Summary

1. Crystal growth of an alloy of 99% of lead and 1% of antimony has been found to take place with a velocity which may be expressed by the same equation as a monomolecular reaction, that is the velocity at any instant is proportional to the ultimate volume less the mean crystal volume at that instant.

2. The velocity constant calculated in this way is only slightly affected by the temperature.

3. The ultimate or equilibrium volume is an exponential function of the temperature and may be expressed by an equation of the form $V = Be^{(-A/T)}$.

4. The ultimate crystal volume is a linear function of the decrease in height of a cylindrical slug.

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THE OXIDATION OF HYDRAZINE. II. THE EFFECT OF OXYGEN ON THE DECOMPOSITION OF HYDRAZINE. THE REACTIONS WITH FERRICYANIDE IN ALKALINE SOLUTION, AND DICHROMATE IN ACID SOLUTION

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RECEIVED MAY 12, 1924 PUBLISHED AUGUST 5, 1924

The Effect of Oxygen on the Decomposition of Hydrazine

In the first paper[1] the following experimental data had been incidentally collected on the decomposition of hydrazine sulfate solutions at various acid or alkali concentrations.

TABLE I

THE DECOMPOSITION OF HYDRAZINE IN THE PRESENCE OF AIR

Expt.	Concn. of hydrazine M	Acidity or alkalinity of the solution	Time	Decomposed %
19, Table I	0.11	H^+ = about 0.1 M[2]	2 months	0
4, Table IV	.008	H^+ = about 10^{-7}	2 hours	0.9
11, Table IV	.015	H^+ = about 10^{-7}	48 hours	8.1
19, Table II	...	alkaline	10 minutes	2.0
p. 864	.05	OH^- = about 0.5	5 minutes	0.9
p. 864	.05	OH^- = about 0.5	16 hours	20.0

These solutions were all in contact with air, and the opinion was expressed that the presence of oxygen is responsible for the rapid "decomposition" of hydrazine in alkaline solutions.

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[1] Bray and Cuy, THIS JOURNAL, **46**, 858 (1924).

[2] This solution of hydrazine sulfate (0.11 M) gave a green color with methyl violet, indicating that the concentration of H^+ is about 0.1 M. For more exact evidence that the hydrolysis of $N_2H_6^{++}$ into $N_2H_6OH^+$ (or $N_2H_5^+$) and H^+ is nearly complete, see Bredig, *Z. physik. Chem.*, **13**, 314 (1894), and Bach, *ibid.*, **9**, 250 (1892).

There were occasional and highly contradictory statements in the literature in connection with the fact that hydrazine salts in alkaline solution disappear. The brief incidental remark of Sabanejeff,[3] which seems to have escaped the attention it deserves, should be mentioned. He suggests that the difficulty in measuring the conductance of hydrazine salts is due to decomposition, with evolution of gases, under the action of platinum and especially platinum black. In a subsequent publication[4] he found that this effect was due to atmospheric oxygen, platinum acting as a catalyst in the oxidation but not in the decomposition of the hydrazine. This he proved by bubbling oxygen through a hydrazine sulfate solution in which platinum was suspended. However, he did no work either in alkaline solutions or in the absence of platinum.

On the other hand, Tanatar[5] in his study of the decomposition of hydrazine in the presence of platinum black, found that in alkaline solution hydrogen, nitrogen and ammonia were formed in proportions which varied with the experimental condition, while in acid solution no hydrogen was formed. Apparently he was satisfied that he was dealing with catalytic decomposition alone, but it is not impossible that oxidation effects, due to oxygen from the air or platinum black, were involved.

In view of this state of affairs it seemed highly desirable to settle experimentally the question of whether hydrazine in alkaline solution decomposes spontaneously or is merely oxidized.

Experiments in the absence of oxygen were carried out as follows. The vessel consisted of a round-bottom glass flask with three outlets in the upper part. One of these was connected either with a vacuum pump or with a supply of nitrogen gas which was freed from oxygen by washing with ammoniacal cuprous sulfate solution. The second was a vertical tube through which the solution could be introduced and which could be tightly closed with a rubber stopper. The third was for the purpose of withdrawing samples of the hydrazine solution for analysis, in such a way as to avoid completely atmospheric oxidation; it consisted of a sealed-in tube reaching nearly to the bottom of the flask, and leading outside through a stopcock to a calibrated pipet of about 10 cc. capacity, also sealed on. The solution could be forced into the pipet by nitrogen pressure.

A solution of hydrazine sulfate was introduced into the flask, heated twice in a vacuum to remove oxygen, and cooled after each evacuation in the presence of nitrogen. While the nitrogen current was flowing through the vessel, enough sodium hydroxide solution was introduced to make the solution approximately molal with respect to sodium hydroxide, and the flask was again tightly stoppered. At intervals, samples of the

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[3] Sabanejeff, *Z. anorg. Chem.*, **17**, 492 (1898).

[4] Sabanejeff, *Chem. Centr.*, **1899**, II, 33; *J. Russ. Phys.-Chem. Soc.*, **31**, 375 (1899).

[5] Tanatar, *Z. physik. Chem.*, **40**, 475 (1902); **41**, 37 (1902).

solution were withdrawn, run at once into an excess of dil. sulfuric acid and analyzed by the iodic acid method.[1]

Three determinations in the first hour, three more after two hours, and two after 26 hours agreed almost exactly, thus showing that the decomposition of hydrazine at room temperatures even in molal alkali is not appreciable in 26 hours, when atmospheric oxidation is completely eliminated. In a similar set of experiments (and even in more dilute alkali; see Table I) in the presence of air 20 to 25% of the hydrazine decomposed in about 16 hours.

In view of the fact that, at least in the absence of platinum, the disappearance of hydrazine in alkaline solution is entirely due to atmospheric oxidation, it is evident that all work on hydrazine reactions in alkaline solution in the presence of air is to be considered merely as qualitative in nature, and must be repeated with careful exclusion of oxygen before any conclusion can be drawn from it. For it is evident, when the reactions of the various oxidizing agents with hydrazine in alkaline solution are considered, that oxygen, when present, also reacts with hydrazine, whenever the reaction is sufficiently slow. From the fact that iodine reacts quantitatively even under these conditions (1 mole of hydrazine requiring exactly 4 equivalents of iodine), it follows that this reaction is very rapid. However, when the oxygen error is demonstrated to exist, it is not safe to conclude that the reaction is relatively slow, since catalysis of the oxygen reaction or its "induction" by another reaction may occur.[6] As an example may be mentioned the alkaline bromine reaction[1] for which it was shown that the deviations, presumably due to an oxygen error, are actually larger than would have been the case if the two reactions had been taking place independently. In the alkaline iodate reaction,[1] however, the error may have been due merely to the slowness of the iodate-hydrazine reaction. In any event, it seems probable that the reaction would have been quantitative if the oxygen had been excluded.

The Oxidation of Hydrazine by Ferricyanide in Alkaline Solution

The quantitative oxidation of hydrazine to nitrogen by ferricyanide in alkaline solution is the basis of a nitrometric method of analysis studied by Rây and Sen.[7] In the following it is shown that an accurate titration method could also be developed. However, since several other satisfactory oxidimetric methods are known,[1] the ferricyanide reaction is of interest mainly because, as in the case of the iodine reaction, the possible error due to atmospheric oxidation in the alkaline solutions is negligible.

The procedure was as usual to mix known amounts of ferricyanide and

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[6] Similarly in acid solution, in spite of the fact that the oxygen reaction does not take place, it is quite possible that an oxygen effect may be found in certain cases due to catalysis or induction.

[7] Rây and Sen, *Z. anorg. Chem.*, **76**, 380 (1912).

hydrazine, the former in excess, and then to determine the excess iodimetrically.

The ferricyanide was standardized according to the method of Müller and Diefenthäler,[8] that is, an excess of potassium iodide and zinc sulfate was added (the former in about four times and the latter in twice the amount by weight of ferricyanide present) and the liberated iodine titrated with thiosulfate solution. The hydrazine sulfate solution was standardized by the iodic acid method.

After the hydrazine and ferricyanide had been pipetted into a glass-stoppered flask, 10 cc. of 1 *N* sodium hydroxide solution was added. After five minutes the solution was made neutral to litmus, 40 cc. of approximately 0.1 *M* zinc sulfate solution (about 5 g. of $ZnSO_4.7H_2O$) and a large excess of potassium iodide (over 5 g.) were added. When, after titration with thiosulfate, the residue was a milk-white precipitate of zinc ferrocyanide, the error was zero or very small. A green tinge indicated the formation of some ferro-ferricyanide, and the result was invariably high even when the green was very faint.

The alkali was added because the reaction between hydrazine and ferricyanide is slow in acid solution. In the alkaline solution the error of atmospheric oxidation was possible, and would tend to give low results.

The results are given in Table II, where the volumes and concentrations of the solutions are given at the top of the table, and the amount of thiosulfate equivalent to the excess oxidizing agent appears in the second column.

TABLE II

THE OXIDATION OF HYDRAZINE BY FERRICYANIDE IN ALKALINE SOLUTION

Volume of hydrazine = 9.95 cc. Volume of ferricyanide = 14.43 cc.
Concn. of hydrazine = 0.0905 *M* Concn. of ferricyanide = 0.2954 *M*
Normality of thiosulfate = 0.1236 *N*

Expt.	Thiosulfate Cc.	Calculated concn. of N_2H_4	Deviation %	Remarks
1	5.43	0.0903	− 0.2	
2	5.35	.0905	− .0	Alkali added slowly
3	5.38	.0904	− .1	
4	2.26	.1001	+10.5	Heated
5	3.35	.0967	+ 6.8	
6	2.75	.0986	+ 8.8	
7	3.89	.0950	+ 4.9	Alkali added first
8	2.86	.0982	+ 8.5	Alkali added first, 6 *N*
9	0.88	.1044	+15.3	No $ZnSO_4$
10	3.25	.0970	+ 7.1	Heated before addition of alkali

With the procedure described above, in Expts. 1, 2 and 3, the results were satisfactory, being low by only 0.2%, 0.0% and 0.1%, respectively. In the second experiment, in which the alkali was added drop by drop to

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[8] Müller and Diefenthäler, *Z. anorg. Chem.*, **67**, 418 (1910).

decrease the possible error due to atmospheric oxidation, there was no error.

Heating the solution before and during the reaction to avoid the oxygen error is decidedly not advisable as shown by Expts. 4, 5 and 6. In all cases the solution turned greenish-blue and the odor of hydrocyanic acid could be easily detected. The high results can be ascribed to one or all of the following causes: oxidation of the hydrocyanic acid, oxidation of ammonia possibly formed by hydrolysis of the cyanide, vaporization of hydrazine (if the solution is alkaline), and the formation of insoluble ferro-ferricyanide which reacts only slowly with iodide. The mixture after titration of the liberated iodine invariably was green or blue.

In Expts. 7 and 8, alkali (10 cc. of 1 *N* and 6 *N* potassium hydroxide, respectively) was added first. The large deviations show that both increasing the alkalinity and adding the alkali first presumably favor the decomposition of the ferricyanide, and are to be avoided.

To determine the magnitude of the possible error due to incompleteness of the reaction between ferricyanide and iodide to liberate iodine, in Expt. 9 the usual procedure was adopted, but without the addition of zinc sulfate to remove the ferrocyanide and favor the liberation of iodine. A very large deviation (15%) was obtained. It should be mentioned that the end-point kept coming back.

Finally, in Expt. 10 the hydrazine was added to the ferricyanide and the solution was heated until a green precipitate began to appear, and then alkali (10 cc. of 1 *N*) was added. Although the green color disappeared quickly, the result is high, showing that the formation of ferro-ferricyanide is not the sole cause of high results.

The Dichromate-Hydrazine Reaction

The oxidation of hydrazine by dichromate in acid solution is an example of a reaction in which the results obtained vary with the experimental conditions. The reaction

$$3N_2H_5^+ + 2Cr_2O_7^{--} + 13H^+ = 3N_2 + 4Cr^{+++} + 14H_2O \qquad (1)$$

which requires four equivalents of dichromate per mole of hydrazine, may be accepted as the upper limit in respect to the amount of oxidizing agent required per mole of hydrazine. This limit can be approached under favorable conditions; but, as it is not actually realized, the reaction cannot serve as the basis of a method for analyzing hydrazine.[9] In the present investigation we have endeavored to make the deviation from Reaction 1 as large as possible, in the hope of finding a definite limit in this direction. If there is such a limit, and it can be determined, it would throw some light on the mechanism of the hydrazine oxidation.

The factor which has the greatest influence on the results was found to

[9] Compare Ref. 1, and the work of Browne and Shetterly there mentioned.

be the rate of addition of one reagent, for example dichromate, to the reaction mixture containing sulfuric acid and the other reagent. Thus, if in two experiments, with all other conditions identical, dichromate is added more slowly in one case than the other, the effect of the slow addition is to decrease the amount of oxidizing agent required, and therefore to increase the deviation from Reaction 1. Also, when hydrazine sulfate is added slowly to the acid dichromate solution, the deviation from Reaction 1 is diminished, which is consistent with the result first mentioned.

Three series of experiments in which dichromate was added last are summarized in Table III and Fig. 1. In the first and second series 10 cc. of 6 *N* sulfuric acid was used, and in the last series 10 cc. of concd. sulfuric acid. The excess of dichromate, added in all cases, was determined iodimetrically, and the concentration of hydrazine was calculated on the assumption that the reaction had corresponded to Equation 1.

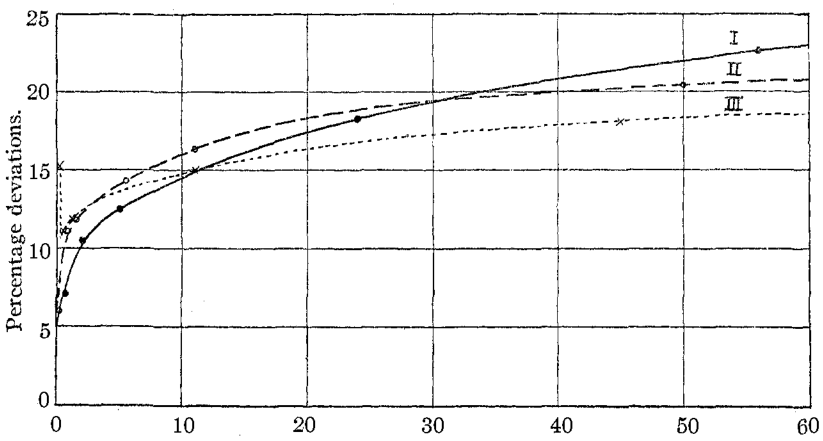

Fig. 1.—Compare Table III.

In Fig. 1 the percentage deviations (see the last column) are plotted against the time intervals taken in adding the dichromate (see the third column). In each experiment the solution was stirred or shaken during the addition, and the rate of addition was roughly constant. The times were varied from approximately 0.2 minute, corresponding to free delivery from the pipet, to nearly one hour, when the dichromate was added drop by drop. The small variation in the volume of solution delivered was negligible in comparison with the effects obtained.

The marked influence of the rate of addition of the dichromate is evident. The curves in Series I and II rise rapidly at first, and then more slowly, thus indicating that the percentage deviation cannot be increased indefinitely, and therefore that a limit exists.

TABLE III

DEVIATIONS IN THE HYDRAZINE-DICHROMATE REACTION AS A FUNCTION OF THE TIME OF ADDITION OF THE DICHROMATE

Compare Fig. 1

Volume of $N_2H_6SO_4$ solution = 9.95 cc. Concentration of $N_2H_6SO_4$ solution = 0.09054 M. Order of mixing, H_2SO_4-$N_2H_6SO_4$-$K_2Cr_2O_7$.

	Expt.	Time of addition Min.	0.1 M thiosulfate Cc.	Concn. of N_2H_4 calcd. M	Deviation %
Series I	1	0.5	9.70	0.0841	7.1
Vol. of $K_2Cr_2O_7$ = 35.1 cc.	2	2	10.93	.0810	10.5
Concn. of $K_2Cr_2O_7$ = 0.1231 N	3	5	11.65	.0792	12.5
Initial acidity = about 3 N	4	24	13.43	.0747	17.3
Final acidity = about 1.1 N	5	56	15.29	.0701	22.6
Series II	1	0.2	15.05	.0851	6.0
Vol. of $K_2Cr_2O_7$ = 9.94 cc.	2	.8	16.88	.0805	11.1
Concn. $K_2Cr_2O_7$ = 0.4922 N	3	1.5	17.13	.0799	11.8
Initial acidity = about 3 N	4	5.5	18.07	.0775	14.3
Final acidity = about 2 N	5	11	18.75	.0758	16.3
	6	50	20.46	.0716	20.4
	7[a]	0.2	15.13	.0849	6.2
Series III	1	.2	18.41	.0767	15.3
Vol. of $K_2Cr_2O_7$ = 35.1 cc.	2	.5	16.90	.0805	11.1
Concn. of $K_2Cr_2O_7$ = 0.1231 N	3	1.2	17.18	.0798	11.9
Initial acidity = about 17 N	4	11	18.30	.0770	15.0
Final acidity = about 6 N	5	45	19.41	.0742	18.1

[a] In Expt. II,7, 7 cc. of 0.16 M $(NH_4)_2SO_4$ was added before the dichromate; compare II,1.

Most of the experiments mentioned in the first paper were performed under conditions similar to those in Series II, and these later results agree fairly well with the earlier ones. The average value of the deviation, in experiments in which the reagents were mixed rapidly was about 6%, which is the same as the value in II,1 for 0.2 minute time of addition. This deviation was lowered to 4.5% when the hydrazine was added last and the time of addition was about 70 min. A comparison of II,7 with II,1 shows that the presence of NH_4^+, one of the products of the side-reaction, has little or no effect. In the earlier work it was found that the presence at high concentration of Cr^{+++}, a product of the main reaction, also had no effect. This last result makes it impossible to account for the deviation by assuming a rapid *primary* formation of a Cr^{+5} or Cr^{+4} compound by the interaction of Cr^{+++}, $Cr_2O_7^{--}$ and H^+.

Evidence that the deviation at zero time would be smaller in Series I than in Series II is furnished by an experiment in which the hydrazine was added rapidly to the dichromate solution, all other conditions being the same as in Series I; the deviation was 5.3%. As implied in the preceding paragraph, the corresponding value in Series II would be nearly as high as 6%.

The difference in the experimental conditions in Series I and II consists in a fourfold increase in the concentration of the dichromate solution added in the experiments of Series II, and a resulting increase in the concentration of acid except at the beginning of these experiments. The effect of these variations is not great, but it is evident that the deviation (in Series II) is increased at low times of addition, and decreased at higher times. Comparison with Series III, in which the acid concentration is much greater, shows a further change in the same direction: a high concentration of sulfuric acid thus has the effect of greatly increasing the deviation, but only at low times of addition. The high result in III,1 is not an experimental error, since it was confirmed by other experiments.

The most favorable conditions for obtaining a large deviation thus seem to be (1) the use of a dilute solution of dichromate; (2) the very slow addition of this solution to the acidified hydrazine solution; and (3) the avoidance of high concentration of acid. As a confirmation, there may be mentioned an experiment in which the dichromate was still more dilute than in Series I and the time of addition was very long (about one hour); the deviation was found to be over 25%.

The slow addition of dichromate has the effect of maintaining in the reaction mixture a relatively high concentration of hydrazine, $N_2H_5^+$, until nearly all the hydrazine is used up; and therefore corresponds to an experiment in which the hydrazine is present in very large excess over the dichromate. The hydrazine thus has an opportunity to react with any intermediate products formed in Reaction 1, and this may be accepted as a necessary condition for a large deviation from this reaction.

However, this condition was not maintained during the latter part of each experiment, since the dichromate was always added in excess. It follows that the percentage deviation must have been greater at the beginning of an experiment than near the end, and therefore that the average deviation actually found is smaller than the theoretical limiting value. We must, therefore, conclude that the limit is higher than a 25% deviation. It may indeed greatly exceed this value.

Evidence that Reaction 1 takes place in steps is furnished by the large number of molecules involved, 18 in the equation as written. Definite proof is supplied by the rate measurements of Seubert and Carstens,[10] who found that the reaction was first order with respect to both $N_2H_5^+$ and $Cr_2O_7^{--}$. This may be considered a first approximation, even though the reaction measured did not correspond exactly to Equation 1. For the mechanism they assume the oxidation of hydrazine to nitrogen and the reduction of sexavalent chromium to quadrivalent, and write the equation

$$N_2H_5^+ + Cr_2O_7^{--} = N_2 + 2CrO_2 + OH^- + 2H_2O \qquad (2)$$

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[10] Seubert and Carstens, *Z. anorg. Chem.*, **56**, 357 (1908).

for the rate-determining reaction. The following equation also conforms to their assumptions.

$$N_2H_5^+ + Cr_2O_7^{--} = N_2 + HCr_2O_5^- + 2H_2O \qquad (2')$$

Other reactions which agree with the kinetic data may, of course, be written, such as for the formation of N_2H_2 and a compound of quinquivalent chromium; and the choice of a probable mechanism should be based on a careful study of many reactions of hydrazine and dichromate, respectively.

If we assume that there is only one rate-determining reaction, and that it is represented by Equation 2 or 2′, then deviations from Reaction 1 may be explained by a reaction between $N_2H_5^+$ and quadrivalent chromium, which requires x equivalents of oxidizing agent per mole of hydrazine, where x is less than 4. The deviation is increased by the presence of excess hydrazine, and the "limit" will be reached when all the intermediate chromium compound reacts in this way. If x has the value 1, the one mole of hydrazine oxidized by Reaction 2 or 2′ requires four equivalents of oxidizing agent, and the two moles oxidized in the following reaction require two equivalents, thus giving a limit of six equivalents for three moles of hydrazine or two equivalents per mole, which is a decrease of 50%. Similarly, if x has the value 2 or 3, the limit is 2.67 or 3.33 equivalents per mole, and the deviation is 33.3 or 16.7%, respectively. The last case, 16.7% deviation, is excluded by our experimental results; but either of the others, 33.3 or 50%, is a possible limit.

To explain the approach to Reaction 1, when the dichromate is present in large excess, assumptions such as the following may be made. The +4 chromium compound, formed by Reaction 2 or 2′, reacts with $Cr_2O_7^{--}$ to form a Cr^{+5} compound, and four equivalents of this oxidizing agent then oxidize one mole of hydrazine. Or, in the acid solution the Cr^{+4} compound is spontaneously transformed into Cr^{+++} and $Cr_2O_7^{--}$, a reaction which appears not to be excluded by the data on the behavior of the known compounds of +4 chromium.

Another possible mechanism deserves mention. If N_2H_2 may be formed as an intermediate product, it will probably tend to accumulate in the solution when hydrazine is present in excess and the concentration of dichromate is thereby lowered. Its decomposition into NH_3 and N_3H,[11] or into N_2 and H_2, would account for the observed deviations. A complete quantitative study of the reaction should therefore be made. This study would ensure the detection of all the products, and would also decide whether oxygen of the air reacts with any of the intermediate products. Work along these lines was begun, but the investigation was interrupted before definite results were obtained.

[11] This was suggested by Browne and Shetterly, THIS JOURNAL, **31**, 794 (1909).

Summary

1. It is shown that the presence of oxygen is responsible for the fairly rapid "decomposition" of hydrazine in alkaline solution. When air is excluded the concentration remains unchanged for 26 hours at room temperature. It is evident that earlier work on hydrazine reactions in alkaline solution should be repeated with careful exclusion of oxygen.

2. When alkali is added to a solution containing a hydrazine salt and excess ferricyanide, the oxidation of hydrazine to nitrogen is quantitative even in the presence of oxygen of the air. This reaction can be made the basis of an accurate volumetric method of analysis of hydrazine, in which the excess of ferricyanide is determined iodimetrically. The only other hydrazine reaction in alkaline solution in which the oxygen error is known to be negligible is that with iodine; both of these reactions must, therefore, be very rapid in comparison with the oxygen-hydrazine reaction.

3. The quantitative oxidation of one mole of hydrazine to nitrogen by *four* equivalents of dichromate is a limiting reaction which can be approached but not realized. The favorable conditions for approaching the maximum value of four are a moderate rather than high concentration of acid, and the presence during the reaction of dichromate in excess. There are large deviations from this reaction, however, when the presence of hydrazine, $N_2H_5^+$, in excess is ensured, such as by adding the dichromate solution very slowly. There is evidence that a limit exists which corresponds to less than three equivalents of oxidizing agent per mole of hydrazine.

Evidence that the reaction takes place in steps is presented. If in the rate-determining reaction hydrazine is oxidized directly to nitrogen, then it is probable that a quadrivalent chromium compound is formed as an intermediate step, and that its reaction involves one, or possibly two, equivalents per mole of hydrazine.

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