[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

A STUDY OF THE MERCURY SULPHOCYANATE COMPLEXES.

BY M. S. SHERRILL AND S. SKOWRONSKI.

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I. INTRODUCTION.

ANY theory of valence to be fully satisfactory must be capable of explaining the existence of at least all complex compounds which are stable enough to exist either in solution or the gaseous state. From a valence standpoint, therefore, a study of such complexes and a determination of their molecular formulas is very important.

Moreover, an interesting relation between the tendency of the elements to form complexes and their position in the electrochemical series has been pointed out by Abegg and Bodländer.[1] This principle states that the tendency towards complex formation increases with decreasing electro-affinity, of which the decomposition-potential may be taken as a measure. The stability of a complex is a measure of the tendency of its constituents to combine, and is greater the smaller the amount of the complex which is dissociated into its component ions. It may be expressed mathematically in the form of a constant, called by Bodländer[2] the *stability constant*, which is equal to the concentration of the complex divided by the product of the concentrations of the component ions raised to that power which, according to the law of mass action, corresponds to the number of single ions constituting the complex.

To compare quantitatively the tendency of the halogens to form complexes, a study of the complexes formed by dissolving the mercuric halides in a solution containing a common anion is especially suitable. As has been established by many kinds of observations, this solution takes place with the formation of a complex anion according to the general reaction,

$$m\text{HgX}_2 + n\text{X}^- \rightleftarrows (\text{HgX}_2)_m(\text{X}^-)_n .$$

The more stable this complex is, the less will it be decomposed into its single ions according to the reactions,

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[1] *Ztschr. anorg. Chem.*, **20**, 472 (1899).

[2] *Ber. d. chem. Ges.*, **36**, 3935 (1903).

$$(HgX_2)_m(X^-)_n \rightleftarrows m\text{Hg}^{++} + (2m+n)X^-,$$

and the larger will be its stability-constant,

$$K_1 = \frac{[(HgX_2)_m(X^-)_n]}{[\text{Hg}^{++}]^m[X^-]^{2m+n}}.$$

According to the principle of Abegg and Bodländer stated above, the value of this constant should increase in the series, $HgCl_2$, $HgBr_2$, HgI_2, $Hg(CN)_2$, in the order named. One of us[1] has studied the complex formation and determined the stability constants of these four salts. It was the purpose of this work to extend this investigation to mercuric sulphocyanate.

II. SOLUBILITY OF MERCURIC SULPHOCYANATE IN POTASSIUM SULPHOCYANATE SOLUTIONS.

One method of determining the formula of the complex is to measure the solubility of mercuric sulphocyanate in varying strengths of potassium sulphocyanate solution; for the increase of solubility over that in pure water is a quantitative measure of the complex formation as represented by the general equation,

$$m\text{Hg(SCN)}_2 + n\text{SCN}^- \rightleftarrows (\text{Hg(SCN)}_2)_m(\text{SCN}^-)_n. \qquad (1)$$

From this equation and the law of mass action it follows that

$$\frac{[(\text{Hg(SCN)}_2)_m(\text{SCN}^-)_n]}{[\text{Hg(SCN)}_2]^m[(\text{SCN}^-)]^n} = K_2. \qquad (2)$$

Here, as well as in the following discussions, we will let a represent the original concentration of the potassium sulphocyanate solution, b the concentration of the free mercuric sulphocyanate existing as such in the solution, and c that of the mercuric sulphocyanate present in the complex. It follows then from equations (1) and (2) that

$$K_2 = \frac{\dfrac{c}{m}}{b^m\left(a - \dfrac{n}{m}c\right)^n}. \qquad (3)$$

Complete dissociation of the potassium sulphocyanate and of the complex salt into the corresponding ions is here, as in subsequent considerations, assumed. Although this assumption is certainly not exact, it cannot affect the order of magnitude of the constants.

Since in these solubility experiments mercuric sulphocyanate is

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[1] *Ztschr. phys. Chem.*, **43**, 705 (1903).

present as a solid phase, the concentration b of the free mercuric sulphocyanate in the solution must be constant and equal to its solubility in water. The concentration c of the mercuric sulphocyanate bound as complex in the solution is equal to its total concentration or total solubility diminished by the concentration of the part uncombined, b.

The values of a, b and c being now known, to determine the formula of the complex, it would seem only necessary to make such assumptions as to m and n as would make the expression remain constant. It is, however, to be borne in mind that in saturated solutions, the concentration of the SCN^- ion, owing to its disappearance in the form of the complex is very small, and that therefore a small error in the determination of c will cause a large error in $\left(a - \frac{n}{m}c\right)$, and since this term is raised to the nth power it will render the whole expression uncertain. For this reason exact values for m and n cannot be determined by such solubility experiments. When, however, the concentration of the SCN^- ion is negligibly small, the ratio $\frac{a}{c}$ must approximate to $\frac{n}{m}$; for in case all of the SCN^- ions disappear in the form of the complex according to equation (1), $\frac{a}{c}$ must become equal to $\frac{n}{m}$. For this same reason Jander,[1] who has measured the solubility of mercuric sulphocyanate in potassium sulphocyanate solutions, was not justified in concluding that n is equal to 1 from the fact that the ratio $\frac{a}{c}$ remains constant.

The solubility experiments were made by rotating potassium sulphocyanate solutions of various concentrations in a thermostat at 25° for several hours with an excess of mercuric sulphocyanate, which had been purified by crystallizing twice from hot water. The exact concentration of the potassium sulphocyanate solutions was obtained by titrating them with a silver nitrate solution of known strength with ferric alum as an indicator. After settling, samples were pipetted off, and the mercuric salt dissolved was determined by precipitating with hydrogen sulphide and weighing the mercuric sulphide in a Gooch crucible after drying it at 110°.

The results of the solubility experiments are given in the fol-

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[1] Inaug. Dissert., Breslau, 1902; *Ztschr. Elektrochem.*, **8**, 688 (1902).

lowing table, which for the sake of comparison also includes the results of Jander's measurements (indicated by the letter (J)), All concentrations are expressed in mols per liter. The solubility of mercuric sulphocyanate in water at 25° was found to be 0.0022 mol per liter.

TABLE I.—TEMPERATURE 25°.

Concentration of KSCN (*a*).	Solution taken for analysis cc.	Weight HgS.	Solubility of $Hg(SCN)_2$.	Increase of solubility of $Hg(SCN)_2$ (*c*).	Ratio total KSCN to combined $Hg(SCN)_2(a/c)$.
0.101	..	......	0.057	0.055	1.84 (J)
0.125	20	0.3276	0.071	0.069	1.81
0.248	..	......	0.141	0.139	1.79 (J)
0.251	10	0.3272	0.141	0.139	1.80
0.542	..	......	0.181	0.179	3.02 (J)
0.503	5	0.2715	0.233	0.231	2.18
0.730	..	......	0.274	0.272	2.65 (J)
0.765	5	0.3449	0.298	0.296	2.58

At the lower concentrations the results agree very closely with those of Jander, and it is to be noted that the ratio $\frac{a}{c}$ though somewhat smaller than 2 approximates that value. This would indicate that there exists at these concentrations principally a complex with the ratio $\frac{n}{m} = 2$ mixed with a small amount of a complex for which that ratio is less than 2.

At the higher concentrations no agreement with Jander's results was obtained. This lack of agreement is to be explained, however, by the fact pointed out by Jander and illustrated by the following table, that the solubility decreases with the time of rotation.

TABLE II.—TEMPERATURE 25°.

Time of rotation.	Original concentration KSCN.	Solubility of $Hg(SCN)_2$.
4 hours	0.503	0.233
2 days	0.503	0.220
3 weeks	0.503	0.200

This phenomenon might be caused by the gradual separation of a solid complex salt and a consequent change in concentration of the potassium sulphocyanate. In this case a true equilibrium would be reached either on the complete disappearance of the mercuric sulphocyanate as solid phase, or when the potassium sulphocyanate had reached such a concentration as would correspond to equilibrium with the two solid phases, the complex salt and the mercuric sulphocyanate. If the latter conditions are realized by keeping an excess of mercuric sulphocyanate present, the concentration of the final solution must be independent of the initial concentration of the potassium sulphocyanate solution used.

To test this point the following solubility experiments were carried out at 0°, a temperature more favorable to the formation of the complex. Two solutions of potassium sulphocyanate of different concentrations were shaken with a large excess of mercuric sulphocyanate for twenty hours, and then 20 cc. were analyzed for both mercury and potassium. The potassium was determined as sulphate by evaporating the filtrate from the hydrogen sulphide precipitate with sulphuric acid and strongly igniting. The results of the experiments are given in Table III.

TABLE III.—TEMP. 0°.

Initial KSCN conc.	Weight. K_2SO_4.	Weight. HgS	Final KSCN conc. a.	Solubility of $Hg(SCN)_2$.	Increase of solubility c.	$\frac{(a)}{c}$
0.125	0.1344	0.1909	0.0770	0.041	0.039	1.97
0.250	0.1332	0.1854	0.0765	0.040	0.038	2.01

The table shows very clearly the constancy of the final concentrations and therefore the correctness of the explanation given above. It is also to be noted that when a is put equal to the final potassium sulphocyanate concentration, the ratio $\frac{a}{c}$ becomes very nearly equal to 2.

From all these solubility experiments, we may draw the conclusion that at the concentrations in question a complex is formed in solution with the ratio $\frac{n}{m}=2$, the simplest assumption being a complex of the formula $K_2Hg(SCN)_4$. A solid complex salt also separates from solution but our experiments do not determine its composition.

III. FREEZING-POINT DETERMINATIONS.

The change of the freezing-point of a potassium sulphocyanate solution caused by successive additions of solid mercuric sulphocyanate offers another means of studying the constitution of the complex anion formed. Thus, in case no complex formation takes place on the addition of the mercuric sulphocyanate, the freezing-point would be lowered by an amount corresponding to the number of mols added. Should one mol $Hg(SCN)_2$ combine with one SCN^- ion, the total number of mols in the solution, and hence the freezing-point would remain unchanged. Finally, if one mol of $Hg(SCN)_2$ were to unite with two or more SCN^- ions, the total number of mols in the solution would be decreased and the freezing-point correspondingly raised.

The results of such freezing-point determinations, which were made with a Beckmann apparatus in the usual way and with the usual precautions, are given in the following table:

TABLE IV.—FREEZING-POINT.

Conc. KSCN.	Conc. $Hg(SCN)_2$. C.	Raising of freezing-point Δ.	Δ/1.852.	$\frac{\Delta/1.852}{C}$.
0.739	0.000	....	....	...
0.739	0.083	0.220	0.119	1.43
0.739	0.166	0.481	0.259	1.56
0.739	0.249	0.730	0.394	1.58
0.493	0.000	....	....	...
0.493	0.056	0.142	0.077	1.37
0.493	0.111	0.293	0.158	1.42
0.493	0.166	0.452	0.244	1.47
0.247	0.000	....	....	...
0.247	0.042	0.097	0.052	1.24
0.247	0.084	0.199	0.107	1.27
(0.247	0.126[1]	0.331	0.178	1.41)
0.124	0.000	....	....	...
0.124	0.042	0.072	0.039	0.93
0.124	0.063	0.124	0.067	1.06

In the fourth column of the table is given the quotient of the observed change of freezing-point Δ by the molecular change 1.852°. This should represent the total number of mols removed on the addition of the mercuric sulphocyanate. The last column contains the ratio of mols removed to mols of mercuric sulphocyanate added. An inspection of the last column of the table shows that at the concentrations 0.739 and 0.493 normal of the potassium sulphocyanate, for every mol of mercuric sulphocyanate added, a raising of the freezing-point is obtained which corresponds to the removal from the solution of one and a half mols, while at the lowest concentration 0.124 normal, for every mol $Hg(SCN)_2$ added, the change of freezing-point corresponds to a removal of only one mol from the solution. At the intermediate concentration 0.247 normal, the ratio of total number of mols removed

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[1] Precipitation occurred.

from the solution to mols mercuric sulphocyanate added lies about midway between these limits. These changes might be explained by assuming that at the higher concentrations the complex anion $(Hg(SCN)_2)_2(SCN^-)_4$, at the lowest concentration $(Hg(SCN)_2)(SCN^-)_2$, and at the middle concentration a mixture of these two exist. Since the ratio $\frac{n}{m}$ for both of these complexes equal 2, these results agree with the conclusions drawn from the solubility experiments. The results described below, however, obtained from the measurement of the electromotive force of certain concentration cells at 0°, a method which is more reliable in concentrated solutions than the freezing-point one, show conclusively that only the simpler complex $(Hg(SCN)_2)(SCN^-)_2$ exists to an appreciable extent at any of these concentrations. It is probable therefore that at the higher concentrations the freezing-point change is not proportional to the change in molal concentration which would render the conclusions just referred to doubtful. In the dilute solution, where the theoretical significance of the freezing-point results is not doubtful, the results are in full accord with those obtained by the other methods.

IV. SOLUBILITY OF MERCUROUS SULPHOCYANATE IN POTASSIUM SULPHOCYANATE SOLUTION.

It is a well established fact that all mercurous salts decompose of themselves in aqueous solution into metallic mercury and the corresponding mercuric salt. This reaction mentioned by Behrend[1] for mercurous iodide, has beeen studied by Ogg[2] and Abel[3] and corresponds to the equilibrium:

$$(Hg_2)^{++} \rightleftarrows Hg^{++} + \mathbf{Hg}.$$

As has been shown by Richards and Archibald[4] for the chloride, and by Abegg and Immerwahr[5] for the other halides, this decomposition goes much further in the presence of the alkali-metal halides or sulphocyanate. According to these investigations the explanation of this phenomenon is to be found in the fact that a

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[1] *Ztschr. phys. Chem.*, **11**, 474 (1893).

[2] *Ibid.*, **27**, 285 (1898).

[3] *Ztschr. anorg. Chem.*, **26**, 377 (1901).

[4] *Proc. Am. Acad.*, **37**, 347 (1902) ; *Ztschr. phys. Chem.*, **40**, 385 (1902).

[5] *Ztschr. Elektrochem.*, **8**, 688 (1902).

part of the mercuric ions formed by the reaction disappear from the solution by chemical combination. Thus, in the action of potassium sulphocyanate on mercurous sulphocyanate, the mercuric sulphocyanate formed by the decomposition combines with the potassium sulphocyanate to form a complex, whereby the concentration of the free mercuric sulphocyanate and therefore of the mercuric ions is diminished. It will be seen from equation (4) below that, since the influence of the metallic mercury which is present as a solid phase is constant, a diminution of the concentration of the mercuric salt must cause a conversion of some of the mercurous salt into new mercuric salt and mercury, and then more mercurous salt must dissolve till equilibrium is again reached. As has been shown by Abegg and Immerwahr[1] for the bromide and iodide, the same equilibrium may be reached by shaking a solution of mercuric sulphocyanate in potassium sulphocyanate with metallic mercury.

The equilibria which occur in the subsequent discussion and the equations representing them are as follows:

Reactions in equilibrium. Equilibrium equations.

$$Hg_2(SCN)_2 \rightleftarrows Hg(SCN)_2 + \mathbf{Hg} \qquad K = \frac{[Hg(SCN)_2]}{[Hg_2(SCN)_2]} \tag{4}$$

$$m Hg(SCN)_2 + n SCN^- \rightleftarrows (Hg(SCN)_2)_m(SCN^-)_n$$

$$K_2 = \frac{[Hg(SCN_2)_m(SCN^-)_n]}{[Hg(SCN)_2]^m[SCN^-]^n}. \tag{5}$$

$$Hg(SCN)_2 \rightleftarrows Hg^{++} + 2SCN^- \qquad K_3 = \frac{[Hg^{++}][SCN^-]^2}{[Hg(SCN)_2]}. \tag{6}$$

$$Hg_2SCN_2 \rightleftarrows Hg_2^{++} + 2SCN^- \qquad K_4 = \frac{[Hg_2^{++}][SCN^-]^2}{[Hg_2(SCN)_2]}. \tag{7}$$

To determine the formula of the complex which is formed, several methods may be employed. If we have, for example, mercurous salt present as solid phase, its concentration in the solution, and hence according to equation (4) that of the free mercuric salt, must be constant. If we now vary the concentration of the SCN$^-$ ion by varying the concentration of the potassium sulphocyanate solution, the following equation must hold true,

$$\frac{[(Hg(SCN)_2)_m(SCN^-)_n]}{[SCN^-]^n} = K_2[Hg(SCN)_2]^m = K_5. \tag{8}$$

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[1] *Ztschr. Elektrochem.*, **8**, 688 (1902).

By assuming that the total mercuric sulphocyanate in solution is present in the form of the complex, which assumption is justified by the fact that mercuric sulphocyanate is but slightly soluble in water, we may calculate K_5 from the solubility of the mercurous sulphocyanate. If, as before, *a* represent the original concentration of the potassium suplhocyanate, and *c* that of the mercuric salt combined as complex, which here is substantially equal to the total concentration of the mercury, it follows in the solution saturated with mercurous sulphocyanate from equations (5) and (8) that

$$K_5 = \frac{\frac{c}{m}}{\left(a - \frac{n}{m}c\right)^n}. \tag{9}$$

By choosing in equation (9) such values of *m* and *n* as cause the expression to remain constant, the formula of the complex may be determined.

With this purpose in view the solubility of mercurous sulphocyanate in solutions of potassium sulphocyanate of two different concentrations was measured. Equilibrium was obtained by rotating solutions of potassium sulphocyanate almost saturated with mercuric sulphocyanate with metallic mercury in a thermostat at 25° for several days. The dissolved mercury was determined as before by weighing as HgS.

TABLE V.—TEMPERATURE 25°.

Conc. KSCN. *a*.	Solution taken for analysis. cc.	Weight HgS.	Solubility of $Hg_2(SCN)_2$ as $Hg(SCN)_2$. *c*.	$K_5 = \frac{m}{\left(a - \frac{n}{m}c\right)^n}$			
				$m = 1$. $n = 1$.	$m = 1$. $n = 2$.	$m = 1$. $n = 3$.	$m = 2$. $n = 4$.
0.50	10	0.3248	0.140	0.39	2.89	272	29.9
0.25	10	0.1272	0.055	0.28	2.81	90	71.5

It is evident from the above table that the best constancy is obtained when *m* is made equal to 1, and *n* equal to 2, and that the formula of the complex is therefore $(Hg(SCN)_4)^{--}$.

V. ELECTROMOTIVE FORCE MEASUREMENTS.

The measurement of the electromotive force of concentration cells of the type

$$\mathbf{Hg} / \left(\underset{\text{Conc. 1.}}{Hg(SCN)_2 + KSCN}\right) / \left(\underset{\text{Conc. 2.}}{KSCN + Hg(SCN)_2}\right) / \mathbf{Hg},$$

furnishes another method of determining the formula of the complex, which has the advantage over that based on the solubility of the mercurous salt of being independent of the constancy of concentration of the mercurous and mercuric sulphocyanates. This method is, however, limited to such concentrations of mercuric sulphocyanate as correspond *in maximo* to the solubility of the mercurous sulphocyanate, since with higher concentrations the excess would precipitate when brought in contact with the mercury electrode.

From the electromotive forces, values of both m and n may be calculated according to the method of Bodländer,[1] as indicated below. For each solution of mercuric sulphocyanate in potassium sulphocyanate, the equation

$$\frac{[(\mathrm{Hg(SCN)_2})_m(\mathrm{SCN}^-)_n]}{[\mathrm{Hg}^{++}]^m[\mathrm{SCN}^-]^{2m+n}} = \frac{\mathrm{K}_2}{\mathrm{K}_3^{\,m}} = \mathrm{K}_1 \qquad (10)$$

or

$$[\mathrm{Hg}^{++}]^m = \frac{1}{\mathrm{K}_1}\,\frac{[(\mathrm{Hg(SCN)_2})_m(\mathrm{SCN}^-)_n]}{[\mathrm{SCN}^-]^{2m+n}}$$

must hold, where K_1 is the stability constant of the complex. From this it follows for two different solutions 1 and 2 that

$$\frac{[\mathrm{Hg}^{++}]_1}{[\mathrm{Hg}^{++}]_2} = \left(\frac{[(\mathrm{Hg(SCN)_2})_m(\mathrm{SCN}^-)_n]_1[\mathrm{SCN}^-]_2^{\,2m+n}}{[(\mathrm{Hg(SCN)_2})_m(\mathrm{SCN}^-)_n]_2[\mathrm{SCN}^-]_1^{\,2m+n}}\right)^{\frac{1}{m}}. \qquad (11)$$

Substituting for the concentrations in this equation their values in terms of a and c (see Sec. II), it becomes

$$\frac{[\mathrm{Hg}^{++}]_1}{[\mathrm{Hg}^{++}]_2} = \left(\frac{c_1\left(a_2 - \frac{n}{m}c_2\right)^{2m+n}}{c_2\left(a_1 - \frac{n}{m}c_1\right)^{2m+n}}\right)^{\frac{1}{m}}. \qquad (12)$$

When the concentrations of the SCN^- ion in the two solutions are equal, the equation simplifies itself to

$$\frac{[\mathrm{Hg}^{++}]_1}{[\mathrm{Hg}^{++}]_2} = \left(\frac{c_1}{c_2}\right)^{\frac{1}{m}}. \qquad (13)$$

This condition is fulfilled when $a_1 = a_2$ and when c_1 and c_2 are made small in comparison with it; that is, when the two solutions of potassium sulphocyanate are of the same strength, and in each of them is dissolved only a small proportion of mercuric sulphocyanate differing in the two cases.

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[1] "Festschrift zum siebzigsten Geburtstage von Dedekind Braunschweig" (1901); see also *Ztschr. phys. Chem.*, **93**, 547 (1902).

Since now, according to the Nernst formula for concentration cells,

$$E_{25^\circ} = 0.0295 \log_{10} \frac{[Hg^{++}]_1}{[Hg^{++}]_2},$$

it follows from equation (13) that

$$E_{25^\circ} = \frac{0.0295}{m} \log_{10} \frac{c_1}{c_2} \text{ or } m = \frac{0.0295}{E_{25^\circ}} \log_{10} \frac{c_1}{c_2} \qquad (14)$$

where m naturally must be a whole number.

Having once established the value of m, the value for n may be calculated from equation (12) by measuring the electromotive force of any other cell, where the concentration of the SCN^- ions is different in the two solutions. This complicated equation is most easily solved by trial, which is rendered simple by the fact that n also must be a whole number.

By assuming the values of m and n obtained in this way, conversely, the ratio $\frac{[Hg^{++}]_1}{[Hg^{++}]_2}$ can be calculated from equation (12), and from this ratio the electromotive force of any given concentration cell determined. By comparison of the values thus calculated with the measured ones, we may decide how well this formula holds at all concentrations.

In order to obtain an absolute value for K_1 from equation (10) it is necessary to know the concentration of the mercuric ions in some one solution. Now the concentration of the mercurous ions in the normal calomel electrode has been calculated[1] to be

$$[Hg_2^{++}] = 6.3 . 10^{-18}.$$

In the investigation cited, this value was used as a basis for further calculations. Ley and Heimbucher[2] have, however, from the electromotive force of the concentration cell

$$\mathbf{Hg}/Hg_2Cl_2,\ 1.0\ KCl \Big/,\ \frac{0.1\ Hg_2(ClO_4)_2}{2} /\mathbf{Hg},$$

correcting for the hydrolysis and dissociation of the mercurous perchlorate, obtained the more accurate value

$$[Hg^{++}{}_2] = 3.5 . 10^{-18}.$$

According to measurements of Abel,[3] the ratio of mercurous to

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[1] Sherrill: *Ztschr. phys. Chem.*, **43**, 711 (1903).

[2] *Ztschr. Elektrochem.*, **10**, 303 (1904).

[3] *Ztschr. anorg. Chem.*, **26**, 377 (1901).

mercuric ions $\frac{[Hg_2^{++}]}{[Hg^{++}]}$ when in equilibrium with metallic mercury is equal to 120. Using the value given above by Ley and Heimbucher, it follows from this that the concentration of the mercuric ions in the normal electrode is

$$[Hg^{++}] = \frac{3.5 \times 10^{-18}}{120} = 2.9 \times 10^{-20}.$$

We therefore measured the electromotive force of the various sulphocyanate solutions in combination with a normal electrode. From a knowledge of these values for the normal electrode, the concentration of the mercuric ions in the solution may be calculated from the Nernst equation for concentration cells. By substituting the values thus found in equation (10), we obtain the stability constant K_1 for the complex anion in question.

The measurements of the electromotive force were made according to the Poggendorf compensation method, using a capillary electrometer. The following table contains the results and calculations with different concentrations of potassium sulphocyanate containing varying amounts of mercuric sulphocyanate.

Table VI.—Temperature 25°.

Number.	Conc. KSCN. a.	Conc. $Hg(SCN)_2$. c.	E. M. F. against N.E.	E. M. F. against solution No. 8. Meas.	E. M. F. against solution No. 8. Calc.	Conc. Hg^{++}.	$K_1 = \frac{[Hg(SCN)_4^{--}]}{[Hg^{++}][SCN^-]^4}$.
1	1.53	0.400	0.078	0.091	0.099	6.6×10^{-23}	21.4×10^{21}
2	1.53	0.200	0.106	0.064	0.068	7.7×10^{-24}	15.7×10^{21}
3	1.53	0.100	0.120	0.049	0.051	2.4×10^{-24}	13.1×10^{21}
4	1.53	0.050	0.132	0.037	0.039	9.9×10^{-25}	11.9×10^{21}
5	1.53	0.025	0.141	0.028	0.028	4.8×10^{-25}	10.8×10^{21}
6	1.53	0.0125	0.149	0.020	0.018	2.6×10^{-25}	9.5×10^{21}
7	1.53	0.00625	0.160	0.009	0.009	1.1×10^{-25}	10.8×10^{21}
8	1.53	0.00313	0.169	0.000	....	5.5×10^{-26}	10.4×10^{21}
9	1.02	0.200	0.056	0.113	0.116	3.6×10^{-22}	3.8×10^{21}
10	1.02	0.133	0.084	0.085	0.081	4.1×10^{-23}	10.2×10^{21}
11	1.02	0.0665	0.100	0.069	0.067	1.2×10^{-23}	9.0×10^{21}
12	1.02	0.0333	0.112	0.057	0.055	4.6×10^{-24}	9.0×10^{21}
13	1.02	0.0166	0.122	0.047	0.044	2.1×10^{-24}	8.0×10^{21}
14	1.02	0.00831	0.132	0.037	0.035	9.9×10^{-25}	8.0×10^{21}
15	1.02	0.00416	0.140	0.029	0.027	5.1×10^{-25}	7.7×10^{21}

Number.	Conc. KSCN. *a*.	Conc. $Hg(SCN)_2$. *c*.	E. M. F. against N. E.	E. M. F. against solution No. 8.		Conc. Hg^{++}.	$K' = \frac{[Hg(SCN)_4^{--}]}{[Hg^{++}][SCN^-]^4}$
				Meas.	Calc.		
16	0.765	0.200	0.043	0.126	0.127	1.0×10^{-21}	10.6×10^{21}
17	0.765	0.100	0.071	0.098	0.096	1.5×10^{-22}	7.0×10^{21}
18	0.765	0.050	0.088	0.081	0.079	3.1×10^{-23}	8.8×10^{21}
19	0.765	0.025	0.100	0.069	0.066	1.2×10^{-23}	8.2×10^{21}
20	0.765	0.0125	0.111	0.058	0.056	5.1×10^{-24}	8.2×10^{21}
21	0.765	0.00625	0.121	0.048	0.046	2.3×10^{-24}	8.2×10^{21}
22	0.765	0.00313	0.130	0.039	0.037	1.2×10^{-24}	8.6×10^{21}
23	0.503	0.140	0.025	0.144	0.147	4.1×10^{-21}	13.7×10^{21}
24	0.503	0.070	0.057	0.112	0.113	3.4×10^{-22}	11.3×10^{21}
25	0.503	0.035	0.073	0.096	0.095	9.3×10^{-23}	10.4×10^{21}
26	0.503	0.0175	0.086	0.083	0.082	3.6×10^{-23}	10.2×10^{21}
27	0.503	0.00875	0.097	0.072	0.072	1.5×10^{-23}	10.2×10^{21}
28	0.503	0.00438	0.106	0.063	0.062	7.1×10^{-24}	1.0×10^{21}
29	0.503	0.00219	0.116	0.053	0.052	3.4×10^{-24}	10.2×10^{21}
30	0.251	0.035	0.027	0.142	0.142	3.6×10^{-21}	9.3×10^{21}
31	0.251	0.0175	0.043	0.126	0.128	1.0×10^{-21}	8.2×10^{21}
32	0.251	0.00875	0.057	0.112	0.110	3.4×10^{-22}	8.6×10^{21}
33	0.251	0.00438	0.067	0.102	0.099	1.5×10^{-22}	8.4×10^{21}
34	0.251	0.00219	0.077	0.092	0.089	7.1×10^{-24}	8.0×10^{21}
						Mean,	9.7×10^{21}

The value for m was calculated from the concentration cell consisting of solutions 7 and 8 by substituting the values in equation (14) as follows:

$$m = \frac{0.0295}{0.009} \log. \frac{0.00625}{0.00313} = 0.99.$$

Values approximately 1 are also obtained by calculating m from the concentration cells consisting of solutions 14 and 15, 21 and 22, 28 and 29, 32 and 34.

The value for n may now be obtained from any concentration cell where the concentration of the SCN^- ions in the two solutions is different, for example from the cell consisting of solutions 1 and 7. It is found to be approximately equal to 2, and the formula of the complex ion is therefore $Hg(SCN)_4^{--}$. The constancy of the K_1 values, and the good agreement of the measured electromotive forces with those calculated under this assumption as to the complex ion show conclusively the existence of this complex throughout this whole range of concentration.

This conclusion is in agreement with that drawn from all the other methods employed except the freezing-point determinations at the higher potassium sulphocyanate concentrations (see Sec. III), where there were indications, though probably unreliable ones, that *m* was equal to 2 and *n* equal to 4. To see whether the complex really had polymerized at 0°, electromotive force measurements were made at that temperature with the following results:

TABLE VII.—TEMP. 0° C.

Sol. No.	Conc. KSCN.	Conc. $Hg(SCN)_2$.	E. M. F. against normal electrode.	E. M. F. against Sol. No. 1.	
				Measured.	Calculated.
1	1.02	0.200	0.094	0.000	0.000
2	1.02	0.100	0.115	0.021	0.023
3	1.02	0.050	0.128	0.034	0.038
4	1.02	0.025	0.139	0.045	0.051
5	1.02	0.0125	0.148	0.054	0.061
6	1.02	0.00625	0.157	0.063	0.069
7	1.02	0.00313	0.166	0.072	0.077

Here, as before, the calculated values of the electromotive force are found to agree well with the measured ones when it is assumed that $m = 1$ and $n = 2$, and we may draw the conclusion that here as well as at 25° the complex $Hg(SCN)_4^{--}$ is the only one which exists to an appreciable extent in the solution.

When mercurous sulphocyanate is present as a solid phase in a potassium mercuric sulphocyanate solution, it is possible by using the concentration of the mercurous ions in the normal electrode (see above) to calculate its solubility product; for the SCN^- ion concentration is known, and the Hg_2^{-} ion concentration may be calculated from the electromotive force measurement.

Furthermore, the solubility of mercuric sulphocyanate in any particular strength of potassium sulphocyanate may be calculated from electromotive force measurements and from the stability constant K_1, by solving for *c* in the equation

$$K_1 = \frac{\frac{c}{m}}{[Hg^{++}]\left(a - \frac{n}{m}c\right)^{2m+n}},$$

and this calculated value of the solubility compared with that analytically determined. Table VIII contains the results of such measurements and calculations with two solutions of potassium sulphocyanate saturated with mercuric sulphocyanate.

TABLE VIII.—TEMP. 25°.

Concentration. KSCN. *a*.	E. M. F. against normal electrode.	Conc. Hg^{++}.	Conc. Hg_2^{++}.	Solubility of $Hg(SCN)_2$. Analytically determined.	Solubility of $Hg(SCN)_2$. Calculated.	Sol. product. $[Hg_2^{++}] \times [SCN^-]^2$.
0.50	0.028	3.3×10^{-21}	4.0×10^{-19}	0.14	0.13	1.9×10^{-20}
0.25	0.018	7.1×10^{-21}	8.5×10^{-19}	0.055	0.045	1.7×10^{-20}

The agreement between the fifth and sixth columns is further evidence of the existence of the complex $Hg(SCN)_4^{--}$.

From the solubility product (s. p.) of $Hg_2(SCN)_2$ may be calculated the concentration of the mercurous ions in a saturated solution of this salt in pure water, which is identical with its solubility if complete dissociation be assumed, for in pure water

$[SCN^-] = 2[Hg_2^{++}]$ and therefore s. p. $= 4[Hg_2^{++}]^3$ or

$$[Hg_2^{++}] = \sqrt{\frac{\text{s. p.}}{4}} = \sqrt[3]{\frac{1.8 \times 10^{-20}}{4}} = 1.7 \times 10^{-7}$$

VI. COMPARISON OF THE RESULTS WITH THOSE OBTAINED WITH THE MERCURIC HALIDE COMPLEXES.

A comparison of the stability constants of the various mercuric complexes thus far investigated shows the relative tendency of the halogens and of the cyanogen and sulphocyanogen groups to form complexes. These constants are brought together in the following table.

TABLE IX.

Complex salt.	Stability constant.[1]
K_2HgCl_4	1.6×10^{16}
K_2HgBr_4	7.7×10^{21}
$K_2Hg(SCN)_4$	9.7×10^{21}
K_2HgI_4	3.5×10^{30}
$K_2Hg(CN)_4$	4.6×10^{41}

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[1] The stability constants for the chloride, bromide, iodide and cyanide complexes were recalculated from the values given by Sherrill (*Loc. cit.*), using the concentration of mercurous ions in the normal electrode obtained by Ley and Heimbucher (*Loc. cit.*).

According to the above table, the tendency towards complex formation increases in the following order: Cl, Br, SCN, I, CN. Grossman,[1] from a large collection of qualitative data, and Bodländer and Eberlein,[2] by comparing the stability constants of the corresponding complex silver salts, have arrived at the same conclusion.

According to Abegg and Bodländer[3] with different salts of the same metal, the solubility as a rule increases with increasing electroaffinity of the anion. The order of decreasing solubility should therefore be the same as that of increasing stability of the complex.

The following table shows the solubility in water of the mercurous salts, the salts being arranged in the order of decreasing solubility.

TABLE IX.

Cl.[4]	SCN.	Br.[5]	I.[5]
0.8×10^{-6}	1.6×10^{-7}	5.6×10^{-8}	2.5×10^{-10}

Here, as Bodländer and Eberlein[6] also found by comparing the solubility products of the silver halides, Br and SCN have reverse positions from what they do in the series of the stability constants of the complex, but, as the differences in the two values are not large in either case, this is not a serious anomaly.

VII. SUMMARY.

The existence in aqueous solution of a complex salt of the composition $K_2Hg(SCN)_4$ has been shown by a number of physicochemical methods. Its degree of stability has been determined, and incidentally the solubility-product of mercurous sulphocyanate has been deduced.

1. The increase of solubility of mercuric sulphocyanate caused by the addition of potassium sulphocyanate was found, when expressed in mols per liter, to be always approximately equal to one-half of the number of mols of potassium sulphocyanate added. This indicated in saturated solutions the quantitative formation of a complex of the general formula

$$K_{2m}Hg_m(SCN)_{4m}.$$

2. The change of the freezing-point of moderately dilute solu-

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Ztschr. anorg. Chem., **37**, 433 (1903).

[2] *Ibid.*, **39**, 238 (1904).

[3] *Ibid.*, **20**, 458 (1899).

[4] Ley and Heimbucher (*Loc. cit.*).

[5] Recalculated from values of Sherrill (*Loc. cit.*).

[6] *Loc. cit.*

tions of potassium sulphocyanate caused by the addition of varying amounts of mercuric sulphocyanate was found to correspond to a removal from the solution of one mol for every mol of mercuric sulphocyanate added. This, taken in conjunction with the preceding conclusion, can be explained only by the formation of the complex $K_2Hg(SCN)_4$.

3. The solubility of mercurous sulphocyanate in potassium sulphocyanate was determined. This solubility results in virtue of the following reactions:

$$Hg_2(SCN)_2 \rightleftarrows Hg(SCN)_2 + \mathbf{Hg},$$

$$m\ Hg(SCN)_2 + n\ SCN^- \rightleftarrows (Hg(SCN)_2)_m(SCN^-)_n\,.$$

The law of mass acton therefore requires that, when mercurous sulphocyanate as solid phase is in equilibrium with a solution of potassium sulphocyanate, the following equation must hold.

$$\frac{[(Hg(SCN)_2)_m(SCN^-)_n]}{[SCN^-]^n} = K_1[Hg(SCN)_2]^m = K$$

Since mercuric sulphocyanate is but slightly soluble in water, the total amount of mercuric salt in solution may be taken as a measure of the concentration of the complex. It is therefore possible by assuming the existence of any one complex, to calculate K from the solubility of the mercurous salt and the concentration of the potassium sulphocyanate. From the solubility of mercurous sulphocyanate in different concentrations of potassium sulphocyanate, the best constancy of the K values was obtained by assuming the complex to be $K_2Hg(SCN)_4$.

4. By measuring the electromotive force of concentration cells of the type

$$\mathbf{Hg}/\left(\underset{\text{Conc. 1.}}{Hg(SCN)_2 + KSCN}\right) / \left(\underset{\text{Conc. 2.}}{KSCN + Hg(SCN)_2}\right)/\mathbf{Hg},$$

and applying the law of mass action to the results, the formula of the complex salt was also found to be $K_2Hg(SCN)_4$.

5. From the electromotive force of such solutions measured against the normal calomel electrode, in which the concentration of the mercury ions is known, the concentration of the mercuric ions in the solution in question could be calculated, and from this was derived the stability-constant of the complex, which is defined by the equation

$$K = \frac{[Hg(SCN)_4^{--}]}{[Hg^{++}][SCN^-]^4}$$

The constancy of this expression gave evidence of the existence of the above complex salt throughout the whole range of concentration taken.

6. A comparison of the value of this stability-constant (9.7×10^{21}) with those of the corresponding mercuric halide complexes showed that the relative tendency of the halogens and of the cyanogen and sulphocyanogen groups to form complexes increases in the following order: Cl, Br, SCN, I, CN.

7. In solutions where the mercury electrode caused precipitation of mercurous sulphocyanate, the concentration of the mercurous ions was calculated from the electromotive force measured against the normal electrode. The concentration of SCN— ions in such solutions was calculable from the concentration of the potassium sulphocyanate and the solubility of the mercurous salt. From these two values the solubility product of mercurous sulphocyanate,

$$[Hg_2^{++}]\,[SCN^-]^2, \text{ was calculated to be } 1.8 \times 10^{-20}.$$

In conclusion we wish to express to Prof. A. A. Noyes our sincere thanks for his friendly interest in the investigation, and for the material assistance he has given us.

MOLECULAR WEIGHT DETERMINATIONS BY MEANS OF PLATINUM THERMOMETERS.

BY H. T. BARNES, E. H. ARCHIBALD AND D. McINTOSH.

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IN the course of an extended investigation on the properties of liquefied gases, we found it necessary to determine the molecular weights of some substances dissolved in these liquids for the purpose of comparison with conductivity measurements; and since these measurements were to be made at temperatures as low as —80 C., we were compelled to modify the apparatus ordinarily used.

We have, therefore, used platinum thermometers; and as these have only, so far as we are aware, been employed in determinations of the rise in boiling-point by Noyes[1] and Abbott and that by a different method, we give here a description of our apparatus and some results of determinations of the molecular weights of inorganic salts when dissolved in water.

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[1] *Ztschr. phys. Chem.*, **23**, 63 (1897).