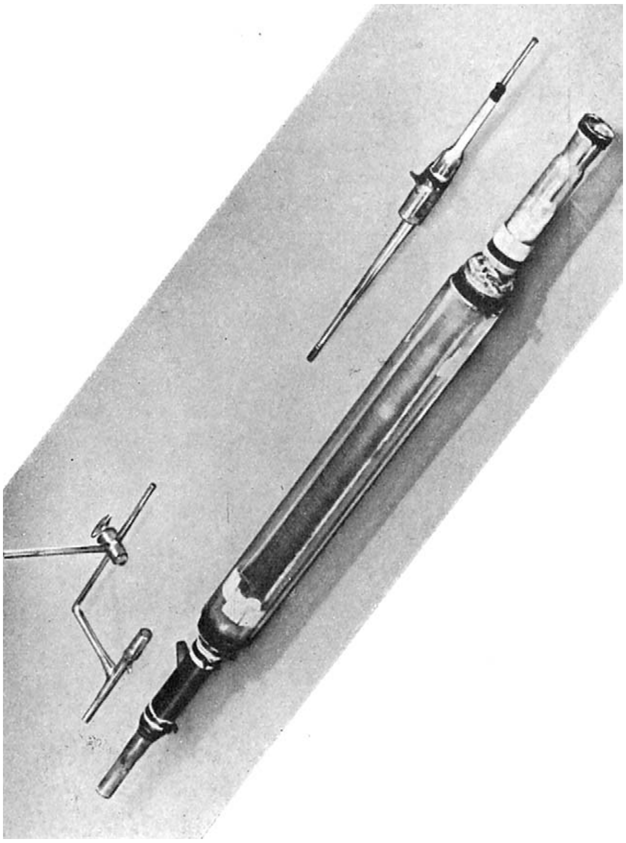


Fig. 2.

regulator (12), the calcium chloride tube (16), the flowmeter (13) and passes into the mixing bottle (14).

When measuring, the inlet gas is taken out by the threeway-stopcock for analysis in (17), whereas the gas normally is passed from the mixing bottle to the converter (18). The converter itself (18), as also the outer insulating glass tube, are made solely of Pyrex glass, making it possible at all time to follow the colors of the catalyst.

As shown in Fig. 1, the gas is preheated in the downward flow and subsequently in the upward flow, before it passes the catalyst layer.

The outlet on the top piece is equipped with a threeway-stopcock (21) so that, for one, the gas may be led to analysis in (22) or may be let out, beforehand bubbling through a pressure regulator giving same pressure-drop as in (22) and (17). This arrangement permits an adjustment to constant gas flow through the system, thereafter changing to gas analysis of the inlet gas or exhaust gas without changing the rate of flow.

The converter is equipped with electric heating coils so that it may be heated to approximately 550 °C. The heating is regulated through a variable transformer.

(19) and (20) are thermometers (0–620 °C, 1°) which register the temperature in the gas immediately before and after the catalyst.

The temperature in the reaction zone itself is not measured. The temperatures given below are the temperatures in the gas immediately before the catalyst.

2. Procedure

The conversion was determined as described by Olsen and Maisner in the said article.

By means of the flowmeters the rate of flow for air and sulfur dioxide was adjusted to the desired value, and subsequently the discoloration period for an acid solution of potassium permanganate with a known quantity of permanganate was measured for inlet gas as well as for exhaust gas. In respect of the procedure, which has proved easy and exact, further reference is made to the said article [14].

3. Catalyst quantities and rate of flow

In practically, all of our measurements 30 cc contact mass has been used and as the inside diameter of the converter is 18 mm, this is equivalent to a catalyst layer of 12–13 cm.

The normal rate of flow applied is $N = 13.5\ \mathrm{l}_{0^\circ,760\ \mathrm{mm}}$ at 7% SO_2/h–225 ml at 7% SO_2/min, equivalent to a speed $v = 90$ cm/min, calculated for the entire cross-section of the pipe filled with contact bodies. The speed is converted to NTP.

Compared with the catalyst quantity our normal velocity is only 2/3 of the normal velocity generally used in technical converters, but we usually try out each catalyst at speed 1, 1.5, 3 and 5 times our normal velocity, just as we have also normally tried each catalyst at different temperatures as, for instance, 449, 424, 408 and 395 °C. The temperatures are here still measured in the gas flow immediately before the catalyst layer.

4. Catalyst preparation

First, we shall briefly describe the preparation of our catalyst A.1, which does not differ greatly from the one described in U.S.P. 1,371,004 [12].

Five grams NH_3VO_3 p.a. is dissolved in water. An aqueous solution of 5 g KOH p.a. is added, and the ammonia is boiled off. The alkaline KVO_3-solution is poured on 35 g acid washed calcinated kieselgur (Merck) in a mortar, and the mixture is thoroughly treated for half an hour.

Subsequently, the mortar is placed in a drying oven at 100–120 °C.

When the mass is of a suitable consistency, it is formed into cylindrical bodies 4 mm in diameter and 4–6 mm long.

The bodies are dried in a drying oven at approximately 100–150 °C and placed in the reaction apparatus where they are activated by passing air and sulfur dioxide through at 450–500 °C.

The catalyst is always kept in constant reaction for 24 h before the conversion is measured.

When the catalyst A.1 is activated it has a vanadium content of about 4%, the molecular proportion K/V being about 2/1.

Hereinafter, the catalysts prepared by us are indicated by a letter having reference to the carrier used, and a number referring to the chemical composition.

Table 1

Temperature (°C)	Rate of flow[a]	Conversion
S.1 30 cc		
449	1.5*N*	96.7
449	3*N*	96.7
449	5*N*	96.5
424	1.5*N*	97.7
424	3*N*	97.8
424	5*N*	97.3
408	1.5*N*	98.3
408	3*N*	98.0
408	5*N*	95.8
395	1.5*N*	78.0
S.10 30 cc		
449	1.5*N*	96.4
449	3*N*	87.4
449	5*N*	70.0
424	1.5*N*	79.0
S.11 30 cc		
449	1.5*N*	91.8
449	3*N*	73.0
449	5*N*	57.0

S.1: K/V = 2/1; S.10: Na/V = 2/1; S.11: Na/V = 2.8/1.7% SO_2, 11% O_2, 82% N_2.

[a] $N = 13.5$ l at 7% SO_2/h.

Table 2

Temperature (°C)	Rate of flow[a]	Conversion
A.2 30 cc		
396	1*N*	98.5
396	1.5*N*	97.6
396	3*N*	97.0
396	5*N*	96.5
A.4 30 cc		
396	1*N*	98.4
396	1.5*N*	97.6
396	3*N*	94.1

7% SO_2, 19% O_2, 74% N_2.

[a] $N = 13.5$ l at 7% SO_2/h.

5. Experimental results and the interpretation of same

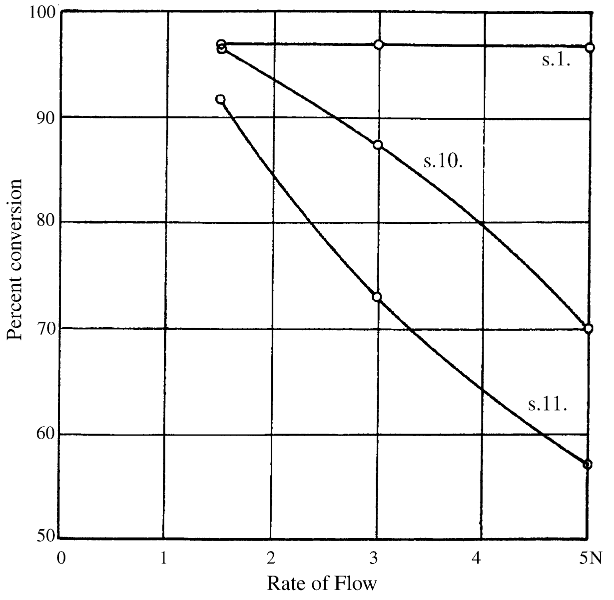
Weber [10] mentions that K, Rb, Cs and Tl produce compounds of the type $K_2O{\cdot}8SO_3$, while Li, Ag and Cu even though they produce pyrosulfates, yet do not produce “achtfachschwefelsaure Salze”. This great affinity for SO_3 which enables certain sulfates to bind SO_3 even at higher temperatures, explains why K, Rb, Cs and Tl are the best activators, as in the formation of these higher sulfatized compounds a considerable reduction of the melting point and viscosity of the molten salts takes place.

We may here mention that the melting points of the pyrosulfates or sulfates themselves do not explain the great difference in activity, which we have found in Na and K promoted catalysts.

This difference in activity may be seen in Table 1, and Fig. 3 concerning trials with catalysts S.1, S.10 and S.11. S.1 differs from A.1 only insofar as a Swedish Gur has been used in its preparation instead of Merck’s Gur (A). S.10 and S.11 differ from S.1 in, that all KOH has been substituted, respectively, by an equimolar quantity NaOH and the same weight of NaOH.

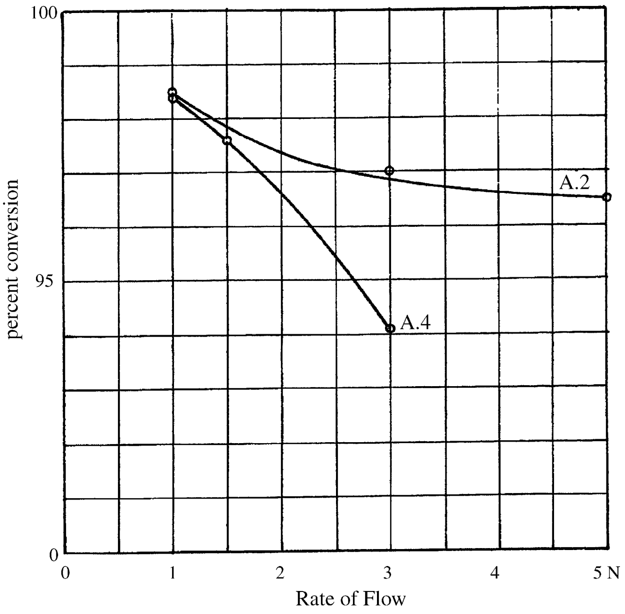
Even when substituting only about 10% of the potassium content of the catalyst with an equimolar amount of sodium, a decrease in activity, though not great, may be noted. This may be seen in Table 2, and Fig. 4 of the catalyst A.2 and A.4, where A.2 is a potassium-pyro-sulfate-vanadium catalyst activated by manganese, and A.4 the corresponding catalyst in which 10% potassium has been replaced by sodium.

Replacement of about 10% of the potassium content of a catalyst with an equimolar amount of thallium is inclined to



S.1, S.10 and S.11 at 449°C.

Fig. 3.



A.4 and A.2 at 396°C.

Fig. 4.

Table 3

Temperature (°C)	Rate of flow[a]	Conversion
449	1.5*N*	97.0
449	3*N*	96.8
449	5*N*	96.5
424	1.5*N*	98.2
424	3*N*	98.0
424	5*N*	97.1
408	1.5*N*	98.5
408	3*N*	98.2
408	5*N*	96.5
395	1.5*N*	97.0
395	3*N*	74.0

7% SO_2, 11% O_2, 82% N_2.

[a] $N = 13.5$ l at 7% SO_2/h.

Table 4

Temperature (°C)	Rate of flow[a]	Conversion		
		S.26	S.27	S.28
449	1.5*N*	96.5	96.7	96.7
449	3*N*	96.7	97.0	96.4
449	5*N*	96.5	96.7	96.4
424	1.5*N*	98.0	98.0	98.2
424	3*N*	98.0	98.0	98.2
424	5*N*	96.7	97.4	96.4
408	1.5*N*	98.1	98.9	77.0
408	3*N*	97.3	98.4	
408	5*N*	92.5	96.8	
395	1.5*N*	69.0	99.0	
395	3*N*		95.6	
395	5*N*		91.4	

7% SO_2, 11% O_2, 82% N_2.

[a] $N = 13.5$ l at 7% SO_2/h.

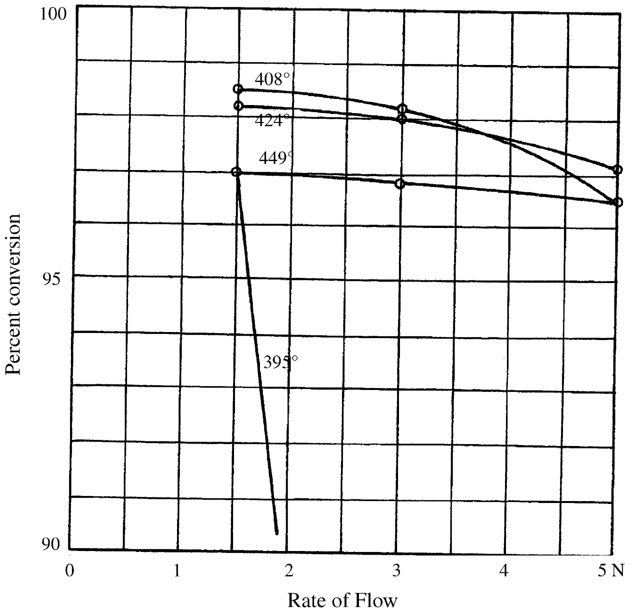
somewhat increase the activity. This may be seen in Table 3, and Fig. 5 for the thallium promoted catalyst S.12 which differs from the catalyst S.1 in the before mentioned way only.

Replacement of about 10 % of the potassium content with an equivalent quantity of rubidium effects a definite increase of the activity of the catalyst, whereas a corresponding replacement of potassium with barium definitely decreases the activity.

This is illustrated in Table 4, covering the conversions measured with the catalyst S.26 (all K), S.27 (K + Rb) and S.28 (K + Ba). All these catalysts are activated by addition of the same amount of manganese and iron.

To explain the observations, briefly set forth in the foregoing, we have set-up the theory developed in the first paragraphs in Section 5. In accordance herewith, the high efficiency of catalysts with, for instance, K is explained by $K_2S_2O_7$'s power to retain further SO_3 quantities, whereas, for instance, the lower efficiency of Na catalysts is explained by the fact that $Na_2S_2O_7$ cannot bind SO_3.

Based on this theory, it may also be explained why many of those metals which may themselves change valence may work as activators. This activating effect is quite different from the before mentioned and is, in our opinion, due to the ability of these compounds to aid in the reoxidation in homogeneous phase of vanadium with lower valence than +5. This activating



S.12. AT 449°, 424°, 408°, 395°C

Fig. 5.

Table 5

Temperature (°C)	Rate of flow[a]	Conversion
S.1		
449	1.5*N*	96.7
424	–	97.7
408	–	98.3
395	–	78.0
S.15		
449	1.5*N*	96.5
424	–	98.0
408	–	98.3
395	–	94.5
S.23		
449	1.5*N*	97.0
424	–	98.0
408	–	98.4
395	–	98.3
S.24		
449	1.5*N*	96.4
424	–	97.9
408	–	98.4
395	–	82.0
S.25		
449	1.5*N*	97.1
424	–	98.2
408	–	94.2
395	–	–

7% SO_2, 11% O_2, 82% N_2.

[a] $N = 13.5$ l at 7% SO_2/h.

effect we have found, for instance, for Mn and Fe. At the same time, as these metals are positive promoters, they would probably work in such a way as to increase the viscosity of the melt. We have found that the optimal concentration of these activators is 15–20% molar percent of the vanadium quantity. A higher Fe- or mix-content increases the viscosity of the melt to such a degree that the ensuing deterioration of the catalyst more than balances the so to say favorable chemical effect of these metals; therefore, causing the over-all efficiency of the catalyst to diminish. This is illustrated in Table 5 given below covering the catalysts S.1, S.15, S.23, S.24 and S.25.

The latter four catalysts are activated through adding a slight quantity of manganese, the quantity being the same for all four catalysts, and increasing quantities of iron, as follows: for S.15 Fe/V-1/15, for S.23 Fe/V-1/7, for S.24 Fe/V-1/5 and for S.25 Fe/V-1/2.4.

From the foregoing, it will be noted that the activated catalysts can work at a lower temperature than the unactivated ones, and at the same time, that an increase of the activator quantity beyond a certain limit decreases the activity.

With the described set-up a total of about 3000 measurements have been made with more than 100 different catalysts. The main part of the measurements were intended to develop the best possible catalyst for technical use. For this purpose, the chemical composition of the catalyst and the carrier as also the suitable form, size and porosity of the contact bodies were examined. Also the influence of temperature, gas composition, space velocity and content of gaseous impurities in the gas mixture were examined. Among all the phenomena noticed in this respect there were none that contradicted the melt theory.

Especially, the questions pertaining to the activating of the catalyst (the induction period) and the poisoning were explained in a natural manner by the melt theory.

Previously, it has often been described that vanadium catalyst before being used are activated in a mixture of air and sulfur dioxide. According to the theory developed above, this process consists in the catalyst absorbing part of the sulfur trioxide produced in starting. The effect is so pronounced, that during the activation process a period may set in where an essential part of the sulfur dioxide let in with the gas mixture is removed from the gas without compensation, even approximately, in a corresponding amount of sulfur trioxide being found.

We have made direct experimental observations of these facts. The activation period varies according to catalyst charge, temperature and so forth but amounts to 5–25 h. It is obvious, that it is of great importance, insofar as the start of converters for sulfuric acid manufacture is concerned to be acquainted herewith. The danger in starting a technical converter with a catalyst, which is only partly activated will easily be understood as sulfur trioxide is bound under great heat development, and also that an active catalyst may be deactivated by passing air, containing no sulfur dioxide, through the catalyst at increased temperature.

Also as to the known phenomena of catalyst poisoning a natural explanation may be found in the melt theory.

On catalysts, which in technical sulfuric acid converters had been poisoned by iron oxide dust, we have established iron contents, which correspond exactly with the content which according to our investigations might be expected for a catalyst with the degree of poisoning found.

In order to establish a direct experimental proof of the melt theory, we made tests with catalyst bodies consisting of an inside cylinder about 1.5 mm diameter which is made up of kieselgur with normal addition of chemicals, excluding vanadium, however, and an outer shell, about 1 mm thick of kieselgur with a standard content of chemicals, including also vanadium.

The bodies were placed in the laboratory converter where they were subjected to normal trial conditions at approximately 450 °C.

After a period of 4 days some of the bodies were taken out and examined. On cutting them through, it was observed that the vanadium had partly passed into the inside cylinder. After a further few days of continuous operation, some bodies were again taken out for examination. The vanadium content was now almost evenly distributed over the cross-section.

We have been able to finally prove the melt theory as we have succeeded in accomplishing the oxidation process by using pyrosulfate-sulfurtrioxide melts with dissolved vanadium compounds. We shall revert to this in a later article.

To complete the present work, we shall briefly set forth some investigations for the purpose of establishing the change of valence of the vanadium.

As yet the part played by vanadium in the catalytical process has not been finally determined. That a shifting valence is essential for its function may be observed directly in the test apparatus used by us.

The catalyst bodies which are first passed by the sulfur dioxide gas will, for instance, at fairly high gas speeds and low temperatures be colored green or bluish green to indicate the presence of vanadium with a valence below 5, whereas catalyst bodies in regions where the main part of the sulfur dioxide already has been oxidized, always is of a yellow, yellowish brown or reddish brown color. Bearing on this fact, and making use of the discovery we have made: that the process may be accomplished through the exclusive use of melts, we have tried to determine the normal valence range of vanadium. Here, we have made a series of absorption spectrum measurements for vanadium melts placed as a film on glass plates that were placed inside a glass pipe, heated to 450–500 °C through which the gas mixture was passed. Here, the vanadium melt also shows different colors, viz. greenish where the sulfur dioxide concentration is highest, and brownish where the sulfur dioxide concentration is less. This is, of course, also shown in the spectrums taken. Experimental difficulties, however, have brought about that the preliminary absorption spectrum measurements have not been sufficiently uniform to arrive at a final conclusion. The experiments will be continued at a later date.

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