must be kept within the limits $189 < n < 191$. A comparison of the two examples makes clear of how great importance it may be to know how to do the shaking in order to get the best effect.

In conclusion I wish to thank Professor Dr. Niels Bjerrum, whose advice and helpful criticism of my work have been of great value.

Summary

The supersaturation error in measurements of velocity of chemical reactions by rate of gas evolution has been examined.

The velocity of the evolution of carbon dioxide from supersaturated solution follows the unimolecular law. The dependence of its velocity constant h on the number of horizontal shakings n per minute has been determined. h has a maximum and falls rapidly when n is diminished or increased.

A mathematical expression for the velocity of the evolution of gas in the course of the reaction $A \longrightarrow B + C$ (dissolved), followed by the reaction C (dissolved) $\rightleftarrows C$ (gas), has been derived.

The importance of the results for the measurement of a fairly quick unimolecular reaction has been discussed.

COPENHAGEN, DENMARK

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, NO. 557]

SILVER ION CATALYSIS OF PERSULFATE OXIDATIONS. I SALT EFFECT ON THE VELOCITY OF OXIDATION OF AMMONIA. II. COMPARISON OF THE VELOCITY WITH VARIOUS REDUCING AGENTS

BY CECIL V. KING

RECEIVED MAY 16, 1927 PUBLISHED NOVEMBER 5, 1927

I. Introduction

It has been shown that persulfates react with ammonia, in alkaline solutions, in the presence of silver salts, with a measurable velocity,[1] and Yost has represented the reaction as taking place in two steps, as follows (the silver ion, however, being in an ammonia complex):

$$S_2O_8^{--} + Ag^{+} \longrightarrow 2SO_4^{--} + Ag^{+++} \text{ measurable} \qquad (1)$$
$$3Ag^{+++} + 2NH_3 \longrightarrow 3Ag^{+} + N_2 + 6H^{+} \text{ extremely rapid} \qquad (2)$$

There seems to be no question that trivalent silver is formed, as indicated by two things: the analysis of the insoluble compound formed when persulfates and silver salts are mixed, and the fact that the reaction rate, when ammonia or chromic salts are oxidized, is proportional to the *first* power of the silver-ion concentration.

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[1] (a) Marshall, *Proc. Roy. Soc. Edinburgh*, **23**, 163 (1900). (b) Yost, THIS JOURNAL, **48**, 374 (1926).

Yost found that when this reaction was carried out in alkaline solution increase in ammonia concentration increased the velocity of reaction, while increase in hydroxide concentration decreased it. Since in any one experiment ammonia and hydroxyl ions both disappear and the silver-ion concentration remains constant, rather good "pseudo-unimolecular" rate constants can be obtained. Since Yost attributes the measurable velocity entirely to reaction (1), he concludes that the effect of increased ammonia concentration is to increase the concentration of a silver ion with more ammonia groups attached than in $Ag(NH_3)_2^+$, and that this higher complex makes reaction (1) faster. The effect of hydroxide he treats rather as a specific effect than a general salt effect, though he suggests that perhaps "a decrease in the activity coefficient of peroxysulfate ion is superposed upon the effect of producing a less reactive substance" $[Ag(NH_3)_2OH]$. It is the purpose of this paper to show that the effect of hydroxides is not a specific but is a perfectly general salt effect; to show that the reaction is "pseudo-unimolecular" only in a certain range of salt concentration (that is, where change in ionic concentration during the course of the reaction counteracts the loss of ammonia); and to discuss the question of possible dependency of the velocity of the reaction on the nature of the reducing agent.

Theoretical

If the velocity-determining reaction is $S_2O_8^{--} + Ag^+ \longrightarrow Ag^{+++} + 2SO_4^{--}$, then, according to Brönsted's theory of kinetic salt effect,[2] the expression for the velocity should be

$$V = k'C_{S_2O_8^{--}} \cdot C_{Ag^+} \cdot \frac{f_{S_2O_8^{--}} f_{Ag^+}}{f_{(S_2O_8,\ Ag)^-}}$$

where f represents activity coefficient; and we may consider that $f_{(S_2O_8,\ Ag)^-}$ (the activity coefficient of the first complex formed between Ag^+ and $S_2O_8^{--}$) is approximately equal to f_{Ag^+}, since both are univalent ions, thus reducing the velocity expression to

$$V = k'C_{S_2O_8^{--}} \cdot C_{Ag^+} \cdot f_2$$

where $f_{S_2O_8^{--}} = f_2$ if $f_{S_2O_8^{--}}$ approximates the activity coefficient of any bivalent ion. Then

$$k = k'f_2$$

where k = the observed rate constant and k' = the theoretical rate constant in a solution containing no ions; and k as measured and plotted later in this paper is directly proportional to the activity coefficient of a bivalent ion, provided that Brönsted's theory is correct and that the velocity is actually determined by the reaction assumed.

Even if the second reaction

$$3Ag^{+++} + 2NH_3 \longrightarrow 3Ag^+ + N_2 + 6H^+$$

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[2] Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); *ibid.*, **115**, 337 (1925); Lecture, Columbia University, Columbia University Press, New York City, **1926**.

were slow, according to Brönsted's theory the salt effect would be small and linear and the total salt effect would be nearly the same; but if this were true it should be evidenced by accumulation of the trivalent silver and precipitation of the insoluble black compound, and this is not the case.

Experimental

Method of Measuring Velocity.—Since in a closed system the pressure of nitrogen above the solution is directly proportional to the amount of persulfate decomposed (provided thorough shaking of the reaction vessel insures equilibrium at all times), the velocity can be measured by following this pressure. The same type of apparatus described before for measurements of this sort was used.[3] The space above the solution in the velocity apparatus was evacuated to practically the vapor pressure of the solution; evacuation was continued for as short a time as possible in order to avoid undue volatilization of ammonia. The volume of solution used was 100 cc. and the space above the solution was about 100 cc. It can be shown from the vapor pressure of ammonia from the solutions used that the amount of ammonia in the gas phase was always considerably less than 1% of the total amount present, so this factor is unimportant.

In making the measurements, suitable amounts of standard persulfate, ammonia, hydroxide and salt solutions were mixed and made up to 98 cc., put in the reaction flask and allowed to come to temperature. A 2 cc. portion of standard silver nitrate solution was carefully measured into a glass capsule with a small glass hook near its open end, and this capsule suspended from a platinum loop fused into the side of the neck of the reaction flask. The flask was closed and the apparatus evacuated with shaking to aid evolution of dissolved air in the solution, the apparatus closed, the pressure read and the capsule with the silver nitrate dropped into the solution and thoroughly mixed by the shaking. The time was noted from the time the silver nitrate solution became thoroughly mixed with the other solution.

The rate constants were calculated in the same way as Yost's, that is, from the integrated form of the equation

$$\frac{\mathrm{d}C_{\mathrm{S_2O_8}^{--}}}{\mathrm{d}t} = k \cdot C_{\mathrm{S_2O_8}^{--}} \cdot C_{\mathrm{Ag}^+}$$

Solutions Used.—Potassium persulfate was prepared by recrystallizing the C. P. salt two or more times from water between 50 and 0°; the crystals were drained on a cotton plug in a funnel, washed with cold water, dried by sucking dried, dust-free air through them for two or three hours and further allowed to stand several days in a desiccator over sulfuric acid before use. Standard solutions were made by direct weighing of the salt, and were made fresh every four or five days.

C. P. ammonia water was diluted to the desired strength and standardized by running a sample from a pipet into excess of standard hydrochloric acid, titrating back with standard potassium hydroxide with methyl red as indicator.

Potassium and sodium hydroxides were made from saturated solutions that had stood for some time to allow the insoluble carbonates to settle out, and standardized

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[3] (a) Brönsted and Duus, *Z. physik. Chem.*, **117**, 299 (1925); (b) Brönsted and King, THIS JOURNAL, **47**, 2523 (1925).

against resublimed benzoic acid. The solutions were made in carbon dioxide-free, distilled water and protected from the air.

Potassium and sodium nitrates were recrystallized from the C. P. salts, dried at 100°, pulverized and dried again at 100° and allowed to stand in a desiccator over sulfuric acid for several days before use; the standard solutions were made by weighing the salts.

Silver nitrate was made by recrystallizing the C. P. salt. A 0.15 *M* solution was made by weighing the salt, and a 2 cc. portion was pipetted out of this same solution for every experiment. The solution was kept in a dark closet. The 2cc. pipet used could easily deliver the same amount with a maximum error of less than 0.5%, well within the error of measurement of the reaction-velocity constants.

In all experiments the concentration of the catalyst was the same; the concentration of ammonia was the same (within 0.5%) and was much higher than that of the persulfate; and the concentration of persulfate was the same (except in two experiments which are noted later). The concentration of persulfate used was chosen to give a suitable increase in pressure in the apparatus, and the concentration of ammonia was chosen so that the proportion oxidized was not too great, and the change in ionic concentration during the reaction would practically balance the loss in ammonia, except in a few experiments noted later. All measurements were made at 20° ± 0.01°.

Results of the Measurements.—Experiment 40 in Table I shows the results of a typical experiment with a solution containing sufficient potassium hydroxide so that no NH_4^+ ion was formed during the reaction, that is, so that the solution did not become much less alkaline. In some experiments such a small amount of potassium hydroxide was used that it would all be neutralized before the reaction was over; NH_4^+ is then formed and the ammonia disappears much more rapidly. In these cases the velocity constants fell off towards the end of the reaction and only those over the first half of the reaction were used for the averages. Experiments 28 and 26, Table I, show how the "constants" fall off when no potassium hydroxide is used and so ammonia disappears both from the oxidation and neutralization of H^+ ion formed—even though sufficient inert salt (potassium nitrate) is present so that the change in ionic concentration is small.

TABLE I

RESULTS OF TYPICAL EXPERIMENTS (TEMPERATURE, 20°)

Expt. 40		Expt. 28		Expt. 26	
0.04 *N* $K_2S_2O_8$, 0.08 *N* NH_3, 0.20 *N* KOH, 0.003 *N* $AgNO_3$		0.04 *N* $K_2S_2O_8$, 0.08 *N* NH_3, 0.16 *N* KNO_3, 0.003 *N* $AgNO_3$		0.04 *N* $K_2S_2O_8$, 0.08 *N* NH_3, 0.20 *N* KNO_3, 0.003 *N* $AgNO_3$	
Time, min.	*k*	Time, min.	*k*	Time, min.	*k*
30	2.74	15	2.44	20	2.25
40	2.66	35	2.42	40	2.27
50	2.68	55	2.42	60	2.23
60	2.72	85	2.30	80	2.19
70	2.69	125	2.33	100	2.17
80	2.71	155	2.25	120	2.17
100	2.73	215	2.21	170	2.07
120	2.72	245	2.21	290	2.03
140	2.68				
170	2.72				
Mean	2.71				

In Table II are given the mean constants for a number of experiments in which varying amounts of potassium hydroxide, sodium hydroxide, potassium nitrate and sodium nitrate were added. When potassium nitrate and sodium nitrate were used, it was, as stated, necessary to start with some alkali present, if the "pseudo-unimolecular" constants were to be obtained; and so 0.02 *N* potassium hydroxide was present in all these experiments, this being about the minimum amount possible. It is unfortunate for the comparison between the effect of sodium and potassium ions that sodium ion could not constitute the entire positive ion present in those experiments with sodium ion; but due to the difficulty of preparing pure sodium persulfate this was not attempted. It would also have been possible to prepare pure ammonium persulfate and then have

TABLE II

CONSTANTS (TEMPERATURE, 20°)

Summary of effect of KOH
0.04 *N* $K_2S_2O_8$, 0.08 *N* NH_3,
0.003 *N* $AgNO_3$

c_{KOH}, *N*	Total salt, equiv. concn.	*k*
0.02	0.063	4.22
.02	.063	4.23
.04	.083	3.64
.08	.123	3.25
.08	.123	3.28
.12	.163	3.05
.12	.163	3.05
.16	.203	2.85
.20	.243	2.68
.20	.243	2.71

Summary of effect of KNO_3
0.04 *N* $K_2S_2O_8$, 0.08 *N* NH_3,
0.02 *N* KOH, 0.003 *N* $AgNO_3$

c_{KNO_3}, *N*	Total salt, equiv. concn.	*k*
..	0.063	4.22
..	.063	4.23
0.02	.083	3.58
.04	.103	3.17
.08	.143	2.71
.10	.163	2.50
.12	.183	2.42
.14	.203	2.23
.16	.223	2.13

Summary of effect of NaOH
0.04 *N* $K_2S_2O_8$, 0.08 *N* NH_3,
0.003 *N* $AgNO_3$

c_{NaOH}, *N*	Total salt, equiv. concn.	*k*
0.02	0.063	4.30
.04	.083	3.84
.08	.123	3.52
.12	.163	3.32
.16	.203	3.15
.16	.203	3.21
.20	.243	3.11

Summary of effect of $NaNO_3$
0.04 *N* $K_2S_2O_8$, 0.08 *N* NH_3,
0.003 *N* $AgNO_3$, 0.02 *N* KOH

c_{NaNO_3}, *N*	Total salt, equiv. concn.	*k*
0.125	0.188	2.62
.175	.238	2.41

Summary of results with no inert salt present
0.08 *N* NH_3, 0.003 *N* $AgNO_3$

$c_{K_2S_2O_8}$, *N*	$c_{NH_4^+}$ at start, *N*	Total salt, equiv. concn.	*k* (start)
0.02	0.0013	0.024	7.34–7.00
.02	.0013	.024	6.89–6.71
.04	.0013	.044	6.44–5.94
.04	.0013	.044	5.78–5.40

included the ammonia formed in the alkaline solution from this in the total ammonia concentration. This was also not attempted, chiefly because a qualitative, not a quantitative, comparison between the potassium and sodium ions was desired. Of course, only a qualitative comparison between the hydroxide and nitrate ions can be made, as these must both be present in all solutions.

It was feared that when a solution became low in hydroxyl-ion concentration, some nitrate might be formed—that is, not all the oxidation resulted in nitrogen gas.[4] But in no case was there evidence that less nitrogen was evolved than in the most alkaline solutions.

In Table III are given full data for experiments made with the lowest possible salt concentrations. No ionic substances were present except those actually necessary; and in Experiments 45 and 46 the persulfate concentration was reduced to the minimum necessary for accurate measurements by the method used. It was known that ammonia would disappear rapidly, and that the ionic concentration would increase, as indicated in the equation

$$3S_2O_8^{--} + 8NH_3 + (6K^+ + nAg^+ + nNO_3^-) \longrightarrow 6SO_4^{--} + 6NH_4^+ + N_2 + (6K^+ + nAg^+ + nNO_3^-)$$

(ions whose concentrations are unchanged being enclosed in the parentheses). Since both these effects would decrease the velocity, it is to be expected that the "constants" would fall off very rapidly, and that this happened is shown in the table. Only the very first "constants" can give a measure of the true velocity for the ionic concentrations specified for these solutions in Table II; and these values, due to the difficulty of accurate measurement, are less accurate than those in Table II. Never-

TABLE III

EXPERIMENTS WITH LOW SALT CONCENTRATIONS (TEMPERATURE, 20°)

Expts. 43 and 44			Expts. 45 and 46		
0.04 N $K_2S_2O_8$, 0.08 N NH_3, 0.003 N $AgNO_3$			0.02 N $K_2S_2O_8$, 0.08 N NH_3, 0.003 N $AgNO_3$		
Time, min.	k (43)	k (44)	Time, min.	k (45)	k (46)
4	6.44	5.78	4	7.36	6.89
6	5.94	5.40	6	7.00	6.71
8	5.43	5.24	8	6.72	6.61
10	5.43	5.11	10	6.60	6.30
15	5.13	4.90	15	6.41	6.24
20	4.99	4.85	20	6.39	6.27
30	4.74	4.72	30	6.24	6.13
60	4.54	4.49	40	6.33	6.12
80	4.41	4.37	50	6.11	5.94
95	4.37	4.38	60	6.17	5.91

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[4] (a) Marshall, *Proc. Roy. Soc. Edinburgh*, **23**, 168 (1900); (b) Marshall and Inglis, *ibid.*, **24**, 88 (1902).

theless, they show the order of magnitude of the velocity and indicate very clearly how different it is in these solutions of lowest ionic concentration.

It is evident that in solutions of very low ionic concentration the salt effect due to changing ionic concentration during the course of the reaction entirely masks the character of the reaction. It is necessary, of course, to determine the character of such a reaction in high concentrations of some neutral salt, where the change will have little influence.

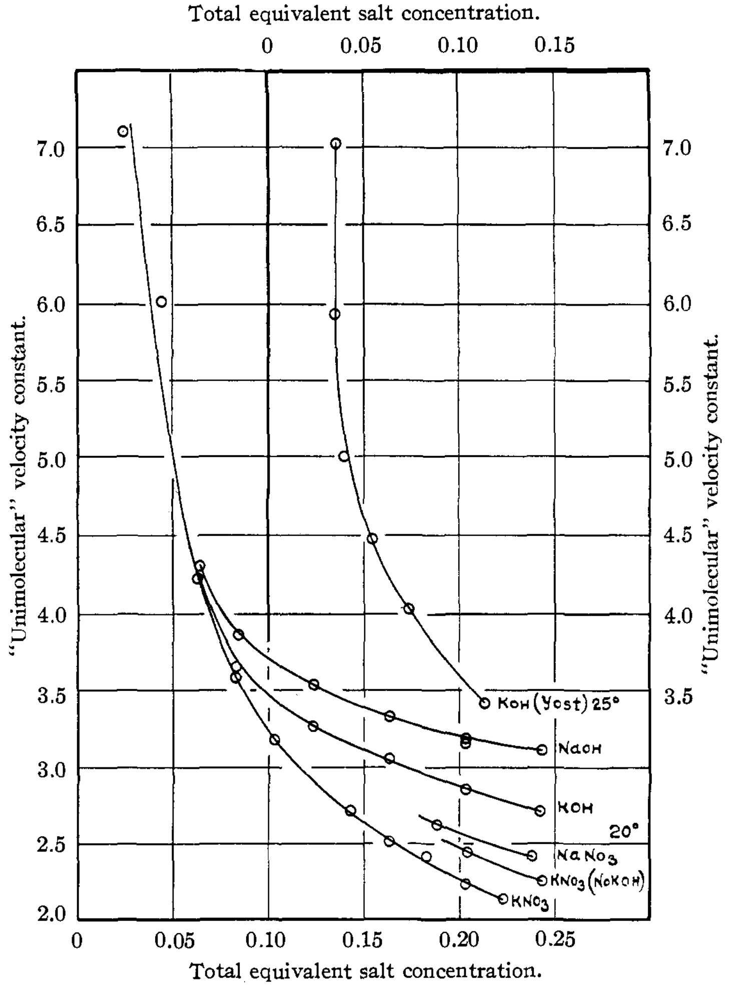

Fig. 1.—Effect of added salts on the persulfate-ammonia reaction.

Discussion of Results

The results given in Tables II and III are plotted in Fig. 1. A glance at this figure shows again how useless it is to record a velocity constant for a reaction between ions unless not only their concentration but the total ionic concentration of the solution is given. This is especially true for very low salt concentrations where the velocity changes very rapidly with changing salt concentration.

The curves make it plain that the effect is not a specific one for hydroxides, since the effect of the salts used is of the same character and magnitude. Both positive and negative ions show an effect, since changing either one changes the salt effect. Sodium ion shows less effect than potassium ion, and this is in agreement with the measurements of the effect of sodium and potassium salts on activity coefficients of ions by other means, for example, from solubility measurements. Slightly soluble salts are as a rule less soluble in sodium salts than in potassium salts at corresponding concentrations,[5] and this means that the activity coefficient of the saturating salt is greater in the sodium salt than in the potassium salt solution. Here, since k is proportional to f_2, it is seen that f_2 is greater in the presence of the sodium salt than in the presence of the potassium salt.

There are in the literature no direct comparisons available between the effects of hydroxides and nitrates on the activity coefficients of other ions. However, as a rule hydroxides have a greater "salting out effect" than other ionic substances, both on non-electrolytes and electrolytes.[6] This would indicate that the activity coefficients of other ions should be lower in the presence of nitrates than in the presence of hydroxides, and this is in accordance with the data here presented and shown in Fig. 1.

It is impossible to extrapolate the curves to zero concentration and so get any accurate measure of the absolute magnitude of the salt effect, but the sign, general character and magnitude agree with the Brönsted theory. It is sufficient to say that in this solution, containing some bivalent and some monovalent ion, at a concentration of 0.04 N, f_2 = about 0.40, the velocity of the reaction should be only about four-tenths its value in a solution of zero ionic concentration.

In the inserted figure some of Yost's measurements have been replotted on the same scale as the others. The data are given in Table IV. The first two measurements were with ammonium persulfate, with no addition of potassium hydroxide, and, as noted before, these "constants" fall off rapidly during the reaction. Consequently the first "constants" only are taken and these are recalculated to the same concentration of ammonia as the other measurements, using Yost's curve for the effect of ammonia on the reaction rate to make this correction. The values obtained are,

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[5] See, for example, (a) Brönsted, This Journal, **44**, 877 (1922); (b) *Kgl. Danske Videnskab. Selskab., Math.-fys. Medd.*, **4**, No. 4 (1921).

[6] See, for example, Rørdam, "Studies on Activity," *Dissertation*, H. H. Thieles Bogtrykkeri, Copenhagen, **1925**, pp. 44–45; Brönsted, This Journal, **42**, 785 (1920).

of course, not very accurate but it is evident that the curve as a whole is of exactly the same type and the salt effect of the same magnitude as found in the present investigation. It is difficult to make a direct comparison due to the difference in ammonia concentration and difference in temperature (Yost's measurements were at 25°).

TABLE IV

YOST'S MEASUREMENTS AT 25°

$C_{S_2O_8^{--}}$	C_{Ag^+}	C_{NH_3}	C_{KOH}	Total salt, equiv. concn.	k
0.0138 *M*	0.0059	0.1123	....	0.0355	7.00[a]
.0138	.0059	.0687	....	.0345	5.90[a]
.0086	.005	.0383	0.017	.039	5.00
.0086	.005	.0383	.034	.056	4.45
.0086	.005	.0383	.0519	.0741	4.01
.0086	.005	.0383	.0904	.1126	3.41

[a] Calculated for $C_{NH_3} = 0.0383\ N$.

II. Comparison of the Velocity with Various Reducing Agents

According to the assumptions made, any substance oxidized by persulfate in the presence of silver ion (at negligible speed otherwise) should be oxidized at the same rate, the total salt concentration being the same, provided the second reaction is very rapid, and in case the persulfate and silver ions are in the same condition of solvation, etc. At least, no such oxidation should be faster than the oxidation of Ag^+ to Ag^{+++}. Now Marshall and Inglis have measured the velocity of oxidation of NH_4^+ to NO_3^- by persulfate in the presence of silver ion at 25°,[4b] with only NH_4^+, $S_2O_8^{--}$ and $AgNO_3$ present, and also in the presence of other salts. Yost has measured the velocity of oxidation of chromic ion by persulfate in the presence of silver ion.[7] Some typical total salt concentrations and rate constants (those of Marshall and Inglis recalculated in the same manner as those in this paper) are given in Table VI. From these figures it seems quite possible that the velocities of the NH_4^+ and the Cr^{+++} oxidations are controlled in exactly the same way, the small differences being due to salt effect. But the ammonia oxidation is 10 times as fast; Yost concludes that this is due to the fact that not Ag^+ but $Ag(NH_3)_2^+$ is reacting. This appears to be a plausible explanation.

The author has also carried out some experiments involving silver ion as the catalyst for the reaction

$$S_2O_8^{--} + C_2O_4^{--} \xrightarrow{Ag^+} 2SO_4^{--} + 2CO_2$$

In these solutions the Ag^+ was expected to be in the same state of solvation as in the Cr^{+++} and NH_4^+ solutions and, consequently, the velocity of reaction should be about the same. But the experiments indicated that it was *about 4000 times as fast* as in the Cr^{+++} and NH_4^+ oxidations,

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[7] Yost, THIS JOURNAL, **48**, 152 (1926).

and *300 to 400* times as fast as in the ammonia oxidation. The results of one experiment are given in Table V and also in Table VI.

TABLE V

EXPERIMENTAL RESULTS

0.02 N $Na_2C_2O_4$
0.01 N $K_2S_2O_8$
0.00002 N Ag_2SO_4
Total salt concentration, 0.03 N

Time, min.	Pressure of CO_2, cm. Hg	k
10	1.10	989.0
20	2.27	1162
30	3.11	1184
40	3.49	1208
60	4.33	1127
90	5.57	1047
∞	6.10	..

TABLE VI

TYPICAL VALUES

Total salt equiv. concn.	k	
1.0	0.218	Marshall and Inglis, NH^+ oxidation (25°)
0.5	.267	
0.2–0.36	0.30–0.36	Yost, Cr^{+++} oxidation (25°)
.2	2.25–3.25	King, NH_3 oxidation (20°)
.03	7.0	King, NH_3 oxidation (20°)
.03	1100–1200	King, $C_2O_4^=$ oxidation (20°)

These experiments were not continued, as it was difficult to reproduce results within less than 10 to 15%, and only with certain concentrations of reactants was the reaction as nearly "pseudo-unimolecular" as the above example. Nevertheless, it seems that the mechanism of the silver ion catalysis may not be altogether explained yet. It is possible that the nature of the reducing agent influences the velocity, in spite of the other evidence to the contrary.

Summary

I. The effect of various salts on the velocity of oxidation of ammonia by persulfate, catalyzed by silver ion, has been measured, and the following conclusions have been reached.

1. The effect of hydroxides, as measured by Yost, is not specific, but a general salt effect (except in so far as the equilibrium $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ is concerned).

2. The salt effect is of the sign, general character and magnitude predicted by the Brönsted theory of salt effect, assuming the velocity-determining reaction to be that deduced by Yost.

3. The specific effect of the ions K^+, Na^+, OH^- and NO_3^- is in accord with their effect on the activity coefficient of other ions as indicated by solubility and other measurements.

4. It is pointed out again that the magnitude of the salt effect on velocity of reaction between ions is very great in dilute solutions, and that at low concentrations changing salt concentration during the course of a reaction may mask the true character of the reaction.

II. Finally, it is shown that in the case of the reaction $S_2O_8^{--} + C_2O_4^{--} \xrightarrow{Ag^+} 2SO_4^{--} + 2CO_2$, the velocity is not as predicted from the other reactions.

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[Contribution from the Gates Chemical Laboratory, California Institute of Technology, No. 147]

FLUORESCENCE IN MIXTURES OF AMMONIA AND MERCURY VAPOR

By Allan C. G. Mitchell

Received May 23, 1927 Published November 5, 1927

Introduction

While making experiments on the decomposition of ammonia by optically excited mercury vapor, Dickinson and Mitchell[1] observed a greenish fluorescence which appeared when a mixture of ammonia at a few millimeters' pressure and mercury vapor at room temperature was illuminated by the radiation from a cooled quartz mercury arc; they showed that the resonance radiation 2537 Å. was necessary to the production of this fluorescence. Observations with a direct vision spectroscope showed the fluorescence to be a diffuse band with a maximum around 5100 Å. Photographs with a quartz prism spectrograph showed an additional diffuse band in the ultraviolet with a maximum around 3370 Å. The green fluorescence was also observed visually when nitrogen was used instead of ammonia.

In the present experiments the ultraviolet fluorescence and the conditions under which it is excited were examined further.

Experimental Arrangement

A spherical resonance vessel (volume about 500 cc.) with a plane quartz window sealed to one end with sealing wax was connected to a vacuum system. About 2 cc. of mercury was placed in the resonance vessel to give a partial pressure of mercury corresponding to its vapor pressure at room temperature. Ammonia, nitrogen, hydrogen and argon could be admitted to the apparatus in the desired amounts and their pressures read on a McLeod gage. The method of purifying and admitting the gases to the resonance vessel was the same as that described by Mitchell

[1] Dickinson and Mitchell, *Proc. Nat. Acad. Sci.*, **12**, 692 (1926).