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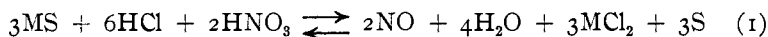
AQUA REGIA: PRELIMINARY PAPER.

BY WILLIAM C. MOORE.

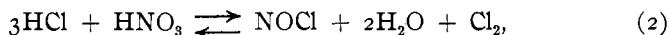
Introduction.

There seems to be a wide-spread belief that the efficacy of the mixture known as aqua regia when used as an oxidizing agent is due to the free chlorine it may yield under certain conditions.¹

Its action on a metallic sulfide, for instance, is generally expressed in accordance with this view, somewhat after the following manner:



an equation obviously derived from the equation



first developed by Goldschmidt² to express the changes occurring when concentrated hydrochloric acid and nitric acid are mixed in the proper proportions and the mixture heated.

Lunge and Pelet,³ however, in an investigation into the commercial methods for the preparation of chlorine, showed that when the chlorine from nitrosyl chloride formed by the above action from aqua regia at 100° was calculated to hydrogen chloride, and the nitrogen oxides were calculated as nitric acid there was too much of the former, and too little of the latter. These same investigators also showed that aqua regia becomes colored at 14°, begins to evolve gas at 35° and that between 95° and 100° a vigorous action occurs. When the temperature of the mixture was raised to 108.9° chlorine and other decomposition products were no longer evolved but a distillate containing an aqueous solution of hydrochloric and nitric acids was obtained. A study of the real nature of the course of oxidation reactions effected by aqua regia seems, however, to have been neglected. In seeking a full and consistent explanation of the action of aqua regia, the first question we have to answer is: "Is aqua regia always more effective than nitric acid as an oxidizer?" Böttger⁴ mentions the general tendency of analysts to utilize aqua regia as an oxidizing agent, and without committing himself, hints that their faith in its efficacy may not always be well founded. It is obvious that in many cases it is a valuable reagent, and to explain why, in certain cases, it is so effective as an oxidizer and solvent Ostwald⁵ has stated:

¹ Morgan, *Qual. Analysis*, p. 43, 1906 edition; Prescott and Johnson, *Qual. Analysis*, 5th edition, pp. 279, 333 (1904); Treadwell (Hall's translation), 1st edition, p. 247 (1905).

² Goldschmidt, *Ann.*, 205, 372 (1880).

³ Lunge and Pelet, *Z. angew. Chem.*, 8, 3 (1905).

⁴ Böttger, *Qual. Analysis*, trans. by Smeaton, p. 217 (1906 edition).

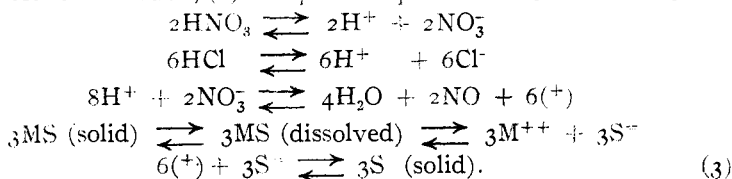
⁵ Ostwald, *Principles of Inorg. Chem.* (Findlay's trans.), 3rd edition, p. 339 (1905).

"The explanation is found in the consideration that the chlorine compounds which are formed of the above metals (gold and platinum) have a much more stable character than the nitrates which would be formed by the action of nitric acid. The fall from the initial substance to the end product is therefore greater in the case of aqua regia than in the case of nitric acid, not because aqua regia stands higher, but because the products of its action stand much lower." Thus, chloroplatinic acid possesses a smaller energy content than a possible platinum nitrate, so aqua regia dissolves platinum while nitric acid does not. But there are many cases where aqua regia is used to effect solution to which it is possible that such an explanation will not apply. It is obvious, for instance, that it holds perfectly good, with respect to the action of aqua regia upon mercuric sulfide; for mercuric chloride is much less highly ionized in aqueous solution than is mercuric nitrate;¹ but will it hold good for the action of aqua regia on lead sulfide, or upon such sulfides as arsenious, nickel and cobalt sulfides?

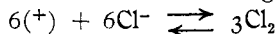
In the case of lead, lead chloride and lead nitrates are ionized at 25° to almost the same extent;² aqua regia and nitric acid each produce arsenic acid when arsenious sulfide is acted upon by either; cobalt and nickel chlorides are about as highly ionized as are their nitrates;² so if aqua regia in these special cases really is more effective as an oxidizer some other explanation than that free chlorine is the effective agent in aqua regia must be sought.

Again: a mixture of dilute nitric and hydrochloric acids, or of diluted "aqua regia" is sometimes used as an oxidizing agent; is chlorine set free from *these* mixtures?

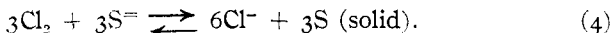
If we write the reaction, (1) as separate equations in ionic form it becomes



It is also possible to include the following additional steps:



and

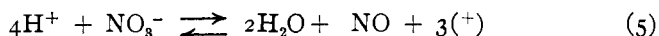


Now, if the formulation of the action is correctly represented in the various steps of (3) it is at once apparent that the function of the hydrogen chloride is simply to furnish hydrogen ions. Simplified then, the essential features of (3) are depicted in the following scheme:³

¹ Ley, *Z. physik. Chem.*, **30**, 247 (1899); Morse, *Z. physik. Chem.*, **41**, 709 (1902).

² Kohlrausch and Holborn, *Leitvermögen*, p. 166 (1898 edition).

³ This identical equation is given in Tower's *Qualitative Analysis* (1909 edition,



obviously the same scheme which expresses the action of nitric acid alone as an oxidizing agent when nitrogen dioxide is the only reduction product of the acid; in either case the three positive charges would be available to oxidize any substance, the oxidation product of which has a lower oxidation potential than nitric acid itself. In the case cited in (3), the sulfide ion is oxidized to elemental sulfur.

If, however, we include in the process the steps formulated in (4), the chloride ion actually does play a part in the oxidation, since according to this scheme the intermediate formation of chlorine and its subsequent reduction to chloride ion constitutes one of the essential steps. If this is true then the *chloride ion possibly acts as a catalytic agent*.¹ It has long been known² that a nitrate with hydrochloric acid, or a chloride with nitric acid, when heated behaves as does aqua regia; in fact, patents³ have been obtained for the manufacture of chlorine by these processes.

In order to ascertain whether the ionic explanation outlined above is a legitimate one, the author has been conducting, for some time, a series of experiments upon the oxidation of various sulfides and other oxidizable substances. It must be stated at the outset that these experiments have in the main been conducted as preliminary experiments for the purposes of orientation. It is not possible, so far as the author is aware, to control the action either of nitric acid, or of any of the oxidation mixtures studied so that only one oxidation product of the sulfide ion is obtained, and so actual quantitative measurements of the rate of oxidation of sulfide ion, seem, for the present at least, out of the question. It is hoped, however, that a quantitative comparison of the effectiveness of nitric acid alone, and mixtures of nitric acid and hydrochloric acid as oxidizing agents can be made in some other way, such as by using some other substance than the sulfides so far studied.

Experimental Part.

Experiments on Mercuric Sulfide.—In order to study the comparative oxidizing effect of nitric acid alone, and that of mixtures in which the concentrations of the hydrogen and nitrate ion differed, a series of mixtures of nitric acid and sulfuric acid was prepared, and the action of mercuric sulfide of these mixtures and of nitric acid alone was studied. If possible, it would have been better to have used some stronger acid than p. 14) to express the oxidation of ferrous to ferric ions, but apparently the author offers no explanation as to any difference that may exist between nitric acid and aqua regia as oxidizing agents.

¹ See, in this connection, Alex. Smith's "General Inorganic Chemistry," p. 448 (1096).

² See Gmelin-Kraut, Vol. 1, 3, p. 53 (1909).

³ See Lunge and Pelet, *loc. cit.*

sulfuric, but hydrogen iodide, which was thought of, itself acts on mercuric sulfide, while trichloroacetic, another possibility, could not be used on account of the low temperature at which it decomposes. In addition, the action on mercuric sulfide of mixtures, containing hydrogen, nitrate, and chloride ions in varying concentration, was superficially investigated.

These experiments with mercuric sulfide may be divided into three series: In Series A mercuric sulfide was treated with mixtures of nitric and sulfuric acids, in the cold (first, at 25.75° and then at room temperature). Where mixtures of 4 *N* nitric acid and 4 *N* sulfuric acid or 4 *N* nitric acid alone was used there was no apparent oxidation, even after many days. For instance, 4 *N* nitric acid had no effect after standing in contact with mercuric sulfide at ordinary temperature for 100 days. When a mixture of equal volumes of 4 *N* nitric acid and *concentrated* sulfuric acid was allowed to act on precipitated mercuric sulfide at 25.75° for 14 days some oxidation had occurred, as evidenced by the gray color of the solid and the brown gas in the upper part of the vessel. On standing at room temperature for 48 days longer this change in color of the solid was much more pronounced.

In Series B, mixtures of mercuric sulfide, 4 *N* nitric, and 4 *N* sulphuric acid were boiled, using a reflux condenser. Four-normal nitric acid effected the most rapid oxidation, then came in order: 66.7 per cent. 4 *N* sulfuric acid with 33.3 per cent. 4 *N* nitric acid mixture, then 33.3 per cent. 4 *N* sulfuric with 66.7 per cent. nitric acid, and lastly 4 *N* sulfuric acid alone.

In Series C, mercuric sulfide was boiled with mixtures containing hydrogen, nitrate, and chloride ions in varying proportions, a reflux condenser being used in each case, and the apparatus so arranged that any chlorine evolved would pass into 0.1 *N* silver nitrate acidified with nitric acid. A few details will probably be interesting:

Experiment 33.—0.5 g. HgS, 50 cc. 4 *N* HNO₃, 0.6 cc. 3 *N* KCl were boiled. Action began before the boiling point (105.1°) was reached; 5 min. after the heating began the action was vigorous and in 7 min. all the mercurous sulfide was oxidized to a light colored product. No indications of the evolution of chlorine were noted till after 44 min. of vigorous boiling when a slight cloud was produced in the silver nitrate. The yellow oxidation product weighed 0.42 g.

Experiment 34.—0.48 g. HgS, 40 cc. 4 *N* HNO₃, 0.5 cc. 3 *N* KCl were boiled under same conditions as in Exp. 33. Action began at 50° , with vigorous action at 95° ($1\frac{1}{2}$ min. after heating began), when the solid became yellow-gray in color. There were no indications of the evolution of chlorine. The residue weighed 0.54 g.

Experiment 38.—50 cc. of 4 *N* HNO₃ and 0.5 cc. 3 *N* KCl were boiled 30 minutes. There was almost no evolution of chlorine. The mixture was cooled, 1 g. of HgS added, and the heating resumed. A little action took place on adding the mercuric sulfide; there was brisk action 1 minute later, at 75° ; 2 minutes after heating began, at 95° , brisk evolution of oxides of nitrogen, with no chlorine, and at 103.8° the solution boiled, 3 minutes after the heating began. The solid was partially oxidized.

After 1 hour and 56 minutes' boiling the oxidation was not complete as there were still black particles left.

Experiment 41.—Practically a duplicate of No. 38; considerable chlorine evolved. In this experiment the preliminary boiling was omitted. In No. 42, 0.25 cc. 3 *N* HCl, 0.65 g. HgS and 50 cc. 4 *N* HNO₃ were boiled. In 41 minutes' boiling a large part of the sulphide was oxidized, and the oxidation was practically complete after 8 hours, and 47 minutes' boiling.

In all these experiments the mercuric sulfide employed was precipitated from a mercuric chloride solution, thoroughly washed and then dried before use.

Experiments with Lead Sulfide.—In the first set of experiments with lead sulfide, 0.5 g. precipitated lead sulfide was treated with 15 cc. *N* nitric acid; 0.5 g. was likewise treated with 15.0 cc. *N* nitric acid mixed with 0.25 cc. 3 *N* potassium chloride; and another 0.5 g. treated with 15.0 cc. *N* nitric acid and 0.25 cc. 3 *N* hydrochloric acid. Each of these mixtures was heated about 1 min. and allowed to stand one week. At the end of this time, the tubes in which chloride ion was present contained a mass of sulfur, permeated by crystals of lead chloride. The other tube still contained solid lead sulfide. In another set of experiments 0.25 g. lead sulfide was boiled (a) with 10 cc. 2 *N* nitric acid and 1 cc. 3 *N* hydrochloric acid; (b) with 10 cc. of 2 *N* nitric acid; and (c) 0.1 g. lead sulfide was boiled with 10 cc. 2 *N* nitric acid and 0.25 cc. 3 *N* potassium chloride. Again, the action was most rapid and complete in the cases where chloride ion was present. In each case a reflux condenser was used, and in all the experiments sulfur was deposited in the condenser tube. On repeating the experiments varying the concentration of the chloride ion, it was seen that the most sulfur was deposited in condenser tube of the flask containing the greatest concentration of chloride ion. Sulfate ions were produced in every case (precipitated as barium sulfate), and hydrogen sulfide was likewise evolved, as was shown by the precipitation of black silver sulfide when the evolved gases were passed through decinormal silver nitrate.

Experiments with Arsenious Sulfide.—When 0.185 g. of arsenious sulfide was heated, (a) with 50 cc. of 4 *N* nitric acid and (b) with 2.20 cc. 3 *N* hydrochloric acid, and 47.80 cc. of 4 *N* nitric acid, action began immediately in both instances. After heating 20 minutes only a little residue was left in either case. These mixtures were allowed to stand for two weeks, but no indications of further action were noted. In (a) the residue left weighed 0.04 g.; in (b) it weighed 0.06 g. 10 cc. of each mixture were taken and the arsenate ion determined by precipitation as magnesium ammonium arsenate, ignition and weighing as magnesium pyro-arsenate. In (a) the weight was 0.0415 g.; in (b) it was 0.0528 g.

When 0.1 g. of arsenious sulfide was treated with 20 cc. of 4 *N* nitric

acid and 0.5 cc. 3 *N* potassium chloride, action began immediately, and on standing over night a sulfur-yellow residue, weighing 0.005 g. and consisting largely of sulfur, was left. A second experiment was performed at the same time, substituting 0.5 cc. water for the chloride solution; the yellow residue left had the color of arsenious sulfide and weighed 0.045 g. Ten cc. of the solution from these experiments gave about the same volume of magnesium ammonium arsenate when precipitated under exactly the same conditions. These precipitates were not weighed.

Experiments on the Oxidation of the Ferrous Ion in Ferrous Ammonium Sulfate Solutions.—A series of experiments was carried out, in which tenth-normal ferrous ammonium sulfate was oxidized, (a) by means of nitric acid alone, (b) by means of solutions containing hydrogen, nitrate, and chloride ions in varying concentrations. The procedure was, in general, as follows: 25.06 cc. of 0.1 *N* ferrous ammonium sulfate were diluted to 45.06 cc. by means of the oxidizing solution; at definite intervals 10 cc. portions were removed and titrated with dilute potassium permanganate. When chloride ion was present, excess of manganous¹ ion (MnSO_4 solution generally) and excess of sulfuric acid was added, before titrating.

The temperature was ordinary room temperature (about 20°). In some of the series, one set of experiments was made (as will be seen) with nitric acid alone. The original titer for zero time was found by titrating 10 cc. of the ferrous solution before dilution, with the permanganate, and from the figure so obtained, the initial permanganate, value of 10 cc. of the 25.06 cc. of ferrous solution diluted to 45.06 cc., was calculated. All concentrations refer to total equivalent weights per liter.

SERIES A.

I. 25.06 cc. 0.1 *N* $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4$; 10 cc. *N* HNO_3 ; 10 cc. *N* HCl .

II. 25.06 cc. 0.1 *N* $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4$; 20 cc. *N* HNO_3 .

Time. Hrs.	I.	II.
0.0	5.89	5.89
5.5	6.00	5.80
23.0	5.87	0.85
29.25	5.92	0.45
47.00	5.71	0.18

Concentrations: Fe^{++} (total) 0.055; H^+ (total) 0.44 NO_3 ; I, 0.22; II, 0.44; Cl I, 0.22.

¹ See Zimmerman, *Ber.*, 15, 779 (1884); also Mixter and Dubois, *THIS JOURNAL*, 17, 405 (1895).

SERIES B.

- I. 25.06 cc. 0.1 *N* FeSO₄(NH₄)₂SO₄; 10 cc. *N* FeCl₃; 10 cc. *N* HNO₃.
 II. 25.06 cc. 0.1 *N* FeSO₄(NH₄)₂SO₄; 10 cc. *N* HNO₃; 10 cc. *N* HCl.

Time. Hrs.	I.	II.
0	5.28	5.28
3.75	6.18	5.78
48	5.21	5.69
51.75	5.59	5.91
72	5.61	5.40

Concentrations: Total Fe⁺⁺ I, II, 0.055. H⁺, I, 0.22; II, 0.44; NO₃⁻, I, II, 0.22; Cl⁻, I, II, 0.22.

SERIES C.

- 25.06 cc. 0.1 *N* FeSO₄(NH₄)₂SO₄; 8.9 cc. *N* HNO₃; 11.1 cc. H₂O.

Time, hours.....	0.0	4.5	22.5	32.17
cc. KMnO ₄	6.17	6.15	6.18	6.17

Concentrations: Fe⁺⁺, 0.055; H⁺, 0.19; NO₃, 0.19.

SERIES D.

- I. 25.06 cc. 0.1 *N* FeSO₄(NH₄)₂SO₄; 15 cc. *N* HNO₃; 5 cc. H₂O.
 II. 25.06 cc. 0.1 *N* FeSO₄(NH₄)₂SO₄; 15 cc. *N* HNO₃; 5 cc. *N*/1HCl.
 III. 25.06 cc. 0.1 *N* FeSO₄(NH₄)₂SO₄; 15 cc. *N* HNO₃; 5 cc. *N*/KCl.

Time. Hrs.	I.	II.	III.
0	5.83	5.83	5.83
4.57	0.50	5.96	5.95
65	0.10	5.96	5.99
109	0.00	..	6.00

Concentrations: Fe⁺⁺ (total I, II, III), 0.055; H⁺ I, III, 0.33; II, 0.44; NO₃⁻, I, II, III, 0.033; Cl⁻, II; 0.11 III, 0.33.

Experiments with Ferrous Chloride.—0.28 g. of pure iron wire was dissolved in 25 cc. of hot *N* hydrochloric acid. This solution was diluted to 100 cc. the next day. Three experiments were carried out. In I, 25.06 cc. of the ferrous chloride were mixed with 20 cc. of *N* nitric acid; in II, 25.06 cc. of the ferrous solution were mixed with 20 cc. 2 *N* nitric acid; in III, 25.06 cc. of the ferrous solution were mixed with 20 cc. 0.5 *N* nitric acid. 10 cc. of the original ferrous chloride were titrated with dilute permanganate, and from the number of cc. of this solution required for oxidation, the original or zero value for a 10 cc. portion of 25.06 cc. diluted to 45.06 cc. was calculated. At definite intervals 10 cc. portions of I, II, III were removed and titrated with permanganate, using excess of manganous sulfate and sulfuric acid as in the work with ferrous ammonium sulfate.

The temperature was that of the room—about 20°. The results for 10 cc. portions titrated as above, follow:

Time (hrs.).	I. cc. KMnO_4 .	II. cc. KMnO_4 .	III cc. KMnO_4 .
0	5.81	5.81	5.81
48	5.43	4.61	5.80
72	5.31	4.43	5.85
96	5.32	4.59	5.52

Discussion and Conclusions.

The results with mercuric sulfide show that mixtures containing hydrogen, nitrate and chloride ion more effectively and completely oxidize it than dilute nitric acid alone. This was to have been expected, from a knowledge of the great difference in the degree of ionization of mercuric nitrate and chloride. The formation of free chlorine, however, does not necessarily occur when such oxidizing mixtures as those just mentioned are heated, and if chlorine is set free it is largely, if not completely, reduced again to the ionic form. The results with hot mixtures of sulfuric and nitric acids show that if the total concentration of hydrogen ion is much greater than that of nitrate ion, such a mixture oxidizes mercuric sulfide more rapidly than a mixture where the opposite is true, which would be expected from a consideration of the active masses of the reacting substances. The difference noted, however, was slight.

Although lead sulfide is more rapidly oxidized by nitric acid when chloride ion is present than when it is absent, the difference in rate of oxidation might possibly be due to the difference in degree of dissociation of lead nitrate and lead chloride, the latter being less dissociated. For this reason, the experiments on arsenious sulfide have a greater value in the light they afford on the problem under consideration. The results with this substance show that in the cold a relatively greater amount of sulfur is formed by mixtures containing hydrogen, nitrate and chloride ion, from a given weight of arsenious sulfide, than is formed by the action of nitric acid alone; in hot solutions, while the weight of the *residue* is greater where chloride ion is present, likewise the amount of arsenate ion produced is greater than where nitric acid alone is used. The greater weight of the residue may be due to a relatively larger proportion of the sulfide ion being oxidized to sulfur by the diluted mixture containing chloride ion, while when nitric acid alone was used a greater amount of hydrogen sulfide could possibly have been formed. This point will bear further investigation.

The most important results are those obtained by oxidizing ferrous salts by means of mixtures containing hydrogen, nitrate and chloride ions, and by means of nitric acid alone. A glance at the tabulated results shows that oxidation is practically completely stopped in several of the experiments where chloride ion was present, and that nitric acid can oxidize ferrous sulfate more rapidly than ferrous chloride, because of this retarding action of the chloride ion. That the ferric ion retards

the oxidation of ferrous in some cases is known¹ but this is hardly a case of that sort since nitric acid alone oxidizes ferrous solution in the cold easily, as is seen from the results above. This peculiar result will be thoroughly and carefully investigated.

Taking a survey of all of this preliminary work as a whole, it seems that there is some ground, then, for the following conclusions:

1. Dilute nitric acid and dilute mixtures containing hydrogen, nitrate and chloride ions may effect the oxidation of certain substances at different rates, even when the final products of the two oxidations do not differ in their energy content.

2. This difference may be due (*a*) to the influence of excess of hydrogen ions where chloride ion is absent, and (*b*) when chloride ion is present, to a possible catalytic action of this ion.

3. The most striking example of chloride ion acting as a catalytic agent is in the oxidation of ferrous salts, when it acts as a negative catalytic agent.² Finally it must again be emphasized that this work here reported is purely preliminary, and serves to outline a field of work in which it is hoped some important results may be achieved, in the future.

NEW YORK CITY.

A VOLUMETRIC ESTIMATION OF PHOSPHORIC ACID.

BY J. ROSIN.

Received April 26, 1911.

The reaction between silver nitrate and a soluble phosphate whereby silver phosphate is precipitated has served as the basis of several attempts at a volumetric estimation of phosphoric acid. Perrot,³ who was the first to propose a method based on this reaction, precipitated the phosphoric acid with silver nitrate in the presence of acetic acid and determined the residual silver by sodium chloride. Holleman⁴ converted the phosphoric acid or the mono-alkali salt into the dialkali salt by means of caustic soda and precipitated the phosphoric acid with silver nitrate in the presence of sodium acetate. The residual silver was then titrated in an aliquot portion by Volhard's method. Lieberman⁵ adds a considerable amount of nitric acid to the solution of the phosphate, then adds an excess of silver nitrate and follows this with ammonia water until blue litmus paper is no longer affected. He then determines residual silver by Volhard's method.

Holleman's method recommends itself and it is in fact the best of the

¹ Benson, *J. Physic. Chem.*, 7, 1-14; 7, 356-77 (1903).

² See also in this connection, Benson (*loc. cit.*) with respect to the influence of iodide ion, and for other theories.

³ *J. Soc. Chem. Ind.*, 1888, 311.

⁴ *Z. anal. Chem.*, 1895, 85.

⁵ *Analyst*, 1909, 361.