TABLE III

HEAT OF SOLUTION OF Ag_2WO_4 IN 0.16 *M* NH_3

Moles Ag_2WO_4/950 ml. soln.	ΔH_3 (kcal./mole Ag_2WO_4)
0.004435	−12.22
.009520	−12.28
.010013	−12.30
.012845	−12.11

TABLE IV

HEAT OF SOLUTION OF $AgNO_3$ IN 0.16 *M* NH_3

Moles $AgNO_3$/950 ml. soln.	ΔH_4 (kcal./mole $AgNO_3$)
0.003492	−8.08
.003694	−8.09
.009345	−8.08
.019239	−8.06
.047520	−8.04

TABLE V

HEAT OF SOLUTION OF $AgNO_3$

Moles $AgNO_3$/950 ml. soln.	ΔH_5 (kcal./mole $AgNO_3$)
0.004010	+5.45
.004501	+5.44
.009998	+5.47
.010707	+5.46
.031557	+5.45
.062937	+5.46

tungstates. We believe that our value for the heat of solution of $AgWO_4$ (14.7 kcal./mole) is better than Pan's value.[7]

Our heats of reactions 4 and 5 are in good agreement with the heats reported by Smith, Brown and Pitzer,[18] Lange and Martin[19] and Roth.[20] On the basis of our ΔH_4^0 and ΔH_5^0 we calculate the standard heat of formation of $Ag(NH_3)_2^+$(aq) to be −26.87 kcal./mole and the standard partial molal entropy to be 57.8 cal./deg. mole. For these calculations we have used heats of formation and entropies given by the Bureau of Standards[2] and the equilibrium constant for the dissociation of $Ag(NH_3)_2^+$[aq) given by Vosburgh and McClure.[21]

We are unable to make a completely reliable calculation of the entropy of solution of Ag_2WO_4 because we do not have a completely reliable free energy of solution of Ag_2WO_4. The best free energy of solution available is that due to Pan,[7] but our calorimetric measurements indicate his results are in error—probably due to the presence of polytungstates. We therefore use Pan's free energy of solution (15.4 kcal./mole) as a lower limit and our heat of solution (ΔH_2^0) to calculate that the entropy of solution is at least as negative as −2.4 cal./deg. mole. On the basis of a comparison with Ag_2CrO_4[8] and Ag_2MoO_4[9,11] we would expect the entropy of solution to be about ten entropy units more negative than the limiting value calculated above. This corresponds to a free energy of solution about 3 kcal./mole more positive than that reported by Pan[7] and seems reasonable in view of the importance of polytungstates in these investigations.

All of the heats of formation of tungsten compounds reported in this paper are based on the heat of formation of H_2WO_4(c). Any change in the accepted value for the heat of formation of this compound will change the heats of formation of $WO_4^=$(aq), Na_2WO_4(c) and Ag_2WO_4(c) but will not change the heat of solution of Ag_2WO_4 we have calculated from our heats of reaction and solution.

Acknowledgment.—We are grateful to K. Pan for sending us reprints of his papers, to L. P. Fernandez and C. N. Muldrow for assistance with some of the calorimetric measurements, and to the Research Corporation for the necessary financial support of this research.

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CHARLOTTESVILLE, VIRGINIA

[CONTRIBUTION FROM THE RUAKURA ANIMAL RESEARCH STATION, NEW ZEALAND DEPARTMENT OF AGRICULTURE]

A Spectrophotometric Study of Some Molybdenum Thiocyanate Complexes

BY D. D. PERRIN[1]

RECEIVED SEPTEMBER 10, 1957

Molybdenum(V) forms a series of complexes with thiocyanates in molar hydrochloric acid. For the amber-colored complex used in chemical analysis the Mo:CNS ratio is 1:3. The complex is uncharged and is probably $MoO(CNS)_3$. A yellow complex, of Mo:CNS ratio 1:2, is described, and a colorless 1:1 complex is postulated to explain observed changes in absorbancy with changes in thiocyanate concentration. The three complexes exist in equilibrium with molybdenum(V) and thiocyanate ion. Association constants in 60% acetone–water have been calculated from the absorbancy data.

Reduction of molybdates in acid thiocyanate solutions gives a characteristic amber to orange-red color. This reaction, which is commonly used to estimate low concentrations of molybdenum, requires for maximum color development a hydrogen ion concentration approximately one molar and a high concentration of thiocyanate ion.

A wide range of formulas have been assigned to the molybdenum thiocyanate complex which is formed under these conditions.[2-4] Recent work confirms that the complex contains pentavalent molybdenum.[2,4,5] Molybdenum(V), prepared by

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[1] John Curtin School of Medical Research, The Australian National University, Canberra, Australia.

[2] C. F. Hiskey and V. W. Meloche, THIS JOURNAL, **62**, 1565 (1940), who also review earlier formulations.

[3] A. T. Dick and J. B. Bingley, *Nature*, **158**, 516 (1946).

[4] A. K. Babko, *J. Gen. Chem.* (*U.S.S.R.*), **17**, 642 (1947).

[5] C. E. Crouthamel and C. E. Johnson, *Anal. Chem.*, **26**, 1284 (1954).

reduction of molybdate in a silver reductor, gives with thiocyanate ion absorbances in water, aqueous acetone and ether identical with those obtained using cuprous plus stannous reduction of molybdates.[5] No evidence of mixed valence complexes has been found.[5] Using different mathematical procedures based on the variation of absorbance of solutions with reactant concentrations Hiskey and Meloche[2] and Babko[4] have claimed Mo:CNS ratios of 1:3 and 1:5, respectively. Babko also suggested that under appropriate conditions a colorless molybdenum thiocyanate anion and cation occur in solution.

The present investigation was undertaken in an endeavor to decide between these alternatives by determining the association constant of the complex over a range of concentration. Results reported below indicate a Mo:CNS ratio of 1:3 for the familiar amber complex (A). In addition, a yellow complex (Y), for which this ratio is 1:2, is the main colored component present at lower thiocyanate concentrations. A third, colorless, complex (C), with a Mo:CNS ratio of 1:1, is also formed.

The instability of these complexes and the ease with which they dissociate render their isolation and chemical characterization difficult. Spectrophotometric techniques similar to those used for ferric thiocyanate[6–8] are applicable, but the range of valence states possible for molybdenum makes the interpretation of results less certain. The enhancing effects of ferric and cupric ions on the absorbancy, using conventional analytical procedures for molybdenum,[3,9–12] illustrate this difficulty: in the absence of iron and copper half of the molybdenum(VI) is reduced to the trivalent state and is not available for complex formation.

In aqueous solutions, especially at low thiocyanate concentrations, the molybdenum complexes decompose rapidly and quantitative measurements are difficult to obtain. Extraction into suitable immiscible solvents such as ethers, esters or higher alcohols, considerably increases the stability of the complexes; it also considerably increases the complexity of quantitative mathematical treatment because of the need to include the distribution coefficients of the reacting species. On the other hand. 60% acetone–water provides a single phase system in which the amber complex (A) is stable[5] and the yellow complex (Y) decomposes sufficiently slowly to allow correction for the observed rate of fading. This solvent was used for most of the present work.

Experimental

Except where otherwise indicated all reagents were B.D.H. AnalaR and were used without further purification.

A standard molybdenum(VI) solution was prepared by dissolving 1.840 g. of ammonium molybdate in 1 l. of distilled water (1 ml. ≡ 1.000 mg. Mo). More dilute solutions were prepared from this solution immediately before use. For more concentrated solutions 0.500 *M* sodium molybdate (J. T. Baker Analyzed) was used.

All absorbance measurements were made using a Beckman model DU photoelectric quartz spectrophotometer. Silica inserts and a range of optical cells provided light paths from 0.12 to 100 mm.

Initially, the method of Crouthamel and Johnson[5] was used, but with potassium thiocyanate as the source of thiocyanate ion. Subsequently, a more convenient modification based on an earlier extraction procedure[12] gave results agreeing with those of Crouthamel and Johnson. The reaction procedures for producing the complexes consisted essentially in the addition of reagents, with mixing, in the following orders:

I. 1 ml. of molybdenum solution, 1 ml. of concentrated hydrochloric acid, 0.5 ml. of 0.1 *M* cuprous chloride in concentrated hydrochloric acid, 5 ml. of water, acetone, potassium thiocyanate in acetone (final volume of acetone, 15 ml.), 0.5 ml. of 10% stannous chloride in concentrated hydrochloric acid, water to give final volume of 25 ml.

II. 4 ml. of constant boiling point hydrochloric acid, 0–3 ml. of molybdenum solution, 1 ml. of iron(III) solution, 3–0 ml. of water, acetone, potassium thiocyanate in acetone (final volume of acetone, 15 ml.), 2 ml. of 10% stannous chloride in 1.2 *M* hydrochloric acid, water to 25 ml.

In both procedures there was a slight temperature rise during mixing. The final solutions were cooled rapidly to 23°, the time between addition of stannous chloride and first spectrophotometer reading being about 1.5 minutes. Color development was complete within this time, except at low concentrations of thiocyanate ion where maximum intensity was reached 2–3 minutes after mixing.

Absorption Spectra.—Reduction of molybdates in approximately molar hydrochloric acid solutions, in the presence of high concentrations of thiocyanate ion, leads to almost complete conversion to the amber complex, A. In 60% acetone–water the complex so formed is stable for at least several hours and has an absorption maximum near 4600 Å. in the presence or absence of iron. Using cuprous reduction and assuming one molybdenum atom per molecule of complex, the apparent molar absorbance index at 4600 Å. for A was 18,800 in 0.33 *M* potassium thiocyanate, in good agreement with the reported[5] value, obtained under similar conditions, of 18,700 ± 150, in 0.60 *M* ammonium thiocyanate. For procedure II the values were 19,700 and 10,500, depending on the presence or absence of iron. Correction for incomplete conversion to A, using the association constant calculated below, leads to a value for the true molar absorbance index of A, at 4600 Å., in 60% acetone–water, of 20,500.

In very dilute thiocyanate solutions containing molybdenum(V) in excess, a yellow complex, Y, with an absorption maximum near 4250 Å., is formed. This decomposes more rapidly than A, 60% acetone–water solutions fading at room temperature by about 5% per minute. The spectra recorded in Fig. 1 were obtained by taking readings as rapidly as possible after mixing and correcting using the observed rates of fading.

At intermediate thiocyanate concentrations both A and Y are present in solution. The contribution of each to the observed absorbancy was obtained as follows.

For procedure II Beer's law was obeyed at 4200 and 4600 Å. over a range of molybdate concentrations from 2×10^{-5} to 8×10^{-4} *M* for a series of constant thiocyanate concentrations ranging from 2×10^{-3} to 0.4 *M*. Previous workers[5] have also found this relation to hold over a range of wave lengths for procedure I if a high thiocyanate concentration is present. It appears reasonable to conclude that under the experimental conditions both Y and A obey Beer's law. Where two light absorbing species, A and B, fulfilling this requirement, have different absorption spectra, it follows that

$$A_1{}^{\mathrm{B}} = \frac{\alpha A_1{}^{\mathrm{obsd}} - A_2{}^{\mathrm{obsd}}}{(\alpha - \beta)} \qquad (1)$$

and

$$A_2{}^{\mathrm{A}} = \frac{\alpha A_2{}^{\mathrm{obsd}} - \alpha\beta A_1{}^{\mathrm{obsd}}}{(\alpha - \beta)} \qquad (2)$$

where superscripts identify the absorbing species, subscripts

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(6) H. E. Bent and C. L. French, THIS JOURNAL, **63**, 568 (1941).

(7) S. M. Edmonds and N. Birnbaum, *ibid.*, **63**, 1471 (1941).

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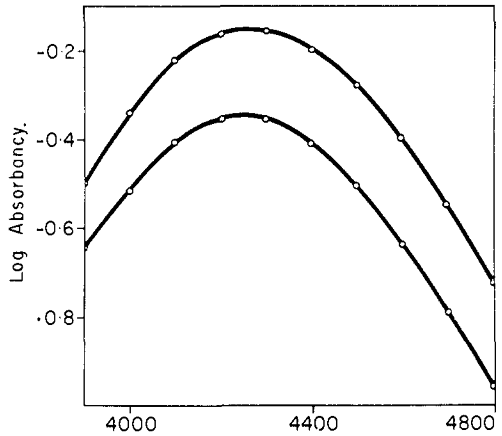

Fig. 1.—Absorption spectrum of molybdenum thiocyanate complex, Y, in 60% acetone-water; [HCl], 1.02 *M;* [Fe^{+++}], 2×10^{-3} *M.* Upper, [MoO_4^{--}], 8.00×10^{-4} *M;* [CNS^-], 8.20×10^{-4} *M.* Lower, [MoO_4^{--}], 1.20×10^{-3} *M;* [CNS^-], 4.10×10^{-4} *M.*

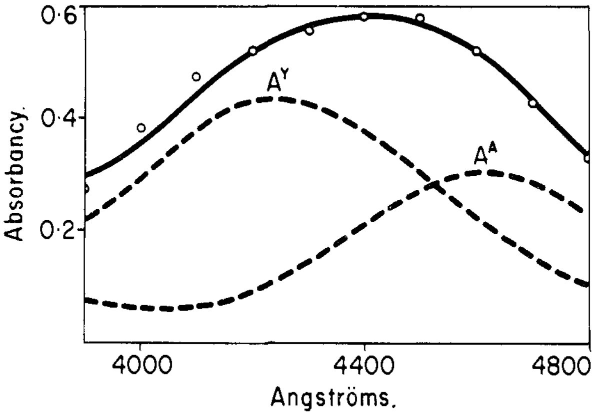

Fig. 2.—Analysis of absorption spectrum for intermediate thiocyanate concentration; light path, 0.45 mm. [MoO_4^{--}], 4.00×10^{-3} *M;* [CNS^-], 8.20×10^{-3} *M;* [Fe^{+++}], 2.0×10^{-2} *M;* [HCl], 1.07 *M;* 60% acetone-water; exptl., O; $A^Y + A^A$, ——.

1 and 2 refer to the selected wave lengths, $\alpha = A_2^A/A_1^A$, and $\beta = A_2^B/A_1^B$. These relationships can be deduced from

$$A_1^{\text{obsd}} = A_1^A + A_1^B \qquad (3)$$

$$A_2^{\text{obsd}} = A_2^A + A_2^B \qquad (4)$$

For example substitution of $A_2^A = \alpha A_1^A$, $A_2^B = \beta A_1^B$, in equation 4 and elimination of A_1^A between equations 3 and 4 gives A_1^B as above.

Provided that the individual absorption spectra of A and B can be obtained, α and β can be evaluated. Because these ratios depend only on the shape of each spectral curve, it is not necessary for this purpose to know the actual concentrations of A and B that are present. This is important for the molybdenum thiocyanate complexes: calculations using the equilibrium constants reported in the present paper indicate that for the conditions under which the two absorption spectra shown in Fig. 1 were obtained relatively large amounts of the molybdenum were present as the colorless complex, C. However, because Y is the only light absorbing species present, it follows from Beer's law that the curves in Fig. 1 should be of the same shape. Their vertical separation should be equal to the (constant) difference between the logarithms of the (unknown) concentrations of Y present in the two solutions. The desired ratio of the absorbancies for Y at the selected wave lengths is obtained from either curve as the antilogarithm of the difference between the appropriate ordinates.

For the molybdenum thiocyanate complexes, A and Y, substitution of values obtained from the absorption spectra gives

$$A_{4200}^{Y} = 1.174A_{4200}^{\text{obsd}} - 0.348A_{4600}^{\text{obsd}} \qquad (5)$$

$$A_{4600}^{A} = 1.174A_{4600}^{\text{obsd}} - 0.600A_{4200}^{\text{obsd}} \qquad (6)$$

Figure 2 shows a typical absorption curve obtained from a solution of intermediate thiocyanate concentration. From the observed absorbancies at 4200 and 4600 Å. and the absorption spectra of A and Y, the separate contributions of Y and of A to the observed spectrum were calculated. Their sum reproduced closely the experimental values.

The Method of Continuous Variations.[13,14]—An attempt was made to determine the Mo:CNS ratios for Y and A by this method. Over the wave length range 3900–4200 Å., where Y absorbs more strongly than A, a rather diffuse absorbance maximum was obtained, with a Mo:CNS ratio lying between 1:2 and 1:3 and probably closer to the former value (Fig. 3). At longer wave lengths, where A absorbs more strongly, the maximum was shifted to greater molar fractions of thiocyanate ion but, even in light paths down to 0.12 mm., its position was not sufficiently sharp for accurate location.

The Association Constants of the Complexes.—When the molybdenum thiocyanate complexes are formed at constant molybdenum concentration, the absorbancy increases with increasing thiocyanate concentration, as shown in Fig. 4. Using equations 5 and 6 the absorbancy can be expressed in terms of the contributions due to A_{4200}^{Y} and A_{4600}^{A}. As the molar absorbance index of A is known, the concentration of A, and hence $[\mathrm{Mo}]_0 - [\mathrm{A}]$, can be determined. With increasing thiocyanate concentration this quantity approaches [Y]. Hence the limiting slope of the plot of A_{4200}^{Y} against $[\mathrm{Mo}] - [\mathrm{A}]$ provides an estimate of the molar absorbance index of Y. Values from the data of Fig. 4, together with two more concentrated solutions, are plotted in Fig. 5. A straight line drawn through the origin gives a value of ϵ_{4200}^{Y} of approximately 4,550.

As [A] and [Y] can now be obtained, it is possible to confirm that Y and A are in equilibrium by determining *n* for the reaction $\mathrm{Y} + n\mathrm{CNS}^- \rightleftarrows \mathrm{A}$. Since $[\mathrm{A}] = K[\mathrm{Y}][\mathrm{CNS}^-]^n$, the plot of $\log [\mathrm{A}] - \log[\mathrm{Y}]$ against $\log [\mathrm{CNS}^-]$ should be linear and of slope *n*.

If the Mo:CNS ratio for Y is 1:2, the uncombined thiocyanate concentration is

$$[\mathrm{CNS}^-] = [\mathrm{CNS}^-]_0 - 2[\mathrm{Y}] - (n + 2)[\mathrm{A}] \qquad (7)$$

The correction for [A] is quite small and is not significantly affected by setting $n = 1$, 2 or 3. At low thiocyanate concentrations correction for the presence of the colorless complex, C, becomes important and can be made using the association constants reported below.

The data of Fig. 6 are consistent only with a value of $n = 1$. This was also found to be true if the Mo:CNS ratio of Y was assumed to be 1:3. Equations derived on the assumption that two or more ions or molecules of Y or A were concerned in the equilibrium did not fit the experimental results.

If Y is formed by direct addition of thiocyanate ions to molybdenum, it should be possible, in the same way, to determine the number of thiocyanate ions, *x*, involved in the formation of Y. However, the assumption that $[\mathrm{Mo}\bar{v}] = [\mathrm{Mo}]_0 - [\mathrm{Y}] - [\mathrm{A}]$, where $\mathrm{Mo}\bar{v}$ represents the form in which pentavalent molybdenum is present under the experimental conditions, did not give consistent results. Thus, from results by the method of continuous variations, Y contains at least two thiocyanate ions. Taking $x = 2$, the logarithm of the proposed equilibrium constant decreased steadily from 6.67 to 4.71 as thiocyanate concentration was increased. For $x > 2$, greater drifts in log *K* were observed.

The possibility was then examined that the equilibria occur

$$(\mathrm{Mo}\bar{v}) + \mathrm{CNS}^- \rightleftarrows (\mathrm{Mo}\bar{v})(\mathrm{CNS}) \qquad (\mathrm{C})$$

$$(\mathrm{Mo}\bar{v})(\mathrm{CNS}) + \mathrm{CNS}^- \rightleftarrows (\mathrm{Mo}\bar{v})(\mathrm{CNS})_2 \qquad (\mathrm{Y})$$

$$(\mathrm{Mo}\bar{v})(\mathrm{CNS})_2 + \mathrm{CNS}^- \rightleftarrows (\mathrm{Mo}\bar{v})(\mathrm{CNS})_3 \qquad (\mathrm{A})$$

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(13) P. Job, *Ann. chim.*, **9**, 113 (1928).

(14) P. Job, *ibid.*, **6**, 97 (1936).

where the complex, C, is colorless. Charges on molybdenum ions and complexes have been omitted.

From the data presented in Fig. 4 it is possible to calculate the association constant, $K_1 = [\mathrm{A}]/[\mathrm{Y}][\mathrm{CNS}^-]$. Strictly, activities should be used, but under the experimental conditions, where a high and almost constant ionic strength is maintained, the various activity coefficients should be relatively constant and may be included in the equilibrium constant.

Table I summarizes the data used in this calculation, including values of [A] and [Y] derived from Fig. 4.

TABLE I

ASSOCIATION CONSTANTS OF AMBER AND YELLOW COMPLEXES

$[\mathrm{Mo}]_0 = 8.0 \times 10^{-4}\ M$

$[\mathrm{CNS}^-]_0 \times 10^4$	$[\mathrm{A}] \times 10^4$	$[\mathrm{Y}] \times 10^4$	$\log K_1$	$\log K_2$	$\log K_1'$
6.0	0.013	1.15	1.49		
8.0	.023	1.51	1.49		
12.0	.073	2.17	1.65		(2.30)
16.0	.144	2.87	1.71	3.07	2.02
20.0	.230	3.35	1.74	2.97	1.93
24.0	.330	3.98	1.74	2.98	1.86
32.0	.421	4.71	1.62	2.95	1.67
40.0	.822	4.93	1.78	2.94	1.82
60.0	1.456	5.19	1.79	2.94	1.81
80.0	1.946	5.21	1.77	2.99	1.77
120.0	2.95	4.60	1.80	3.00	1.80
160.0	3.56	3.94	1.81	2.75	1.81
240.0	4.76	2.64	1.92	3.28	1.92

The values of $[\mathrm{CNS}^-]$ used in calculating K_1 were obtained from equation 7. For the temperature range 20–23°, log K_1 lay within the limits 1.70 ± 0.22. The ionic strength varied between 1.07 and 1.10.

However, if at the higher thiocyanate concentrations effectively all of the molybdenum is present as C, Y or A

$$[\mathrm{C}] = [\mathrm{Mo}]_0 - [\mathrm{Y}] - [\mathrm{A}] \tag{8}$$

$$[\mathrm{CNS}^-] = [\mathrm{CNS}^-]_0 - [\mathrm{Mo}]_0 - [\mathrm{Y}] - 2[\mathrm{A}] \tag{9}$$

The thiocyanate concentrations given by equation 9 are somewhat less than by equation 7. Values of log K_1 recalculated using equation 9 are listed in Table I under "log K'_1" and range between 1.85 ± 0.18 for $[\mathrm{CNS}^-]$ varying from 4.8×10^{-4} to $2.20 \times 10^{-2}\ M$.

Substitution of values from Table I in $K_2 = [\mathrm{Y}]/[\mathrm{C}][\mathrm{CNS}]$, using equations 8 and 9, leads to values of log K_2 which lie within the limits 3.01 ± 0.27, over a range of $[\mathrm{CNS}^-]$ from 4.8×10^{-4} to $2.20 \times 10^{-2}\ M$.

At lower thiocyanate concentrations the incompleteness of conversion of $\mathrm{Mo}\bar{v}$ to C, Y and A prevents values of [C] and $[\mathrm{CNS}^-]$ from being obtained to test the constancy of K_1 and K_2 at these concentrations. However, by using the value of log K_1 obtained earlier, it is possible to estimate $[\mathrm{CNS}^-]$ from $K_1 = [\mathrm{A}]/[\mathrm{Y}][\mathrm{CNS}^-]$, and hence [C] and $(\mathrm{Mo}\bar{v}]$ from

$$[\mathrm{Mo}]_0 = [\mathrm{Mo}\bar{v}] + [\mathrm{C}] + [\mathrm{Y}] + [\mathrm{A}] \tag{10}$$

$$[\mathrm{CNS}^-]_0 = [\mathrm{CNS}^-] + [\mathrm{C}] + 2[\mathrm{Y}] + 3[\mathrm{A}] \tag{11}$$

Knowing [A], [Y], [C], $[\mathrm{Mo}\bar{v}]$ and $[\mathrm{CNS}^-]$ it then becomes possible to calculate K_2 and K_3, where $K_3 = [\mathrm{C}]/[\mathrm{Mo}\bar{v}][\mathrm{CNS}^-]$. Relevant data from Table I and Fig. 2 are presented in Table II.

TABLE II

ASSOCIATION CONSTANT OF COLORLESS COMPLEX, C

$[\mathrm{A}] \times 10^4$	$[\mathrm{Y}] \times 10^4$	$[\mathrm{C}] \times 10^4$	$[\mathrm{Mo}\bar{v}] \times 10^4$	$[\mathrm{CNS}^-] \times 10^4$	$\log K_2$	$\log K_3$
0.013	1.15	2.06	4.78	1.60	3.54	3.43
.023	1.51	2.76	3.71	2.15	3.41	3.54
.073	2.17	2.89	2.87	4.74	3.20	3.33
3.29	20.9	8.10	7.70	22.2	3.08	2.68

In view of the limitations of accuracy of the experimental data the estimates of log K_2 are in good agreement with the value in Table I. The approximate constancy of log K_3

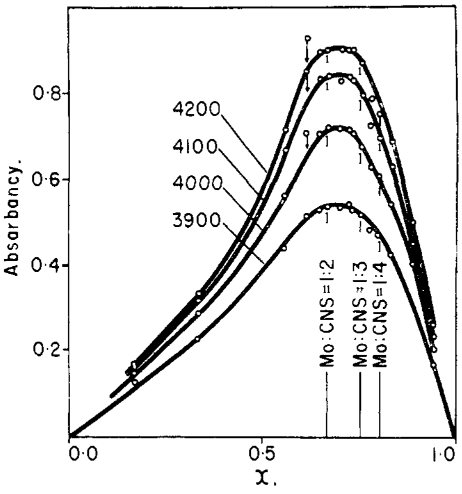

Fig. 3.—Method of continuous variations: mol. fraction $\mathrm{CNS}^- = x$; $[\mathrm{MoO_4}^{--}] + [\mathrm{CNS}^-] = 1.80 \times 10^{-2}\ M$; $[\mathrm{Fe}^{+++}]$, $2.0 \times 10^{-2}\ M$; [HCl], $1.07\ M$; 60% acetone-water; 3900–4200 Å.; light path 0.45 mm.

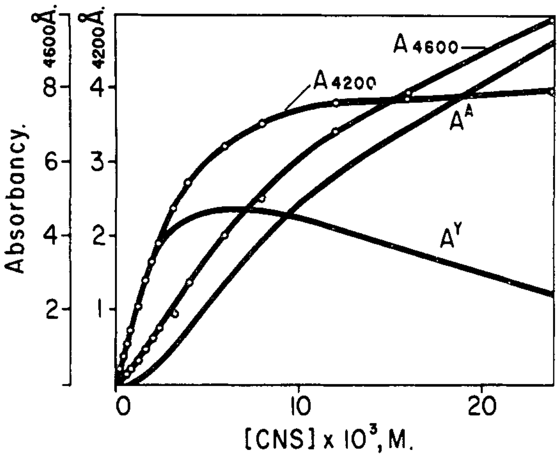

Fig. 4.—Increase of absorbancy with $[\mathrm{CNS}^-]$: $[\mathrm{MoO_4}^{--}]$, $8.0 \times 10^{-4}\ M$; $[\mathrm{Fe}^{+++}]$, $2.0 \times 10^{-3}\ M$; [HCl], $1.00\ M$; 60% acetone-water.

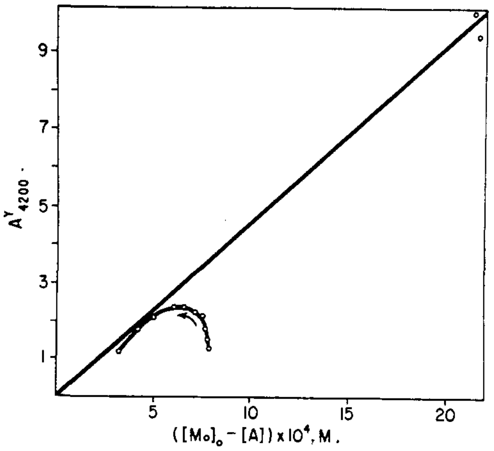

Fig. 5.—Estimate of $A^{\mathrm{Y}}_{\mathrm{molar}}$, data from Fig. 4, arrow indicates increasing $[\mathrm{CNS}^-]$. Upper points, duplicates, $[\mathrm{MoO}^{--}]$, $3.0 \times 10^{-3}\ M$; $[\mathrm{CNS}^-]$, $1.54 \times 10^{-2}\ M$; $A^{0.45\ \mathrm{mm.}}_{4200}$ 0.690, 0.660; $A^{0\ 45\ \mathrm{mm.}}_{4600}$, 1.03, 1.00.

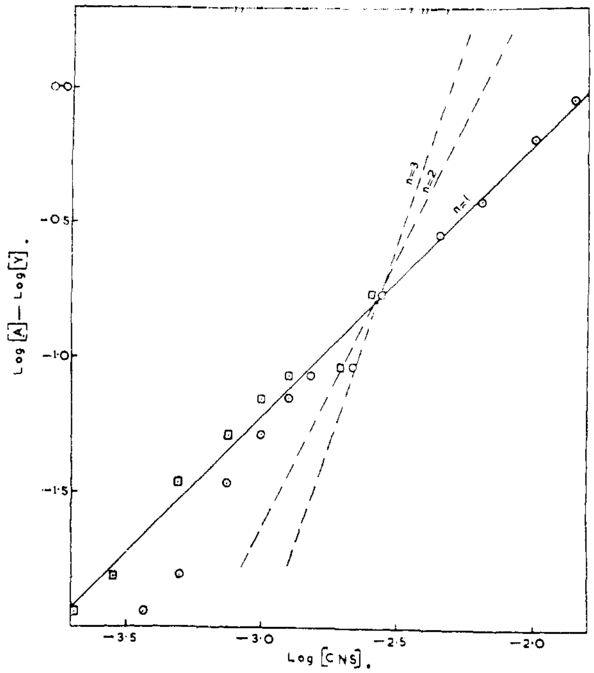

Fig. 6.—Estimate of n in Y + n[CNS$^-$] ⇄ A, data as for Fig. 4: uncorrected, ⊙; corrected for colorless complex, C, using log K_3 = 3.2, ⊡.

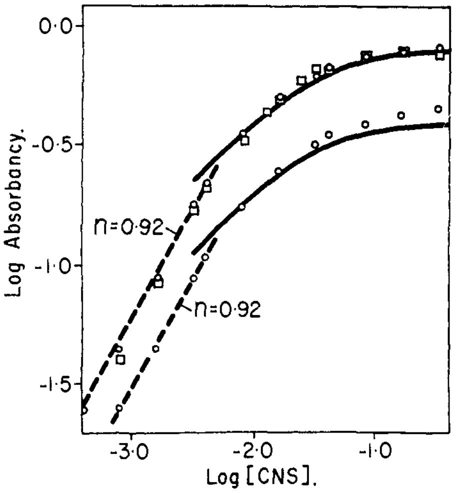

Fig. 7.—Change of absorbancy at high [CNS$^-$], at 4600 Å. [MoO$_4^{--}$], 4.16 × 10^{-5} M; [HCl], 1.00 M; 60% acetone–water. Procedure 1, ⊡; procedure 2, ⊙. Lower values, iron-free solution. Curves calculated for log K_1 = 1.85.

supports the scheme outlined above, and its value is comparable with log K_1 and log K_2.

The possibility that A and Y are 1:4 and 1:3 complexes, respectively, also was examined. The assumption that over the range 2 × 10^{-3} to 2.4 × 10^{-2} M [CNS$^-$]$_0$ only A (as 1:4), Y (as 1:3) and a colorless 1:2 complex were present, gave values of log K_1 which decreased from 3.88 to 1.83. Similarly, log K_2 varied from 4.93 to 2.77. Attempts to reduce these variations by assigning arbitrary values to log K_3 and a postulated log K_4 led to inconsistent results at lower thiocyanate concentrations. It was therefore concluded that A is the 1:3 complex.

This conclusion was supported by a mathematical analysis of the results obtained by the method of continuous variations. Irrespective of whether A is the 1:3 or the 1:4 complex the main reaction taking place for CNS:Mo ratios greater than about 2:1 or 3:1, respectively, is the interconversion of Y and A and not the direct formation of A from molybdenum and thiocyanate ions. It can be deduced that, for wave lengths where A absorbs more strongly than Y, the absorbance maximum occurs at a higher thiocyanate ratio than corresponds to the composition of A. At high concentrations the ratio should approach 5 or 7 depending on whether A contains 3 or 4 thiocyanate ions, respectively. For the experimental conditions the values should be slightly less. Although subject to considerable uncertainty, the observed absorbance maxima at 4500, 4700 and 4900 Å., for a total concentration of 0.036 M, lay between CNS:Mo ratios of 3 and 5.

The results of Krauskopf and Swartz[15] are in agreement with the conclusion that A is the 1:3 complex. By direct analysis a Mo:CNS ratio of 1:3 was obtained for ethereal extracts of the complex formed by low temperature reduction, with zinc, of ammonium molybdate and potassium thiocyanate in hydrochloric acid solutions.[15]

The Charge on the Complex, A.—Measurements were made of the velocity of A under a potential gradient by a moving boundary method similar to that of Bent and French.[6] The aqueous phase was approximately 1 M in hydrochloric acid, 0.6 M in potassium thiocyanate and 0.035 M in stannous chloride. The 60% acetone–water phase carefully introduced into the central part of the apparatus was approximately 1 M in hydrochloric acid, 0.32 M in potassium thiocyanate, 0.02 M in sodium molybdate and 0.035 M in stannous chloride. Under these conditions any molecule of A migrating into the aqueous phase should have been reasonably stable over the short period during which observations were made.

At 19°, under a potential gradient of about 1.6 volts per cm., the observed movement of the amber boundary was less than 1 mm. in 40 minutes toward the anode and less than 3 mm. in 40 minutes toward the cathode. The darkening which took place around the anode did not extend beyond the outer arm of the apparatus and did not affect the observation of the boundaries. Ionic velocities calculated from the measurements are much lower than are found for monovalent ions and indicate that A is an uncharged molecule.

The Formation of an Anion.—It has been suggested[4] that at higher thiocyanate concentrations a colorless anion is formed by molybdenum(V). Evidence in support of this was sought by determining the effect on the absorbancy of increasing thiocyanate concentrations at a constant concentration of molybdenum, with and without the presence of iron(III), and using both procedures I and II (Fig. 7). The upper solid curve in Fig. 7 was calculated for log K_1 = 1.85, assuming that only A and Y were present and summing the values of A_{4600}^{A} and A_{4600}^{Y} so obtained. This approximation is more exact at higher thiocyanate concentrations, where neglect of Mo$\bar{v}$ and C becomes less significant. Up to at least 0.3 M potassium thiocyanate, which approaches the limit of useful concentration of this salt in aqueous acetone (potassium chloride separating at higher concentrations), experimental points lie close to predicted values and no decrease in absorbancy is observed. The lower solid curve in Fig. 7, calculated assuming that only half the molybdenum present could form complexes, gives reasonable agreement with the values obtained in iron-free solutions.

However, Crouthamel and Johnson[5] found with ammonium thiocyanate in 60% acetone–water a 3.5% reduction in molar absorbance index when the thiocyanate concentration was increased from 0.56 to 1.92 M. If this slight reduction is assumed to be due to the formation of a colorless anion

$$(\text{Mo}\bar{v})(\text{CNS})_3 + \text{CNS}^- \rightleftharpoons (\text{Mo}\bar{v})(\text{CNS})_4^-$$

and the value of log K_1 = 1.85 is used to obtain the true molar absorbance index of A, an approximate estimate can be obtained of the association constant, K_4 = [(Mo$\bar{v}$)(CNS)$_4^-$]/[(Mo$\bar{v}$)(CNS)$_3$][CNS$^-$]. From the data of Crouthamel and Johnson for 0.93, 1.44 and 1.92 M ammonium thiocyanate, log K_4 was calculated to be −1.7, −1.6 and −1.6.

Data from the same paper also provide a check of the value of log K_1. From the reported apparent molar absorbance indices at 0.049, 0.140 and 0.240 M ammonium thiocyanate, values of log K_1 may be calculated to be 2.31,

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(15) F. C. Krauskopf and C. E. Swartz, THIS JOURNAL, **48** 3021, (1926).

2.04 and 2.10, respectively, in reasonable agreement with the present value of 1.85.

The Method of Bent and French.[6]—From Fig. 7 the number of thiocyanate ions per molecule of complex may be determined by the method of Bent and French.[6] The limiting slopes in Fig. 7 for low concentrations of thiocyanate are close to unity, indicating the addition of one thiocyanate ion to form the main light absorbing species. From the association constants obtained earlier, it can be calculated, as is also apparent visually, that under these conditions almost all of the absorption is due to Y, so that this result provides evidence in support of the reaction C + $CNS^- \rightleftarrows$ Y.

The assumption that only one molybdenum atom is present in each of the molybdenum complexes has enabled consistent association constants to be calculated. Although results obtained by the method of Bent and French (Fig. 8) might appear to justify this assumption, use of the experimental values of the association constants shows that under the conditions chosen almost all the observed change in absorbancy at 4600 Å. is due to the conversion of Y to A. The observed slope of unity indicates that there is one ion of Y involved in this reaction but provides no information as to the number of molybdenum atoms in Y.

The Reversibility of the Equilibria.—Early in this work an attempt was made to demonstrate the reversibility of the reactions by dilution of solutions containing molybdenum(V) and thiocyanate ions. For this purpose relatively low concentrations of thiocyanate must be used, otherwise the absorbancy tends to vary inversely with the dilution and no evidence of equilibria can be obtained. Absorbance measurements indicated that dissociation took place, but until K_1, K_2 and K_3 were known, it was not possible to interpret the results quantitatively.

In two typical experiments solutions were 4.17×10^{-5} *M* in molybdenum, 1.00 *M* in hydrochloric acid, 0.035 *M* in stannous chloride, 7.2×10^{-4} *M* in ferric ammonium sulfate and 0.31 *M* in potassium chloride, in 60% acetone–water. In (1), color was developed by making the solution 8.0×10^{-3} *M* in potassium thiocyanate, and the solution was then diluted with an equal volume of molybdenum-free, thiocyanate-free solution. Absorbancies were measured at 4600 Å. before and after dilution. In (2), treatment was similar but 1.6×10^{-2} *M* potassium thiocyanate was used. From K_1, K_2 and K_3 and the molar absorbance indices of A and Y the absorbancies of the diluted solutions were calculated and compared with experimental values. These were: solution (1), before dilution, $A_{4600}^{1\text{ cm}} = 0.357$; after dilution, observed $A_{4600}^{5\text{ cm}} = 0.525$, calculated $A_{4600}^{5\text{ cm}} = 0.560$; solution (2), $A_{4600}^{1\text{ cm}} = 0.508$, $A_{4600}^{2\text{ cm}} = 0.314$ and $A_{4600}^{2\text{ cm}} = 0.342$, respectively. The slightly lower experimental values may have been due to slight fading owing to the longer time between initial mixing and final measurement.

In another experiment, reagents were added in the order molybdenum, acid, iron, stannous chloride, thiocyanate. The observed absorbancy was in good agreement with the calculated value.

Molybdenum Thiocyanates in Water.—Attempts to study equilibria involved in the changes Mo $\rightleftarrows$ C $\rightleftarrows$ Y $\rightleftarrows$ A, in water, were unsuccessful, owing to the rapid fading of solutions at low thiocyanate concentrations. Estimates of the association constant of A were comparable with the value in 60% acetone–water.

Maximum absorption for molybdenum in strong aqueous thiocyanate solutions occurs at 4600 A., the apparent molar absorbance index for A being 12,300 at 22°, in 0.60 *M* potassium thiocyanate and 1.00 *M* hydrochloric acid, in the presence of iron. Correction for incomplete formation of A using the value of log K_1 reported below gives the true molar absorbance index of A in water as 12,900. In the absence of iron the apparent molar index was 6,300 in 0.123 *M* potassium thiocyanate.

Table III gives the results of a series of experiments using a constant concentration of molybdenum and varying concentrations of thiocyanate.

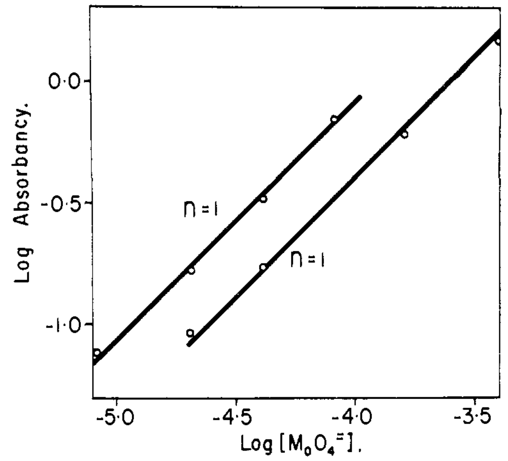

Fig. 8.—Estimate of number of Mo atoms in complexes: $[CNS^-] = 8.22 \times 10^{-3}$ *M*; 60% acetone-water measurement at 4600 Å. Upper values, procedure 1; lower values, procedure 2, no iron.

TABLE III

ASSOCIATION CONSTANT FOR AMBER COMPLEX IN WATER

1.00 *M* HCl, 0.018 *M* $SnCl_2 \cdot 2H_2O$, KCl to give $\mu = 1.65$.

$[Mo]_0 = 8.34 \times 10^{-5}$ *M*

$[CNS^-] \times 10^3$	$A_{4600}^{1\text{ cm}}$	"[A]" $\times 10^5$	$(\log K_1)_{\text{approx}}$	$(\log K_1)_{\text{cor}}$
0.20	0.0066	0.092	1.74	1.74
2.0	.0228	.32	1.30	1.29
4.0	.0676	.95	1.51	1.49
8.0	.148	2.08	1.62	1.60
16.0	.250	3.52	1.66	1.63
32.0	.371	5.22	1.72	1.68
40.0	.423	5.96	1.80	1.75
80.0	.441	6.21	1.56	1.51
160	.538	7.59	1.80	1.66
320	.571	8.05	1.94	1.64
600	.592	8.34		

Readings were taken within one minute of mixing, a series of measurements being made over several minutes to give a short extrapolation back to the time of mixing. This value was taken to be the desired absorbancy, except at low thiocyanate concentrations where maximum intensity was reached after about two minutes. As an approximation all absorption was assumed to be due to A and conversion to A was assumed to be complete at the highest thiocyanate concentration used. In this way values of $(\log K_1)_{\text{approx}}$ were obtained. From similar results in acetone–water, it is likely that the agreement at the lower thiocyanate concentrations is fortuitous, the main reaction under these conditions being, probably, the interconversion of C and Y. From $(\log K_1)_{\text{approx}}$ the incompleteness of conversion to A at the highest thiocyanate concentration was calculated and a more exact estimate of the true molar absorbance index of A obtained. The corrected values of [A] so obtained led to values of log K_1 between 1.50 and 1.75 at 20 ± 1°.

Uncorrected values of log K_1 for other molybdenum solutions over a range of thiocyanate concentration were

(1)	0.016–0.400 *M* KCNS	4.17×10^{-4} *M* Mo	log K_1 = 1.56–1.93
(2)	0.008–0.160	2.09×10^{-5}	1.67–1.84
(3)	0.004–0.080	2.09×10^{-5}	1.83–2.10

In (1) and (2), which were iron-free solutions, conversion to A was assumed complete in 0.60 *M* potassium thiocyanate: in (3), which contained 1.43×10^{-3} *M* ferrous ammonium sulfate, the reference solution was 0.40 *M* in thiocyanate. In each series potassium chloride was added to all except the strongest solution to maintain constant ionic strength.

These results, together with the transient yellow color observed in aqueous solutions when molybdates are reduced in the presence of low thiocyanate concentrations, indicate that the reactions postulated above for aqueous acetone probably occur also in water. No diminution of optical density was observed as thiocyanate concentration was increased to 0.6 *M*.

A small series of measurements was made using an amyl alcohol extraction method.[12] The apparent molar absorbance index of A in amyl alcohol (5 ml. shaken with 25 ml. of aqueous phase) was 15,500 at 4650 Å., the wave length of maximum absorption. Using this value to calculate the concentration of A in amyl alcohol, and hence the apparent molybdenum and thiocyanate concentrations in the aqueous phase, again indicated an equilibrium involving thiocyanate to the first power, but no attempt was made to determine the constant.

The lower values of the molar absorbance indices of A in water and amyl alcohol are due in part to the broadening of the absorption band; in both solvents the curves of log *A* against wave length are flatter on the long wave length side of the maximum than in acetone.

Discussion

Formation of the series of complexes, C, Y and A, provides a quantitative explanation of the observed absorbance changes in aqueous acetone solutions as thiocyanate and molybdenum(V) concentrations are varied. Limited measurements with aqueous solutions also accord with the formation of Y and A, while the closeness of the absorbance maxima, the shape of the absorption spectra and the comparable values for the molar absorbance indices in water, aqueous acetone, ether[5] and amyl alcohol suggest that the complex, A, is present in all these solvents under conditions commonly employed in analysis.

The possibility that these complexes are formed by the addition of thiocyanate ion to an ion containing more than one molybdenum atom is considered unlikely because of the formation of A over a wide range of conditions[5] and the agreement of molar absorbance indices using different molybdates, different analytical procedures and a range of storage conditions.[5]

Data presented in this paper are consistent with the formula $MoO(CNS)_3$ for A, and complexes of this type are known. Sand and Burger[16] and Rosenheim and Koss,[17] by the action of pyridine on the red and violet liquids obtained from acidified solutions of molybdates and thiocyanates, either by boiling or by treating in the cold with zinc, tin or other reducing agents, isolated a complex, $MoO(CNS)_3 \cdot (C_6H_5N \cdot HCNS) \cdot H_2O$. The complex $Mo(OH)_2(CNS)_3 \cdot 2C_6H_5N$ also was obtained, but Barbieri[18] and James and Wardlaw[19] suggest that the latter is $MoO_2(CNS) \cdot (C_6H_5N \cdot HCNS)_2$, one of their reasons being its convertibility to the other complex on treatment with thiocyanic acid. Molybdenylammonium chloride, $MoOCl_3 \cdot 2NH_4Cl$, gives an orange-red coloration in hydrochloric acid solutions containing excess ammonium thiocyanate.[18] Barbieri[18] considers that nearly all molybdenum(V) compounds that have been isolated are double salts of the types $MoOX_3 \cdot RX$ and $MoOX_3 \cdot 2RX$, and contain the molybdenyl radical. Quniolinium, tetramethyl- and trimethyl-ammonium salts of the type, $R_2MoO(CNS)_5$ have been isolated.[19] The pyridinium complex is decomposed by water but dissolves in dry alcohol or chloroform, giving a deep red color.[17] The corresponding chlorides are known,[19] and by using boiling solutions of thiocyanic acid or hot concentrated hydrochloric acid the following equilibrium may be driven either to the right or to the left[19]

$$R_2(MoOCl_5) + 5HCNS \rightleftharpoons R_2(MoO(CNS)_5) + 5HCl$$

In dilute aqueous solution pyridinium molybdenyl thiocyanate gives a molecular conductivity consistent with complete hydrolysis.[19]

It is not known whether the high chloride ion concentrations used in the present work lead to partial formation of molybdenyl chloride complexes in competition with the thiocyanate complexes. The possibility that molybdenum(V) is present in molar hydrochloric acid as the complex, $MoOCl_3$, and the various thiocyanate complexes arise by successive replacement of the chloride ions, is unlikely if the interpretation given below of the relation between successive association constants for C, Y and A is correct.

Estimation of the thermodynamic association constants for the various reactions is not possible owing to the high ionic strengths of the solutions in which the complexes are formed. Using concentrations, the values of the logarithms of the association constants in 60% acetone–water for the complexes, which are suggested to be $MoOCNS^{++}$, $MoO(CNS)_2^+$ and $MoO(CNS)_3$, are approximately 3.2, 3.01 and 1.85, for $\mu = 1$, at 20–25°. In water at 20 ± 1° the logarithm of the association constant for the third complex is approximately 1.7 for $\mu = 1.65$.

The agreement as to order of magnitude of the first two constants and the greater drop to the third parallels the observations of Rabinowitch and Stockmayer[20] for the series $FeCl^{++}$ $FeCl_2^+$, $FeCl_3$, where the values were 0.62, 0.11 and −1.40, for $\mu = 1$, at 26.7°. Rabinowitch and Stockmayer explain the relatively large difference between the second and third association constants in terms of the replacement by chloride ions of water molecules in the hydration sphere of the ferric ion. The second chloride ion must be bound on the opposite side of the ferric ion from the first chloride ion, since this is a position of minimum electrostatic energy, and the difference between the first and second association constants can then be ascribed mainly to the differences in statistical probabilities. The third chloride ion, in replacing another water molecule, is exposed to repulsive forces from the other two chloride ions and hence its association constant is substantially reduced. As thiocyanic acid is apparently a strong acid,[21] it is probable that the reactions between the molybdenyl radical and thiocyanate ions are governed by similar considerations. If so, an even greater drop in the value of the association constant should be expected for the formation of an anion and the estimate of log $K = -1.6$ for $MoO(CNS)^-_4$, based on the data of Crouthamel and Johnson,[5] is consistent with this prediction. The more uniform decrease in the association constants for the series $FeOH^{++}$,

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$Fe(OH)^{+}_{2}$, $Fe(OH)_3$, as reported by Lamb and Jacques,[22] has been suggested to be due to less purely ionic binding.[20]

Using the method of continuous variations, with a light filter transmitting around 5000 Å., Babko[4] found that for aqueous molybdenum thiocyanate solutions the ratio for maximum absorbancy was near 1:5. He concluded that this was also the Mo:CNS ratio for the amber complex. However, if the stability constants for the aqueous complexes are assumed to be roughly of the orders now reported for 60% acetone–water, it can be shown mathematically, as discussed earlier, that the observed maximum occurs at a significantly higher thiocyanate ratio than is found in A.

Although Hiskey and Meloche reported[2] a Mo:CNS ratio of 1:3 for the complex they studied, over the range 1–2 M hydrochloric acid, it is doubtful that their complex was A. The slow, uniform rate of formation of the complex, reaching a maximum after about one hour, contrasts with the very rapid development of color when A is formed under comparable conditions, nor is it consistent with the catalyzed oxidation of lower valence molybdenum such as can follow the reduction of molybdates by stannous chloride in the absence of iron and copper.[5] The absorption curves of Hiskey and Meloche show a maximum near 5100 Å. which is absent from A, while the data indicate significantly less complete formation of the complex at high thiocyanate concentrations in 1 M hydrochloric acid than was found for A in the present work. Finally, application to the present results of the mathematical treatment of Hiskey and Meloche, for the dependence of absorbancy on thiocyanate concentration gave, at 4600 Å., good agreement for $n = 1$, corresponding to the conversion of Y to A at the high thiocyanate concentrations involved. The value of $n = 3$, reported by Hiskey and Meloche, is incompatible with the equilibria proposed in the present work.

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[CONTRIBUTION NO. 68 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

2,3-Dithiabutane, 3,4-Dithiahexane and 4,5-Dithiaoctane: Chemical Thermodynamic Properties from 0 to 1000°K.[1]

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RECEIVED JANUARY 9, 1958

Thermodynamic properties of the first three members of the symmetrical alkane disulfide series were investigated. Measurements were made of the heat of vaporization and vapor heat capacity of 2,3-dithiabutane; the low temperature thermal properties, vapor pressure and entropy of 4,5-dithiaoctane; and the heats of combustion and formation of 2,3-dithiabutane, 3,4-dithiahexane and 4,5-dithiaoctane. The new experimental data were used in revising previously published tables of thermodynamic functions for 2,3-dithiabutane and 3,4-dithiahexane. A table of thermodynamic functions for 4,5-dithiaoctane was calculated by an incremental method. Values of the heat, free energy and logarithm of the equilibrium constant of formation between 0 and 1000°K. were computed for the three compounds. The S–S thermochemical bond energy is the same in the three disulfides as in S_8 within experimental uncertainty.

Chemical thermodynamic studies of alkane disulfides are included in the program of American Petroleum Institute Research Project 48A in this Laboratory. Earlier publications reported experimental thermodynamic studies and tables of thermodynamic functions for 2,3-dithiabutane (dimethyl disulfide)[2] and 3,4-dithiahexane (diethyl disulfide).[3] This paper reports additional experimental studies for those two compounds and the next higher symmetrical alkane disulfide, 4,5-dithiaoctane (di-*n*-propyl disulfide). The experimental work included: for 2,3-dithiabutane, vapor flow calorimetry and combustion calorimetry; for 3,4-dithiahexane, combustion calorimetry; and for 4,5-dithiaoctane, low temperature calorimetry, comparative ebulliometry and combustion calorimetry. Detailed results are presented later in the Experimental section. However, the more pertinent results, to which reference will be made in the subsequent discussion, are collected for ready reference in Table I.

The experimental results were used in calculating more reliable tables of thermodynamic functions for 2,3-dithiabutane and 3,4-dithiahexane. A similar table for 4,5-dithiaoctane was obtained by an incremental method. The values of $\Delta Hf^{\circ}_{298.16}$ were used to calculate the standard heat, standard free energy and logarithm of the equilibrium constant of formation for all three substances over the temperature range of interest. Finally, values $\Delta Hf^{\circ}_{298.16}$ for the related symmetrical alkane sulfides, also determined in this Laboratory, made possible calculations of the S–S thermochemical bond energy. The several calculations are discussed in the next section.

Chemical Thermodynamic Properties

Thermodynamic Functions of 2,3-Dithiabutane.—The thermodynamic functions given for 2,3-

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[1] This investigation was part of American Petroleum Institute Research Project 48A on "The Production, Isolation and Purification of Sulfur Compounds and Measurement of their Properties," which the Bureau of Mines conducts at Bartlesville, Okla., and Laramie, Wyo. The authors wish to acknowledge the assistance of Thelma C. Kincheloe with the low temperature calorimetry, James P. Dawson with the comparative ebulliometry and Frankie R. Frow with the combustion calorimetry.

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