

free and combined, is shown by the linearity of the molecular volumes of the cobalt halides, as well as those of numerous other metal halides, when plotted against the atomic volumes of the halogens at the boiling point. Such linearity is not maintained after the formation of amines or hydrates.

5. Analysis is given of 5 factors which parallel and perhaps partly determine secondary valence strength.

6. The great importance of percentage contraction in the formation of hydrates, amines and polyhalides is shown by straight line proportionality to stability.

7. The theoretical approximate calculation of molecular volumes and specific gravities of compounds very difficult to prepare is briefly outlined.

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THE OXIDATION OF NITRIC OXIDE AND ITS CATALYSIS.

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Introduction.

In a previous article¹ it has been shown that the chief reactions occurring during the absorption of the oxides of nitrogen to form nitric acid in aqueous solution are the following



Reaction 1, the reaction of nitrogen peroxide with dilute aqueous nitric acid is a very rapid reaction when carried out under conditions of efficient washing action of the gas by the liquid. It is a reaction which does not, however, proceed to completion, being halted at an equilibrium condition, which in the case of nitric acid of fair concentration, is far short of complete conversion of the nitrogen peroxide. The presence of nitric oxide above a certain equilibrium concentration will prevent the reaction of absorption from proceeding at all, and only as this nitric oxide is re-oxidized and removed by the excess oxygen in the gases (according to Reaction 2) can the process of absorption go on.

Reaction 2, the re-oxidation of the nitric oxide liberated during the absorption process is a slow reaction. Since the reactions of absorption and oxidation (1 and 2) progress simultaneously, and are really mutually interdependent, it is evident that, should it be found possible by some means to cause an acceleration in the rate of the oxidation reaction, the retarding

¹ Burdick and Freed, *THIS JOURNAL*, 43, 518 (1921).

influence of equilibrium effects on the absorption reaction would cease to be so great a factor.

The relatively large time required by the oxidation process suggests at once that it may be feasible to cause the processes of absorption and oxidation to proceed separately. Since the absorption reaction is rapid, this can be accomplished in small units. Interposed between the small absorption units would be reaction chambers to serve as intermediate oxidizing chambers to secure complete re-oxidation of the liberated nitric oxide. With the aid of a material which catalyzes or accelerates the rate of the oxidation of nitric oxide to nitrogen peroxide it would be possible to reduce very materially the time of the oxidizing period and, therefore, the size of these reaction chambers. The following experiments were designed to determine the properties of the substances which it was anticipated might have a catalytic influence upon the reaction of oxidation.

Description of the Experiments.

1. **Experimental Apparatus for the Study of the Possible Catalysis of Oxidation and Absorption Reactions Simultaneously.**—The experiments were an attempt to find some contact material which when wet with acid would catalyze the oxidation reaction. The material should supposedly either be of a highly absorptive character or should form unstable additive compounds with the nitrous gases, or should be readily reduced by the nitric oxide present in the gas and as readily re-oxidized by the excess oxygen.

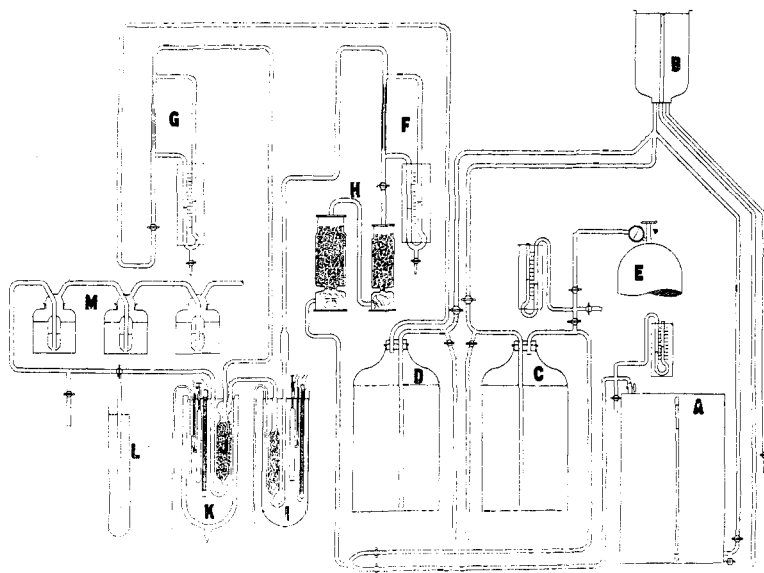


Fig. 1.

The apparatus for these experiments consisted essentially of a miniature absorption tower made completely of glass and filled with packing material crushed to 4-6 mesh. The gas current entered from the bottom and the nitric acid was circulated by means of a glass acid pump. The apparatus was essentially that of Fig. 1, with the catalyzer chamber replaced by the small absorption tower. Nitrogen peroxide from the storage reservoir and air were metered by flow gages and were mixed in a chamber. The gas was then passed in at the bottom of the tower and emerged into the alkali absorption train. A slow stream of nitric acid flowed continuously from the storage reservoir down over the contact material in the tower and out into a over storage reservoir. From this reservoir it was again raised by the action of a glass pump to the upper reservoir. Since the quantity of acid used was always large relative to the quantity of nitrogen peroxide there was no appreciable change in the concentration of the acid.

From the analysis of the emerging gases, the percentage of the entering nitrogen peroxide which had been absorbed was computed, and the relative efficiency of the contact material determined.

The entering gas mixture contained 3% of nitrogen peroxide and 19% of oxygen, the rate of flow was 20 liters per hour and the strength of acid used was 40% by weight.

All experiments yielded negative results; that is, in no case was any improvement in absorption noted over the results obtained with a standard packing of glass fragments. The materials tested were the following: glass, pumice, charcoal, coke, and pumice impregnated with platinum, manganese dioxide, cobalt and nickel and their oxides, tungstic acid, and vanadic acid. The manganese dioxide, which is almost completely insoluble in nitric acid, dissolves readily and completely in the presence of nitrogen peroxide or nitric oxide and contaminates the acid. Practically all the other impregnating materials dissolved likewise.

2. Experimental Apparatus for the Study of the Catalysis of Oxidation Reactions Independently of Absorption Reaction.—The apparatus for the study of the oxidation rate of nitric oxide is shown in Fig. 1.

The oxygen-nitrogen mixture, prepared by diluting air with the proper amount of nitrogen in the measuring carboy C, was transferred by water displacement into the large storage and supply gasometer A, the gas in which was maintained under the constant head corresponding to the height of the water inlet at B. The emergent mixture of oxygen and nitrogen passed through the flowmeter F, through the water saturating apparatus in I and into the top of reaction chamber J, where it was mixed with nitric oxide from the storage carboy D, the proportion of nitric oxide admitted being regulated by the gage and valve at G. The mixed gases passed directly down through the catalyzer material in J and up through the 3-way stopcock L to the alkali absorption train M. Except when making an analysis, the gas current was deflected down into the tube L filled with alkali. The height of the liquid in L, was the same as the total height in the wash bottles, so that in turning the cock no change in the rate of flow or gas proportions was produced.

To introduce water vapor into the gas the thermostat I was so arranged that it could be set to maintain any desired temperature. The gas passing through the long glass column filled with water became saturated with vapor at a temperature chosen to give the desired percentage concentration. The connecting tube from the water saturator to the reaction chamber was heated electrically to a temperature such that there was no condensation of water in the apparatus. The connection between the

reaction chamber and alkali absorption train was short and of small bore glass tubing. It was also kept warm by a heating arrangement in order that no condensation of nitric acid should take place.

Since the catalytic efficiencies of the materials tested varied over wide ranges, in order to secure a suitable degree of oxidation of the nitrous gas reaching the alkali, it was necessary to provide reaction chambers of various sizes and to vary considerably the oxygen concentration in the gas. In the experiments on inert materials (glass, coke, etc.) the reaction chamber had a volume of 30 cc., and the entering gas contained 20% of oxygen, whereas for the active charcoals the catalyzer chamber was reduced in size to 6 cc., and the oxygen concentration in the gas was kept at 3%.

The method of making a run on a new material was as follows. After the catalyzer or contact material had reached a state of equilibrium with the steady flowing current of gas (this taking nearly 24 hours in the case of the active charcoals and only a few minutes in the case of inert materials) the gas current was deflected for a period of 20 minutes to the alkali absorption train M containing a known amount of standard alkali. The analysis of the alkali,² the free volume of the contact space and the gage reading on the air gage furnished the data for calculating the reaction rate constant K . The apparatus was run continuously, analyses being made at suitable intervals. The only shut-down required was for changing the catalyzer material.

Results of the Experimental Measurements.

The equation for the reaction of nitric oxide with oxygen, $2\text{NO} + \text{O}_2 = 2\text{NO}_2$ indicates that the rate of oxidation will be proportional to the square of the nitric oxide concentration and directly proportional to the oxygen concentration.³ The mathematical equation expressing these conditions is, therefore,

$$-dC_{\text{NO}} = K(C_{\text{O}})(C_{\text{NO}})^2 dt$$

in which $-dC$ represents the decrease in concentration of nitric oxide in the time dt ; C_{O} , the concentration of oxygen; C_{NO} the concentration of nitric oxide at any given instant, and K the factor of proportionality, or the rate of reaction constant. The above equation transformed into form for integration is

$$-dC = K \left[C_{\text{O}} - \frac{C_1 - C}{2} \right] C^2 dt$$

In this equation C_{O} represents the concentration of the oxygen at the time when the concentration of nitric oxide is C_1 . In the case of the follow-

² For the method of analysis and calculation of gas compositions, see Ref. 1. p. 522.,

³ Cf. Bodenstein and Meinecke, *Z. Elektrochem.*, 16, 876 (1910) and Briner and Fridori, *J. chim. phys.*, 16, 280 (1918).

ing experiments C_0 and C_1 represent the respective concentrations of oxygen and nitric oxide at the moment of mixing.

The integrated⁴ form of the equation is

$$Kt = \frac{2}{2C_0 - C_1} \left[\frac{1}{C} - \frac{1}{C_1} \right] - \frac{4.6}{(2C_0 - C_1)^2} \log_{10} \frac{(2C_0 - C_1 + C)C_1}{2C_0 C}$$

Since K varies inversely as t , a large value of K indicates a high rate of oxidation and a correspondingly low value for t . The value of this number K as calculated from the experimental data is the best measure of comparative oxidation rates, and thus represents the relative efficiency of the contact material tested.

In the case of reactions catalyzed by solid substances and taking place at the surfaces of gas absorption, it does not follow that the rate of combination will be strictly according to that predicted from the chemical equation. However, in this instance since the catalytic activities of the substances investigated were tested under nearly identical conditions, the preceding equation may be accepted as sufficiently accurate for purposes of comparison.

In Table I are given the data embodying the experimental measurements of the reaction rate constant for the various substances tested. The relative reaction rates are given in the last two columns, the first giving the reaction rate constant and the second the time required for the oxidation of 90% of the nitric oxide in an arbitrarily assumed gas containing 2% nitric oxide and 3% oxygen in contact with the material under consideration. The latter figures show clearly the order of the rate of oxidation as it might actually be found in the final stages of the absorption system in an ammonia oxidation plant.

From the table it is seen that no one of the first series of substances tested exhibited any marked catalytic activity. The experiments indicate that any highly porous material has an accelerating influence on the rate. Impregnation with materials which might react chemically with the nitrous gases seemed to have no effect, for none of the samples of impregnated pumice was more effective than ordinary pumice.

The substances, metallic cobalt and nickel, their oxides and nitrates, were not found to possess any catalytic ability to oxidize the oxides of nitrogen as has been claimed by Classen.⁵ The metals and metallic oxides are rapidly converted to nitrates, which in the presence of water vapor except at elevated temperatures, immediately deliquesce.

The influence of temperature on the rate of reaction in the presence of

⁴ The general formula for integration is

$$Kt = \int_{c_1}^c \frac{dc}{c^2(k-c)} = -\frac{2}{k} \left[\frac{1}{c} \right]_{c_1}^c - \frac{2}{k^2} \left[\log \frac{(k-c)}{C} \right]_{c_1} \quad k = (a-2c)$$

⁵ Classen, *Brit. pat.* 18065, 1915.

TABLE I
EXPERIMENTAL DATA

Contact substance	Temp.		Composition of entering gas			Issuing gas NO %	Per cent. Oxidation in passage	Time of contact of gases with catalyzer Sec.	K	Time for 90% oxid. of 2% gas
	° C	Rate of flow of gas per min.	NO %	O ₂ %	H ₂ O %					
Glass container empty	0	123	3.11	20.4	0.1	0.53	83.0	19.2	21	480
	25	144	2.91	20.4	0.1	0.96	67.1	16.5	11	910
	50	159	2.74	20.4	0.1	0.91	66.9	14.9	12	840
Crushed glass	25	146	2.82	20.4	0.1	0.98	65.2	11.6	15	670
	50	148	3.45	20.3	0.1	1.19	65.4	11.0	13	770
Untreated pumice	25	137	2.97	20.4	0.1	0.86	71.0	11.9	18	560
Pumice impregnated with tungstic acid in HNO ₃	50	142	3.06	20.4	0.1	0.78	74.6	11.5	21	480
	50	151	3.20	20.3	0.1	0.92	71.1	10.8	18	560
With tungstic acid in soln. of hydrogen peroxide	25	143	3.04	20.4	0.1	0.92	69.9	11.5	17	590
	25	142	3.00	20.4	0.1	0.98	67.3	11.0	16	630
With NiO	25	147	2.86	20.4	0.1	1.00	65.1	11.0	15	670
With CoO	25	151	3.07	20.4	0.1	0.82	73.2	11.8	19	530
With metallic Ni	25	146	3.02	20.4	0.1	0.90	70.1	10.5	19	530
With metallic Co	25	149	2.98	20.4	0.1	0.91	69.9	12.5	15	670
With MnO ₂	25	145	2.97	20.4	0.1	0.94	69.2	11.4	17	590
Platinized pumice	25	158	2.62	20.4	0.1	0.75	71.4	14.2	17	590
Platinized asbestos	25	147	2.62	20.4	0.1	0.78	70.1	11.3	20	500
Coke	25	140	2.98	20.4	0.1	0.82	72.5	11.7	19	530
Common charcoal	25	140 ^a	3.0	20.4	0.1	0	100	11.7		
Coconut charcoal	50	140	3.0	20.4	0.1	0	100	11.7		
	80	140	3.0	20.4	0.1	0	100	11.7		
	25	124.7 ^b	1.33	2.96	0.1	0.102	92.4	1.88	10,000	1.0
Coconut charcoal in small reaction tube	25	118.4	1.39	2.96	0.1	0.084	94.0	1.98	12,000	0.8
	80	148.5	1.63	2.59	0.1	0.163	90.0	1.58	8800	1.1
	25	119.2	1.87	2.94	1.0	0.540	71.4	1.96	1400	7.0
	25	116.0	1.86	2.94	1.0	0.608	67.3	2.02	1100	9.0
	25	124.6	1.77	2.94	1.0	0.690	61.0	1.87	930	11.0
	25	130.7	1.31	2.96	1.0	0.48	63.3	1.64	1350	7
Coconut charcoal	80	136.6	1.96	2.90	1.0	0.39	80.0	1.71	2650	4
Peach-kernel charcoal	80	114.7	1.87	2.90	1.0	0.406	78.3	2.04	2010	5
	80	112.5	1.71	2.90	1.0	0.335	77.2	2.08	2430	4
	80	211.5	1.23	2.79	5.7	0.431	64.9	1.11	2710	4
	80	141.7	2.22	2.76	5.6	0.392	82.4	1.65	3110	3
	55	136.2	1.79	2.66	5.8	0.568	68.3	1.72	1590	6
	55	145.3	1.66	2.80	5.7	0.654	60.6	1.61	1165	9
	53	109.4	1.51	2.78	5.7	0.647	57.2	2.11	808	12
	53	120.7	1.59	2.77	5.7	0.495	68.8	3.23	910	11
	53	113.6	1.66	2.78	5.7	0.568	65.8	2.81	765	13
Steamed coke	100	167.9	1.27	2.45	14.7	0.305	76.0	2.00	3440	3
	80	105.0	2.63	2.81	3.9	1.12	57.5	3.37	329	30

^a Volume of empty reaction chamber = 30 cc.^b Volume of empty reaction chamber = 6 cc.

inert materials is unusual.⁶ Above 25° the rate of reaction is practically

⁶ The temperatures recorded in the table are the temperatures maintained in the thermostat. Inasmuch as the oxidation of 1% by volume of nitric oxide in a gas is sufficient theoretically to raise its temperature 20° above the surroundings, assuming no radiation, the actual temperatures of the gases may be somewhat higher than those given.

independent of the temperature, a slight decrease in the rate of reaction with increase of temperature appearing to be the general rule. Below 25°, however, a rapid increase in the rate of reaction with decrease in temperature, was noted, the rate at 0° being twice that at 25°.

The only materials possessing catalytic properties of any pronounced value were the special charcoals and the activated coke. The two samples which were most reactive were the coconut and peach-kernel charcoals. A sample of coke subjected to steaming at 600° to 800° was found to possess a pronounced but much lower catalytic activity. It is to be expected that the highly absorptive silica gels would act in the same manner as the charcoals, but at the time these experiments were performed such material was not available for testing. The order of catalytic activity that these materials possess is quite remarkable; thus, the specific reaction rates for coconut charcoal was found to be about 11000, or more than 500 times that observed for ordinary porous materials. The time required therefore to produce a given degree of oxidation in a given gas mixture is less in the same proportion. For example, to secure the conversion to nitrogen peroxide of 90% of the nitric oxide in a gas containing 3% of nitric oxide and 3% of oxygen requires with inert material 500 seconds and in the presence of the catalyzer only 1 second.

Water vapor has a very considerable effect on the catalytic properties of the charcoals. To retain activity the catalyzer must be maintained at a temperature above the condensation point of the aqueous nitric acid which would be in equilibrium with the gas phase in contact with it. Condensation on the catalyzer or soaking in nitric acid had no permanent harmful effect, as the material after drying resumes its activity.

In Table II are tabulated experimental results to show the influence on the catalysis of the moisture content of the gases and also the effect of change in temperature. With dry gases the catalytic activity is only slightly decreased by an increase of temperature. When, however, moisture is introduced into the gases, the reaction rate drops greatly, in the case of the coconut charcoal at 25°, 1% of water vapor in the gas causing a decrease in the rate of reaction constant from 11000 to 1100. With moist gases the effect of temperature is the opposite of that found with dry gases, the rate of reaction increasing as the temperature difference above the condensation point of the aqueous nitric acid becomes greater.

A slight amount of water vapor present in the gases inhibits the activity of the catalysis to a considerable degree, but except in the immediate neighborhood of the condensation point where the catalysts are very sensitive to changes in water vapor concentrations, concentrations of water vapor in excess of 1% seem to exert no further depressing effect. Even with a water vapor content as high as 15%, as would be encountered, for instance, in the gases from ammonia oxidation, the catalytic activity

TABLE II
EFFECT OF TEMPERATURE AND WATER VAPOR CONCENTRATION

Contact substance	Temp. ° C.	Water vapor in gas used Percentage by volume	K Obs.
Coconut charcoal	25	dry	11000
	80	dry	8800
	25	1.0	1100
	50	1.0	1400
	80	1.0	2700
Peach-kernel charcoal	80	1.0	2200
	53	5.7	800
	55	5.7	2400
	80	5.7	2900
	100	14.7	3400

of the charcoals is well maintained, provided the temperature of the reaction space is sufficiently elevated.

The decrease in the rate of reaction with elevation of temperature observed in the case of the dry gases is probably occasioned by the decreased absorptive ability of the charcoal at the higher temperatures. The increase in the rate of reaction with temperature rise in the presence of water vapor is likewise probably to be explained by the lowering of the surface concentration of absorbed water on the charcoal caused by the temperature increase, thus enabling a relatively greater proportion of the active mass of the catalyzer to take up its duty.

With respect to the life of the charcoal catalysts, their properties do not seem to be impaired at all with time, tests over many weeks duration showing no decrease in activity. The charcoals were also tested for possible slow combustion, but in no case was there any evidence of carbon dioxide formation.

Summary.

A study of the rate of the reaction $2\text{NO} + \text{O}_2 = 2\text{NO}_2$ has shown that ordinary porous materials either impregnated or unimpregnated possess no specific catalytic action, but that in the presence of the highly absorptive forms of carbon or charcoal the rate of the reaction may be accelerated as much as 500 fold.

The presence of water vapor in the gas mixtures greatly decreases the activity of the charcoal catalysts. Increase of the temperature interval above the point of condensation of the aqueous vapor counteracts to some extent this effect.

The temperature coefficient of the rate of reaction for the uncatalyzed and the catalyzed reaction is in general negative. For the catalyzed reaction in the presence of water vapor the temperature coefficient is apparently positive. This is probably due to the decreased absorption of water by the catalyzer at elevated temperatures.