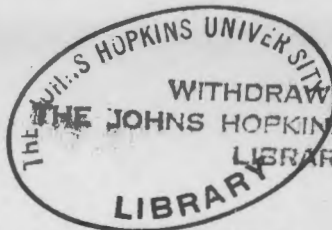


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THE CATALYTIC EFFECT OF ANIONS ON
REDUCTION REACTIONS INVOLVING METAL IONS

By
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THE CATALYTIC EFFECT OF ANIONS ON REDUCTION REACTIONS
INVOLVING METAL IONS¹

By

Richard C. Pinkerton and Frederick R. Duke

I. ABSTRACT

A model is proposed for a general activated complex AXB in oxidation-reduction reactions involving two metal ions (A) and (B). The symbol (X) would indicate the anions or other groupings which might be present, and which ordinarily would be complexed to the metals separately. The effectiveness of (X) is related to its ability to be oxidized or reduced in itself. In the case that (X) consists of oxidizable anions, the probability of electron transfer from (X) to the oxidizing metal (A) is correlated with the strength (energy) of the bond between (X) and (A). Two previous explanations of the catalytic effect of anions on such reactions are discussed, and some experiments outlined which will test the validity of the proposed model.

The disproportionation of uranium (V) is of interest because it occurs between oppositely charged ions and because an excess proton is necessary for reaction. The rates of disproportionation are studied in heavy and light water in an attempt to distinguish between paths in which a proton or deuteron is involved and those in which our (X) grouping is OH⁻ or OD⁻. Of the two courses, the latter is judged to be more likely and the reaction is therefore placed in the general class of anion catalyzed oxidation-reductions.

In the next study, it is confirmed that the chloride catalyzed ferric-stannous reaction is first order in ferric ion concentration. In the range of chloride ion concentrations studied, fourth order dependence on chloride is dominant. It is probable that a minimum of three is required in the activated complex for any appreciable reaction rate. When bromide is added, a third order dependence is observed. Only two iodide ions appear necessary for reaction, but third order dependence may be important at higher iodide ion concentrations. The reaction is depressed when large amounts of metal ions are present due to the complexing and removal of halide ions. This is markedly so in the case of high stannous ion concentrations. Approximate values for the equilibrium constants for the formation of SnCl⁺ and SnBr⁺ are estimated. In the order of increasing effectiveness in promoting reaction we have that Cl⁻ is less than Br⁻ is less than I⁻.

¹This report is based on a Ph.D. thesis by R. C. Pinkerton.

Attention is directed to the fact that the complexing affinity of the halides for both ferric and stannous ions decreases in this order, while the order observed is the order of increasing ease of oxidation of the halide ions.

In the next studies, it is found that hexammine-cobaltic ion is reduced by stannite ion by a path independent of the cobalt concentration. Instead, the reaction is first order HSnO_2^- and OH^- . No significant amount of SnO_2 is found, but some dimerization of the stannite is necessary to explain the results. When the hydroxypentammine-cobaltic ion is used, the reaction is similarly zero order in cobalt, showing that one anion is insufficient. When the complex is allowed to stand in strong basic solution, the reaction is faster and a bimolecular path is possible. It is found that chloride ion will not accelerate these reactions, but traces of cyanide ion will. Cyanide is the only anion tried which can displace ammonia from the complexes. Stannite will apparently not reduce the hexacyanocobaltate (III) ion because of an adverse over-all free energy change.

The probable generality of the model is discussed and the results applied to the explanation of the rates of some of the isotope exchange reactions which have been studied recently. It would seem that some account must be taken of the equivalence of the oxidation changes in the two reactants as well.

II. INTRODUCTION

When dealing with the stoichiometry oxidation-reduction reactions, the chemist has long been in the habit of assigning an oxidation number to each of the atoms or radicals in his system. Sometimes he is fairly certain that this formalism has some physical significance. The oxidation number of sodium ion in aqueous solution is the same as the charge of the solvated ion. A certain arbitrary factor is introduced as soon as collections containing more than one element are considered. Whenever the elements concerned have similar electron affinities, a dilemma arises in assigning separate numbers. The organic chemist seldom speaks of oxidation number simply because the physical reality of the concept is low and hence of slight utility,

For simple inorganic reduction reactions* the connection between ionic charge and oxidation number is so convenient that the whole idea

*The full term "oxidation-reduction reaction" is clumsy and redundant. The term "red-ox reaction" has not been generally used. The single adjective will be used throughout.

of oxidation has been redefined in terms of the electron. If one examines only the initial and final states of such reactions, there is an apparent net gain and loss of electrons for certain participants. The trouble is that the idea has been carried over to describe the kinetic process. Thus the exchange of oxidation number between two isotopic forms of the same metal ion is now referred to as "electron transfer." Such a term implies that the course of the reaction may be followed by the observation of a single electron. It implies that an electron as a distinct entity leaps from one metal ion to another. The term is misleading and should be abandoned.

In aqueous solutions, where the possible number of intermediates in an oxidation is large, tracing the path of a reaction is particularly difficult. It is more profitable to forget about the electrons and attempt to find only certain low energy collections or elements and their combined oxidation states.

Let us restrict our attention to those reduction reactions which occur between metal ions in solution. These ions are always closely associated with molecules of the solvent or with certain anions which may be present. Different complexed forms of a metal in the same oxidation state may have different latent reactivities, because their free energies are not the same. More important as far as the actual course of a reduction reaction is concerned, the presence of particular anions or neutral molecules may affect the energy of the transition state. They are capable of changing the over-all rate and order of a reaction quite aside from their influence on the free energies of the reactants and products.

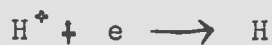
Considered by themselves, the metal ions concerned are always positively charged. Now if a direct electron transfer is to take place between two metal ions, it is reasonable to require that they approach so that their orbits overlap appreciably. Otherwise the probability of transfer is small unless tunneling occurs.¹ In addition to overcoming this unfavorable charge repulsion, the colliding ions might further be required to eliminate any of the surrounding complexed groups which come between them. The process we have been considering here has been shown to require energies in great excess of the normal thermal energy.^{2,3} We may conclude that reaction by such a path rarely happens.

Instead, let us suppose that our activated complex is of the form AXB. In this contracted notation, (A) will stand for some metal in its higher oxidation state and (B) the metal to be oxidized. The quantity (X) is to mean any anion or neutral group which by its presence will lower the potential energy of the system. It may even stand for more than one such group. In addition to lowering the potential energy,

two or more anions might be required so that they could act conjunctively in the process. That is, a number of closely associated anions might have chemical properties different from the individuals.

Now if the activated state in the reduction reaction is of the sort described above, the nature of (X) must be taken into account. An electron could not be expected to pass from (B) to (A) without interacting strongly with (X). Viewed as a process in time, one of the following two events are likely. An electron might move from (B) to (X), thus "reducing" (X) temporarily, followed by (X) reducing (A). Or else (A) might temporarily oxidize (X) which in turn would oxidize (B). The effectiveness of the complex will then be influenced by the "oxidizability" or "reducibility" of the grouping (X). A more satisfactory way of saying this is as follows. If we were able to look at the activated complex, we would find that that portion of it which corresponds to (X) resembles somewhat (X) in an oxidized or reduced state. By oxidizability we imply the ability of an atom or group to undergo transient one-electron deficiencies and by reducibility the opposite. As examples of oxidizable anions we might list CN^- , CNO^- , CNS^- , Cl^- , Br^- , I^- , OH^- and I_3^- . The oxidized or neutral forms of the foregoing have been postulated as intermediates in free radical reactions and the existence of many of them in the gaseous state has been demonstrated.

Reducible groups are more difficult to enumerate. Those which come immediately to mind contain hydrogen, so that the fundamental change could be the conversion of a proton to hydrogen atom. The reactions



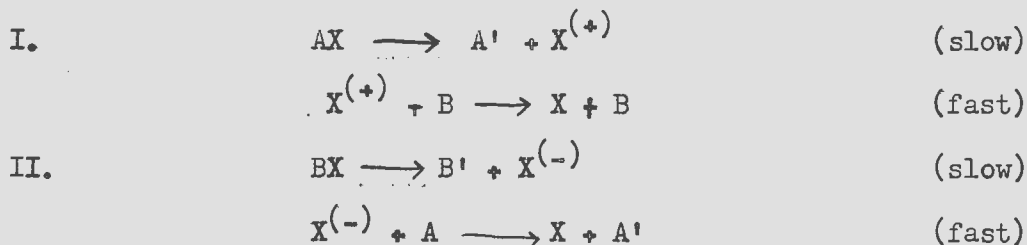
require so much energy that they are unlikely steps in processes which occur in aqueous solution at room temperature.

So far we have not considered how the activated state AXB might arise. In fact, as long as it is in equilibrium with its precursors, it is meaningless to inquire whether it is formed by the paths,



or by a termolecular reaction. We will note in passing two extreme cases, in which reduction reactions take place via non-concerted paths.

In the two limits, the group (X) in an oxidized or reduced form appears as a distinct species, and is no longer the activated complex. We may write down the steps



In these symbolic reactions, primes refer to the product oxidation states of (A) and (B) and (+) and (-) to the relative state of oxidation of the intermediate (X) and not necessarily the ionic charge.

Now if the first of the reactions in I and II are rapidly reversible equilibria, the over-all kinetics will be first order in both metal ions. It will be impossible to distinguish between these cases and the concerted case. But if the initial reactions are slow (as they might ~~well~~ be because of the high energy required to produce free $\text{X}^{(+)}$ or $\text{X}^{(-)}$), and the following reactions rapid, the orders will be different. Thus I will tend to be zero order in the reducing agent (B) and II will tend toward zero order in (A).

We are now able to comment further on the nature of the activated complex AXB. If the group (X) is oxidizable, there will be some contributions to the structure of the form



and if (X) is reducible, we have the corresponding



This is the same as saying that if (X) is oxidizable, it should be more closely bonded to (A) in the activated complex and the complementary statement concerning (X) and (B) in the case that (X) is reducible. One cannot say the same about the other metal involved, so that the bond of (X) to (B) in the first of the above structures need not resemble bonding of the sort found in Werner type complexes at all. We may postulate that if an oxidizable group (X) is present, but the metal (A) cannot form a tight bond with it, activated complexes of the type AXB would not be important. To a limited extent, we may test these ideas experimentally.

It has been noted that certain anions have a remarkable accelerating effect on reduction reactions of the sort we have been discussing. The classic example is the catalysis of the ferric-stannous reaction by chloride ion.^{4,5,6,2} No specific mechanism has been advanced to explain how the actual "electron transfer" takes place. However, two reasons have been proposed to explain the catalysis which deserve serious consideration. If either had any general validity, it would not be profitable to speculate as to the more exact mechanism.

The first proposal is an extension of the idea of charge repulsion outlined previously, and was first applied to the ferric-stannous case by Gorin.² From the collision point of view, chloride or hydroxide ions complex with ferric ion, reduce its positive charge, and thus make it possible for stannous ion to make an approach. Presumably the metal ions would still have to react through some surrounding sphere of chloride, hydroxide or water. Weiss⁷ took up this idea and carried it to absurdity by insisting that the reaction occurred between Fe^{+++} and SnCl_4^- . To his mind this would be the most favorable charge arrangement. The best criticism that one can make is that any such view treats the complexes as though they were point charges. Further, if one accepts the theory of the activated complex, it would not be possible to distinguish between any of the collisions involving iron and tin chloride complexes which have the same number of chloride ions in total. On the experimental side, one may cite many cases where reactions occur rapidly "against the charge", and still other cases in which reaction is slow in spite of a favorable charge distribution. Remick⁸ has collected a number of such examples, and we shall have occasion to examine some in the course of the present investigations.

The second proposal was originally stated by Shaffer,⁹ and later extended by Remick.⁸ It is concerned with the equivalence of the changes in oxidation state for the two metals involved. So far, in our general discussion, we have tacitly treated these reactions as though they were one step processes and so that a unitary change in oxidation number occurred. But if we examine even the simple ferric-stannous reaction, we see that the ferric ion gains one electron and the stannous ion loses two in the over-all process. In any such case, two things might happen. A higher order collision than bimolecular might be necessary (in other words, more than two metal ions might be present in the activated complex) or the reaction might occur in steps. This means that unusual oxidation states of one of the metals would be produced. This requires higher than normal energies and would explain the slowness of some of these reactions. The example originally used by Shaffer was the oxidation of thallous ion by ceric ion. He also observed that placing certain organic dyes in the solution which were capable of undergoing one-electron oxidations speeded up the reaction.

Remick has somewhat extended this idea and would explain the catalytic effect of chloride ion in the ferric-stannous reaction as follows. Since some form of tin (III) has been proposed as an intermediate,² anything present which would stabilize this oxidation state might also lower the energy of the transition state. Chloride ions might serve this purpose. In such an event, the activated complex would have the chloride ions (our (X) grouping) more closely associated with tin (our (B) metal). There would be contributing structures which would resemble closely a tin (III) chloride complex product. Thus it differs from the model we have proposed.

The following series of three studies was designed to test our ideas concerning the role of anions or other catalytic agents in the reduction reactions involving two metal ions. Those systems were chosen which, as far as possible, would distinguish between the consequences of our ideas and the two previous lines of reasoning.

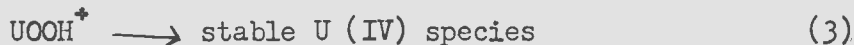
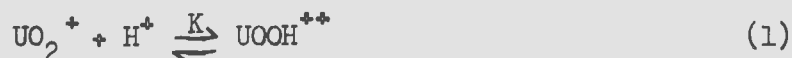
The first reactions studied were the disproportionations of uranium (V) in heavy and light water solutions. The original intention was to find out whether or not a hydrogen atom transfer was involved in the rate controlling step. This would correspond to an (X) grouping of the reducible type in our general picture. These are reactions which also proceed in violation of the charge repulsion criterion.

The second group of reactions studied were the halide catalyzed reductions of ferric ion by stannous ion. They serve to establish the connection between the oxidizability of the anion and its effectiveness in promoting reaction.

The third section deals with the oxidation of stannite ion by various complex cobalt (III) ions. These are reactions in which the rate of complexing of possible accelerating anions with cobalt is slower than the usual path of reduction. Much information is gained concerning the behavior of alkaline tin (II) solutions as well.

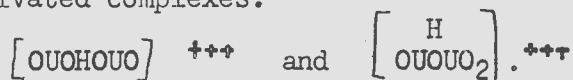
III. A REACTION WHICH PROCEEDS COUNTER TO CHARGE REPULSION: THE DISPROPORTIONATION OF URANIUM (V) IN LIGHT AND HEAVY WATER

The kinetics of the disproportionation of uranium (V) ion in perchloric acid solutions has been studied by Heal,¹⁰ and by Kern and Orleman.¹¹ The conclusions from both investigations are that the reaction is second order in uranium (V) ion and first order in hydrogen ion. Kern and Orleman formulate the steps as follows:



The rate determining step (2) is noteworthy because reaction apparently occurs between two positively charged species and the prior equilibrium involving the proton serves only to increase the charge of one of the uranium (V) ions. Since Kern and Orleman could detect no appreciable concentration of the ion UOOH^{++} , there is no reason to insist on its presence as an intermediate. What one might better say is that the activated complex is - 3 charged and that in its formation a concentration of charge is certainly necessary. Now from the criterion of charge repulsion one would expect that an activated complex could be formed easier from two ordinary UO_2^+ ions. Also, since a one-to-one change in oxidation state takes place, there is no question as to equivalence. The uranium ions are already in their least stable oxidation state in the beginning of the reaction.

A simple electron transfer between the uranium metal ions themselves is extremely unlikely. What needs to be explained is the necessity of the proton. We write down the following two symbols which are supposed to represent the approximate configurations for two possible activated complexes:



The first of these has as its best recommendation a reasonable charge distribution. The uranium centers are separated and shielded, and it looks as if hydrogen bonding might be important. The difficulty is that if the proton serves only as a hydrogen bond, the reduction cannot take place. This arrangement corresponds to our general AXB with a reducible (X) unit, (X) being in this case the proton. As mentioned in our introduction, unreasonably high activation energies might be required for such a path.

The second of these models corresponds to our general model with an oxidizable (X) grouping, here represented by OH^- . It is possible that such a mechanism is involved in the reaction of hydrolyzed ferric and stannous ions.² Furthermore, many hydroxides of mixed valence state are known in which there may be an exchange of oxidation state by such a mechanism. Prestwood and Wahl¹² found that the exchange between Tl (I) and Tl (III) is quite extensive during their separation precipitation of Tl $(\text{OH})_3$.

In view of the success attained by the use of deuterium in the investigation of mechanisms, it was decided to determine the relative rates of the disproportionation of UO_2^+ ions in water and in deuterium oxide. If the actual model is ~~the~~ second one we have discussed, one would expect little difference in the rates of reaction from substituting OD^- for OH^- as our (X) grouping. One would expect differences due to solvent effects. We will postpone discussion of these until later, except to say that such effects would tend to give an increased rate in heavy water due to the difference in basicity in the two solvents. In the first model, the H^+ or D^+ plays a more direct role. Reactions which involve directly hydrogen or deuterium are as a rule considerably slower in the deuterium case. Bonhoefer¹³ has collected the results of a number of such experiments. Bigeleisen¹⁴ has calculated that if the hydrogen or deuterium is less strongly bound in the activated complex than in the reactants, the rate of reaction should be slower in the deuterium case. We would certainly expect this to be true in our first model, perhaps enough so the opposing solvent effect would be offset.

Before going on to our experimental results, we must add that the two models proposed above are not intended to exclude other possibilities. However, they are the lowest energy configurations which we can think of.

Experimental Part

Materials.

A perchloric solution of $\text{UO}_2(\text{ClO}_4)_2$ was prepared by boiling down $\text{UO}_2(\text{NO}_3)_2$ several times with 70% HClO_4 . The uranium solution was standardized gravimetrically as U_3O_8 . Stock solutions of 0.5 M. NaClO_4 were prepared by dissolving a weighed quantity of the anhydrous salt in light or heavy water.

Apparatus.

The polarographic method of Kern and Orleman¹¹ was used. A simple manual instrument was constructed and provided with a switching arrangement so that the circuit could also be used as a potentiometer for the measurement of pH. A combined electrolysis and polarograph cell was employed, similar to the model of Kern and Orleman except that it was of reduced dimensions and provided with a water jacket to maintain a temperature of $25.0 \pm .2^\circ$.

Procedure;

A preliminary examination was made in which it was found that the polarographic wave for the couple $\text{UO}_2^{++} = \text{UO}_2^+ + e$ was almost identical in heavy water to that ordinarily obtained.² Hence the same potentials were employed for electrolysis and analysis in D_2O as in H_2O . The values of the diffusion coefficients of UO_2^+ were assumed to be the same for the purpose of calculating the concentrations from the diffusion current, and the value by Kern and Orleman in light water was used.

In a typical run, 20 ml. of salt solution in light or heavy water and 1 ml. of stock $\text{UO}_2(\text{ClO}_4)_2$ solution in light water were electrolyzed for 20-30 min. at a current of about 3 ma. With the smaller cathode area used, the current density was sufficient to maintain a proper potential for the reduction. The mercury cathode was stirred and nitrogen was bubbled through the main cell and the anode compartment throughout the electrolysis. Then 0.5 or 1.0 ml. of dilute HClO_4 solution (in ordinary water) was added and the polarograph was used to follow the diffusion current for 40 minutes.

After the completion of the reaction, the hydrogen ion activity was determined with the use of the quinhydrone electrode balanced against the saturated calomel electrode. In the case of the heavy water solutions (mole fraction of $\text{D}_2\text{O} = 0.91$) the reference potential used was 0.4865 v. This value was obtained by interpolation from the data of Rule and LaMer,^{1b} who have found the quinhydrone electrode most satisfactory for measuring activities in light and heavy water mixtures.

Interpretation of the Results

The values of k''/a_{H^+} (or $k''/(a_{\text{H}^+} + a_{\text{D}^+})$) in the second pair of runs given in Table 1 correspond to the quantities reported by Kern and Orleman, and the reader is referred to their paper for the definitions and methods of evaluation. The greatest source of error involved is in the determination of the quantities $a_{\text{H}^+} + a_{\text{D}^+}$. This is due to an uncertain liquid junction potential between the calomel cell and the solution. However, if we may assume that the difference in liquid junction potentials for light and heavy water is small, the error involved will cancel out in the ratio of the two constants k'_D / k'_H . Here k'_D stands for the value of $k''/(a_{\text{H}^+} + a_{\text{D}^+})$ in the light and heavy water mixture and k'_H for the same quantity in the ordinary water solutions.

TABLE 1

The Rates of Disproportionation of Uranium (V)

Solutions for Various Values of ($a_{H^+} + a_{D^+}$)

Mole Fraction D_2O	k''	E quinhydrone vs. S. C. E.	($a_{H^+} + a_{D^+}$)	$k'' / (a_{H^+} + a_{D^+})$
0.0	1.17	0.3281	7.60×10^{-3}	154
0.0	1.24	0.3288	7.80×10^{-3}	159
0.0	2.17	0.3238	1.14×10^{-2}	154
			Avg. =	$156 = k'_H$
0.91	1.56	0.3547	5.90×10^{-3}	264
0.91	3.89	0.3791	1.53×10^{-2}	255
			Avg. =	$260 = k'_D$

All runs were made at ionic strength 0.5

It is seen that the rate constant for the heavy water mixtures is about 1.7 times the value of that for the disproportionation in light water. This may be the result of two effects, which are inseparable in these experiments since no appreciable concentration of the supposed intermediate $UOOH^{++}$ is built up. That is, we cannot determine the exact effect of deuterium oxide on the value of K for reaction (1) as reported by Kern and Orleman. It will be more convenient to discuss the reaction using their stepwise notation, since anything that we may say concerning the effect of the difference in basicity between light and heavy water on the relative concentrations of the hypothetical intermediates $UOOH^-$ and $UOOD^-$ will apply equally to the relative concentrations of the activated complexes in the two media. The other effect, the one in which we are primarily interested, is the effect on the values k for reaction (2). Unfortunately, all that may be found experimentally are the products $k' = kK$. If it is assumed that the various influences are

separable in a product of this sort, it is possible to determine a reasonable value of K_D/K_H . We may then set down the ratio

$$k_D/k_H - (k_D'/k_H') / (K_D/K_H) = 1.7 / (K_D/K_H).$$

Since no concentration of any intermediate acid such as $UOOH^-$ is detected, the acidic property of any intermediate is strong. This means that the ratio K_D/K_H , which is certainly between the values 1.0 and 3, is more near to the value 1.0.¹⁶ This effect alone could explain the observed experimental results, that is, the ratio k_D/k_H might well be unity. As for the probable effect on this ratio if the activated complex were the symmetric one, we would expect a much smaller value. The transfer of a deuteron from carbon to oxygen is said to be 3.5 to 10 times as slow as that of a proton.¹³ There remains to be considered the possible differences between light and heavy water in their action as solvents, apart from the differences in their intrinsic basicities. These factors are generally not taken into account or lumped in with the latter effect in studies of acid catalyzed reactions in the two media, since the increased rate observed in deuterium oxide is in line with the expected difference in acid dissociation constants.

We may consider the solvent effect on the activities under the general headings of mobility so far as it is related to viscosity, and electrostatic effects. Since the dielectric constants of light and heavy water are very similar, one would expect that differences in electrostatic effects would be negligible.

There have been reports of three reactions whose rates are independent of the deuterium oxide concentration.^{17,18} In the simplest of these, Hughes et al.¹⁷ found that the rate of hydrolysis of palmityl chloride was the same up to concentrations of 87% D_2O . The conclusion was that viscosity differences had no effect on the rate. On the other hand, Champetier¹⁹ found that the rate of hydrolysis of $CrCl_3$ was lower in D_2O . This may be a base catalyzed reaction. The paper was cited as an example of the effect of the higher viscosity of D_2O by Yamasaki,²⁰ who found that the catalytic oxidation of pyrogallol by O_2 in the presence of complex cobalt salts was slower in heavy water. Again this might be a base catalyzed reaction, but it is true that ionic mobilities are lower in deuterium oxide.

Although these examples do not provide any conclusive evidence, it may be said that if there is any solvent effect other than that due to the difference in the intrinsic basicities, it would be such that the reaction would go at a slower rate in deuterium oxide than in ordinary water.

The ratio of the rate constants reported here is, in fact, in line reported for acid catalyzed reactions in which the hydrogen (or deuterium) is not directly affected. We may tentatively conclude that the activated complex is one in which the hydrogen is fairly strongly bonded, and accept the second of our models. Now even though the OH^- ion does not appear in the kinetic equations, the similarity of the proposed model to those for our general case leads us to place this reaction in the category of the anion catalyzed reactions.

IV. A TEST OF THE CRITERION OF OXIDIZABILITY OF THE ANION: THE HALIDE CATALYZED FERRIC-STANNOUS REACTIONS

The reaction between ferric and stannous ions was observed by Gorin² to be very slow in perchloric acid solutions, particularly at high hydrogen ion concentrations where hydrolysis is suppressed. One possible explanation for the failure of the unhydrolyzed ions to react is the coulombic repulsion between them, as we have indicated in our introduction.^{2,3,7} Many studies have been made of the reaction in the presence of chloride ion.^{4,5,6} In this case it is rapid, and it is usually concluded that chloride complexes of ferric and stannous ions are involved, since they are known to exist. No definite conclusions concerning the order in chloride ion may be drawn from the data in these papers, although Weiss⁷ has made some attempt. However, he had no exact values for the various equilibrium constants for the chloride complexing involved, and made some rather inconsistent assumptions concerning their magnitude.

At first glance, it would seem desirable also to gain information as to the exact species which participate. Although it is theoretically impossible to obtain such information when all the complexing reactions are rapid (or all complexes are in equilibrium with the activated complex), several views have been advanced. Thus Gorin has stated that the probable reactants are FeCl_3 and either SnCl_2^+ or SnCl_3^- . One may infer from his paper² that his reasoning is based on the conclusion (not very well substantiated even in the hydroxide ion catalyzed case) that the last complexing reaction of ferric ion with the anion is slow. That is, the reaction $\text{FeCl}_2^+ + \text{Cl}^- \longrightarrow \text{FeCl}_3$ might be slower at low chloride concentrations than the actual reduction step and become rate determining. This was not confirmed in the work reported below, although it may be true for the iodide catalyzed reaction. On the other hand, Weiss believes the reaction to be between Fe^{+++} and SnCl_4^- solely because he thinks that the charge distribution would be more favorable in this case. He further suggests that at higher chloride ion

concentrations, the apparent order in chloride ion decreases for the reason that large amounts of FeCl^{++} start to form. It is his conception that FeCl^{++} would not be capable of reacting because of a less favorable charge relation. He then describes the reaction between the pair mentioned as a "simple electron transfer," whatever that may mean. Many have quoted him. Thus Krishna²¹ has observed that increasing the ionic strength depresses the rate of reaction, and writing the reaction as Weiss does concludes that the Bronsted theory is thereby confirmed.

More recent data on the equilibrium constants for the formation of the ferric²² and stannous²³ chloride complexes are now available and enable a more exact evaluation of the chloride ion dependence. In this series of experiments, the order in chloride ion is investigated and the studies extended to systems in which bromide and iodide ions are used to catalyze the reaction.

Experimental Part

Materials

A solution of 2.03 N HClO_4 was prepared and used to make up all stock solutions and dilutions. An approximately 0.3 solution of $\text{Sn}(\text{ClO}_4)_2$ was made by dissolving the salt in 2.03 N HClO_4 and was standardized before each series of runs against standard ceric sulfate solution. A solution of 0.150 N $\text{Fe}(\text{ClO}_4)_3$ was prepared by dissolving the salt in 2.03 N HClO_4 and was standardized by tin reduction and titration with standard ceric sulfate. A solution of 2.01 N HCl was made and diluted when necessary with 2.03 N HClO_4 . Solutions of 0.5 N NaBr and NaI were made by dissolving the salts in water and standardizing by means of a Fajans titration.

Procedure

With the stock solutions made up as described, all reacting mixtures were of ionic strength 2 except for negligible contributions from the metal salts themselves and small corrections in the cases where NaBr or NaI were added. By using high acidity, hydrolysis was suppressed and the ionic strength remained essentially unchanged during the reaction. All reactions were carried out in a 200 ml. flask immersed in a water bath held at $25.0 \pm 0.2^\circ$. The metal constituent to be present in the smaller concentration was usually added last to start the reaction, although the order was found to be unimportant. Usually 7 samples of 5 ml. each were withdrawn, quenched in HgCl_2 solution and titrated for

ferrous ion with standard ceric sulfate solution, using diphenylamine as indicator. Quenching with HgCl_2 repeatedly has been shown not to catalyze the reaction, and this was confirmed before attempting these experiments. In the case of runs reported in Table 6, 25 ml. samples were taken.

Results and Discussion

The rate expression used was

$$\frac{dx}{dt} = k' (a-x) (2b-x) \quad (4)$$

where (x) is the concentration of ferrous ion at time (t) , (a) the initial concentration of ferric ion and (b) the molar concentration of stannous ion. Included in k' are functions of chloride concentration. The integrated form is

$$\frac{2.303}{a-2b} \log_{10} \frac{a-x}{2b-x} = k't + \text{constant} \quad (5)$$

In the tables, the quantity S reported is the slope of a plot of $\log_{10} (a-x) / (2b-x)$ vs. the time in minutes. Then

$$k' = \frac{2.303}{a-2b} S. \quad (6)$$

There has been some disagreement in the past as to the exact order in ferric ion, since when a plot is made as above to test for the order, the reaction rate as indicated by the slope S appears to decrease toward the end of the reaction. Yet as shown below the actual order in ferric ion is one, and not two. Since the apparent decrease in rate must be due to some other effect (such as the consumption of chloride ion because of higher complexing ability in the products) the slopes have been found for the initial phase of the reaction.

To determine the true order in ferric ion, a series of runs were made in which the initial ferric ion concentration was varied (Table 2). The results show that the dependence is first order as concluded by Gorin².

Table 2

Effect of Varying Initial Ferric Concentration

Initial Stannous Concentration: 0.00875

Total Chloride Concentration: 0.136 (c_t)

Fe^{+3}	S	k'	k'/c_t^3
0.101	0.0720	1.96	822
0.0312	0.0590	2.14	898
0.0609	0.0455	2.42	1014
0.0406	0.0226	2.28	956
0.0203	0.00280	2.32	976

Because it is known that stannous ion forms relatively stable complexes with chloride ion, the determination of the rate dependence on chloride concentration was carried out in solutions of low tin content. An examination of the quantities k' / c_t^3 in table 3 shows that there is an apparent third order dependence. The symbol c_t refers to the total chloride ion concentration.

Table 3

The Effect of Varying Chloride Concentration with Ferric Ion in Excess.

Initial Ferric Concentration: 0.101

Initial Stannous Concentration: 0.00875

Cl^- or c_t	S	k'	k' / c_t^3
0.217	0.265	7.27	715
0.163	0.112	3.07	715
0.136	0.0694	1.90	800
0.108	0.0358	0.982	771
0.0813	0.0137	0.377	701
0.0542	0.00398	0.109	686

Next the effect of varying the initial stannous ion concentration was studied. The results in Table 4 show that the rate actually decreases when the stannous ion concentration is increased, although the reaction is first order in tin. This is the consequence of the removal of chloride ions from action by the formation of complexes with stannous ion. If the chloride ion concentration is varied in a series of high stannous ion concentration, the third power dependence on chloride is obscured (Table 5). However, if one assumes that the true dependence in this particular range is third order, one may use the results to estimate a value of the equilibrium constant

$$K_1^S = \frac{y}{(b-y)(c_t-y)}$$

for the reaction $\text{Sn}^{++} + \text{Cl}^- \rightleftharpoons \text{SnCl}^+$. Here (y) refers to concentration of SnCl^+ ion. This is done by taking a value of k'/c_t^3 under conditions in which there is a minimum of complexing (for example the last value of Table 2). This value may then be used to calculate the value of chloride concentrations where much of it is present as SnCl^+ (for example, the first run of Table 4). The difference between the total chloride and "free" chloride as determined from the rate may then be taken as the concentration of SnCl^+ , and K_1^S may be evaluated.

Table 4

The Effect of Varying Initial Stannous Concentration

Total Chloride Concentration: 0.125

Initial Ferric Ion Concentration: 0.183

$[\text{Sn}^{++}]$	S	k'	k'/c_t^3	$k'/(c_t-y)^3$
0.121	0.0320	0.329	167	911
0.0809	0.0351	0.567	237	903
0.0607	0.0337	0.756	383	907
0.0405	0.0258	0.954	483	858
0.0202	0.0129	1.374	697	932

Table 5

The Effect of Varying Chloride Concentration with Stannous Ion in Excess.

Initial Ferric Concentration: 0.0188

Initial Stannous Concentration: 0.0809

$[\text{Cl}^-]_t$ or c_t	S	k'	k'/c_t^3	$k'/(c_t-y)^3$
0.251	0.333	5.36	399	722
0.201	0.163	2.62	325	780
0.151	0.0620	0.998	292	828
0.125	0.0352	0.567	287	903
0.100	0.0166	0.267	265	938
0.0752	0.00584	0.0940	221	899

At first approximation, $K_1^S = 13$. Duke and Courtney²³ have since used an improved concentration cell to measure the constants for the stannous chloride complexes and have found a value of $K_1^S = 11.3$ in 2 N HClO_4 . If this latter value is used to correct for the chloride ion concentration for SnCl^- , a major improvement is brought about in the agreement of the data. This is seen in the quantity $k'/(c_t - y)^3$.

From the above approximations it can be seen that the formation of complexes cannot be ignored when determining the chloride ion dependence. A more exact treatment will now be undertaken. This becomes necessary when it is realized that the actual dependence may be higher than third order, due to the large proportion of the metal ions present in the complexed form. In the following treatment it is assumed that the reaction occurs between chloride complexes of iron and tin, due to the high improbability of the simultaneous collisions of more than two bodies. Next, those reactions occurring between complexes containing less than a total of three chloride ions are neglected, since data show that no significant portion of the reaction can occur by those paths. We may then write the following rate expression:

$$\begin{aligned} \frac{1}{2} \frac{dx}{dt} = & k_{03} [\text{Fe}^{+++}] [\text{SnCl}_3^-] + k_{12} [\text{FeCl}^{++}] \\ & [\text{SnCl}_2] + k_{21} [\text{FeCl}_2^+] [\text{SnCl}^+] + k_{30} [\text{FeCl}_3] [\text{Sn}^{++}] + \\ & k_{04} [\text{Fe}^{+++}] [\text{SnCl}_4^{--}] + k_{13} [\text{FeCl}^{++}] [\text{SnCl}_3^-] + \\ & k_{22} [\text{FeCl}_2^+] [\text{SnCl}_2] + \dots + k_{05} [\text{Fe}^{+++}] [\text{SnCl}_5^{--}] \text{ etc.}^* \end{aligned} \quad (7)$$

Next the concentrations of each of these species is solved for in terms of total ferric ion, total stannous ion and "free" or uncomplexed chloride ion. When this is done, each term is found to contain in its denominator the product of two polynomials which we shall call $f(c)$:

$$f(c) = (1 + K_1^f c + K_1^f K_2^f c^2 + K_1^f K_2^f K_3^f c^3) (1 + K_1^S c + K_1^S K_2^S c^2 + K_1^S K_2^S K_3^S c^3).$$

*After Gorin, it may be assumed that the product of these reactions is a form of Sn (III) which reacts immediately with more ferric ion. Since the initial reaction is rate determining in the ranges studied, nothing may be said of the following reaction.

Higher terms in (c) have been neglected. The K's are the constants for the complexing of one, two and three chloride ions successively with the metal ions; the superscripts f and s refer to ferric and stannous ions respectively. From the data of Rabinowitch and Stockmayer²² we have that $K_1^f = 3.8$ (corrected for ionic strength 2 by their equation), $K_1^f K_2^f = 4.94$ and $K_1^f K_2^f K_3^f = 0.198$. From Duke and Courtney²³, $K_1^s = 11.3$, $K_1^s K_2^s = 58.0$ and $K_1^s K_2^s K_3^s = 14.0$, all at ionic strength 2. We must collect all terms containing the same powers of chloride and write

$$\frac{dx}{dt} = \frac{(a-x)(2b-x)}{f(c)} (dc^3 + ec^4 + \dots) \quad (8)$$

Here (d), (e) etc. are not specific rate constants, but linear combinations of rate constants multiplied by equilibrium constants. For example,

$$d = k_{03} K_1^s K_2^s K_3^s + k_{12} K_1^f K_1^s K_2^s + k_{21} K_1^f K_2^f K_1^s + k_{30} K_1^f K_2^f K_3^f.$$

The k's may not be separated. From equation (6) we see that

$$k'f(c)/c^3 = d + ec + fc^2 + gc^3 + \dots \quad (9)$$

Data from Table 3 have been used to evaluate the constants (d) and (e) (Table 3A). The free chloride (c) has been calculated by subtracting the concentrations of FeCl^{++} and 2FeCl_2^+ (found by graphical methods) and SnCl^+ from the total chloride (c_t). Concentrations of the other species are small compared with total chloride. Then $k'f(c)/c^3$ is plotted vs. (c), from which the intercept, (d), is found to be 1.2×10^3 while the slope at low values of (c) gives (e) = 72×10 (Figure 1). The range of chloride concentration has been extended in the graph by a series of runs reported in Table 6, where the metal concentrations are very small and (c_t) has been taken equal to (c). The constant (f) appears to be very small, and a value of (g) = 27×10^4 estimated from these higher values permits a good fit of the curve over the entire range. The data cannot be fit without considering that activated complexes with at least six chlorides may carry part of the reaction.

We interpret the foregoing to mean that a minimum of three chlorides is necessary to the activated complex and that more than this number considerably enhance the possibility of reaction. It would be of interest to find the separate values of the constants (k) in equation (7), but kinetic data alone can furnish no further information. Certain assumptions are required concerning relations among the values (k) which are of a highly questionable nature and will not be discussed here.

Table 3 A

Data for Determining the more Exact Dependence on
Chloride Ion Concentration

$$c = c_t - [\text{FeCl}^{++}] - 2 [\text{FeCl}_2^+] - [\text{SnCl}^+]$$

$$f(c) = (1+3.8c+4.84c^2+0.198c^3) (1+11.3c+58.0c^2+14.0c^3)$$

k' are from Table 2

k'	c	$f(c)$	$k'f(c)/c^3$
7.27	0.158	7.428	13.59×10^3
3.07	0.117	4.732	9.13×10^3
1.90	0.0961	3.705	7.95×10^3
0.982	0.0760	2.900	6.49×10^3
0.377	0.0564	2.244	4.72×10^3
0.109	0.0370	1.714	3.70×10^3

Table 6

The Effect of Varying Chloride at High Chloride
Concentrations and Low Metal Concentrations

$[\text{Fe}^{+3}]_0 = 2 [\text{Sn}^{+2}]_0$	c_t	k'	$k'f(c_t)/c_t^3$
0.00360	0.111	2.50	8.82×10^3
0.00370	0.270	24.1	25.0×10^3
0.00351	0.359	44.2	37.9×10^3
0.00326	0.476	80.9	62.3×10^3

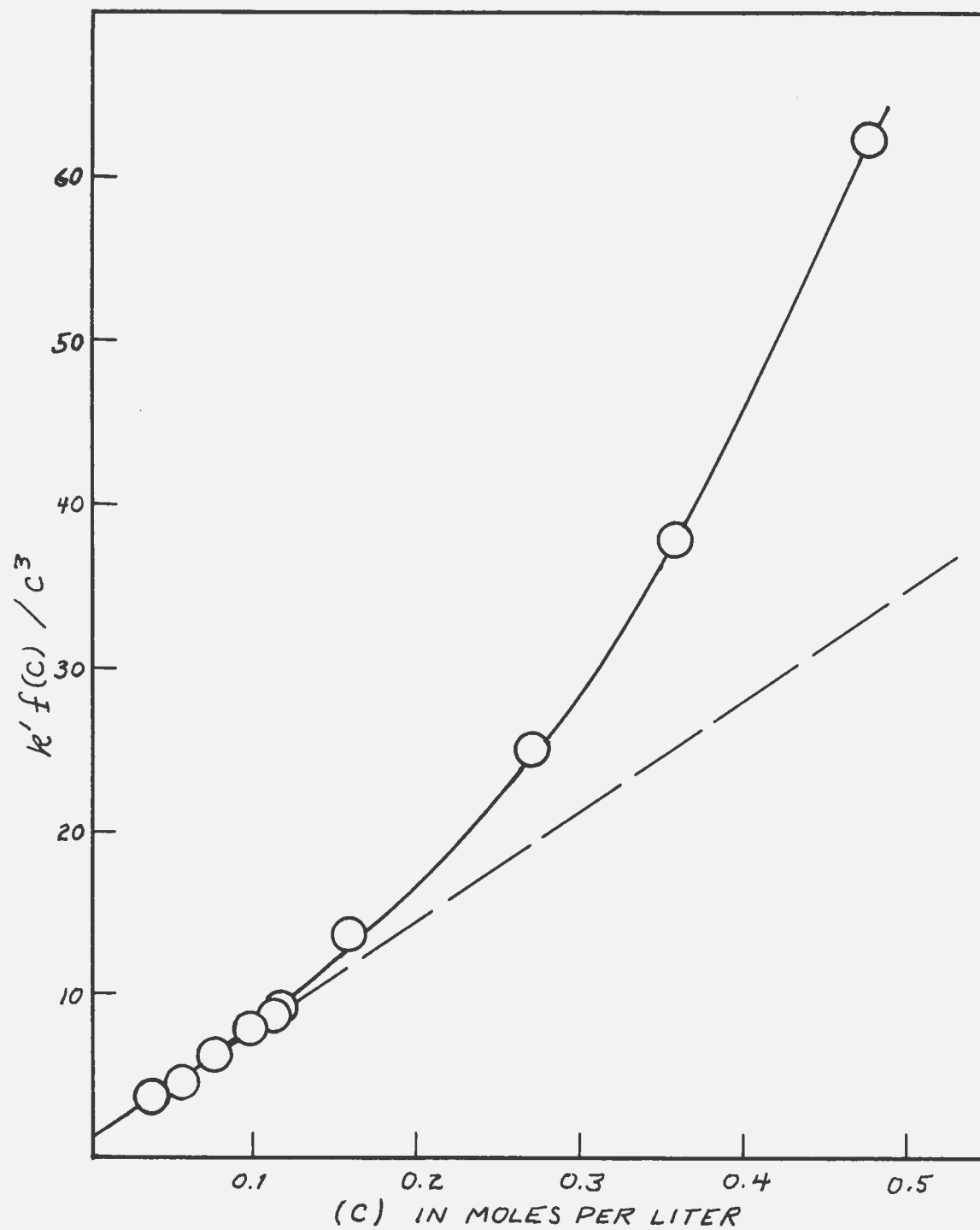


Figure 1 Graphic Evaluation of the Constants (d) and (e)

The criterion of charge repulsion seems of slight importance here. There is nothing apparent to prevent the collision of neutral SnCl_2 from reacting with Fe^{+++} even though these are the major species present at some concentrations. The conclusions of Krishna²¹ regarding the ionic strength effect are invalid, as we have indicated previously.

A simple way of looking at this reaction is to imagine that a chlorine atom (or units such as Cl_2 or Cl_3^-) is effectively transferred from iron to tin. The collections corresponding to the above units in which the chlorine is all in its (-1) state of oxidation are our (X) grouping, whatever the actual motion of the centers of mass. It follows that if the chloride ions were to be replaced by bromide, the transition state would be lower in energy, other factors being equal. Since bromide does not complex as well with ferric and stannous ions, there would be two tendencies affecting the energy of the transition state in opposite directions. Of parallel interest here is the discussion of Rabinowitch²⁴ on what he calls electron transfer in ionic bonding. For the ferric halides, he finds that while the complexing constants decrease as the atomic weight of the halides increases (due to an unfavorable entropy change), the energies of bonding increase. This means that the stabilization by resonance of the form $\text{Fe}^{+3}\text{Cl}_3 \longleftrightarrow \text{Fe}^{+2}\text{Cl}_2\text{Cl}^0$ is less for chloride than for bromide. It is a simple matter to extend this reasoning to the transition states.

From the data listed in Table 7 it can be seen that the apparent order in bromide ion is three. From the value in the table, high stannous concentrations are observed to depress the rate. The last figure may be used as before to make a rough estimate of the value of K_1^S for the reaction $\text{Sn}^{++} + \text{Br}^- = \text{SnBr}^+$ etc. K_1^S is found to be about 2.7.

Table 7

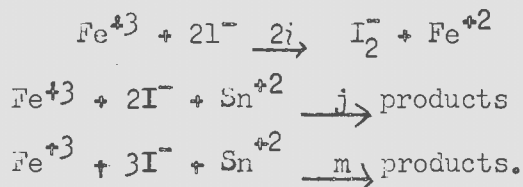
The Effect of Varying Bromide Concentration

$[\text{Fe}^{+3}]_0$	$[\text{Sn}^{+2}]_0$	$[\text{Br}^-]$	S	k'	$k'/[\text{Br}^-]^3$
0.0739	0.00683	0.0676	0.308	11.8	3.81×10^4
0.0739	0.00683	0.0541	0.163	5.84	3.70×10^4
0.0739	0.00683	0.0405	0.0595	2.27	3.41×10^4
0.0739	0.00683	0.0270	0.0179	0.684	3.46×10^4
0.0171	0.239	0.0375	0.427	0.427	0.810×10^4

The corresponding value for the formation of FeBr^{++} (at ionic strength 1) is given as 0.5 by Rabinowitch and Stockmayer²². These values are quite small compared with those for the formation of the chloride complexes, and we may conclude that third order terms are the important ones in the case of the bromide catalyzed reaction. It should be noted that the values $k'/[\text{Br}^-]^3$ show bromide ion to be much more effective than chloride ion even though the concentrations of complexed forms are smaller. In terms of the rate constants for the actual reactions, bromide complexes must be several thousands of times as reactive as chloride complexes.

The iodide catalyzed case is much more complicated due to the fact that ferric ion is capable of oxidizing iodide ion to free iodine. Presumably liberated iodine could oxidize stannous ion immediately. It is then not surprising that multiple reaction paths were found. In the runs reported in Table 8, high concentrations of stannous ion were usually present so that no high concentrations of free iodine were built up.

In earlier work, Hershey and Bray²⁵ found that ferric ion oxidizes iodide by a path which is first order in ferric ion and second order in iodide. Accordingly, we shall set down the following possible reaction paths:



The rate of the equation may then be written as

$$(10) \quad \frac{dx}{dt} = i(a-x)[\text{I}^-]^2 + (a-x)(2b-x)(j[\text{I}^-]^2 + m[\text{I}^-]^3).$$

Now at high tin concentrations, the term $(2b-x)$ is almost the same as $(2b)$. At low tin concentrations, it turns out that the bulk of the reaction is carried by the path which is zero order in tin. Dividing each side of the equation by $(a-x)$ and integrating,

$$\ln \frac{(a-x)/a}{[\text{I}^-]^2} = i + (j + m[\text{I}^-])2b \quad t. \quad (11)$$

The quantity S as reported in Table 8 is found from the initial slope of the logarithmic plot as before, and we then obtain

$$\frac{2.303 S/I}{2b} - i = j + m[\text{I}^-]. \quad (12)$$

Using the last value of S in the table, which is for a run at a lower tin concentration, and two other values, it is possible to solve three linear equations simultaneously to find (i).

Table 8
The Effect of Varying Iodide Concentration

$[\text{Sn}^{+2}]_0$	$[\text{Fe}^{+3}]_0$	$[\text{I}^-]$	S	$S/[\text{I}^-]^2$
0.0649	0.0163	0.00120	0.00862	6.11×10^3
0.0664	0.0167	0.00307	0.0590	6.27×10^3
0.0649	0.0163	0.00600	0.2417	6.77×10^3
0.0634	0.0159	0.00879	0.553	7.17×10^3
0.00558	0.0175	0.00646	0.129	3.09×10^3

We obtain 6.2×10^3 , which is to be compared with the value 3.8×10^3 (at ionic strength 0.09) reported by Hershey and Bray. The exact magnitude is unimportant, however, since it will not affect the quantity (m) to be found next. It is only necessary to plot the quantity on the left hand side of (12) vs. the iodide concentration, using the first four values in the table. The intercept gives us a value of 5.52×10^4 for (j), which will be only as accurate as (i), and a value of 2.7×10^6 for (m). Now it is clear that there must be a path dependent on the tin concentration, since there is a path which is third order in iodide which would not ordinarily be present. Also, a value for (j) is obtained which is of some magnitude. Yet there is not a wide enough over-all variation in the tin concentrations used to conclude that the path is first order in tin. As a matter of fact, the plot we have described (not shown here) is more straight if the quantity (2b) is not divided into the left of (12). Otherwise there are small variations of the same order as the variations in tin concentration used. It may be that the new paths are almost zero order in tin due to a slow prior reaction, such as the complexing of a second or third iodide ion with the ferric ion. In that event, the value (m) which we want would be even higher than that found.

In any event, the value 2.7×10^6 for the reaction depending on three iodide ions is to be compared with the value 3.4×10^4 for three bromides and 1.2×10^3 for three chlorides. Since the amounts of halides increase, the correlation between oxidizability of the anions and their catalytic influence on this reaction is established.

V. CASES IN WHICH THE RATE OF COMPLEXING OF THE
ANION IS SLOWER THAN THE REDUCTION STEP: THE REDUCTION
OF SOME COBALT (III) COMPLEXES WITH STANNITE ION

In the beginning, the requirement was made of the anion that it be capable of forming a strong bond with the oxidizing agent. The reasoning was that a high energy of bonding (which is correlated with the oxidizability of the anion) means a high probability of electron transfer from anion to metal. This applies only to our oxidizable groupings (X). It just happens that the cases of anion catalysis encountered thus far fit into that class.

It is plain that the halide catalyzed ferric-stannous reactions are incapable of demonstrating anything about the specific configuration of the activated complexes AXB. With the possible exception of the iodide ion, the halides all readily associate with both iron and tin, and all complexes are apparently in rapid equilibrium with one another. Suppose that we wished to test the postulate that chloride ion be able to form a strong bond with ferric ion in order for reaction to occur, and decided to add phosphate ion to the solution. Phosphate is known to displace chloride ion from ferric ion. It is also known to slow down the rate of reduction. But phosphate ion is equally capable of displacing chloride ion from stannous ion. Hence no conclusion may be drawn. Further, the addition of phosphate ion merely reduces the total concentration of chloride complexes. It does not entirely eliminate any of the species formerly present.

The particular type of metal complex needed is one whose rate of formation or decomposition is slower than its reduction. Then in favorable cases it is possible to deal with only one complex species at a time, and the effect of changing the number and configuration of oxidizable anions on the oxidizing metal ion may be investigated independently.

In order to show that the Shaffer-Remick ideas about equivalence are inadequate, and to be free from any restrictions at all as to the charge repulsion, a test case was sought having special characteristics. The case selected, the reduction of cobalt (III) complexes by stannite

ion, is one in which the reactants are oppositely charged but which are shown not to react directly. Preferably, the reducing agent should have been one known to undergo a one electron oxidation. Stannite ion will reduce ferricyanide ion almost instantaneously. Finally, the cobaltic ion is able to form a large variety of Werner complexes either with or without the anions we have labeled as oxidizable. Although they are not all stable, their rates of decomposition are usually much slower than the main reduction reaction which occurs.

The reduction of the hexamine-cobaltic ion was found most convenient for study. The ammonia molecules surrounding the cobalt should in theory act as an insulator except for reactions where the tunnel effect is important. The methods described for it apply to the other complexes studied with slight modification.

Before describing the experimental results, the reader is warned that the quality of the data is by no means comparable to that previously obtained. The many difficulties inherent in working in basic solutions make for extremely poor reproducibility, especially since oxygen strongly influences these reactions. At no time will we attach any significance to the absolute values of the rate constants obtained, nor will any essential comparisons be made between the rate constants. Before, such comparisons were necessary to the arguments. In the following, we are really interested only in the orders of reaction. For this purpose, the data are adequate.

Experimental Part

Material.

The hexamine-cobaltichloride used was prepared as described in "Inorganic Syntheses"²⁶. The solid salt was purified by twice recrystallizing from water. Solutions were made by dissolving the salt in concentrated NH_4OH , since fairly high amounts of ammonia had to be present in the runs and this formed a convenient way of adding it. The solutions were analyzed for cobalt by electrolytically depositing it on platinum. The stannite solution was prepared by dissolving about 50 g. of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 100 ml. of H_2O in a 500 ml. volumetric flask. To the milky suspension of the hydrolyzed salt was then added 150 ml. of conc. NH_4OH followed by 250 ml. of 5 M. NaOH . After standing a few days all remaining suspended matter settled out and metallic tin was deposited until equilibrium was reached. The solution prepared in this manner was found to be reasonably stable and easily duplicated. It was standardized on the day of each series of runs by titration with standard ceric sulfate. An approximately 5 M solution of NaOH was made

and standardized against $\text{KHC}_8\text{H}_4\text{O}_4$. Solutions of 5 M. concentration of various salts such as NaCl , NaNO_3 and NaClO_4 were made simply by dissolving the correct weighed amounts in water.

Procedure.

In the first runs made with the hexamine-cobaltic ion it was impossible to reproduce the results because of an induction period of varying length during which there was no apparent reaction. This was felt to be due to the presence of dissolved oxygen in the strongly basic solutions, which would be capable of reoxidizing the cobaltous form to the cobaltic. This proved to be quite serious in mixtures of low tin content. Because of the impracticality of sweeping out oxygen from a basic, strongly ammoniacal solution, the following method was devised. All components of the run except stannite were placed in a test tube and to them one ml. of an approximately 2 N solution of Na_2SO_3 was added. The test tube was then stoppered and allowed to stand over night. When the run was made, the proper volume of stannite was added with a fast flowing graduated pipette, the contents of the test tube poured rapidly into a cuvette for determination by spectrophotometric absorption, and the top of the solution covered with a half cm. of white mineral oil. This kept out air, oxygen and had the additional advantage of decreasing the loss of ammonia from the solution, a factor which would otherwise have caused considerable cooling.

For analysis, a Coleman Model 14 Spectrophotometer was used. The spectra of the various cobaltic complexes and their reduction products were originally determined on a Cary Recording Spectrophotometer. It was found that the cobaltic amines had little absorption in the red region, while the blue reduction products absorbed strongly around $630\text{m}\mu$. This was the wave length used for all analyses. The optical density of the reaction mixture against a solution of the cobaltic ammine at the initial concentration was determined at ten times ranging in interval from 50 - 200 seconds. The final extinction of each run was found several minutes after completion of the reaction and taken as a measure of the molar extinction of the product.

All mixtures were immersed in a water bath held at $25 \pm 0.2^\circ\text{C}$ before the runs. Between determinations during the runs the cuvettes were kept in the water bath.

The Reduction of the Hexamine - Cobaltic Ion and the Behavior of Stannite Ion

Even when the precautions outlined above were taken, the oxygen interference at low tin concentrations was serious. Hence all reaction mixtures contained an excess of stannite.

It was first found that the rate was independent of cobalt concentration. At high stannite, a simple plot of optical density vs. time yielded straight lines. A variation of initial cobalt concentration also did not affect the rate of production of the cobaltous ammine.

The behavior upon variation of hydroxide concentration was next investigated. The results are listed in Table 9.

Table 9

The Effect of Varying Hydroxide Concentration

$[\text{OH}^-]$	$R = E/E_{\text{max.}} \text{ per min. } \times 10^2$	$R/[\text{OH}^-]$	% dev. from avg.
0.561	1.89	3.37	+ 1.5
0.913	2.94	3.22	- 3.0
1.45	4.58	3.35	+ 0.9
1.89	6.33	3.34	+ 0.6
2.33	7.77	3.32	0.0
		Avg. 3.32	
$[\text{Co}(\text{NH}_3)_6^{+++}] = 0.00351$		$[\text{NH}_4\text{OH}] = 6.8$	
$[\text{HSnO}_2^-] = 0.0156$		$[\text{Na}_2\text{SO}_3] = 0.18$	

To maintain the ionic strength, 5 M. NaNO_3 was used. In basic solution, nitrate will not oxidize stannite. In the earlier investigations with the pentammine complex, sodium chloride, perchlorate and sulfate were all used to control ionic strength with substantially the same results. Reproducibility is more difficult with the pentammine complex, however. In the table, all concentrations are given in moles / liter. The quantity R was found by plotting the extinctions E vs. the time in minutes and then dividing the slope by the final extinction, E_{max} . The result was then multiplied by a factor of 10^2 to obtain R. The concentrations of hydroxide are not simply those due to NaOH solution added because there was a large contribution from base in the stannite solution used. In the stannite solution, it was figured that three hydroxides

were consumed by each stannous ion present in the original mixture. If this assumption were incorrect, that is, if the equilibrium constant for a reaction of the type



were at all significant, a marked drift would appear in the values $R/[\text{OH}^-]$ reported. The results show that the reaction is first order in hydroxide, but that there is no large amount of tin in the form of SnO_2^- even in solutions of 2 M. base. This suggests that stannous acid might not be dibasic.

Next the effect of varying chloride ion concentration was studied. This was done for two reasons. First, small amounts of chloride were present at all times because the cobalt and tin solutions were originally prepared from the chlorides, and it had to be shown that chloride did not influence the reaction. The chloride salts were used as a matter of convenience. The perchlorates were originally tried for the pentammine-cobaltic reduction with the same general results, but stannite solutions were found harder to prepare from stannous perchlorate. Second, chloride ion satisfies our condition of oxidizability, and since it so effectively catalyzes the ferric stannous reaction, it might be expected to do so in the cobalt case. We shall use the results to test our condition that the anion should be able to form a bond with the oxidizing agent. The results are collected in Table 10. In this series of runs, all factors except chloride concentration were held constant and the variation in chloride compensated by adding NaNO_3 when necessary. The concentrations of chloride reported are in error by a small residual factor due to the use of the chloride salts but which is of the magnitude of 10^{-4} moles per liter. The over-all variation is then by about a factor of 10^4 . Although there is a slight increase in rate at high chlorides, the over-all change in rate is within experimental error. We conclude that chloride does not catalyze the reaction and offer as the reason the following. Chloride will not displace ammonia from either the hexammine or pentammine complexes at any rate fast enough to be significant.

Table 10

The Effect of Varying Chloride Concentration

$[Cl^-]$	$R = E/E_{max}$ per min. $\times 10^2$	% Dev. from avg.
0.000	2.88	-1.7
0.455	2.86	-2.4
0.919	2.92	-0.3
1.36	3.07	+4.4
Avg. = 2.93		
$[Co(NH_3)_6^{+++}] = 0.00351$	$[Na_2SO_3] = 0.18$	
$[HSnO_2^-] = 0.0150$	$[NH_4OH] = 6.8$	
	$[OH^-] = 0.913$	

The behavior upon varying the stannite concentration, was next investigated. Although it was assumed at first that the dependence would be first order, the situation was found to be more complicated. It was not possible to get reproducible results except in a medium range of tin concentrations. The reasons are that at low values, the induction period mentioned before interfered seriously; at high concentrations precipitates formed. These were presumably cobaltous ammine stannites. The results are listed in Table 11. Because of the precipitation the final extinctions varied somewhat. It was assumed that they should all be equal and the value for one of the lower tin concentrations which was fairly clear was taken as correct. The quantity of So reported in the table is the initial slope of a plot of $\log_{10} (2b - x)$ vs. (t) in minutes. Here $2b$ refers to the extinction which would be obtained if an amount of hexammine cobaltic ion equivalent to the number of moles of stannite initially added were completely reduced in the volume of solution used. That is, b is the concentration of initial tin in terms of extinction units. The quantity (x) is the running extinction found at time (t) . An examination of So shows

Table 11

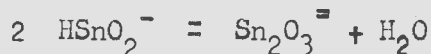
The Effect of Varying Stannite Concentration

$\left[\text{HSnO}_2^- \right]_0$ = B	$S_0 \times 10^3$	$B S_0 \times 10^5$ (experimental)	$B S_0 \times 10^5$ (calculated)	% dev.
0.00975	4.08	3.98	4.29	- 7.2
0.0104	4.85	5.09	4.53	-12.4
0.0195	3.50	6.83	7.47	- 8.6
0.0208	3.62	7.53	7.83	- 3.8
0.0390	3.30	12.87	12.37	- 4.0
0.0416	2.88	11.98	12.96	- 7.6
0.0623	2.92	18.20	17.20	- 5.8
0.0975	2.10	20.48	22.74	- 9.9
0.1039	2.61	27.12	23.74	-14.3
$[\text{Co}(\text{NH}_3)^{+++}] = 0.00307$		$[\text{OH}^-] = 1.62$		
$[\text{NH}_4\text{OH}] = 4.8$		$[\text{Na}_2\text{SO}_3] = 0.17$		

that it is not constant. In addition to the erratic fluctuations due to poor reproducibility, there is an over-all decrease by an approximate factor of two as the tin is increased tenfold. The order is not strictly first.

The results may be explained by assuming that stannite ion, whose formula we take to be HSnO_2^- , can dimerize. This is not unlikely, since some now hold the view that the basic forms of amphoteric hydroxides such as stannous acid are not true solutions but colloids which have been peptized by the base²⁷. The fact that kinetic data can be obtained in the case of stannite is an argument against this

extreme view, but possible polymerization is not to be overlooked. We shall write down the simple equilibrium



If we let B equal the total tin, the concentration of monomer is given by

$$[\text{HSnO}_2^-] = (\sqrt{1-8BK} + 1) / 4K \quad (13)$$

where K is the equilibrium constant for the dimerization reaction. To simplify the equations for the kinetics we shall let (m) stand for the concentration of monomer HSnO_2^- and (c) stand for the concentration of hydroxide ion. Then the rate expression is

$$\frac{dx}{dt} = 2kcm \quad (14)$$

Here (x) will stand for the concentration of cobaltous complex ion formed.

$$\frac{dx}{2B-x} = \left[\frac{2kcm_0}{2B-x} + q \right] dt \text{ where } q = \frac{2kc(m-m_0)}{2B-x} \quad (15)$$

$$\text{or } \frac{dx}{2B-x} = \left[\frac{2kcm_0}{2B} + q + p \right] dt \text{ where } p = kcx(2m_0 - B) / (2B-x)$$

$$\ln \left[\frac{(2B-x)}{2B} \right] = kcm_0 t/B + \int_0^t p dt + \int_0^t q dt. \quad (16)$$

Now both (p) and (q) vanish as (t) approaches zero, and hence the integrals vanish in the limit. This justifies the use of a logarithmic plot and initial slopes, even though the reaction is not first order in the total tin concentration. Actually the deviation from linearity of a plot of $\log_{10} (2B-x)$ vs. time is so small that it can hardly be detected. Now from (13) and (16) we have that

$$2.303 S_0 = kc (\sqrt{1+8KB} - 1) / 4BK \quad (17)$$

Using equation (17) for any two values of S_0 and B we may write

$$\frac{B'S_0'}{B''S_0''} = \frac{\sqrt{1+8B'K} - 1}{\sqrt{1+8B''K} - 1} \quad (18)$$

By choosing values from the beginning and end of Table 11, for which there is about a tenfold variation in B, a value of $K = 17$ may be obtained. This is the easiest done by inserting values in trial-and-error fashion rather than by solving a quartic. It also turns out that the expression is not very sensitive to the value of K and so no more than

one significant figure should be set down. Although the exact value is doubtful, K is large enough to show appreciable dimerization if we assume it to be the cause of the observed order.

To find (k) we rearrange (17) to read

$$BS_0 = (\sqrt{1 + 8BK} - 1) \text{ kc/4} \times 2.303K. \quad (19)$$

Now if BS_0 from Table 11 is plotted vs. the quantity in parentheses, the slope is equal to $\text{kc/4} \times 2.303 K$ (Figure 2). The value of the slope is 8.3×10^{-2} which gives a value of k equal to $7.9 \times 10^{-3} \text{ min.}^{-1} [\text{OH}^-]^{-1}$.

From the values of (k) and K found, the quantity BS_0 was calculated for each run and listed with the experimental value in Table 11. The poor reproducibility can also be inferred from the erratic nature of the graph in Figure 2. Some of the deviations are as much as 14 per cent, but with the correction for K they are no longer systematic.

At one time, it was felt that the wide variations were due to heterogenous effects. The reaction was therefore run in the presence of some broken glass tubing and also, in a length of "tygon" tubing which ought to be without surface as far as this reaction is concerned. There was no systematic variation in the rates and it was concluded that no substantial portion could react via the surface. Nevertheless all runs were made in the same cuvette for purposes of comparison, and the cuvette was washed after each run with a neutral detergent. In the middle range of stannite where the hydroxide dependence was investigated, the reproducibility is well within ordinarily expected error.

The ammonia dependence was next investigated, mostly with the pentammine complex (see below). In the case of the hexammine the effect is very slight. At first it was thought that ammonia either complexed with stannite or formed undissociated salts which were inactive. This was because increasing ammonium hydroxide concentration caused an apparent decrease in rate. However, most of this effect could be explained by slight variations in the molar extinction of the product. Since the ammonia concentration can be changed only about twofold without running into serious difficulty, and since the variation in rate was only a fraction of this, no conclusions could be drawn. However it does seem that the addition of ammonia to stannite solutions contributes somewhat to their stability.

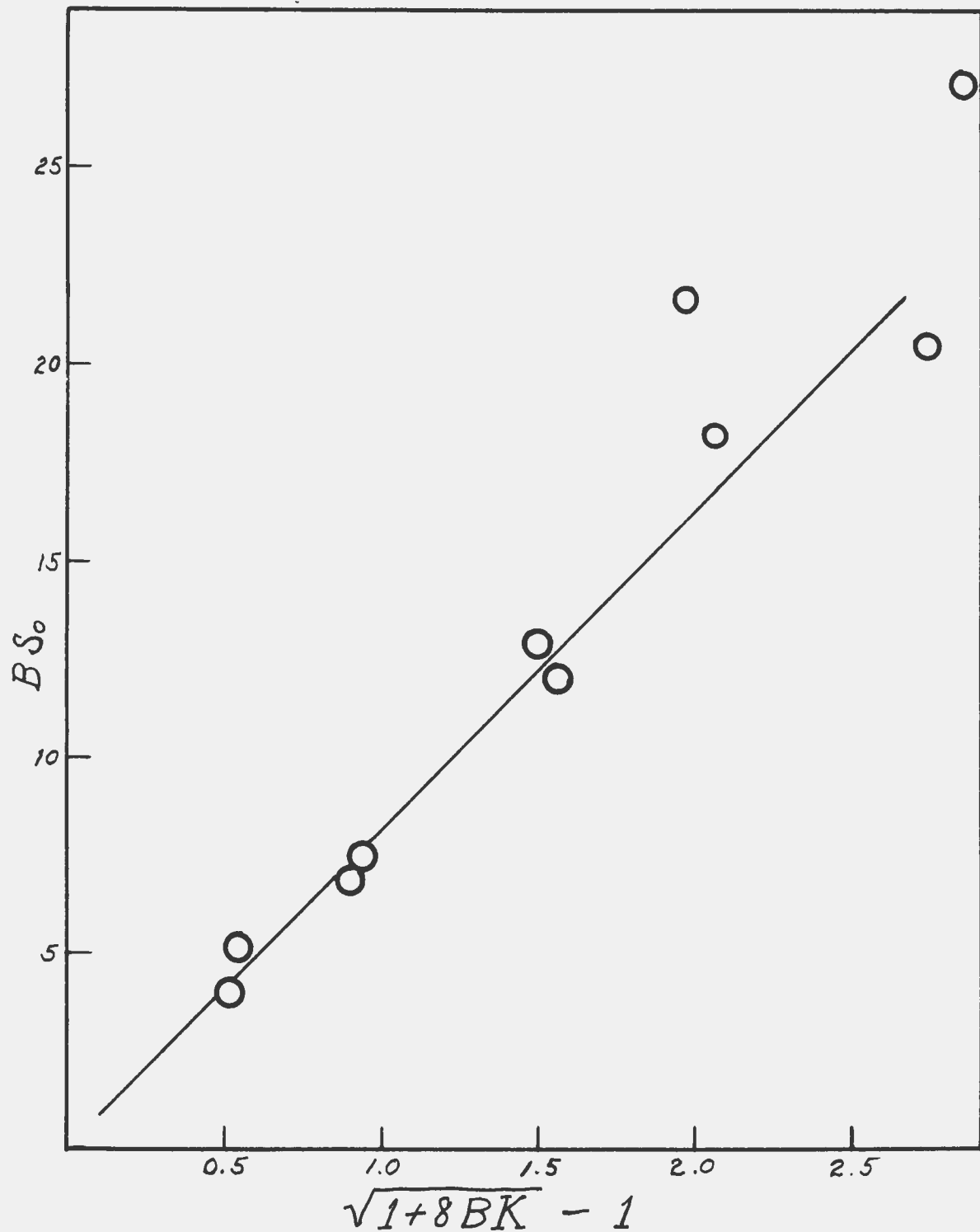


Figure 2 Determination of the Product kK

The Reduction of the Hydroxypentammine-Cobaltic Ion

We now turn to an investigation of the behavior of pentamine-cobaltic ion. In the highly basic solutions used, the complex was in the hydroxy- rather than aquopentammine form. The sulfate and perchlorate were prepared along the lines of the procedure described in "Inorganic Syntheses"²⁸ for bromo-pentammine-cobaltibromide. The oxidation was carried out with hydrogen peroxide. The salt was never separated from its solution but was used in its impure state.

In the preparation of solutions for rate runs, it was found impossible to deoxygenate by the sulfite method. Due to the instability of the hydroxypentammine-cobaltic ion in basic solutions, the runs had to be started as soon as the cobalt complex was added. The induction period observed in the hexammine case was absent anyway, perhaps because oxygen might not so readily attack the pentammine.

It was first noted that all rates were independent of cobaltic concentration as before. Next an attempt was made to determine the dependence on hydroxide ion concentration. Surprisingly enough it was not found to be simple first order as before. The results are summarized in Table 12.

The values S_o reported are slopes of the sort described previously. The tin concentrations given are total stannite concentrations and not those of the monomer. The first thing to be noted is that within the large limits of experimental error present there is no special effect due to using either the chloride or sulfate as an addendum and that there is no great ionic strength effect. Second, it is plain that the hydroxide ion order lies somewhere between zero and first.

Now if we had not known from the previous experiments that there is no large consumption of stannite in a more highly hydroxylated form than HSnO_2^- , we might have tried to fit the present data by using an equilibrium constant. Instead we suppose that there exist two parallel paths of reaction in this case and set about finding the rate constants. To begin, we calculate a quantity k' defined as

$$k' = 4BK \times 2.303 S_o / (\sqrt{1 + 8BK} - 1) \quad (20)$$

which is the same as the (k) used before except that the hydroxide concentration has not been divided into it. Next we plot k' vs. $[\text{OH}^-]$ for the chloride and sulfate cases (Figure 3), and attempt to draw a straight line through the points, disregarding the two higher values.

Table 12

The Effect of Varying Hydroxide Concentration

$$[\text{Co}(\text{NH}_3)_5\text{OH}^{++}] = 0.00580 \text{ in all runs}$$

(A) Chloride used to control ionic strength

$$[\text{HSnO}_2^-] = 0.0114$$

$[\text{OH}^-]$	1.05	1.49	1.94	2.84	3.73
$\text{Sox} \times 10^3$	2.44	2.63	2.69	3.32	4.42
$k' \times 10^3$	7.36	7.92	8.10	10.02	12.80

(B) Sulfate used to control ionic strength

$$[\text{HSnO}_2^-] = 0.0150$$

$[\text{OH}^-]$	1.49	1.94	2.39	2.84
$\text{Sox} \times 10^3$	2.41	2.53	2.88	4.04
$k' \times 10^3$	7.57	7.95	9.05	12.70

(C) No control used

$$[\text{HSnO}_2^-] = 0.0145$$

$[\text{OH}^-]$	1.05	1.49	1.94	2.84	3.73
$\text{Sox} \times 10^3$	2.59	2.66	2.55	3.77	3.84

In spite of the insensitivity of the method we find a rough value of the intercept $i = 5.7 \times 10^3$ and a value for the slope $j = 1.5 \times 10^{-3}$. We freely accept the fact that these values may be in error by as much as 100%. Now the strange thing is that if there were a reaction zero order in hydroxide ion whose effect were superimposed on the first order reaction, we should find that the value of j was that of the former $k = 7.9 \times 10^{-3}$. Instead it is much less. Due to the generally poor quality of the data, we shall not attempt any conclusions based on the absolute values obtained. What is more remarkable here is that there should exist a path zero order in hydroxide concentration at all, since all rate determining steps are apparently dependent on stannite and not

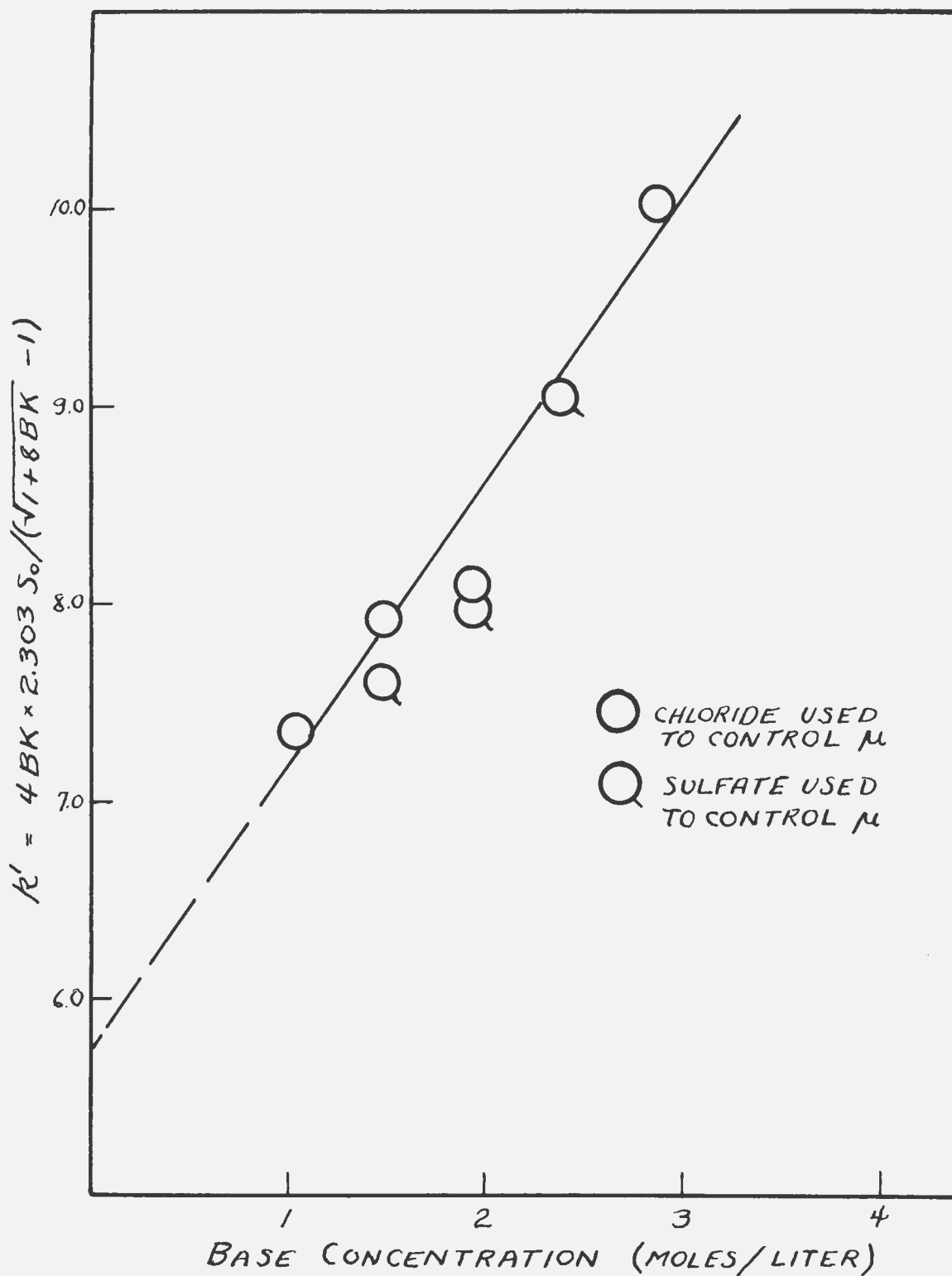
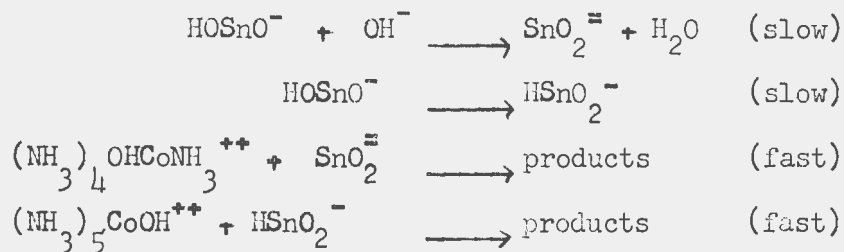


Figure 3 Determination of the base Dependence for the Reduction of the Pentammine-Cobaltic Complex

on cobalt. If a path now exists which was not possible in the hexamine case, it must be due to the presence of the hydroxyl group on the cobalt. An intriguing possibility is that the reacting complexes (not the activated complexes) involve active hydrogen. To show how this might happen we write the following equations:



Since the whole of this anomalous behavior could be laid to some spurious effect, such as the failure to deoxygenate the solutions, we leave this phase of the problem to consider anion catalysis.

We stated before that the aquo- (or hydroxy-) pentammine complex is unstable in basic solutions. If allowed to stand 24 hours or more, the brown hydroxide is precipitated, even in highly ammoniacal solutions. Long before this occurs, marked changes take place. These changes are not readily found spectroscopically because it seems that more highly hydroxylated cobaltic amines have much similar spectra. This effect is illustrated in the curves shown in Figure 4. The middle curve was obtained in the usual manner, the cobalt being added last to start the reaction. It shows a fairly uniform slope in the beginning. The top curve was obtained by allowing the cobalt pentammine to stand in the basic solution for one hour at 25° before starting the run. During this time there was little detectable change in its spectrum. The lower curve was made in the reverse manner by allowing the tin to stand. This shows that the effect is not due to absorption of oxygen by the solvent from the air, or any similar cause.

The top curve in fact will give fairly good first order plots for cobalt. This shows two things. First, more highly hydroxylated cobalt complexes are capable of participating in a rate determining reaction. Second, this reaction must be with the ordinary stannite in solution, or must not be dependent on any "active" form of tin (II). The investigations were not continued because the kinetic analysis is too complex. It involves both parallel and consecutive reactions of comparable rate. Because of the low reproducibility of the data, approximation methods are of doubtful validity when used to test for the various steps involved.

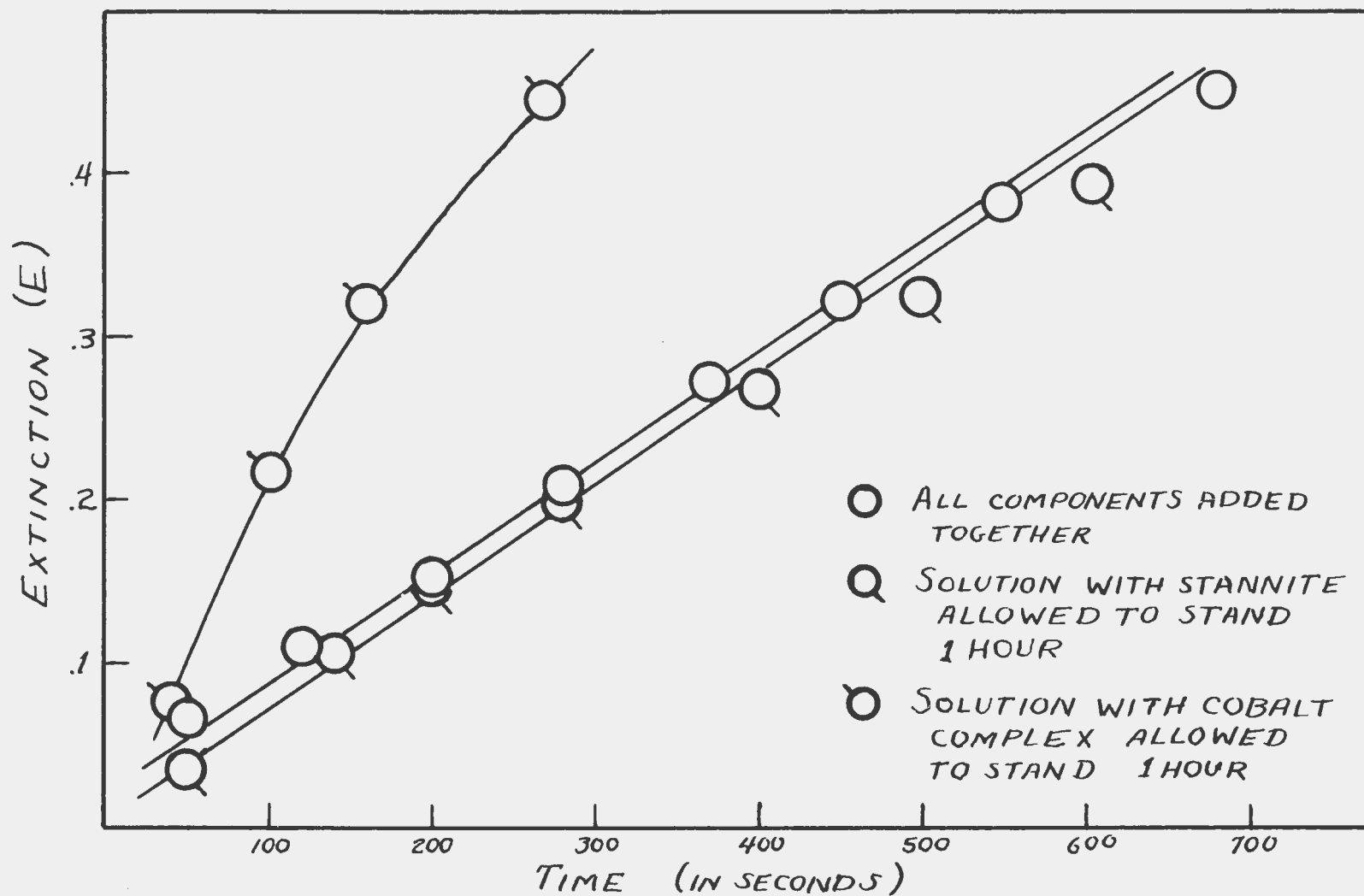


Figure 4 Rate Runs Showing the Effect of Base on the Pentammine-Cobaltic Ion

Qualitatively, the above behavior verifies the predictions made. what is worthy of note is that more than one hydroxyl group must be present in the nucleus for any reaction via the new path. This is comparable to the ferric halide cases, in which it appears that the reduction never proceeds unless two, or more likely, three halide ions are present. In the cobalt-stannite case it is perfectly clear that we cannot blame the effect on any charge repulsion argument, since any anion inserted in the cobalt nucleus lowers its charge and (except for the possible reversing tendency of the ionic strength effect) decreases the probability of collision with stannite ion.

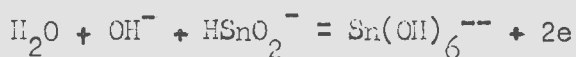
A comparison of the products of reduction in the cases of the hexammine and pentammine is interesting. The absorption spectra appeared almost identical. However, if after a partial reduction a solution of the hexammine was vigorously shaken in air, the original orange color was restored. If very small amounts of dilute hydrogen peroxide were added to the solution of the reduced pentammines complex, the original color was produced. Hydrogen peroxide added to a hexammine solution which had been reduced gave a brown colored solution of peroxides rather than the original orange, but no trace of the hydroxy-pentammine-cobaltic ion. It was concluded that the nuclear structure of the complexes was not disturbed by reduction and that the products in the two cases were different despite the similarity of their spectra.

The Catalytic Effect of Cyanide Ion

We will now qualitatively describe some experiments more in line with the original course of investigation. First, it was found that cyanide ion acts as a specific catalyst for the reduction. No other anion of the series SCN^- , OH^- , Cl^- or Br^- was found to do this except OH^- in the sense described above. The cyanide catalyzed reaction is much more rapid and hard to follow. On the basis of our theory the reason is obvious - cyanide ion is the only one capable of a rapid displacement of ammonia in these complexes. In addition, it is "oxidizable". The difficulty of accurate kinetic analysis is again that parallel reaction paths are involved and that the products are markedly dependent on the amount of cyanide added. Small amounts give the usual product. Larger amounts give successively green, brown and red colored solutions. Supposedly these are due to $\text{Co}(\text{CN})_6$ and polynuclear cyanides. The compound $\text{K}_2\text{Co}(\text{CN})_6$ is described as green. Somewhat strange is the fact that, when excess cyanide is added, the product is yellow rather than red. Also, when stannite is added to a solution of potassium hexacyanocobaltate (III), there is no noticable change at first. Then gradually a deeper yellow color is produced. The red color of the supposed $\text{Co}(\text{CN})_6$ ion is never

formed under any circumstances. When more cyanide is added to this solution, the color becomes pale again. When the solution is heated, the color of the deeper yellow solution becomes pale, but returns again upon cooling.

Offhand, we might explain the results by saying that no reaction has taken place with the hexacyano complex because of an adverse free energy change. Latimer's book³⁰ gives the necessary information, except that the half-cell reactions of interest are of the type which must be calculated indirectly. With some reservations, then, we write down the following:



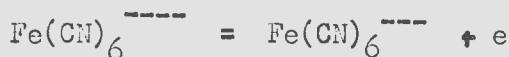
$$E_B^\circ = 0.96$$



$$E^\circ = -0.83$$

The reaction could be pushed to completion then only by abnormal base concentrations. Even if the potentials are adverse, we must explain why the red hexacyano-cobaltate (II) ion is formed in the cases where cyanide is added to the amine reduction systems. To do this we must assume that less than six cyanides are present in the complexes at the time of their reduction. After the reduction, more cyanide can enter to form the red complex, and we must suppose that the oxidation of stannite is "irreversible", that is, the form of stannate produced cannot oxidize the hexacyanocobaltate (II) ion. Upon addition of excess cyanide, the tin (IV) species is complexed and now falls into our category of oxidant - oxidizable anion systems. This is because CN^- is more oxidizable than OH^- . The tin (IV) can now oxidize the cobaltous species to yellow hexacyano-cobaltate (III) ion.

Finally, we are in a position to examine the equivalence principle of Shaffer-Remick. Let us call on Latimer³⁰ for the following half-cell potentials:



$$E^\circ = -0.356$$



$$E^\circ = 0.1$$

Hence the equilibrium constant for the reaction



is (very roughly) 5×10^{-5} . To this we add the fact that stannite reduces ferricyanide ion instantly. This in itself is hard to explain after Shaffer and Remick. The equilibrium above is not so far to the left that ferrocyanide could not act as a catalyst in the reduction of hexammine cobaltic ion.

Ferrocyanide ion and hexammine cobaltic ion form a precipitate which is orange in color. It is not changed when acted upon by stannite ion, only the supernatant solution being slowly turned blue. When ferrocyanide is added to the pentammine solutions, the rate of reduction by stannite is not increased very significantly. Usually the rates appear equal. At other times there seems to be a slight increase which could be due to small amounts of KCN present in the ferrocyanide as an impurity. Interestingly enough, there is a change in color when ferrocyanide is added to basic solutions of the pentammine which may not be additive, indicating some sort of interaction. This may be of the kind described by Davidson³¹ in his studies of the chloride complexes.

Due to the small value of the equilibrium constant calculated above, and the uncertainty in its value, we can reach no final conclusion concerning the question of equivalence. The principle is one which may be useful in the future.

We will save the discussion of the results of electron exchange experiments on some cobalt complexes for the section following.

VI. A COMPARISON WITH THE RESULTS OF OTHER WORK

The availability of many radioactive metals in recent years has led to numerous so-called exchange experiments. Many examples have been collected in a short review paper by Rona³². In these experiments, a solution of some metal with added radioactive tracer in a particular oxidation state and complex form is mixed with another solution of the same metal in a different form. The reaction usually intended is the one involving interchange of the two isotopes. The chemical free energy is almost zero for this reaction, but due to a positive entropy of mixing, the real ΔF is always negative. However, the interchange is often not the reaction which occurs. If the complexes involved are stable, exchange of oxidation state may take place without destruction of the complexes. The reactants and products are then unsymmetric. The only reactions which need concern us are those in which reduction occurs.

Lewis³³ has reported that the interchange between cobaltous and cobaltic hexammines is extremely slow. It is also slow for the ethylene diammine complexes, although somewhat faster than is the case of the amines. What is significant is that the heat of reaction in the case of the amines is higher than the calculated repulsion energy. Somewhat harder to explain is the rather rapid cross reaction between the cobaltous ethylenediammine and the cobaltic hexamine. Apparently the half-life for the concentrations used is about five minutes. The largest free energy decrease occurs for this pair of reactants. The³⁴ reaction is still far from instantaneous. On the other hand Thompson reported complete exchange between ferro- and ferricyanide within the time of separation. This is to be expected, and is simply another example where charge repulsion is too weak an effect to be important. Cobble and Adamson³⁵ have repeated the experiment with the same result. In passing it is noted that the cyanide ions are not disturbed in such reactions. Adamson, Welker and Volpe³⁶ have shown that there is no interchange between cyanide ion in solution and the cyanide complexes of iron (II), iron (III) and cobalt (III).

The other experiments of Thompson with the iron cyanide complexes and ferric and ferrous ion were not designed to test interchange of oxidation state alone and are not pertinent to our subject.

Somewhat harder to interpret are the results of exchanges between ferric and ferrous ion and thallic and thallous ion. Although there has been some controversy over the ferric-ferrous case, the latest report of Betts et al.³⁷ indicate that interchange is very fast in 3M HClO₄ and in the absence of chloride ion. However it is not certain that hydroxylated ferric ions are not responsible for the reaction. The number of anions necessary may be less than three in this one-to-one exchange of state where no high energy intermediates are required. The interchange of thallic and thallous ion goes by a path which is third order in chloride ion for higher chloride concentrations. It also appears that there is a path independent of chloride. Dodson et al.³⁸ have indicated that increasing acidity decreases the rate of reaction. Since the acidity constants for thallic ion are not known, it is possible here that hydroxylated complexes are responsible. These authors also report similar results for the ceric-cerous exchange.

The presence of oxidizable anions is thus able to explain a number of apparently anomalous effects in radioactive exchange experiments. The explanation alone is probably not adequate for the whole body of reactions between metal ions in solution. The original example of Shaffer - the failure of ceric ion to oxidize thallous ion - still seems to hang on the high energy of any possible thallium (III) ion

which might be needed. Another odd example is the failure of titanous chloride to reduce mercuric ion, with or without excess chloride ion. This may be due to the high energy of a possible single mercurous ion intermediate.

For those reactions which do require oxidizable anions, the problems which next suggest themselves are these. What are the geometric requirements of the activated complexes? That is, how many anions are actually required ~~and how much~~ bonding is there to the oxidizing and reducing metals? These questions have been partially answered. Future information will probably come from the great variety of the stable complexes of iron, cobalt and nickel.

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