phoric iron prepared seems to be dependent primarily upon the amount of residual oxide contained in the iron.

3. Iron prepared from colloidal iron oxide by Sorum's method was worthless as an ammonia catalyst. The incorporation of colloidal aluminum oxide in this colloidal iron oxide produced an active catalyst.

4. It appears as though inactivation of an iron catalyst through processes of recrystallization is hindered by an iron oxide core within the iron particles.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF WASHINGTON]

THE EQUILIBRIUM OF THE REACTION BETWEEN NITROGEN AND CARBON DIOXIDE IN THE ELECTRIC ARC

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This study was undertaken as a natural consequence of former work performed in this Laboratory on the equilibrium of gaseous reactions in the electric arc.[1] The reaction between nitrogen and carbon dioxide seemed to offer a very interesting problem because of the appearance of a recent article[2] which indicated that a much higher concentration of nitric oxide could be obtained with a mixture of these gases than could be realized with a mixture of nitrogen and oxygen. The earlier work of Muthmann and Schaidhauf[3] seemed to indicate that this view is erroneous; for they obtained concentrations of nitric oxide from carbon dioxide and nitrogen mixtures which compare unfavorably with those obtainable from air. However, it seemed desirable to collect a more complete series of data in which conditions were varied and in which equilibrium was known to be realized.

Description of Apparatus.—The power supply available was 110-volt, 60-cycle alternating current. The high voltage necessary to maintain the arc was obtained by means of an oil-cooled, closed core transformer of 3.5 kilowatts capacity. Reactance coils in the primary circuit served to stabilize the arc and to give the desired value of secondary current. A milliammeter in the secondary circuit indicated the value of the current. The line voltage varied somewhat, but the current through the arc was substantially constant.

The arc furnace was that used by Colin and Tartar[4] in their study of the equilibrium of the reaction of nitrogen and oxygen in air and other mixtures, to form nitric oxide. It consisted of a 5-liter pyrex flask with platinum electrodes sealed into the neck of the flask. The electrodes were originally of the horn-gap type, and were about 0.8

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[1] (a) Tartar and Perkins, *J. Phys. Chem.*, **30**, 595–616 (1926); (b) Colin and Tartar, *ibid.*, **31**, 1539–1558 (1927).

[2] Krase and Mackey, *ibid.*, **32**, 1488–1494 (1928).

[3] Muthmann and Schaidhauf, *Z. Electrochem.*, **17**, 497 (1911).

[4] Ref. 1 b, see Fig. 2, p. 1544.

cm. apart, but at the temperature of the arc the platinum was gradually volatilized and fused down, so that only small hooks remained upon the ends. The neck of the flask was drawn out and sealed to a two-way stopcock, and another outlet was provided in the bottom of the flask. To each side of the two-way stopcock (a in Fig. 1) was sealed a T-tube; one side of each T-tube was joined to a manometer and the other to a tube containing phosphorus pentoxide (b in Fig. 1). Nitrogen was admitted to the furnace through one of these drying tubes after having passed successively through alkaline pyrogallol, concentrated sulfuric acid and a tube containing heated metallic copper. This latter tube was closely packed with alternate layers of copper gauze, tightly wound into rolls, and of granulated copper. The copper was heated to a dull red during the passage of nitrogen; the oxide formed was periodically reduced with hydrogen.

The tube (e) was filled with carbon dioxide snow and by means of the by-pass (d-g) leading directly to a Cenco Hivac pump was subjected to direct evacuation until nearly one-half of it was gone. This served to purify the carbon dioxide by removal of the gaseous impurities. The purified gas was then admitted to the furnace after passing through the drying tube (b).

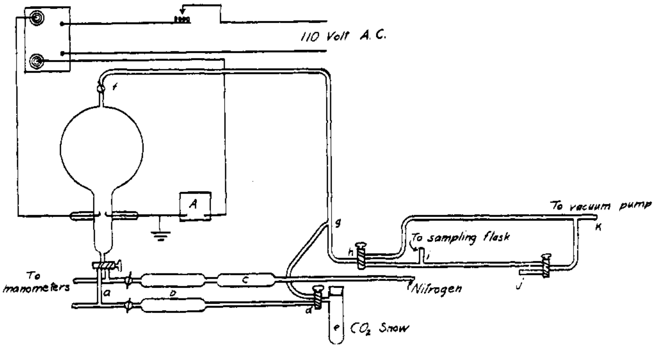

Fig. 1.

Between the points (h) and (k) (Fig. 1) were two lines leading to the pump; one was used for evacuation; the other for sampling the reaction products. The sampling flask was connected in the line by means of a T (i in Fig. 1) and was evacuated down to the limit of the pump when preparing for use. The sampling flask consisted of a 5-liter pyrex flask with a stopcock sealed into the bottom. An absorption train between (i) and (j) served to absorb residual gases after the sampling had been accomplished. Air was first admitted to oxidize the nitric oxide and the gases were then drawn through towers containing hydrogen peroxide and caustic soda solutions (in separate towers).

Method of Procedure

The furnace was evacuated by means of the direct line to the pump. It was then flushed out four times with the oxygen-free nitrogen and with the aid of the manometer in that line was filled to the desired pressure. Carbon dioxide snow was then introduced into the tube (e) and purified as described heretofore. The furnace was filled to the desired total pressure with carbon dioxide. The arc was started and allowed to run for at least three hours, although tests indicated that equilibrium essentially was attained in a somewhat shorter period. At the end of this time a sample of the reaction gases was drawn for analysis. The sampling flask was evacuated and the gases were allowed to distribute themselves through the system. When constant pressure and temperature had been attained, the flask was withdrawn, sodium hydroxide solution was drawn into it (since it was still under reduced pressure) and air was admitted to oxidize the nitric oxide. The flask was allowed to stand with occasional vigorous shaking until the nitrous gases were completely absorbed. The solution was then washed into a 500-cc. Kjeldahl flask and the nitrogen compounds reduced with Devarda's alloy to ammonia, which finally was distilled into standard sulfuric acid. In order to avoid carrying over alkali spray during the distillation, an apparatus was used which was quite similar to that of Mitscherlich.[5] This method was found to be quite reliable. All results were calculated as percentage of nitric oxide by volume of the actual amount of gas present in the furnace.

Discussion

The equation for the reaction of nitrogen and carbon dioxide to form nitric oxide may be written

$$N_2 + 2CO_2 = 2NO + 2CO$$

Thus a two-to-one mixture of carbon dioxide to nitrogen should, theoretically, give the best yield of nitric oxide. Also, it is apparent that three volumes of reacting gases give four volumes of reaction products at constant pressure. The fact that these experiments were performed at substantially constant volume made it difficult to obtain exactly similar conditions when approaching the equilibrium from both sides for, in the one case, there was a slight increase in pressure, while in the other there was a slight decrease. Furthermore, when equilibrium was attained, starting with a nitrogen–carbon dioxide mixture, there was undoubtedly some excess of oxygen and of carbon monoxide present, resulting, of course, from the decomposition of some carbon dioxide not taking part in the reaction with nitrogen; this amount was not precisely known. However, starting with 5% of nitric oxide and 5% of carbon monoxide, with 60% of carbon dioxide and 30% of nitrogen, it was possible to arrive at an equilibrium mixture differing by but 0.1–0.2% from that reached when starting with the theoretical mixture of carbon dioxide and nitrogen. Carbon monoxide was generated by dropping formic acid into concentrated sulfuric acid; nitric oxide by dropping dilute nitric acid through copper gauze so as to keep the nitrate solution formed out of contact with the metal.

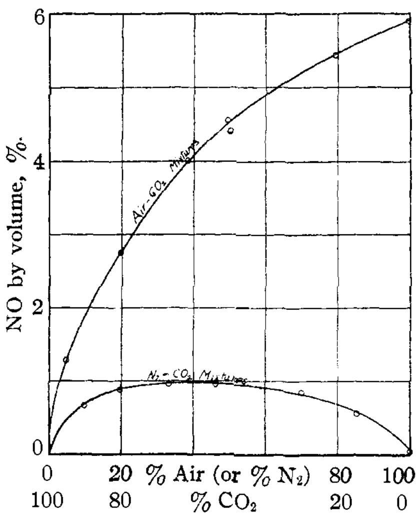

Fig. 2.

A series of runs was made with a current of 65–67 milliamperes and at 760 mm. pressure, in which mixtures of air and carbon dioxide ranging

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[5] Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., New York, 1922.

from 100% of the former to 95% of the latter were used. The results are reported in Table I and are shown graphically in Fig. 2. These data indicate that carbon dioxide acts largely as a diluent under these circumstances, for the concentrations of nitric oxide obtained range from 1.3% in a mixture containing 95% of carbon dioxide, to 5.9% for pure air. This view is substantiated for the most part by the results obtained from nitrogen–carbon dioxide mixtures under similar conditions of current and pressure. The data are given in Table II and are plotted in Fig. 2. Here a maximum of about 1% of nitric oxide was obtained, or only one-sixth the concentration resulting from air alone. In all runs but those having

TABLE I

NITRIC OXIDE FROM AIR AND CARBON DIOXIDE MIXTURES

Run	Pressure, mm.	Current. m. a.	Air, %	Carbon dioxide. %	Nitric oxide, %
N-3	760	67	100.0	0.0	5.92
N-4	760	66.5	80.0	20.0	5.46
N-9	760	67	50.6	49.4	4.43
N-2	760	66.5	50.0	50.0	4.57
N-8	760	65	39.1	60.9	4.02
N-1	760	66	20.0	80.0	2.76
N-7	760	66	5.0	95.0	1.30

TABLE II

NITRIC OXIDE FROM NITROGEN AND CARBON DIOXIDE MIXTURES

Run	Pressure, mm.	Current. m. a.	Nitrogen, %	Carbon dioxide, %	Nitric oxide. %
J-1	760	67	100.0	0.0	0.028
J-6	760	66	100.0	0.0	.014
J-8	760	66	85.0	15.0	.55
J-2	760	67	70.0	30.0	.85
J-4	760	66	46.2	53.8	.95
J-3	760	66.5	33.3	66.7	1.00
J-7	760	66	33.3	66.7	0.94
J-5	760	66	20.0	80.0	.88
J-9	760	65	10.0	90.0	.66
L-4	500	66	85.0	15.0	.83
L-6	500	66	70.0	30.0	.945
L-3	500	67	64.4	35.6	.845
L-2	500	66.5	50.0	50.0	1.03
L-1	500	67	33.3	66.7	0.99
L-5	500	66	14.6	85.4	.83
K-4	300	67	85.0	15.0	.41
K-3	301	67	64.4	35.6	.78
K-2	300	66	50.0	50.0	.93
K-1	301	67	32.2	67.8	.89
K-5	300	68	15.0	85.0	.79
M-3	150	66	65.0	35.0	.99
M-2	150	67	47.3	53.7	1.03
M-1	150	67	33.3	66.7	0.91
M-4	150	66	33.3	66.7	1.13

the highest percentages of nitrogen, the presence of the brown color of nitrogen dioxide demonstrated that some carbon dioxide had been decomposed beyond that required by the foregoing equation. Thus there is also the equilibrium between carbon dioxide and its dissociation products to be considered.

TABLE III

NITRIC OXIDE FROM NITROGEN AND CARBON DIOXIDE MIXTURES

Run	Pressure, mm.	Current, m. a.	Nitrogen, %	Carbon dioxide, %	Nitric oxide, %
O-4	760	97	85.0	15.0	0.82
O-3	760	97	70.0	30.0	0.98
O-2	760	98	50.0	50.0	1.16
O-1	760	99	33.3	66.7	1.23
O-8	760	97	30.0	70.0	1.38
O-5	760	97	20.0	80.0	1.36
O-6	760	98	20.0	80.0	1.33
O-7	760	97	10.0	90.0	1.15

Since Colin and Tartar[1b] had shown that high concentrations of nitric oxide could be attained at reduced pressures from air and other nitrogen–oxygen mixtures, it was decided to try a similar proceeding with nitrogen and carbon dioxide. Series of runs were made, therefore, at 500, 300 and 150 mm. pressure. The results are given in Table II and the first two are compared graphically with the atmospheric runs made with the same current in Fig. 3. The values determined at 150 mm. are altogether too uncertain to more than indicate the order under those conditions. The effect of pressure upon the equilibrium between nitrogen and carbon dioxide seems to be rather slight; in fact, there is scarcely more than 0.1% variation, and this almost comes within the limits of experimental error. As a matter of fact, the two values obtained at 500 mm. pressure with original concentrations of nitrogen of 70 and 85% are, perhaps, a little high for the reason given in the next paragraph. Pressures above atmospheric were not tried but it seems improbable that the reaction would be much favored, if at all, by such a procedure.

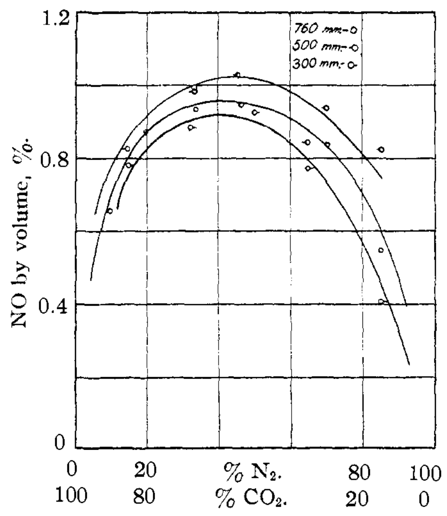

Fig. 3.

Finally, a series of runs was made at atmospheric pressure with a somewhat larger current. Unfortunately this increased current (about 98–100 milliamperes, or approximately a 50% increase) proved to be more than the electrodes could conveniently handle, and the "horn-gap" was completely fused down into stubs. This, of course, had the effect of increasing the current density for the same current. Therefore, this last series is not quite so consistent as those made with the lower current. (The two values made at 500 mm. and 65 milliamperes referred to above as being somewhat high were made after this change in the electrodes.) It was found, however (Table III), that 50% increase in current caused 30–40% increase in the concentration of nitric oxide.

The natural inference from the foregoing results is that not nearly as high a concentration of nitric oxide can be produced by the high tension electric arc from carbon dioxide and nitrogen as can be produced from air or other nitrogen–oxygen mixtures. Krase and Mackey[3] have recently published some thermodynamic calculations which seem to indicate that the very opposite is true, *e. g.*, that four times as high a concentration of nitric oxide could be produced from carbon dioxide and nitrogen mixtures at 3500°, as would be obtained from air. They gave (at 3500°) 5.52% nitric oxide for air, and the present work shows 5.9%, corresponding to some unknown temperature; but where their calculations for nitrogen–carbon dioxide mixtures indicate 23.75% (at 3500°) and 10.88 (at 3000°), the present work shows not more than 1.4%. Now the matter is somewhat complicated by two factors: first, the temperature of the arc (or of the region at the edge just outside the arc where a thermal equilibrium is attained),[6] and, second, the rapidity with which the equilibrium is "frozen." The work of Colin and Tartar[1b] showed that such an equilibrium is "frozen" with almost incredible rapidity. It appears, therefore, that if an equilibrium be attained at some high temperature, say 3000°, it should be little changed during cooling. With this fact established, only the question of the temperature to which the equilibrium corresponds remains to be considered.

In the case of air, it is seen from a comparison with the data of Nernst, Finckh and Jellinek[7] for a purely thermal equilibrium that the concentration of nitric oxide here obtained must correspond to a very high temperature. At 2675° they found 2.23% of nitric oxide (although it appears from the more recent data of Briner, Boner and Rothen[8] that this value may be somewhat low). As a matter of fact, Nernst, Finckh and Jellinek, by extrapolation from their experimental data, estimate that the temperature corresponding to a thermal equilibrium concentration of 6% nitric oxide

[6] Daniels, Keene and Manning, *Trans. Am. Electrochem. Soc.*, **44**, 247 (1923).

[7] Nernst, Finckh and Jellinek, *Z. anorg. Chem.*, **45**, 116–126 (1905); **49**, 213–229 (1906).

[8] Briner, Boner and Rothen, *J. chim. phys.*, **23**, 788 (1926).

is approximately 3500 Å.; and about 6% was obtained in the present work. It seems justifiable, furthermore, to assume that the equilibrium with carbon dioxide–nitrogen mixtures corresponds to a temperature comparable with that in the case of air, particularly in the cases where the current was increased by 50% over that used for air. Moreover, Colin and Tartar[1b] found, in the case of air, that the highest concentrations of nitric oxide were obtained at relatively low values of current, that is, 40 milliamperes or less, so it is improbable that the yield of nitric oxide from nitrogen–carbon dioxide mixtures could be improved by indefinitely increasing the current. The conclusion is, therefore, that only small concentrations of nitric oxide, as compared with air, may be produced from nitrogen–carbon dioxide mixtures in the high tension arc.

The validity of the calculations of Krase and Mackey[2] appears to be in question. One objection to their procedure is the empirical equations used for expressing heat capacity as a function of the temperature. The equations for the heat capacities of nitrogen, oxygen, nitirc oxide, carbon monoxide and carbon dioxide apparently were taken from Lewis and Randall[9] who had formulated them upon the basis of data collected from various sources.[10] These equations, admittedly of a grossly empirical character, and based upon a minimum of reliable experimental data, have been used in the calculations of Krase and Mackey over a temperature range which amounts to an extrapolation of 1000–1500°. This is, no doubt, an unjustifiable procedure; for it is the opinion of Partington and Shilling,[11] who have recently collected data on the heat capacity of gases, that practically no reliable information exists for the region above 2000°. They state: "It will be seen, too, that the tables do not extend above 2000°. This is admittedly a drawback, but reliable tables cannot be constructed for the region where practically no accurate data exist. For approximate estimations in the region 2000–3000°C., several indications may be given, but that is all. For example, the molecular heats of the so-called permanent gases probably reach a maximum value, and continue for some considerable temperature range at that value. . . . It must be emphasized, however, that the final equations given for these tables apply only over the temperature range stated. Extrapolation will not give accurate results. . . ."

Summary

1. Only small concentrations of nitric acid were produced from nitrogen–carbon dioxide mixtures in the electric arc.

2. With a current of 65 milliamperes only one-sixth (1%) the concentra-

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[9] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**.

[10] Lewis and Randall, THIS JOURNAL, **34,** 1128 (1912).

[11] Partington and Shilling, "The Specific Heats of Gases," Ernest Benn, Ltd., London, **1924**.

tion of nitric oxide was produced from nitrogen and carbon dioxide as was produced from air.

3. The effect of reduced pressure upon the equilibrium obtained was very slight.

4. The results obtained show that the concentration of nitric oxide produced from carbon dioxide–nitrogen mixtures was increased by 30–40% when the current was increased by 50%.

5. The results obtained show that the reaction between nitrogen and carbon dioxide holds little promise as a means of fixing nitrogen by the arc process.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MISSOURI]

THE ORIGIN OF PROTOACTINIUM

BY JAMES E. WILDISH

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The major part of this investigation grew out of work started several years ago to separate protoactinium from America's most important uranium ore, carnotite. As expected, after much preliminary work, the presence of protoactinium was established. From the standpoint of radioactivity, it is generally considered as being the parent of actinium and hence takes its place at the head of the actinium series. The fact has long been established that the radioactive elements allow themselves to be arranged in three great divisions, the uranium, the thorium and the actinium series. The exact relation of the actinium series to the uranium and thorium series of radioactive elements is as yet not definitely known. This investigation was undertaken with the hope of throwing some light on this very important relationship.

The uranium disintegration series, as it is now generally represented, shows the actinium series as springing from uranium II, by the way of uranium Y, although it is generally indicated that this is uncertain.[1] According to this scheme, the actinium series is formed in a dual α-ray change from uranium II, the remainder of the uranium II atoms forming the ionium–radium series. At present the most widely accepted percentages for the numbers of uranium atoms forming the ionium–radium and actinium series are ninety-seven and three per cent., respectively. Obviously, if a definite percentage of the uranium atoms disintegrates to form the actinium series, the ratio between this series, or any member of it, to uranium, should be a constant in uranium bearing minerals, just as the radium–uranium ratio is constant.

[1] Meyer and Schweidler, "Radioaktivität," **1927,** p. 347; also Kohlrausch, "Radioaktivität," **1928,** p. 8.