Summary

It has been shown that in a polymer formed exclusively by the addition of monomers to a fixed number of polymer molecules, the numbers of species of various sizes are represented by Poisson's distribution law. Equations representing weight fraction distributions have been derived, and the calculated weight per cents. of various species in several polymers having average sizes of 6 to 500 units are shown graphically.

The distribution for these polymers, typified by the polyethylene oxides, has been contrasted with the distribution in condensation polymers. The former are much more homogeneous. Whereas the ratio of weight average to the number average molecular weight of condensation polymers approaches two as the degree of polymerization increases, for the polyethylene oxide distribution this ratio approaches unity.

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[A CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Nature of the Thiocyanate Complex of Molybdenum

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In the determination of small amounts of molybdenum, the molybdenum as molybdate is reduced with stannous chloride in the presence of an alkali thiocyanate. The red coloration which is formed under these circumstances, is used in a wide variety of colorimetric procedures.[1] The earliest observations of this reaction were made concurrently by Braun and by Skey.[2] About forty years later, Chilesotti[3] electrolyzed acid solutions of molybdates from which he presumably obtained trivalent molybdenum. He reported that when these solutions were treated with potassium chloride or potassium thiocyanate, red salts were formed with a composition of $K_3Mo(SCN)_6 \cdot 4H_2O$ and K_3MoCl_6. Somewhat later Sand[4] and Rosenheim[5] carried out detailed investigations of the complexes which molybdenum formed in the trivalent and pentavalent states. They performed their reductions electrolytically, treating the solutions with an alkali thiocyanate and then extracting the red colored forms with ether. From the ethereal extracts complexes were precipitated with pyridine or quinoline, and, from an analysis of the complexes, these workers attempted to deduce its structure. The complex was variously reported at that time as $MoO(SCN)_3$, $Mo(OH)_2(SCN)_3$ and as $R_2MoO(SCN)_5$ where the R was an alkali atom. In addition to these structures they also were successful in isolating other series of thiocyanate complexes which were formed under nearly identical conditions. In some of these structures the molybdenum was trivalent and the complexes possessed different degrees of hydration. Other compounds differed only in the amount of alkali chloride bound into this complex. In view of the wide variety of structures observed, it becomes extremely difficult to decide which of these formulas should be assigned to the compound under question. Barbieri considered the thiocyanate complex to be $MoO(SCN)_3 \cdot H_2O$. In 1926, Krauskopf and Schwartz[6] reported $Mo(SCN)_3$ on the basis of a simple analysis of the ether extract. However, Wm. Wardlaw and his students[7] reinvestigated the problem of the thiocyanate complex formation and, as a result of a number of experiments decided that the structure of the complex could be either $(H_2MoO_2(SCN)_3)$ or $H_2(MoO(SCN)_5)$ although he also isolated a large number of different salts series of the type $H_2(Mo_2O_3(SCN)_6)$. Thus, again no positive identification of the desired structure could be made.

In considering these variously proposed structures, it seemed somewhat doubtful to us that one could assume that the compounds isolated from the dark colored oily mixtures which these workers obtained were identical with the red thiocyanate used in the analytical determination of molybdenum. In view of the more drastic conditions

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[1] Kedesdy, *Mitt. kgl. Materialprüfungesamt*, **31**, 173 (1913); Maag and McCollam, *Ind. Eng. Chem.*, **17**, 524 (1925); James, *Ind. & Eng. Chem., Anal. Ed.*, **4**, 89 (1932); Hurd and Allen, *ibid.*, **7**, 396 (1935).

[2] Braun, *Z. anal. Chem.*, **6**, 86 (1867); Skey, *Chem. News, Am. Reprint*, **I**, 296 (1867).

[3] Chilesotti, *Atti. accad. Lincei*, **12**, ii, 22, 67 (1903).

[4] Sand and Burger, *Ber.*, **38**, 3384 (1905); also Maas and Sand, *ibid.*, **41**, 1500, 1861, 3367 (1908); **42**, 2642 (1909).

[5] Rosenheim and Koss, *Z. anorg. Chem.*, **49**, 148 (1906).

[6] Krauskopf and Schwartz, THIS JOURNAL, **48**, 3021 (1926).

[7] James and Wardlaw, *J. Chem. Soc.*, 2726–2739 (1928).

which these workers used, it seemed desirable to us to conduct a study in order to establish some of the limiting conditions governing proposals for structure of the complex. To that end, an investigation was begun to determine (1) whether the complex formed in the usual analytical procedure was identical with that formed between quinquevalent molybdenum and thiocyanate and whether it was at all possible for the trivalent molybdenum to form a red colored thiocyanate, (2) whether an equilibrium study of the reaction between the quinquevalent molybdenum and the thiocyanate ion would give some evidence as to the structure of the complex and (3) whether the pronounced color changes, which have been observed in quinquevalent molybdenum solutions, could be correlated with a previous observation of Hurd and Hiskey[8] that varying the acid concentrations resulted in a bleaching effect on the molybdenum thiocyanate complex.

1. **The Valence State of the Molybdenum in the Complex.**—It is recalled that when a molybdate solution, 2 *N* with hydrochloric acid is reduced with such reducing agents as stannous chloride,[9] the silver reductor,[10] or metallic mercury[11] quinquevalent molybdenum is formed. With all three of these agents the procedures have been made quantitative.

The solution of quinquevalent molybdenum, 2 *N* in hydrochloric acid, is amber-red in color. When the solution is in 8 *N* hydrochloric acid, it is emerald-green. These two colored forms of the molybdenum exist in equilibrium with each other. This equilibrium can be shifted from one form to the other simply by varying the hydrochloric acid concentration.

When the amber-colored form of the quinquevalent molybdenum is treated with an alkali thiocyanate solution, an interaction will begin proceeding at an appreciable speed to form a red complex which in appearance and properties seems to be identical with that formed when molybdenum is reduced with stannous chloride in the presence of thiocyanate. If the green colored form is treated with an alkali thiocyanate, no such reaction is observed. On the other hand, if the molybdenum is reduced under more drastic conditions, it can be brought to the trivalent state. Thus, when molybdenum is reduced in the Jones reductor (Zn) in 1–2 *N* sulfuric acid, it forms a green colored trivalent molybdenum compound. If the trivalent compound is treated with an alkali thiocyanate, meanwhile protecting the solution from atmospheric oxidation by blanketing with carbon dioxide or nitrogen, no red colored thiocyanate complex will be formed with the molybdenum even after a half-hour interval. Nor is it possible under these same conditions to extract any red colored complex from this solution with ether or butyl acetate. However, if some oxidant like hydrogen peroxide is added in such amounts as to bring the molybdenum to the five-valent state, the red compound will then be observed.

It is felt that evidence such as this definitely implies that there is no red trivalent complex of molybdenum but that the molybdenum in this complex must be approximately five-valent. In a more striking way, it can be shown that this is so, simply by taking an acid solution of molybdate and alkali thiocyanate and passing it through the Jones reductor. At first, as the solution comes in contact with the zinc, the red molybdenum thiocyanate complex appears but, as it moves down the tube, the solution loses its red color and when reduction is complete it has the blue-green color characteristic of trivalent molybdenum in dilute acid solutions.

The significance of these observations seems to be that as the molybdate passes down the reductor, the action of the zinc brings the molybdenum first to the five-valent state. At this point it reacts with the thiocyanate ion present to form the characteristic red color but, as the reducing action of the zinc is prolonged, the molybdenum is reduced to the trivalent state with the destruction of the red complex.

Besides the green trivalent form of molybdenum there is also a pink form of the trivalent state. It was thought that perhaps this substance reacted with the thiocyanate ion to give red trivalent complex and so it also was studied. This pink modification can be formed in a variety of ways. The essential element of the methods is that the molybdate must be reduced in fairly high concentrations of hydrochloric acid. Foerster[12] formed this pink trivalent molybdenum by electrolytic reduction while in a recent paper Hiskey, Springer and Meloche[13] show that this compound

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[8] Hurd and Hiskey, *Ind. Eng. Chem., Anal. Ed.*, **10**, 623 (1938).

[9] Stěhlik, *Collection Czechoslov. Chem. Commun.*, **4**, 418 (1932).

[10] Birnbaum and Walden, THIS JOURNAL, **60**, 64 (1938).

[11] Furman and Murray, *ibid.*, **58**, 1689 (1936).

[12] Foerster, Fricke and Hausswald, *Z. physik. Chem.*, **146**, 81 (1929).

[13] Hiskey, Springer and Meloche, THIS JOURNAL, **61**, 3125 (1939).

can be formed by reduction in the silver reductor in hydrochloric acid concentrations above 4 *N*. Despite a wide variety of attempts to combine this substance with thiocyanate to form an ether soluble extract, our results were uniformly negative. Consequently it seems reasonable to conclude that trivalent molybdenum does not form any red colored thiocyanate complex.

In an attempt to establish more definitely that molybdenum in the thiocyanate complex is quinquevalent in character, it was decided to obtain the light absorption curves of this complex formed in two different ways. In one case, the complex was formed by reducing molybdate in the presence of an alkali thiocyanate with stannous chloride solution. In the other, the thiocyanate complex was formed by permitting an equivalent amount of a pure quinquevalent molybdenum solution to react with the thiocyanate ion until equilibrium was attained and then to determine its light absorption characteristics. In these experiments the concentration of the molybdenum and the thiocyanate ion in the final solution which were compared were exactly the same. The comparisons were made with the aid of special spectrophotometric equipment. A description has been given by James and Birge.[14]

The absorption curves for the two solutions are plotted in Fig. 1. For the purpose of comparison one of the curves is lowered in relationship to the other, but, on examination, it is apparent that they are practically identical. In addition to studying the absorption characteristics of the aqueous solutions of the thiocyanate complex formed in these two ways, similar studies were made of the butyl acetate extracts of these two solutions. By extracting the two solutions studied in Fig. 1 with butyl acetate, extracts containing approximately the same concentration of molybdenum and thiocyanic acid were obtained. The absorption spectra of these two extracts is given in Fig. 2. From this evidence it seems clear that the color characteristics are the same whether the complex is formed in the conventional manner or by the interaction of thiocyanate and quinquevalent molybdenum.

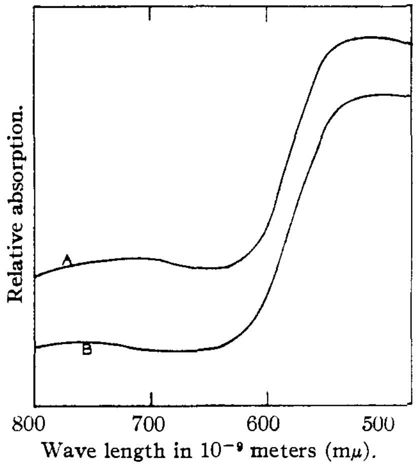

Fig. 1.—A = $Mo^{+6} + SCN^- + SnCl_2$; B = $Mo^{+6} + SCN^-$.

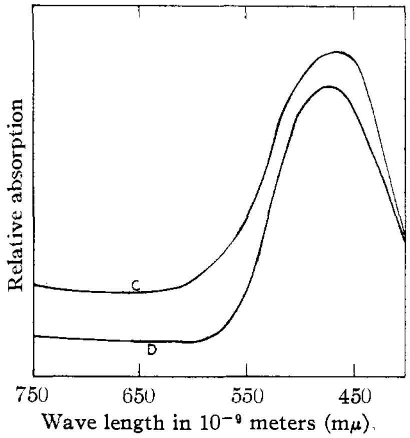

Fig. 2.—Butyl acetate extracts: C, extract of A; D, extract of B.

Therefore, it seems reasonable to conclude that trivalent formulas can be completely eliminated and that one of the limiting conditions concerning the structure of the thiocyanate complex of molybdenum must be a quinquevalent character for the molybdenum.

2. The Reaction between Quinquevalent Molybdenum and the Thiocyanate Ion. General Discussion.—At the outset of these studies it was recognized that the reaction between the thiocyanate ion and quinquevalent molybdenum did not lend itself to the most exact thermodynamical studies because certain difficulties are regularly encountered in the exact measurement of the molybdenum thiocyanate formed. Among those difficulties may be listed the interference due to the pink complex formation of the thiocyanate ion, as well as a fading effect of the molybdenum complex once it has formed.

A characteristic phenomenon of the acidified thiocyanate solutions is the tendency to form a pink colored substance. This pink colored substance is formed under conditions nearly the same

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[14] James and Birge, *Trans. Wisconsin. Acad. Sci.*, **31**, 1 (1938).

as those which might be expected to prevail during the study of the reaction. It has often been observed in this Laboratory that it can be formed by placing a few drops of hydrochloric acid in a 20% solution of potassium thiocyanate. Once formed it can be extracted with any of the usual solvents employed in the molybdenum extraction. Many workers have thought that this pink compound is the ferric thiocyanate, but, even though it does possess a great similarity, it should be emphasized that it can also be formed in carefully distilled thiocyanic acid solutions where no iron could be present. In our particular studies we observed that invariably on mixing hydrochloric acid with a thiocyanate solution, followed by addition of quinquevalent molybdenum, the slow formation of a pure pink color would first be observed. After this color had developed for about ten minutes, the amber tint of the molybdenum complex would appear and reach a maximum while the pink color slowly would fade out. In an approximate fashion the course of these reactions might be represented graphically by the series in Fig. 3.

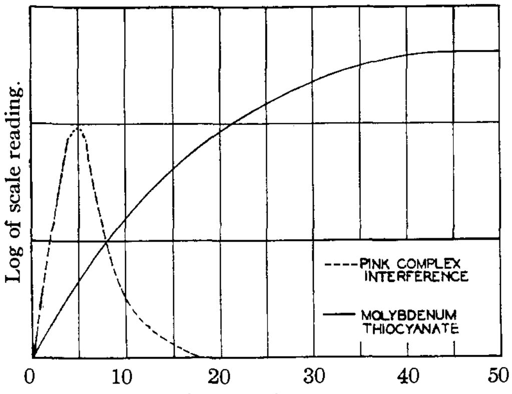

Fig. 3.

A second difficulty encountered in the study of this reaction is one due to an erratic and seemingly unpredictable fading which often occurs during these studies. When solutions of thiocyanate and quinquevalent molybdenum are mixed together and the concentrations are about 0.08 molar and 4.01 × 10^{-5} molar, respectively, the readings obtained from the colorimeter often will show that the color in some of the tubes has faded almost completely while others give perfectly reproducible values. Attempts to find out whether such phenomena were due to the catalyzing influence of traces of impurities seemed to give a negative answer. It did seem, however, that this type of phenomenon occurred with greater frequency in solutions of high hydrochloric acid concentration. Thus, in the four hydrochloric acid concentrations studied, 1.0, 1.5, 2.0, 2.5 *N*, the frequency of this type of fading was greatest in the 2.5 *N* and least in the 1.0 *N* solutions It also was observed that small amounts of stannous chloride solutions hastened the fading of all the solutions to which it was added.

Apart from these erratic fadings, all solutions of the complex showed a very slow fading after the maximum was attained. Thus a typical time *vs.* intensity curve when the hydrochloric acid concentration in the system was about 2.0 *N* appears in Fig. 4. At higher concentrations, the fading was more rapid and at lower concentrations it was much slower.

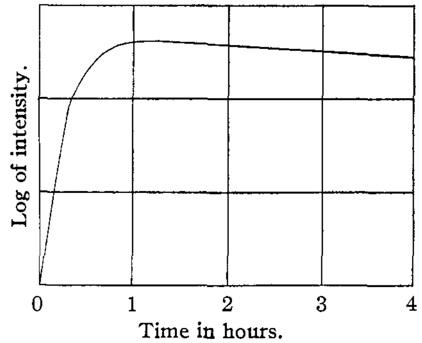

Fig. 4.—Molybdenum thiocyanate intensity as a function of time.

Despite this consecutive fading effect, we felt that we could profitably study the thiocyanate–molybdenum reaction because fading was generally extremely slow and the slight drift was scarcely detectable in the regions where data were of most significance.

Preparation of Materials

A. Approximately 1 Molar Thiocyanic Acid Solution.—This solution was prepared by taking 1 molar alkali thiocyanate, adding 30 ml. of concentrated sulfuric acid per liter and distilling the solution formed in an all glass distilling apparatus. The distillation was carried out at 20 mm. of mercury pressure. Whenever the thiocyanic acid came into contact with certain kinds of organic matter such as the skin, filter paper, cloth, stopcock grease, etc., a pink coloration would be induced. Apparently traces of organic matter or dust would also produce this color effect. In order to obtain a colorless thiocyanic acid solution and keep it so, all apparatus with which it came into contact had to be washed with a small amount of it until a pink coloration no longer formed. Standardization was effected by titration with alkali using phenolphthalein as indicator. This was followed by a Volhard titration as an additional check on the purity of the solution. All of the thiocyanic acid prepared was used within twelve hours or less because, by that time, traces of its decomposition products could already be detected.

B. Quinquevalent Molybdenum Solutions.—This solution was prepared by taking 20.10 ml. of a 0.02495 molar molybdate solution, diluting with an equal amount of 4 *M* hydrochloric acid, heating to 80° and reducing in a silver reductor according to the method of Birnbaum and Walden.[10] The reduced solution was then diluted to one liter with additional 2 *M* acid. The solution was thus 5.01×10^{-4} molar with respect to the molybdenum and 2 *M* with hydrochloric acid. It was always prepared just before an experiment was to be performed.

C.—All other reagents used such as the thiocyanate salts and chlorides of lithium, sodium and potassium were C. P. analyzed and were used without further purification.

Experiments and Results

(1) The Reversible Character of the Reaction.—In this study the attempt was made to demonstrate whether or not the reaction was truly a reversible one. In most cases the usual procedure would be to demonstrate that from whatever side the reaction was begun, the final concentrations of the various components would be the same. But in this instance such an experiment could not be made directly because it was not possible to get pure molybdenum thiocyanate. Therefore, it became necessary to prepare molybdenum thiocyanate solutions of higher concentrations, and then, by proper dilution, to cause the molybdenum thiocyanate to decompose until equilibrium was attained. Then comparing these solutions to others which contained the same total concentration of quinquevalent molybdenum and thiocyanate acid but in which the formation of the molybdenum thiocyanate was performed directly, it became possible to see whether the equilibrium position was the same for the forward and the reverse reaction. In testing this reaction experimentally, two series of solutions were prepared. In one series, which we may designate as the A series, the solutions were prepared in the following manner.

To a 100-ml. volumetric flask, 8 ml. of 5.015×10^{-4} molar solution of quinquevalent molybdenum 2 molar with hydrochloric acid is added followed by 16 ml. of concentrated C. P. hydrochloric acid and varying amounts of water and thiocyanate solution to make up the remaining 100 ml. The solutions were then thoroughly shaken and set aside.

The other series, B was prepared by mixing the same amounts of quinquevalent molybdenum and hydrochloric acid plus 26 ml. of distilled water. To those solutions various amounts of the potassium thiocyanate solution were added and, after mixing, the solutions were permitted to stand until the color density was more than twice that of the corresponding solution in the series A. Then the appropriate amount of distilled water was added to bring the volumes of the solutions to 100 ml. and thus to bring the gross concentration of molybdenum and the thiocyanic acid to the same value as that in the A series. The solutions were permitted to stand while the molybdenum thiocyanate complex slowly decomposed until equilibrium was obtained. The amount of the complex was then determined by measurements in the Evelyn colorimeter using the no. 420 filter manufactured by the Rubicon Company. The results obtained as well as all of the data pertinent to this determination are listed in Table I.

TABLE I

0.9355 *M* KSCN soln., ml.	H_2O[a] added, ml.	Final concn. of KSCN in both series	Log galvanometer deflection Series A	Log galvanometer deflection Series B
10	40	0.0835	0.303	0.290
12	38	.1002	.465	.456
14	36	.1169	.523	.520
16	34	.1336	.557	.553
18	32	.1504	.553	.557
20	30	.1671	.569	.565
22	28	.1838	.561	.569
24	26	.2005	.581	.581
26	24	.2172	.581	.581
24	22	.2339	.581	.585

[a] This was the water withheld in series B.

A comparison of the results for the two solutions reveals that there is little difference in the equilibrium concentrations obtained under a given set of conditions even though the reaction is carried out in widely different manners and from opposite sides of the equation. This is a true test of reversibility and consequently established such a character for the reaction under discussion.

(2) Effect of Electrolyte Concentration on Equilibrium of the Reaction.—During the course of these investigations, it was observed that apparently the equilibrium of the reaction was affected by the character of the cations present. For example, it was observed in several instances that when a given concentration of thiocyanate solutions reacted with a fixed amount of quinquevalent molybdenum, apparently the density of the molybdenum thiocyanate color was greater when the sodium salt of thiocyanic acid was used instead of the potassium salt. Although such effects were known especially from the work of LaMer and others, it was thought worth while to investigate this effect more fully. Besides, any attempt to make equilibrium studies with the end in view of attempting to evaluate the thiocyanate–molybdenum ratio necessitated some knowledge of the degree of these effects so that they could be accounted for properly in any later work.

With this objective in view, another series of solutions was prepared in which the concentration of the molybdenum, as well as the concentration of the free thiocyanate acid, was fixed. To these solutions variable amounts of four different electrolytes were added. These electrolytes were hydrochloric acid and the chlorides of lithium, sodium and potassium. The equilibria for these various systems were established at a temperature of 24.5°, and were attained after two hours. Stock solutions of hydrochloric acid and salts were 2 *M*. Suitable amounts of them were made up with water to a volume of 62 ml. and to this was added 38 ml. of quinquevalent molybdenum and thiocyanic acid mixtures so that their final molarities and that of the hydrochloric acid were 8.018×10^{-5}, 0.305 and 0.167 *M*, respectively. The data obtained are plotted in Fig. 5.

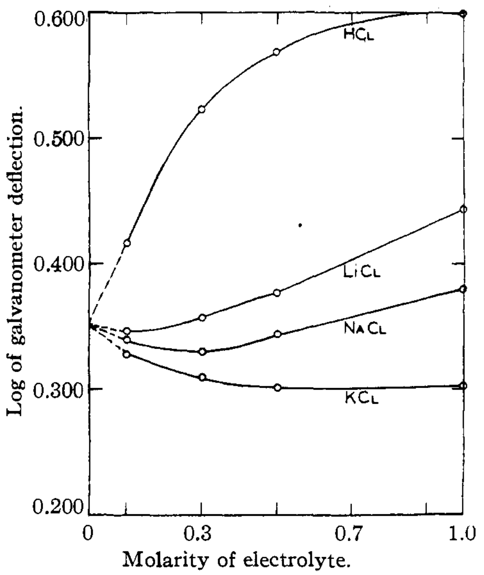

Fig. 5.—Effect of electrolyte concentration on equilibrium.

It is obvious from these data that not only does the ionic concentration of the system have a pronounced effect on the equilibrium of the reaction but that the degree of this effect is specific for the different cations used. It is also apparent that when the concentration of the added electrolytes is at zero (excepting the 0.167 *M* hydrochloric acid in all solutions), the color density indicates that little more than one-half of the quinquevalent molybdenum has reacted with the thiocyanate. The addition of more hydrochloric acid is sufficient to shift the equilibrium of the reaction to completion when its concentration is one molar. With the salts, however, the effect on the equilibrium is much less striking. It is apparent that in order to demonstrate this effect to best advantage it is necessary to choose such a concentration of the thiocyanate that the limiting color density is reached not because of a high thiocyanic acid concentration but rather because of the effect of the added electrolytes. Thus, it would be possible, if more than enough thiocyanate were added to drive the reaction to completion, to observe no effect from small amounts of added electrolytes.

The interpretation of this evidence leads one to believe that the structure of the complex in aqueous solution is not closely related to these salt effects but rather that what is being observed is some change of the apparent activities of the various components of this system due to salting-out or salting-in effects. However, more work would have to be done before any good explanation could be advanced.

Evaluation of the Thiocyanate–Molybdenum Ratio for the Complex.—Throughout this paper it has been postulated that the reaction between quinquevalent molybdenum and the thiocyanate can, in the most general way, be represented by the reaction

$$[\mathrm{Mo}^{5+}\mathrm{R}]^{n+} + n(\mathrm{SCN}^-) \longleftrightarrow [\mathrm{Mo}^{5+}\mathrm{R}]^{n+}(\mathrm{SCN}^-)n \quad (1)$$

It was generally apparent that the most likely value for *n* in this reaction was three, although as had been pointed out in the earlier discussion it had not been established conclusively by any of the previous investigators. In view of this fact, it seemed desirable to attempt an estimation of this ratio from a consideration of the effect which varying concentrations of the thiocyanate would have on the equilibrium of the reaction. Since these studies were to be made by means of colorimetric measurements, certain special details had to be considered. These details were largely associated with the need for exact measurements of all the substances participating in the reaction. Some of these difficulties were resolved by the mathematical treatment which was made of this problem. If we consider the reaction listed by equation 1, it is clear that this formulation does not consider the very pronounced effect of the hydrochloric acid observed in the preceding experiment. It seems better to represent the equation in a modified form such as equation 2.

$$[\mathrm{Mo}^{5+}\mathrm{R}]^{n+} + n(\mathrm{SCN}^-) \longleftrightarrow [\mathrm{Mo}^{5+}\mathrm{R}](\mathrm{SCN})_n + X(\mathrm{OH}^-) \quad (2)$$

The equilibrium constant of this reaction would then be

$$K' = \frac{C[\mathrm{Mo^{5+}R}](\mathrm{SCN})_n C^x(\mathrm{OH})}{C[\mathrm{Mo^{5+}R}]^{n+} C^n(\mathrm{SCN})} \qquad (3)$$

Since the concentrations involved in these studies were to be low, one need not express K' in terms of activities. If the hydrochloric acid concentration is held constant for a series of studies, it then becomes possible to incorporate it in some new constant K and obtain

$$K = \frac{C[\mathrm{Mo^{5+}R}](\mathrm{SCN})_n}{C[\mathrm{Mo^{5+}R}]^{n+} C^n(\mathrm{SCN})} \text{ where } K = \frac{K'}{C^x(\mathrm{OH})} \qquad (4)$$

Now let A = concentration of complex formed, B = total concentration of quinquevalent molybdenum, and C = total concentration of thiocyanate. Then the equilibrium constant can be expressed

$$K = \frac{A}{(B - A)(C - nA)^n} \qquad (5)$$

Since A is small in comparison with C, it may be omitted from $(C - nA)^n$ term. Then

$$K = \frac{A}{(B - A)C^n} \qquad (6)$$

Rearranging, $A = KBC^n - KAC^n$, $A + AKC^n = KBC^n$

$$\frac{A}{B} = \frac{KC^n}{(1 + KC^n)} \qquad (7)$$

Setting $A/B = {}^1/_2$ and writing that value of C where $A/B = {}^1/_2$ as $C_{1/2}$, we have $KC^n_{1/2} = 1$ and $K = (1/C_{1/2})^n$. Substituting this value of K into equation 7, and rearranging we have

$$A = B\left(\frac{\left(\frac{C}{C_{1/2}}\right)^n}{1 + \left(\frac{C}{C_{1/2}}\right)^n}\right) \qquad (8)$$

It is this equation which is used in the evaluation of the thiocyanate molybdenum ratio. By setting up a table in which the values for the term

$$\left(\frac{C}{C_{1/2}}\right)^n \Big/ 1 + \left(\frac{C}{C_{1/2}}\right)^n$$

are expressed as a function of the ratio $C/C_{1/2}$, it becomes extremely easy to calculate the value of A for any value of n and for any value of B. In using equation 8 for the experimental determination of the thiocyanate–molybdenum ratio, the theoretical curves for a plot of the log galvanometer deflection as a function of the thiocyanate concentration were calculated for various values of n. This could be done quite easily given the term for any particular value of B. In order to illustrate the use of the equation, a discussion of the method employed in evaluating the various terms is given.

(a) **Evaluation of A.**—Since A represents the amount of the complex which has formed under a given set of conditions, it can be determined by measuring the density of its color. In the usual colorimetric process, one simply calibrates the galvanometer deflection for these solutions. When monochromatic light is used and when Beer's law holds for the particular system under study, it will be found that the logarithm of the galvanometer deflection equals (kC), the product of the concentration and some constant.

In the process under discussion, this calibration was effected by taking a known amount of quinquevalent molybdenum and adding such an excess of thiocyanate that the reaction was driven to completion. Consequently the concentration of the complex becomes identical with that of quinquevalent molybdenum taken. It was in this way that the calibration curve illustrated in Fig. 6 was obtained.

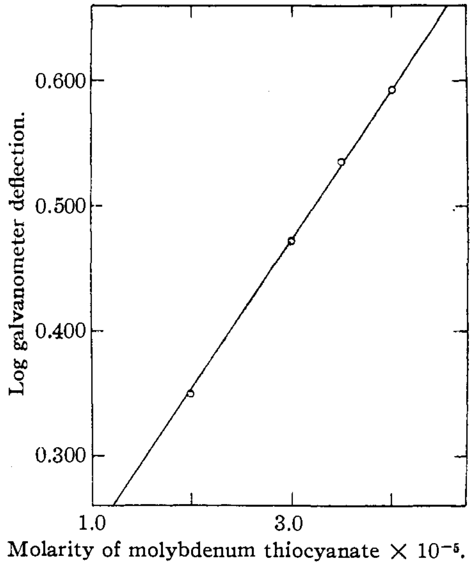

Fig. 6.

(b) **Evaluation of B.**—B was known because the solutions of quinquevalent molybdenum were prepared by quantitative reduction of analyzed molybdate solutions.

(c) **Evaluation of $C_{1/2}$.**—This concentration is determined by plotting the color density of a series of solutions as a function of the thiocyanate concentration. For any fixed amount of quinquevalent molybdenum, this plot will approach a limiting value of the color density. The concentration of the thiocyanate at the half-way point is the $C_{1/2}$ term wanted. In the actual determination of the thiocyanate–molybdenum ratio, a large number of series of solutions were prepared and their color densities determined. In each series the hydrochloric acid concentration and the quinquevalent molybdenum concentration were held constant while the concentration of the thiocyanate was varied. In Figs. 7, 8, and 9 some of the data are plotted.

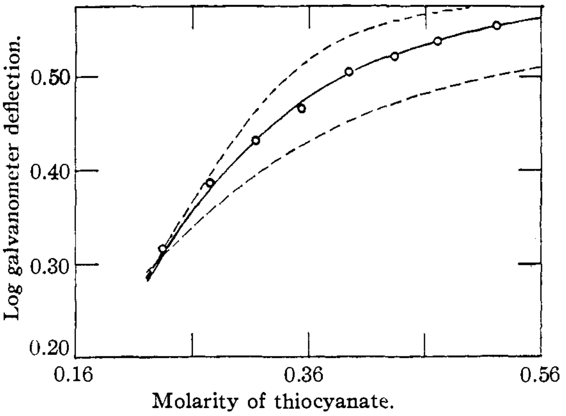

Fig. 7.—Theoretical curves: ---- $N = 2$ and 4; ——— $N = 3$; ○, experimental points; 1.0 molar HCl concentration.

It should be remembered that in the mathematical treatment the hydrochloric acid concentration was incorporated into the special equilibrium constant K; therefore, at any given hydrochloric acid concentration, the $C_{1/2}$ term must be evaluated from the data. After $C_{1/2}$ is evaluated, it then becomes possible to calculate the theoretical curves observed in the figures.

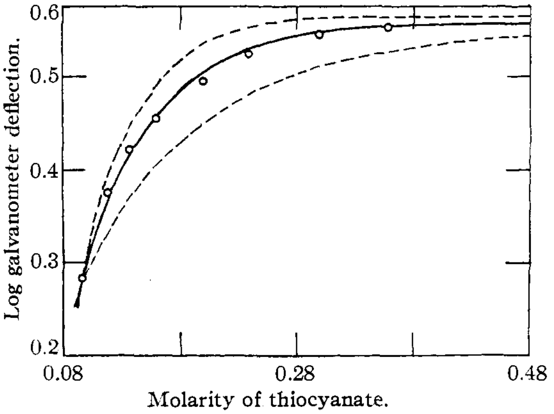

Fig. 8.—Theoretical curves: ---- $N = 2$ and 4; ——— $N = 3$; ○, experimental points; 1.5 molar HCl concentration.

In the above figures only the experimental points are listed. All of the lines drawn represent theoretical lines calculated with aid of equation 8.

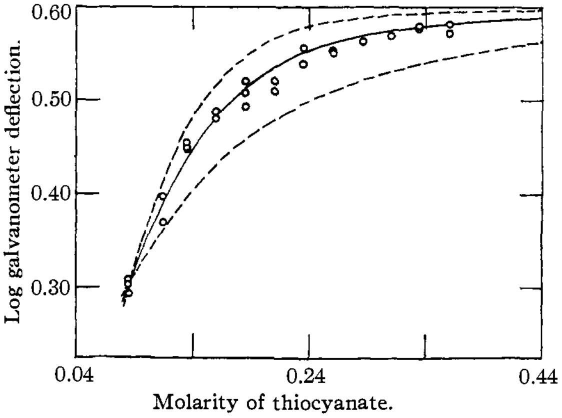

Fig. 9.—Theoretical curves: ---- $N = 2$ and 4; ——— $N = 3$; ○, experimental points; 2.0 molar HCl concentration.

Experiments were also run in hydrochloric acid concentrations above 2.5 N but, since it became virtually impossible to get any semblance of reproducibility at this concentration, those experiments were discontinued. In fact, it can be observed that the results obtained at 2.0 M leave something to be desired. Examination of the data and the plots of these data reveals a close similarity between the theoretical values calculated for a thiocyanate ratio of three and the experimental points observed. It seemed reasonable to conclude that such a close agreement clearly establishes this ratio in a not too ambiguous manner. While one must admit that this ratio has not been established with stoichiometrical exactness from the data presented herein, nevertheless it is important to recognize that no matter how strict the interpretation of the results, a possible deviation greater than 6 or 7% from the value of 3 is not permitted.

If one attempts to solve equation 8 directly for the value of n, a much too rigorous testing of data is obtained. This is due to the fact that we obtain such a term as

$$n = \frac{\log \frac{A}{B - A}}{\log \frac{C}{C_{1/2}}}$$

As A approaches B the value of the $\log A/(B - A)$ term becomes extremely uncertain because a small variation in the value of the $(B - A)$ term causes large variations in $\log A/(B - A)$. As A approaches $B/2$ the expression becomes indeterminate and for values of A greater than $B/2$ it becomes impossible to obtain suitable experimental data.

Despite these general limitations, however, one thing remains clear; these experiments establish this ratio of 3 as a property of the colored substances in solution and not as a property of some dry compound isolated from tarry mixtures of many different substances.

Along with these general observations several other points may be made concerning the character of the reaction. Of these, perhaps the most important is the fact that from the slowness with which equilibrium is attained, one may conclude that this is not an ionic reaction. Additional evidence that the molybdenum complex is not ionic may be surmised from its extreme solubility in a large number of organic solvents. Consequently a representation of the reaction which involves only an exchange of the thiocyanate ion with the chloride ions of quinquevalent molybdenyl chloride must be considered as an over simplification.

3. Fading Effect Induced by Hydrochloric and Sulfuric Acids.—The next problem considered in this study was one associated with the very pronounced fading of the molybdenum thiocyanate observed in high acid concentrations. This effect was used to bleach the molybdenum thiocyanate color and thus prevent the molybdenum from interfering in the colorimetric determination of the rhenium. In view of similar striking color changes observed in pure quinquevalent molybdenum solutions, it was thought desirable to make a study of these two processes in order to determine whether any analogy existed between them.

Experimental

A. Quinquevalent Molybdenum Color Transition.—On taking a solution of quinquevalent molybdenum whose hydrochloric acid concentration is slowly increased, one may observe the series of color changes listed in Table II. This color transition may also be observed by starting with 8 *N* hydrochloric acid and progressively diluting with water whereby the same colors will appear in reverse order.

TABLE II

Molarity HCl	Color of solution	Molarity HCl	Color of solution
0.0–0.5	Faint amber	6.3–7.3	Brown changes to dark olive color
0.5–5.5	Amber color becomes more intense	7.7	Light olive
3.5–5.5	Amber changing to dark brown	8.0	Chrome-green
5.5–6.3	Brown color darkens appreciably	8.0	Above color becomes a pure emerald-green

For the purpose of this discussion, it will only be necessary to consider the color effects at the lower acid concentrations for which the color densities were measured. The measurements were made in the Evelyn colorimeter using the no. 420 filter.

The stock quinquevalent molybdenum solution used was 0.0107 and 2 molar with hydrochloric acid. Solutions of hydrochloric acid prepared by mixing various amounts of water with 5 molar hydrochloric acid had a total volume of 20 ml. To these solutions 5 ml. of the quinquevalent molybdenum solution was added, and the resulting solutions thoroughly mixed. The solutions were transferred to the colorimeter and the galvanometer deflection observed. Data obtained in this manner are plotted in Fig. 10.

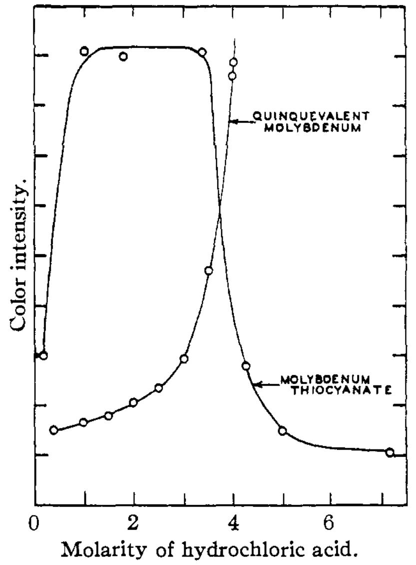

Fig. 10.

In studying the transition caused by the sulfuric acid, small amounts of hydrochloric acid added as a constituent of the stock solution of quinquevalent molybdenum exerted a profound effect upon the action of the sulfuric acid. In order to make the experiments comparable, it was neces-

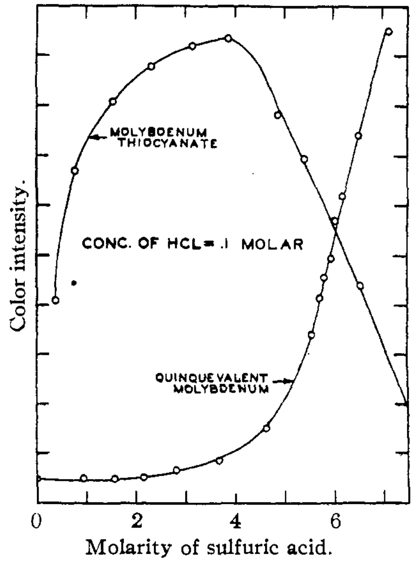

Fig. 11.

sary to adjust the hydrochloric acid concentration in the final solution to 0.1 molar. In these experiments our stock molybdenum solution was 0.015 molar with respect to molybdenum and 1.0 molar with hydrochloric acid. Five ml. of the stock solution was diluted to 50 ml. with a solution whose sulfuric acid concentration was known. After thoroughly mixing the readings of the color density were taken. These data are plotted in Fig. 11.

B. **Fading Effect of the Thiocyanate Complex of Molybdenum.**—The determination of the fading effect of these acids upon the molybdenum thiocyanate complex was done about five years ago, and for those experiments an Eastman Universal colorimeter was used. The principle of the instrument was based on a comparison of the color density of a solution with a standard glass wedge whose color density changed regularly from one end to the other. While the results obtained using such an instrument are not particularly quantitative, they still are sufficiently so to indicate the qualitative aspects of the process we are discussing. In those series, the molybdenum thiocyanate complex was formed by the reduction of alkali molybdate solution with stannous chloride in the presence of potassium thiocyanate while the concentrations of the hydrochloric and sulfuric acids were varied.

The solution, whose color density was to be studied, was prepared by taking 60.5 ml. of an acid solution whose concentration was known and adding to it 2 ml. of the molybdate solution (200 micrograms per ml.) and 2.5 ml. of a 10% potassium thiocyanate solution. Then, 7.5 ml. of 10% stannous chloride was added. The readings were taken after the solution had reached an equilibrium condition showing only a very slight fading effect as a function of time. They are plotted in Figs. 10 and 11.

In plotting these two sets of data, it was necessary to adjust the ordinates in order to properly compare the two curves. When this is done it will be observed how nearly identical the threshold acid concentrations are for these two effects.

It seems clear, therefore, that these two reactions are related to each other in no indirect manner. We feel, therefore, that a possible interpretation of these results is that the two effects are due to similar reactions: that in the case of the quinquevalent molybdenum, a colorless form, which we call "W," is progressively transformed into the amber colored form which we shall refer to as "X." In the case of the molybdenum thiocyanate complex, there is a red colored form W′ corresponding to the W form of the quinquevalent molybdenum and a colorless form of the thiocyanate complex X′ corresponding to the X form of the quinquevalent molybdenum.

If this interpretation is correct, then it is quite logical to agree that whatever the formula for the thiocyanate complex, it must contain within itself the possibility of explaining the fading effect observed.

With the information available from this research it is not possible for us to make any thoroughgoing prediction of what it should be like. Whether the color transitions observed are due to complex formation or to hydration cannot be adequately treated now but the correlation of these two phenomena make it seem likely that a study of the simpler system (*i. e.*, quinquevalent molybdenum without thiocyanate) will give information which has a direct bearing on the structure of the thiocyanate complex.

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Conclusions

An examination of the literature reveals that there is no clear formulation for the structure of the thiocyanate complex of molybdenum. In this research, evidence has been advanced to show that whatever the structure of the molybdenum thiocyanate complex, the formula of it must: (1) indicate quinquevalency for the molybdenum in the complex, (2) show a thiocyanate–molybdenum ratio of three and (3) offer an explanation of the color transitions observed.

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