

*THE EFFECT OF X-RAYS ON THE PLATINUM CATALYST IN
THE CONTACT SULFURIC ACID REACTION*

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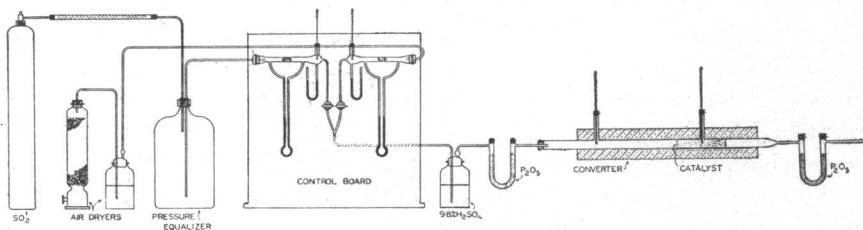
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The work of Schwartz and Klingenfuss¹ seems to show that if platinized asbestos used as a catalyst in the contact sulfuric reaction is exposed to X-radiation under the proper conditions, an increase in activity results. On account of the theoretical and practical importance of this effect and of the possibility of errors in the experimental work of these writers, a careful reinvestigation is warranted.

In the method of Schwartz and Klingenfuss, air and sulfur dioxide were conducted through the converter separately. It is obvious that the composition of the gases would be changing during the entire run and hence the reaction rate would be constantly changing. The conversions obtained could be duplicated only by taking great care to allow the gases to flow for exactly the same length of time for each run and to maintain the tempera-

FIGURE No. 1

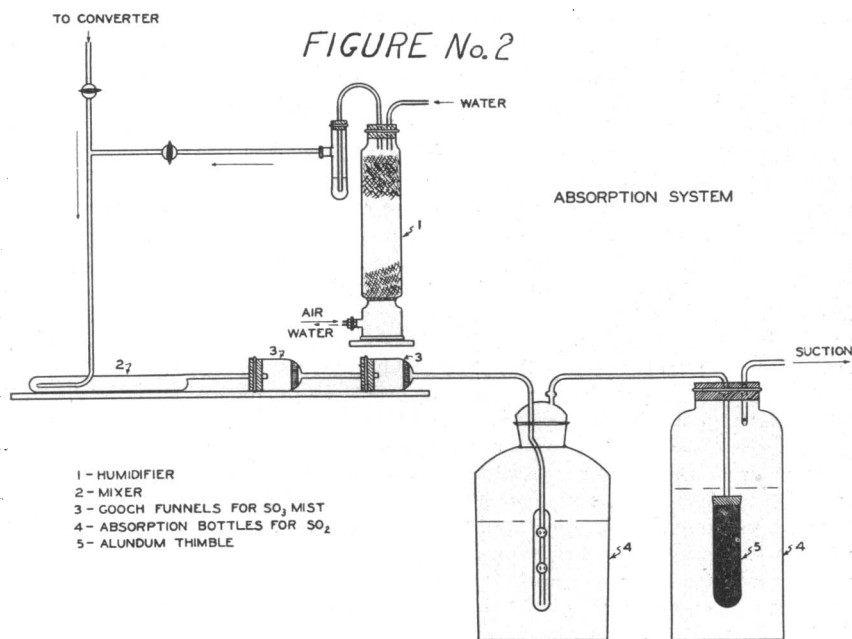
CONVERTER SYSTEM



ture constantly at 260°C. which was adopted for the experiments. Furthermore the method of analysis, consisting in absorption of both sulfur dioxide and trioxide in dilute potassium hydroxide solution, part of which was back-titrated for total acidity and part analyzed for sulfur dioxide with iodine and sodium thiosulfate, was found in the present work to be far from dependable on account of the failure of the solution to absorb completely the sulfur trioxide mist and of actual oxidation of the residual dioxide in the presence of trioxide and moisture after the catalyst was passed.

Experimental.—In the attempt to correct such possible defects as those just outlined and to investigate much more quantitatively the effects of both X-rays and moisture, the apparatus shown in figures 1 and 2

was designed and constructed as the final and satisfactory outcome of a large number of trials of various controlling, absorbing and analyzing methods. Figure 1, which is self-explanatory, shows the converter system as it was connected during the runs in which dry gases were used; when moist air was used the drying agents in the train were removed. The flow of gas was maintained constant by suction on the absorption end of the system assisted by capillary tubing and large bottles as pressure equalizers. In all cases the sulfur dioxide and air stopcocks were regulated so that the manometers on the control board read, respectively, 2 and 1.5 cm., corresponding to 16 cc. of sulfur dioxide and 210 cc. of air



per minute. The gases were passed over the catalyst thoroughly mixed instead of separately as in the experiments of Schwartz and Klingenfuss.

The Converter.—The converter was a pyrex glass tube of 20 mm. bore and 75 cm. length. At 2 points on the tube 30 cm. apart were side tubes, into each of which was fitted a thermometer through an asbestos stopper so that the bulbs were in the axis of the converter tube. The first thermometer registered the temperature of the gases in the preheating zone. Platinized asbestos was placed in the tube, loosely packed, for a distance of about 12 cm. so that the second thermometer registered the temperature at the point of conversion. The converter tube was first wrapped with asbestos paper, then with No. 26 Chromel A resistance wire (spacing 3 mm.) extending the entire length of the converter. This was covered with another layer of asbestos paper and a second coil extending only over the part of the converter containing the catalyst. Finally the entire converter was wrapped with another layer of asbestos paper and magnesia lagging.

At the catalyst the glass tube was blown thin and the lagging was removable so that during irradiation there would be minimum absorption of the X-rays by the converter walls. Wires extending from the ends of the heating coils were connected to 2 potentiometer resistance coils which had a resistance of 50 ohms with 3 amperes. The source of power was 115 volts d. c. The object of the second coil was to enable heating the catalyst to a temperature higher than that of the preheating zone. By trial an adjustment was found on each coil whereby the temperatures, 275°C. for the preheating and 300°C. for the catalyst zone, could be kept constant.

The Catalyst.—The 8% platinized asbestos catalyst was prepared by 2 methods: (1) by impregnation of purified long-fiber asbestos with chlorplatinic acid and subsequent reduction in the converter under operating conditions; (2) by deposition of platinum directly upon the fibers in a solution of chlorplatinic acid by means of sodium formate in the presence of sodium carbonate according to the directions of the British Board of Munitions. The amount of the catalyst used in the converter was 9.5 grams.

Irradiation of the Catalyst with X-Rays.—When the catalyst was to be X-rayed the converter tube was placed 25 cm. from the target of a Coolidge tungsten-target tube and the general, plus the characteristic, tungsten radiation allowed to fall upon the catalyst. When moist air was used, the temperature was raised to the operating point of 300° by means of the heating coils and compressed air, after passage through a tube filled with glass wool, was conducted through the catalyst chamber. In all cases the X-ray tube was operated at 100,000 volts and 3 milliamperes. The time of raying was 3 hours. At the end of this time the converter was set in its position in the apparatus train, the temperatures adjusted and the run made in the usual manner.

The Absorption System.—After unsuccessful trials with the Schwartz and Klingensuss method of absorbing both sulfur dioxide and trioxide in dilute alkali solutions, with various modifications such as the use of alundum thimbles (in which oxidation of the residual dioxide readily occurred), and with filter papers between funnels to remove trioxide mist, the system shown in figure 2 was devised and found entirely satisfactory. It includes a humidifier for mixing moist air with the converter gases and precipitating trioxide mist, 2 Gooch funnels with asbestos mats in series for the removal of the mist, and 2 absorption bottles for residual dioxide, the second with an alundum thimble for removing the last traces, containing standard dilute sodium hydroxide or iodine solutions. For determining trioxide the Gooch funnels were placed in water and the resulting acid solution titrated with standard alkali solution. For the dioxide the alkaline solutions from the absorption bottles were titrated with standard acid or the iodine solutions with standard thiosulfate. This method of analysis was subjected to repeated blank runs in which the gaseous mixtures were passed over the catalyst at room temperature or at 300° and in other cases in the absence of any catalyst.

Discussion of Dry Runs.—The great effect of the presence of moisture in increasing conversion of sulfur dioxide to trioxide is well known.² In order to insure the dryness of the apparatus it was run for a period of about 2 weeks and determinations made daily for the purpose of following the decreasing conversions. When the values of the conversion became constant at about 3.25% the apparatus was assumed to be dry. The effect of X-rays was apparently negligible, since any changes in conversion, after irradiation of the catalyst, were well within the variations around 3.25% in successive runs, with the unrayed dry catalyst.

Discussion of Runs with Moist Air.—In the moist runs tabulated in table 1 atmospheric air was used and all the drying devices were removed from

the system. Hence the air used was at the temperature and humidity of the room. The moisture content of the air was determined by means of a sling psychrometer which had mounted on it a wet and a dry bulb thermometer. The average ratio of H₂O to dry air was 0.0130.

Runs 40 to 43 show the conversion when the unrayed catalyst was used with moist air. The apparatus was allowed to run for 24 hours before any runs were made. This was done to insure that equilibrium conditions were established with regard to moisture. Although this relatively high moisture content prevailed throughout the system, there was no appearance of mist until the moist air was bled in from the humidifier.

Runs 40 to 55 show the change in conversion after raying. A rise of about 6% takes place in the conversion (from 88 to 94%) and then a sudden drop takes place which brings the conversion below its initial value. This is followed by a recovery to the unrayed value and subsequent slow decrease to a constant conversion of 84.3%.

TABLE 1
MOIST RUNS

| RUN | TEMP. | MILLI-MOL SO ₂ | MILLI-MOL SO ₃ | TOTAL MILLI-MOLS | PER CENT CONVERSION | TIME AFTER RAYING | RATIO (H ₂ O/DRY AIR) |
|-----|-------|---------------------------|---------------------------|------------------|---------------------|-------------------|----------------------------------|
| 40 | 299.0 | 7.00 | 14.33 | 16.33 | 87.80 | Unrayed | 0.0130 |
| 41 | 300.4 | 1.84 | 15.40 | 17.24 | 89.24 | Unrayed | .0140 |
| 42 | 300.9 | 2.15 | 17.19 | 19.34 | 88.75 | Unrayed | .0130 |
| 43 | 298.4 | 2.73 | 19.42 | 22.15 | 87.9 | Unrayed | .0130 |

CATALYST X-RAYED FOR 3 HRS.

| | | | | | | | |
|----|-------|------|-------|-------|------|-----------|-------|
| 44 | 302.1 | 1.31 | 19.60 | 20.91 | 93.7 | 1.25 hrs. | .0120 |
| 45 | 302.0 | 1.52 | 18.15 | 19.67 | 93.5 | 2.00 | .0120 |
| 46 | 304.6 | 1.15 | 17.30 | 18.45 | 93.7 | 4.83 | .0140 |
| 47 | 301.4 | 2.88 | 17.88 | 20.76 | 87.1 | 5.29 | .0140 |
| 48 | 301 | 2.88 | 15.60 | 18.48 | 84.5 | 6.65 | .0140 |
| 49 | 299.4 | 2.98 | 18.95 | 21.73 | 87.3 | 8.57 | .0129 |
| 50 | 301.1 | 2.84 | 17.90 | 20.74 | 86.5 | 9.32 | .0129 |
| 54 | 301.4 | 2.24 | 12.30 | 14.54 | 84.3 | 13.40 | .0129 |

Constant thereafter

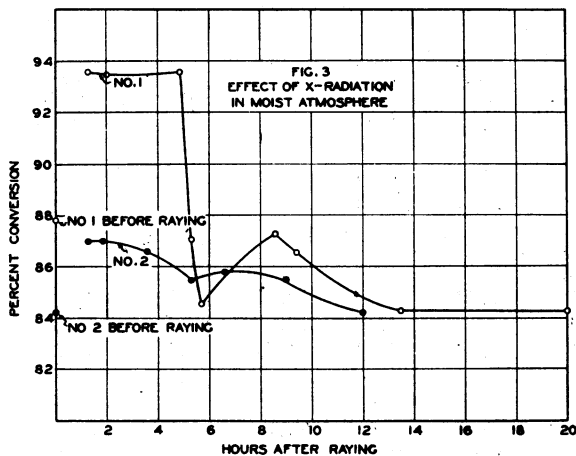
CATALYST X-RAYED FOR 3 HRS.

| | | | | | | | |
|----|-------|------|-------|-------|------|-------|-------|
| 56 | 302.4 | 2.54 | 16.92 | 19.46 | 87.0 | 1.31 | .0129 |
| 57 | 304.0 | 2.51 | 16.60 | 19.11 | 87.0 | 1.89 | .0129 |
| 59 | 304.9 | 2.71 | 17.64 | 20.35 | 86.6 | 3.67 | .0129 |
| 60 | 299 | 2.92 | 16.75 | 19.67 | 85.5 | 5.33 | .0129 |
| 61 | 300.7 | 2.81 | 17.07 | 19.88 | 85.8 | 6.54 | .0129 |
| 62 | 298.8 | 3.04 | 17.70 | 20.74 | 85.5 | 9.00 | .0129 |
| 63 | 300.5 | 2.23 | 12.31 | 14.54 | 84.3 | 12.00 | .0129 |

After the second raying the converter was run continuously for about 8 hours and runs were made at intervals of about 1 hour. The rise in conversion in this case was only to 87%, followed by slight evidences of the minimum and recovery noted after the first raying and a gradual decrease

to the same constant value of 84.3%. These results are shown graphically in figure 3.

The runs made on wet air gave a conversion which was nearly 30 times that obtained when the gases were dried. It would seem almost impossible that moisture could have this effect if the mechanism of the reaction were a simple process such as the absorption of the reacting gases and reaction on the catalytic surface. It would seem essential that the moisture forms some compound with the SO_2 which was easily oxidized or some easily reducible oxide with the catalyst itself. The mechanism suggested by Schwartz and Klingenfuss of the formation of an oxide with the platinum may explain the activation of the catalyst in the presence of moisture. After X-ray activation, probably by ionization, a measurable amount of material is attached to the catalyst, which is reducible by potassium iodide solution. There is actually more oxygen in the platinum catalyst after raying than before.



On the other hand, sufficient data are not yet available to permit an adequate explanation of the sudden drop in activity or "tiring" of the catalyst about five hours after raying, with subsequent recovery, or of the decreased effect of raying after the first time. Undoubtedly an adsorbed film of H_2SO_4 on the catalyst is being built up to a thickness which is less easily ionized by X-rays. To the extreme sensitiveness of most catalysts to heat treatment and to poisons as regards adsorption and activity must be ascribed these complicated phenomena.

It is obvious that the present experiments are but preliminary because of the large number of variables involved, which must be investigated: composition of gases, rate of flow, pressure, moisture content, preheating temperature, catalyst temperature, amount of catalyst, time of raying, X-

ray wave-length, runs after or during raying, aging of catalyst, etc. In further experiments now under way, lower temperature with measurement at 4 points instead of one in the catalyst, constant (and lower) humidity of air independent of the atmosphere, measured volumes of gases passed very slowly over the catalyst so as to insure nearly isothermal conditions, and a smaller amount of catalyst are important improvements which have been introduced.

Summary.—(1) Preliminary experiments indicate that X-rays do not activate the platinum catalyst when the catalyst is rayed in an atmosphere of dry air.

(2) The platinum catalyst is activated when rayed in an atmosphere of moist air. Singular effects are noted with time after raying and following irradiations subsequent to the first.

(3) Moisture has a decided effect upon the percentage conversion of $\text{SO}_2 + \frac{1}{2}\text{O}_2 = \text{SO}_3$ at low temperatures.

(4) A successful laboratory scale apparatus and a proper method for separation of SO_2 and SO_3 have been developed and a satisfactory method of analysis has been devised.

¹ *Zeit. Elektrochem.*, **28**, 472 (1922); **29**, 470 (1923).

² *J. Chem. Soc.*, **65**, 611 (1894); **81**, 272 (1902); cf. Lamb and Vail, *J. Am. Chem. Soc.*, **47**, 123 (1925).

THE JAPANESE WALTZING MOUSE, ITS ORIGIN AND GENETICS¹

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The Japanese waltzing mouse has long been an object of popular and scientific interest, largely on account of its habit of running in circles, the so-called waltzing. However, because of its susceptibility to disease and sensitiveness to temperature changes it is difficult to breed, with the result that its behavior in inheritance, particularly in relation to other characters, has not been thoroughly investigated.

A more or less complete survey of the linkage relationship of waltzing to other characters has recently been made, with some interesting results. It was found, as had previously been suggested by other investigators, that in all probability, the Japanese mouse, of both the waltzing and the non-waltzing form, is a derivative of *Mus wagneri* and not *M. musculus*, the common house mouse. Wagner's mouse is a native of