

shall not be able to bring the discussion to a conclusion on this point.

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Summary

The chemical potentials and partial molar entropies of mixing for lead in liquid lead-gold mix-

tures have been determined by the electromotive force method for compositions up to 79 atomic per cent. gold.

From these data have been calculated for both components activities at 600°, "entropy fractions," and relative partial and integral molar heats of mixing. It was found that the deviation of this mixture from Raoult's law can be largely attributed to a non-ideal entropy of mixing.

The heat and free energies of formation for Au₂Pb(s) from liquid lead and undercooled liquid gold at about 400° were calculated using information from the established equilibrium phase diagram of Au-Pb and from this investigation.

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[CONTRIBUTION FROM GOESSMANN CHEMISTRY LABORATORY, UNIVERSITY OF MASSACHUSETTS]

Composition of Ferric Thiocyanate at High Concentrations

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Several recent investigations²⁻⁵ have established by a variety of methods that in dilute solution the composition of the ferric thiocyanate complex is FeSCN⁺⁺. Møller⁶ used conductivity measurements to identify complexes such as Fe(SCN)₂⁺ and Fe(SCN)₄⁻, in more concentrated solutions. In an earlier study Schlesinger and Van Valkenburg⁷ had concluded that Fe(SCN)₆⁼ was responsible for the red color of ferric thiocyanate solutions on the basis of boiling point elevation and freezing point depression data and absorption spectra.

It has been the purpose of this investigation to study the formation of higher ferric thiocyanate complexes at high concentrations by means of the spectrophotometer, using the method developed by Job⁸ and modified by Vosburgh and Cooper.⁹ Gould and Vosburgh⁶ used this method of continuous variations and found the 1:1 complex at low concentrations, but the method has never been applied to high concentrations of ferric thiocyanate probably because of the very intense color of a concentrated solution. This intense color made necessary the use of very thin absorption cells and the development of a technique for handling these cells.

(1) From a thesis submitted in June, 1948, by Stanley E. Polchlopek to the Graduate School of the University of Massachusetts in partial fulfillment of the requirements for the degree of Master of Science.

(2) Bent and French, *THIS JOURNAL*, **63**, 568 (1941).

(3) Edmonds and Birnbaum, *ibid.*, **63**, 1471 (1941).

(4) Frank and Oswalt, *ibid.*, **69**, 1321 (1947).

(5) Gould and Vosburgh, *ibid.*, **64**, 1630 (1942).

(6) Max Møller, "Studies on Aqueous Solutions of Ferric Thiocyanate," Dana Bogtrykkeri, Copenhagen, 1937.

(7) Schlesinger and Van Valkenburg, *THIS JOURNAL*, **53**, 1212 (1931).

(8) Job, *Ann. chim.*, (10) **9**, 113 (1928).

(9) Vosburgh and Cooper, *THIS JOURNAL*, **63**, 437 (1941).

Experimental

Ferric nitrate and potassium thiocyanate were selected as reactants to avoid the formation of other complexes. The ferric nitrate solutions were standardized against sulfato-ceric acid; the potassium thiocyanate solutions were standardized against silver nitrate. Potassium nitrate solutions were used to maintain constant ionic strength whenever possible. The determinations on 0.1 and 0.25 *M* solutions were made with the potassium thiocyanate solutions brought to the ionic strength and pH of the ferric nitrate. Check determinations were made without bringing the potassium thiocyanate to the pH of the ferric nitrate and it was found that the absorption maxima remained the same as with the pH adjusted potassium thiocyanate. In 1.0 *M* solutions it was not possible because of solubility considerations to bring potassium thiocyanate to the same ionic strength as the ferric nitrate and only the pH was adjusted. In the 2.0 *M* solutions studied neither the pH nor the ionic strength were adjusted. It should be noted that with the high acidity of the thiocyanate solution measurements of optical density had to be made immediately because of the instability of these solutions.

Absorption spectra were determined for solutions in which the ratio of iron(III) to thiocyanate ranged from 1:1 to 1:6 at 0.1 and 0.25 *M* concentrations. These spectra were determined by keeping the volume of the iron(III) solution constant and increasing the volume of thiocyanate. In order that the final volume of ferric thiocyanate be the same for each determination after mixing the components a potassium nitrate solution of the same ionic strength and pH was added each time in appropriate volume.

The absorption measurements were taken with a Beckman D. U. Quartz Spectrophotometer. The band widths used in the determinations ranged from 0.8 *mμ* of spectrum at a wave length of 400 to 4 *mμ* of spectrum at a wave length of 600 *mμ* according to data supplied by the manufacturer. The absorption cells used in these measurements were made from "special grade, colorless" microscope slides (A. H. Thomas Co.). Two thin slips of a plastic sheet (or thin cover glasses) were sandwiched between the microscope slides in such a manner that the plastic or glass separators were at both ends of the cell and the center area could be filled with liquid. The cells were clamped at both ends with spring back metal paper clamps. The

plastic separators used were approximately 0.0038 cm. thick and the glass separators were approximately 0.020 cm. Cells of like construction were used with distilled water to adjust the instrument at each wave length.

The slides used were cleaned by immersion in hot sulfuric acid-potassium dichromate cleaning solution, and then rinsed in several detergents and distilled water. If the water drained evenly and readily from the slide, it was accepted as clean. The slide was then polished with lens paper and handled through lens paper throughout the process of assembly. The plastic film and cover glasses used as separators were never touched by hand.

A cell so constructed was filled by capillarity with the ferric thiocyanate introduced into the top of the cell from a pointed medicine dropper. This procedure was found to fill the cell immediately and completely. That the cell was filled uniformly was indicated by the fact that optical density measurements on the same solution and at a specified wave length remained constant regardless of the position of the cell. It was noted that on standing the solution tended to flow slowly out of the cell. It was, therefore, necessary to refill the cell at more or less regular intervals. This was done by introducing the solution at the top of the cell slowly enough so that it completely replaced the original solution which was thus caused to drain out. These flushings had to be carried out very carefully in order not to soil the optical surface of the cell, for the cells could not be cleaned except by complete dismantling. Measurements on solutions of a given series were carried out in the same cell in order to better control the variables in the investigation. For the same reason in order to eliminate any possible effects which might be attributed to fading, all readings of optical density were taken immediately after mixing and, as with Frank and Oswalt's⁴ investigation, no evidence of fading was found in freshly prepared solutions.

It must be noted that the absorption cells used in this investigation varied in thickness because the solution placed in the cell often formed a thin film over the separators, causing a very slight displacement. No way to overcome this difficulty was found, and consequently the values for the optical densities of the solution varied very slightly every time a new cell was used. The flushing technique proved so satisfactory, however, that it was possible to use the same cell for getting at least two sets of data for either a continuous variation study or an absorption spectrum without dismantling the cell. So long as the same cell was used, the variations in optical density were no more than those normally encountered when using standard one-cm. cells. The determinations of optical density were repeated several times, and the data presented represent the average of at least three determinations. It was observed that the data for any one study always gave the same shaped curves with the maxima occurring in the same place regardless of any slight variation of the thickness of the cells used.

Results and Discussion

Figure 1 presents the absorption curves for volume ratios of 1:1 to 1:6 of 0.100 *M* iron(III) to 0.100 *M* thiocyanate and indicates that maximum absorption does not occur at the same wave length for each ratio. It was determined that the absorption due to ferric nitrate was negligible at wave lengths higher than 350 $m\mu$ with the very thin cells used. This obviated the necessity of corrections for the absorption due to ferric ion at the wave lengths used. Since the total volume for each determination was kept the same by the addition of appropriate volumes of potassium nitrate of equivalent ionic strength, the absorption curves illustrate the mass action effect, and the change in the absorption may be attributed directly to the increase in the thiocyanate concen-

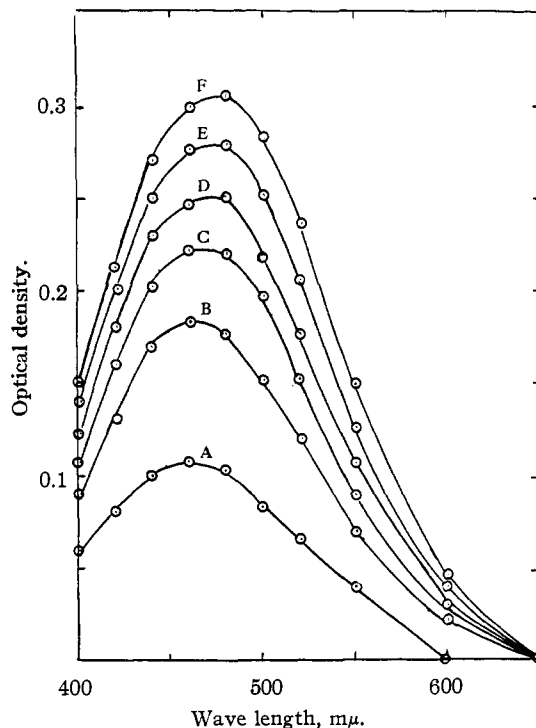


Fig. 1.—Absorption spectra of 0.100 *M* ferric nitrate and 0.100 *M* potassium thiocyanate mixed in ratios of 1:1 (A), 1:2 (B), 1:3 (C), 1:4 (D), 1:5 (E) and 1:6 (F). Iron(III) concentration was constant at 0.0143 *M*. Both solutions were at *pH* 1.7 and ionic strength 0.6. Constant volume was maintained by adding potassium nitrate of like *pH* and ionic strength in approximate amounts. The absorption cell was 0.0038 cm.

tration. It was anticipated, and found, in view of the low stability of ferric thiocyanate, that absorption would increase as the concentration of thiocyanate increased. The shift in absorption maximum suggests that at high concentrations of thiocyanate higher complexes are being formed.

Because the absorption spectra show no tendency to intersect, the rules worked out by Vosburgh and Cooper⁹ for the selection of wave lengths for a continuous variation study do not apply. The wave lengths used for the continuous variations study were those at which maximum absorption was noted and in addition several wave lengths on both sides of the maximum.

The results of the continuous variations studies for 0.100 *M* solutions are presented in Fig. 2. The fact that the maximum falls at a fraction of approximately 0.4 for iron and 0.6 for thiocyanate indicates presumably that 1.5 thiocyanate ions are associated with each ferric ion. A preferable interpretation is that the ferric thiocyanate solution resulting from mixing solutions of 0.100 *M* ferric nitrate and potassium thiocyanate contains not only the 1:1 complex but other, higher, complexes such as the 1:2.

A study of 0.250 *M* solutions of ferric nitrate

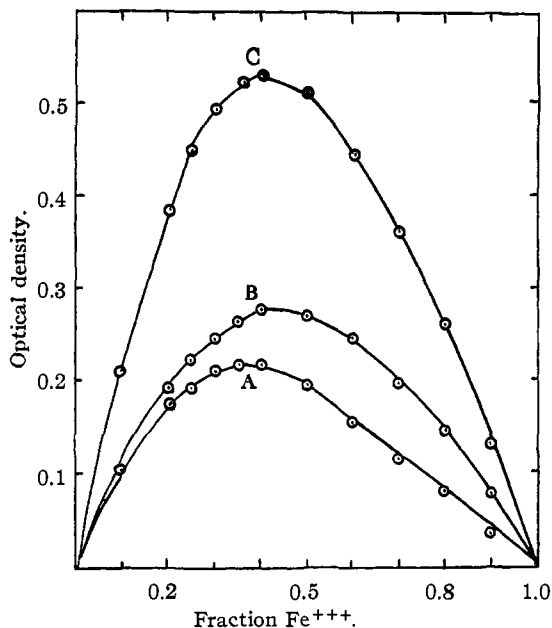


Fig. 2.—Continuous variations studies with 0.100 *M* ferric nitrate and 0.100 *M* potassium thiocyanate, each at *pH* 1.7 and ionic strength 0.6 at wave lengths of 550 $m\mu$ (A), 400 $m\mu$ (B) and 480 $m\mu$ (C). Data for wave lengths of 450 and 500 $m\mu$ follow similar plots. The absorption cell was 0.0038 cm.

and potassium thiocyanate showed (Fig. 3) that the absorption increases and the maximum shifts to higher wave lengths as the ratio of thiocyanate to iron(III) increases, thus again illustrating the mass action effect. The continuous variation study on the same solutions (Fig. 4) indicates that the maximum occurs at almost the same

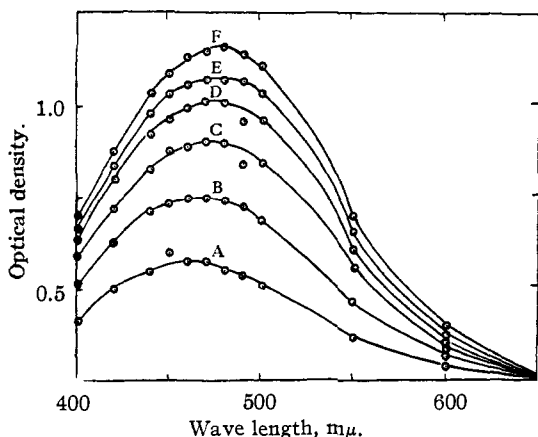


Fig. 3.—Absorption spectra of 0.250 *M* ferric nitrate and 0.250 *M* potassium thiocyanate each at *pH* 1.45 and ionic strength 1.5 mixed in ratios of 1:1 (A), 1:2 (B), 1:3 (C), 1:4 (D), 1:5 (E) and 1:6 (F). Iron(III) concentration was constant at 0.0357 *M*. Constant volume was maintained by adding potassium nitrate of like *pH* and ionic strength in appropriate amounts. The absorption cell was 0.0038 cm.

point as with the 0.100 *M* solutions, again indicating that the solution contains a mixture of complexes.

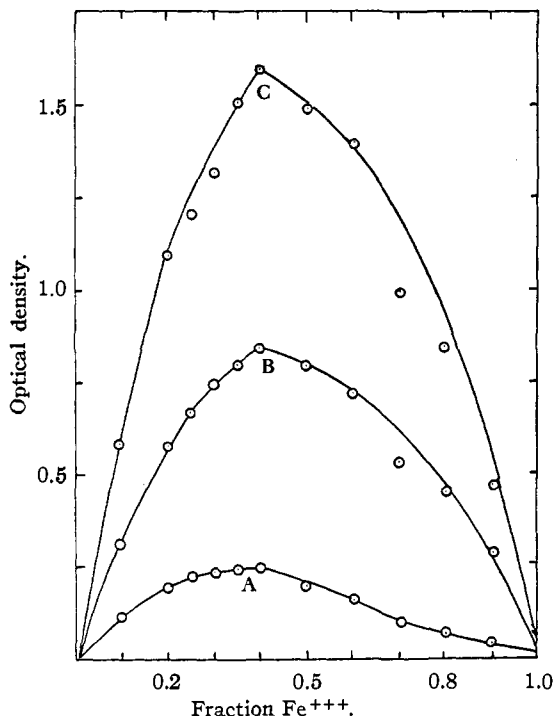


Fig. 4.—Continuous variations studies with 0.250 *M* ferric nitrate and 0.250 *M* potassium thiocyanate each at *pH* 1.45 and ionic strength 1.5 at wave lengths of 600 $m\mu$ (A), 400 $m\mu$ (B), and 450 $m\mu$ (C). Data for wave lengths of 500 and 550 $m\mu$ follow similar plots. The absorption cell was 0.0038 cm.

The optical densities of one and two molar solutions were so high that complete absorption data could not be obtained even with the thin cells used. Consequently, in order to study continuous variation, it was necessary to go to the longer wave lengths. Figure 5 shows the maximum for one molar solution at a ratio of thiocyanate to iron(III) of slightly more than 2:1. In other words, while the presence of some FeSCN^{++} cannot be denied, it appears that the solution contains considerable $\text{Fe}(\text{SCN})_2^+$ and that even higher complexes are present. A study of two molar solutions showed substantially the same thing, as indicated by Fig. 6. The ratio of thiocyanate to iron(III) at the maxima is slightly higher than for the one molar solutions. In the very concentrated solutions $\text{Fe}(\text{SCN})_2^+$ is probably predominant. To check the effect of dilution, samples of the concentrated ferric thiocyanate solutions were occasionally diluted to 0.02 and 0.001 *M* and, as in earlier investigations,^{2,3,4,5} only FeSCN^{++} was found. Doubtless this is the predominant complex involved in colorimetric determinations of iron(III) where thiocyanate concentrations are generally very low.

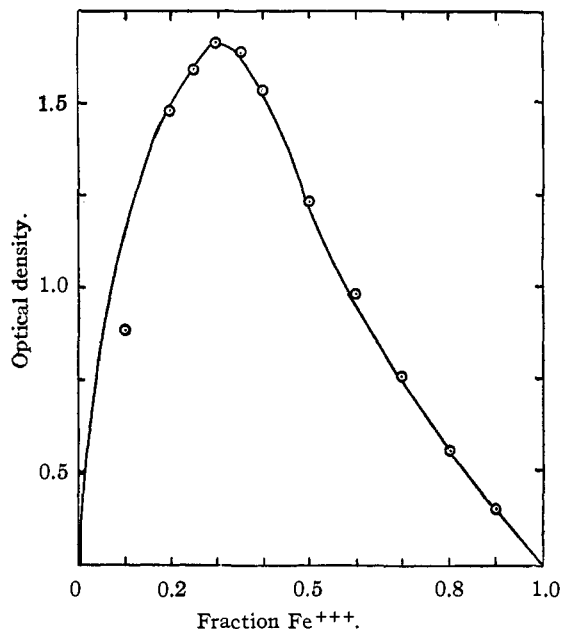


Fig. 5.—Continuous variations study using 1.000 *M* ferric nitrate and 1.000 *M* potassium thiocyanate, each at pH 0.75 at 600 $m\mu$. Ionic strength was not controlled. The absorption cell was 0.0038 cm.

Summary

1. Absorption spectra of ferric thiocyanate solutions with ferric ion at 0.0143 and 0.0357 molar and iron(III) to thiocyanate concentration ratios from 1:1 to 1:6 were determined, and are herewith presented. A shift of the absorption maximum toward longer wave lengths as the thiocyanate concentration is increased is noted and interpreted as an indication of higher complexes than FeSCN^{++} which is found in dilute solution.

2. Data obtained by the method of continuous variations are presented which establish the existence of higher complexes. Definite evidence for higher complexes is found even at concentrations no higher than a few hundredths molar. The complex $\text{Fe}(\text{SCN})_2^+$ is indicated as predominant in the 0.5 to 1.0 molar concentration range.

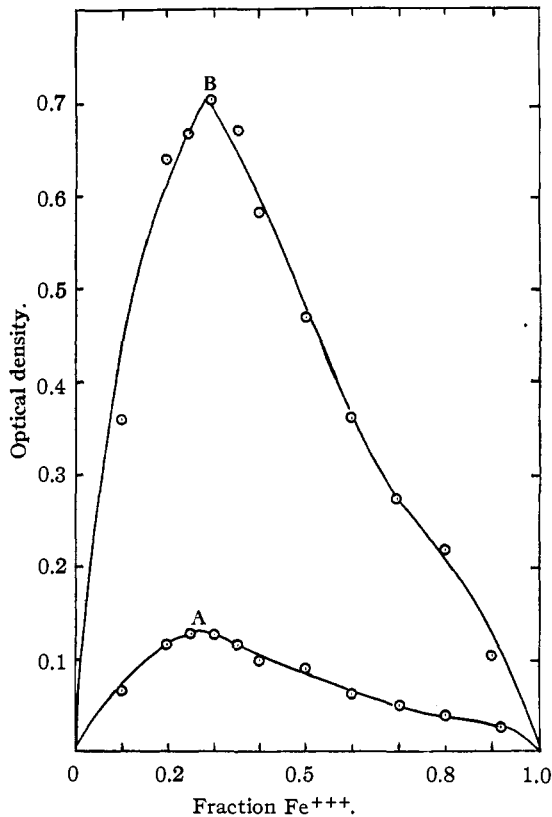


Fig. 6.—Continuous variations study using 2.000 *M* ferric nitrate and 2.000 *M* potassium thiocyanate at 700 $m\mu$ (A) and 650 $m\mu$ (B). Ionic strength and pH were not controlled. The absorption cell was 0.0038 cm.

Evidence for still higher complexes is presented.

3. In view of the complexity of the ferric thiocyanate system at the concentrations studied, no attempt was made to determine equilibrium constants. The several complexes apparently present in any given solution have absorption bands which overlap to such an extent as to make the study of any one particular higher complex extremely difficult, if not impossible, with a spectrophotometric method.