true, and that therefore the values interpolated for the intermediate temperatures between 0 and 156° are doubtless substantially correct. Even at 218° the difference between the observed and calculated values (461 and 512), though doubtless real, is not very large; it lies in such a direction as to indicate that the energy change ΔE is decreasing at a more rapid rate at temperatures above 156° than at the temperatures below it. This is also shown by the fact that the ionization constant at 306° is much less than at 218°, while according to the linear equation the value of ΔE should become zero, and therefore that of the ionization constant K should become a maximum, very near the former temperature, namely, at 302°. The real maximum value of the constant seems to lie between 250 and 275°. Above this temperature ΔE assumes a negative value; and therefore the neutralization of completely ionized acids and bases would be attended by an absorption of heat.

It may also be mentioned that at the lower temperatures the calculated values agree well with the heat of neutralization directly measured by Wörmann,[1] who found for hydrochloric and nitric acids when neutralized with potassium and sodium hydroxides as mean values 14,710 calories at 0° and 13,410 calories at 25°.

It seems worth while to call attention to a possible theoretical explanation of the fact that water, unlike all other substances thus far investigated, continues to increase in ionization up to so high a temperature as 250 or 275°. This phenomenon may well arise from the facts that water at low temperatures is a highly associated liquid containing only a small proportion of H_2O molecules, and that this proportion increases rapidly with rising temperature. Therefore, even through the fraction of H_2O molecules dissociated into H^+ and OH^- ions may decrease steadily, yet the actual concentration of these ions continues to increase until a large proportion of the complex water molecules have been depolymerized.

To the Carnegie Institution of Washington we desire to express our great indebtedness for the financial assistance by which the execution of this investigation has been made possible.

BOSTON, November, 1909.

THE REACTION BETWEEN AMMONIUM CHLORIDE AND POTASSIUM DICHROMATE WHEN HEATED.

BY G. B. FRANKFORTER, V. H. ROEHRICH AND E. V. MANUEL.

Received December 8, 1909.

Doubtless every one who has given a course of lectures in general chemistry has used the potassium dichromate and ammonium chloride method for the preparation of nitrogen, inasmuch as this is one of the methods mentioned in nearly all of the old as well as in some of the new texts of

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[1] *Ann. Physik.*, [4] 18, 793 (1905).

inorganic chemistry. One of us using this method some years ago had reasons to question the correctness of the reaction as ordinarily given:

$$2NH_4Cl + K_2Cr_2O_7 = Cr_2O_3 + 2KCl + 4H_2O + N_2.$$

The matter was not carefully examined until some time later when the subject was taken up and carefully investigated. It required but a few experiments to show that the gas liberated by heating a mixture of ammonium chloride and potassium dichromate is not pure nitrogen. On the contrary, it contains, in addition to nitrogen, such amounts of nitric oxide and nitrogen peroxide as would make the simple equation given above entirely out of the question. In fact, the gas obtained is so rich in nitric oxide that when exposed to the air the brown peroxide color becomes very distinct. It was found, on looking up the literature, that Ramon de Luna,[1] in a letter to Dumas, first described the method and is responsible for the above equation. He intimated, however, that the nitrogen obtained was not pure unless passed through a solution of iron sulphate. It is evident from this last statement that he was aware of the presence of the oxides of nitrogen, although no mention of their presence was made and no attempts made to determine the quantity of gas liberated. From a number of analyses made under widely varying conditions, the writers have concluded that the above reaction is only correct in so far as water, some potassium chloride and some nitrogen are formed in the reaction. Chromic oxide is formed only after prolonged heating at a comparatively high temperature. Nitric oxide and nitrogen peroxide are probably formed when the mixture is heated at any temperature above 210°.

The gas first examined was prepared by using the quantities of salts recommended by de Luna, namely, equal parts of ammonium chloride and potassium dichromate and heating in a hard glass tube containing a delivery tube for collecting the gas over water. In these first experiments we were unable to detect nitrogen peroxide in the gas liberated, doubtless on account of its solubility in water. Later when the gases were collected over mercury, nitrogen peroxide was always found, varying, however, from a very small quantity to 3.5 per cent. Nitric oxide varied from 3 to 50 per cent. of the total gas liberated.

In our first experiments, great difficulty was experienced in preparing the gas for analysis, as it was necessary to remove every trace of air from the apparatus before the analysis was begun. After many experiments with different forms of apparatus, the following figure was constructed and used in most of the subsequent analyses: The hard glass tube A is connected with drying tube D by means of the three-way cock B; tube C is connected with an air pump. D is connected with F by means of a heavy rubber connector and pinchcock, E. F is connected with gas

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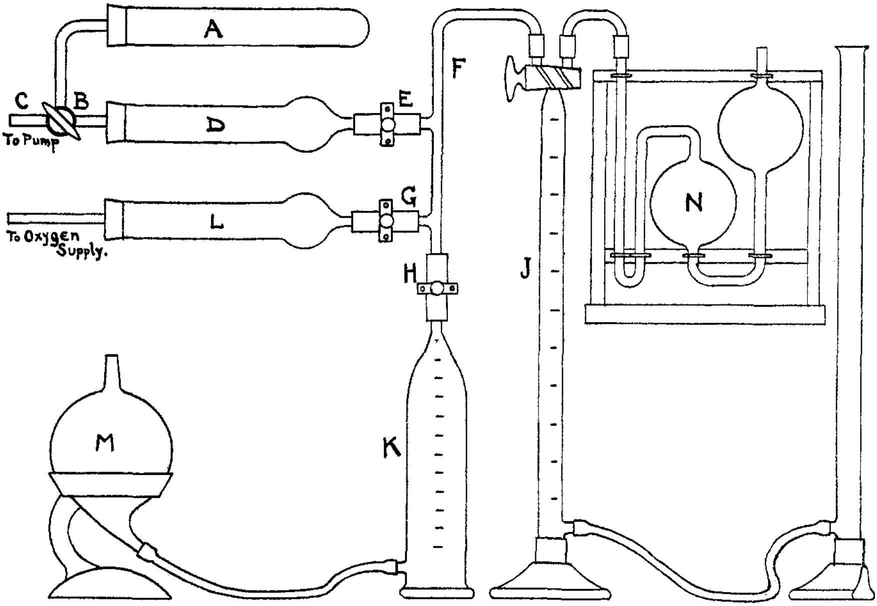
[1] *Ann. chim. phys.*, [3] 68, 183.

burette J, gas holder K, and drying tube L, for furnishing pure oxygen. The leveling tube M is connected with holder K by means of a heavy rubber tube. J is connected with gas pipette N by means of a three-way cock.

To prepare the gas for analysis, the hard glass tube A was filled with the mixture of ammonium chloride and potassium dichromate and connected with B. Gas burette J and reservoir K were filled with mercury up to the capillary tube F. Stopcock B was turned so that A and D were in connection with the air pump. The air was then exhausted and the apparatus washed out twice with pure nitrogen prepared from ammonium nitrite. Finally a vacuum of less than one millimeter was obtained and the experiment begun by gradually heating A. The gases first liberated were collected in the reservoir K until a sufficient quantity was obtained for examination, analysis being made of the gas liberated at different temperatures, beginning at 210°.



Analysis of the Gas.—As both nitric oxide and nitrogen peroxide were present, a method for the determination of these gases was used, depending upon the fact that nitrogen peroxide is soluble in potassium hydroxide, while nitric oxide is not. All the determinations in the first table of analyses were made over mercury with Hempel's apparatus for the exact analysis of gases over mercury. The nitrogen peroxide was first removed by means of caustic potash. The nitric oxide was then determined by adding to the residue a known volume of pure oxygen, and noting the change in the combined volumes as indicated by the following equation:

$$2NO + O_2 = 2NO_2.$$

Finally the results were checked by absorption of the nitrogen peroxide formed by means of potassium hydroxide.

In collecting the gas, preparatory to analysis and during the process of analysis, difficulties arose on account of the nitrogen peroxide attacking the mercury. We were unable to completely prevent this although by carefully drying the gases before coming in contact with the mercury, the action was greatly reduced. The following table gives the percentage by volume of the total amount of gas liberated on heating equal parts of the salts to a dull red heat:

TABLE I.

	N.	NO.	NO_2.
1	55.3	41.1	3.1
2	55.6	42.2	2.2
3	54.6	44.0	1.4
4	50.1	48.5	1.4
5	54.3	44.6	1.1
6	48.7	50.1	1.2
Average	53.1	45.1	1.7

An average of twenty analyses gave numbers differing but slightly from the above average. The first two analyses were made without completely evacuating the apparatus before heating. This doubtless accounts for the increased amount of nitrogen peroxide. It is not possible that the peroxide found in the other analyses can be due to air as the apparatus was thoroughly evacuated before heating.

In the above analyses, no attempt was made to regulate the temperature. These first experiments were made by heating the mixture with a bunsen lamp until no more gas was given. The analysis was then made of a sample of the total amount of gas liberated. Although the reaction apparently began at a low temperature, it required a dull red heat to complete it and to change the dichromate over into chromic oxide.

That exact data might be obtained concerning the changes which take place at different temperatures, an electric heater with a thermostat was constructed. The apparatus consisted of a resistance coil packed in asbestos. This coil enclosed a double-walled mercury jacket which in turn surrounded the bulb containing the mixture of chloride and dichromate. The mercury in this jacket transmitted the heat to the bulb and at the same time, by expansion and contraction, opened and closed a shunt for regulating the temperature. The bulb was made with a neck for introducing a thermometer and a delivery tube for the gases. With this apparatus the whole bulb containing the mixture could be uniformly heated and the temperature could be easily kept within a range of two degrees. The gases were determined gravimetrically. The water formed in the reaction was collected in a phosphoric anhydride bulb and the nitrogen peroxide was taken out by a small potash bulb. In the first experiment the nitric oxide was removed by passing the gas through a piece of apparatus consisting of a sodium peroxide tube followed by a pyrogallate bulb, the latter being used for the purpose of retaining any oxygen which might be liberated by traces of moisture coming in contact with the peroxide. Later this gas was determined by absorption in a ferrous sulphate solution. The nitrogen was collected and measured over water.

The following table of weights was obtained by heating a mixture of two molecules of ammonium chloride and one molecule of potassium dichromate at a temperature of 288–290° until gas ceased to come off. This required about eight hours. Previous to heating, the whole apparatus was carefully swept out with pure nitrogen. The absorption bulbs were removed at the end of the experiment and weighed. That these data may be compared with those of Table 1, the nitrogen and the oxides of nitrogen have been converted into percentages by volume. The following is a result of three analyses:

TABLE 2.

Analysis.	I. Grams.	II. Grams.	III. Grams.
Weight of mixture	7.5000	12.046	12.046
H_2O	0.6470	1.446	1.3280
NO_2	0.0127	0.0272	0.0052
NO	0.0072	lost	0.0269
N_2	0.3280	0.6000	0.4663
$Cr_2O_3.2H_2O$	.	4.520	.....
NO_2 by volume	2.26	.....	0.63
NO by volume	1.97	.....	5.08
N_2	95.77	.....	94.29

In these determinations the ammonium chloride and potassium dichromate were not all decomposed, both being found unchanged in the residue after heating at 290°. In fact, the water and nitrogen liberated were only about one-half of the amount which should have been given off, had the reaction been complete and all of ammonium chloride and dichromate decomposed.

A comparison of this table with Table 1 will show that entirely different reactions take place when the mixture is heated at 290° and at a dull red heat. This is not only evident from the composition of the gas liberated but also from the nature of the residue left after lixiviation.

Hydrated Chromic Oxide, $Cr_2O_3.2H_2O$.—No change takes place in a mixture of ammonium chloride and potassium dichromate until a temperature of 210° is reached. At this point slow decomposition begins and the mixture turns yellowish brown, due to the formation of chromium dioxide.[1] If the temperature is raised to 260° a slate-colored residue remains which, on lixiviating with water, leaves small greenish black iridescent spangles. This substance proved to be a hydrated oxide of chromium containing, however, a trace of chlorine which was very difficult to remove. Two analyses of this substance gave the following:

I. 0.5090 g. substance gave 0.0978 g. H_2O = 19.2 per cent.

II. 2.9608 g. substance gave 0.6474 g. H_2O = 21.6 per cent.

$Cr_2O_3.2H_2O$, $2H_2O = 19.15$.

The samples used in the above analyses were prepared at different times and under different conditions. The oxide used in the first analysis was dried in a vacuum desiccator, while that used in the second was dried in an air bath at 100°.

The change which takes place when a mixture of ammonium chloride and potassium dichromate is heated may be further shown from the fact that not only a change of temperature but also a change in the proportions of the salts will change the reaction. For instance, when a mixture of one part of ammonium chloride and four of the dichromate is heated to 370° a gray residue remains containing a trace of a violet substance, presumably the trichloride, as chromium chloride was found in the residue. When the above proportions were used no unchanged dichromate was found in the residue after heating. However, a strong odor of ammonia was noticed when the retort was opened.

When the proportions were reversed, using one part of ammonium chloride and four of the dichromate and the mixture heated to 370°, a black residue together with some unchanged dichromate remained. No violet compound was found.

The first change which evidently takes place on heating a mixture of ammonium chloride and potassium dichromate is the dissociation of the ammonium chloride. By diffusion, the ammonia passes up through the mixture and into the drying bulbs more rapidly than does the hydrochloric acid. There is left, then, in the mixture, free hydrochloric acid which reacts with the dichromate. By varying the temperature and the amount of hydrochloric acid, a series of reactions may take place giving all of the substances which have been found. The following may represent some of these equations:

1. $2NH_4Cl + 2HCl + 2K_2Cr_2O_7 = 4KCl + 2Cr_2O_3 + NO + NO_2 + 5H_2O$.
2. $3NH_4Cl + 2HCl + 2K_2Cr_2O_7 = 4KCl + 2Cr_2O_3 + N_2 + NO + Cl + 7H_2O$.
3. $2NH_4Cl + 4HCl + 2K_2Cr_2O_7 = 4KCl + 2Cr_2O_3 + 2NO + Cl + 6H_2O$.

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[1] *Bull. soc. chim.*, **40**, 168; *Proc. Chem. Soc.*, **24**, 27.

4. $4NH_4Cl + 6HCl + 2K_2Cr_2O_7 = 4KCl + Cr_2O_3 + 2CrCl_3 + 2N + 11H_2O$.

5. $2NH_4Cl + 8HCl + 2K_2Cr_2O_7 = 4KCl + 2Cr_2O_3 + N_2 + 3Cl_2 + 8H_2O$.

At a high temperature and especially where an excess of the dichromate is used, chlorine is liberated as indicated in equations 2 and 3.

Some of the above equations are only possible, of course, when a part of the dissociated ammonia has been eliminated from the reaction as for instance by the phosphoric anhydride bulb. Any free ammonia left would react with the oxides of nitrogen and chlorine, liberating free nitrogen.

The substances above mentioned are by no means the only ones formed when the above mixtures are heated. There is formed in addition to the above substances, a small amount (representing about one per cent.) of a substance which, when brought in contact with water, liberates pure nitrogen. This substance appears to be a chromyl nitride, and is now under further investigation.

A summary of the principal facts noted above may be stated as follows:

1. The reaction between ammonium chloride and potassium dichromate when heated is not correct as ordinarily given.
2. The oxides of nitrogen are always present in the gas liberated.
3. Both ammonia and chlorine are liberated under certain conditions.
4. Other chromium compounds besides the common oxide are formed.
5. A nitride, presumably trichromyl nitride is formed.
6. The complex nature of this reaction is due in very large measure to the dissociation of ammonium chloride.

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THE ACTION OF THIONYL AND SULPHURYL CHLORIDES ON MERCURY AND MERCURIC OXIDE.

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Received December 7, 1909.

The action of sulphuryl chloride on mercuric oxide has already been studied by Spelta.[1] He states that red oxide of mercury and sulphuryl chloride do not react in the cold or even after prolonged heating in sealed glass tubes.

Yellow oxide of mercury, on the contrary, was found by Spelta to react with sulphuryl chloride when the two are heated together in sealed glass tubes at 150°. He indicates that the reaction proceeds according to the equation

$$(a) \quad 2HgO + SO_2Cl_2 = HgCl_2 + HgSO_4$$

or

$$(b) \quad HgO + SO_2Cl_2 = HgCl_2 + SO_3$$

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[1] *Gazz. chim. ital.*, **34**, 262 (1904).