

THE DISTRIBUTION OF SULFURIC ACID BETWEEN WATER AND KEROSENE SOLUTIONS OF TRI-*n*-OCTYLAMINE AND TRI-*n*-HEXYLAMINE¹

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In this paper a description is given of the distribution of sulfuric acid between water and a kerosene solution with tri-*n*-octylamine or tri-*n*-hexylamine. Assuming ideality in the organic phase no evidence could be obtained that the law of mass action underlies the fundamental processes. Assuming aggregation of the amine salt to a micelle of constant activity a qualitative agreement is found and the empirical formula $K_A = a_{H_2SO_4}[\text{amine}]^n$ seems to be of general interest, the power n changing at inflection points in the titration curves of the weak base anion-exchanger. In the range of acidities where no free amine exists a treatment based on mixed crystal equilibrium between amine sulfate and amine bisulfate leads to results which are much the same for both amines. An empirical formula $K_B = (1/a_{H_2SO_4})(X^2/(1-X))^n$ with X as the mole fraction of the amine bisulfate describes the system.

Introduction

In a previous article⁴ it was shown that the distribution of sulfuric acid between water and benzene solutions of tri-*n*-octylamine (TOA) or tri-*n*-hexylamine (THA) could be based on the formation of the sulfates $(\text{TOAH})_2\text{SO}_4$ or $(\text{THAH})_2\text{SO}_4$.

If it was assumed that the concentrations in the organic phases were equal to the activities the law of mass action gave a satisfactory description of the results, until a certain amine sulfate concentration was reached and deviations occurred. The results were in reasonable agreement with those given by Allen⁵ who explained the deviations as being due to aggregation of the amine salt to micelles.^{5,6}

In the present study it is shown that the processes underlying the distribution show remarkable differences when the benzene is replaced by kerosene.

Experimental

The commercial products TOA and THA are distilled at 1–2 mm. The boiling points are 182–186° and 118–121°, respectively. During the distillation of TOA the fore-run solidifies in the collector. This is probably di-*n*-octylamine. The molecular weight of the main fraction of TOA (boiling range < 2°) is determined by means of potentiometric titration with standard perchloric acid in a benzene–water–alcohol medium. It is found to be 351.6. Assuming that the impurity is di-*n*-octylamine, this value is in agreement with a percentage of 98.6% TOA. The molecular weight of the main fraction of THA is determined as being 278.5. No attempts were made to investigate if the iso-derivatives were present. In all distribution measurements once-distilled amines were used.

Samples of both THA and TOA were exposed to the laboratory atmosphere for three days. No change in weight could be observed and potentiometric titration with standard perchloric acid in a benzene–alcohol–water medium before and after exposure did not show any significant difference.

Ten ml. of a 0.098 *M* amine solution in kerosene,⁷ modified

with 4 vol. % *n*-octyl alcohol to prevent third phase formation, were brought into contact with the same volume of aqueous phases containing known amounts of sulfuric acid (C_i).

We did not find the anomalous behavior which was reported by Allen and McDowell⁸ for the case of uranium extraction. To the aqueous phases, which were brought into contact with the kerosene solution of THA, 0.33 *M* Na_2SO_4 was added to prevent dissolution of the formed $(\text{THAH})_2\text{SO}_4$ in the aqueous phase.

Equilibrium was achieved by means of centrifugal stirring for 1 minute. Thirty minutes after equilibration the layers were separated and the acid content of the water layer (C_t) was determined by means of potentiometric titration using either 0.1 *M* or 0.02 *M* NaOH. To verify the material balance in some cases the organic loading C_o was determined by stripping the acid from the kerosene phases with sodium hydroxide and titrating back the excess alkali.

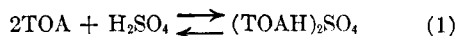
It was found that

$$C_o = C_i - C_t$$

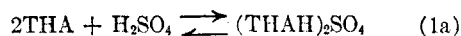
within 1%. From this it might be concluded that the change in volumena is small (unless the changes in the volumena during both extractions compensated each other). Indeed no change in volumena could be detected by measurement after equilibration. From the neutralization curves of the aqueous phases no evidence could be obtained that amine sulfate dissolves in the aqueous phases, if, in the THA case, the salting out agent Na_2SO_4 was added. All experiments were performed at $20 \pm 2^\circ$.

Results

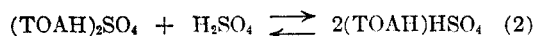
If it is assumed that the reaction between amine and sulfuric acid taking place at the interface is analogous to the reaction between H_2SO_4 and NH_3 , we may write



and



At higher acidities the equilibria could be represented as



If it is assumed that the concentrations in the organic phases are equal to the activities we could write for the equilibrium constants of eq. 1, 1a

$$K_o = \frac{[(\text{TOAH})_2\text{SO}_4]}{[\text{TOA}]^2 a_{\text{H}_2\text{SO}_4}} \quad (3)$$

and

$$(8) \text{ K. A. Allen and W. J. McDowell, } J. \text{ Phys. Chem., } \mathbf{64}, 877 \text{ (1960).}$$

(1) The work, described in this article, forms part of the program of RCN (Reactor Centrum Nederland), The Hague. The experimental results have been obtained in the Laboratory for General and Inorganic Chemistry of the University of Amsterdam.

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(4) J. M. P. J. Versteegen and J. A. A. Ketelaar, *Trans. Faraday Soc.*, **57**, 1527 (1961).

(5) K. A. Allen, *J. Phys. Chem.*, **60**, 239 (1956).

(6) K. A. Allen, *ibid.*, **60**, 943 (1956).

(7) The kerosene used in our experiments was furnished by the Amsterdamsche Chininefabriek. Some physical and chemical properties are: s.w. (at 24°) = 0.778, refractive index n_D^{20} 1.431, boiling range 195–240°, aromates <0.5%.

$$K_e^* = \frac{[(\text{THAH})_2\text{SO}_4]}{[\text{THA}]^2 a_{\text{H}_2\text{SO}_4}} \quad (3a)$$

with brackets denoting activities and $a_{\text{H}_2\text{SO}_4} = 4\gamma_{\pm}^3 C_f^3$.

The sulfuric acid activity which has to be substituted in equation 3 is the activity of the acid in a pure aqueous solution. Values of the mean ionic molal activity coefficient γ_{\pm} can be found in Harned and Owen.⁹ Molarities C_f are obtained from our experiments and as molarities and molalities do not differ very much in our range of concentrations they are combined with γ_{\pm} . Consequently all activities $a_{\text{H}_2\text{SO}_4}$ are expressed in (mole/l.)³. When logarithms are plotted $\sqrt[3]{a_{\text{H}_2\text{SO}_4}}$ is used.

$$\sqrt[3]{a_{\text{H}_2\text{SO}_4}} = 1.59 \gamma_{\pm} C_f \text{ mole/l.}$$

The sulfuric acid activity in equation 3a is the activity in the presence of 0.33 *M* sodium sulfate. Harned and several others¹⁰⁻¹³ calculated from e.m.f. measurements the activity coefficients of sulfuric acid in the presence of several alkali sulfates M_2SO_4 .

The reactions (1, 1a) predominate at low acidities ($C_f < 0.03$ *M*). Thus the formation of $(\text{THAH})_2\text{SO}_4$ according to eq. 1a occurs at about constant ionic strength. The mean ionic molal activity coefficient is taken as $\gamma_{\pm} = 0.22$. Reaction 2a predominates in a range of acidities where the activity coefficient changes from $\gamma_{\pm} = 0.21$ to $\gamma_{\pm} = 0.12$.

ΣTOA is introduced as the total tri-*n*-octylamine content, either in the sulfate, the bisulfate or the free amine form. In our case $\Sigma\text{TOA} = 0.098$ mole/l. When we plot $\sqrt[3]{a_{\text{H}_2\text{SO}_4}}$ vs. $C_0/\Sigma\text{TOA}$ and vs. $C_0/\Sigma\text{THA}$, respectively, the Figs. 1 and 1a are found.

Allen⁵ showed that the curve he obtained when using a 0.1 *M* solution of TOA in benzene showed resemblance to the titration curve of a weak base anion-exchange resin. In our case, the behavior of TOA is somewhat more complicated (Fig. 1), showing a second neutralization step, which starts at an activity $\sqrt[3]{a_{\text{H}_2\text{SO}_4}} \approx 1.4 \times 10^{-1}$ mole/l. The first neutralization step starts at an activity $\sqrt[3]{a_{\text{H}_2\text{SO}_4}} \approx 3.0 \times 10^{-3}$ mole/l. The THA curve (Fig. 1a) shows one neutralization step starting at $\sqrt[3]{a_{\text{H}_2\text{SO}_4}} \approx 9 \times 10^{-4}$ mole/l.

From our results no evidence could be obtained that K_e and K_e^* given in equations (2,2a) are constants. Thus, the law of mass action is not followed and the processes occurring must be explained on another basis. If it is assumed that the amine sulfates withdraw from the system under formation of a micelle with constant activity we may rearrange (2,2a) as

$$K_1 = [\text{TOA}]^2 a_{\text{H}_2\text{SO}_4} \quad (4)$$

and

$$K_1^* = [\text{THA}]^2 a_{\text{H}_2\text{SO}_4} \quad (4a)$$

However, when $\log a_{\text{H}_2\text{SO}_4}^{1/2}$ is plotted vs. $\log [\text{TOA}]$

(9) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," New York, N. Y., 1943.

(10) H. S. Harned and G. Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

(11) H. S. Harned and R. D. Sturgis, *J. Am. Chem. Soc.*, **47**, 945 (1925).

(12) G. Åkerlöf, *ibid.*, **48**, 1160 (1926).

(13) M. Randall and C. T. Langford, *ibid.*, **49**, 1447 (1927).

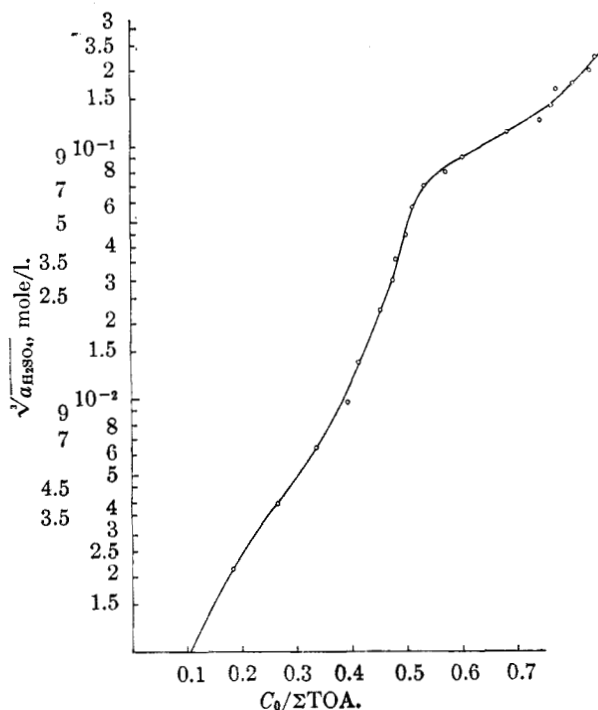


Fig. 1.—Anion-exchange titration curve for TOA.

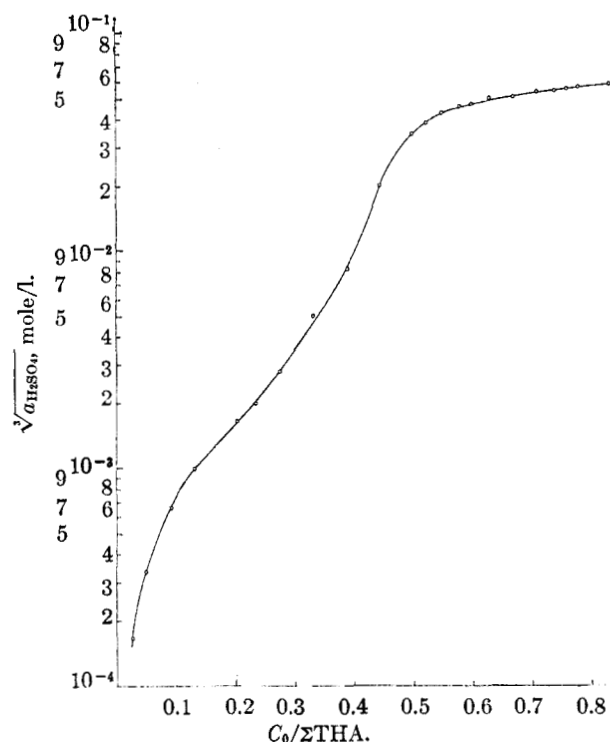
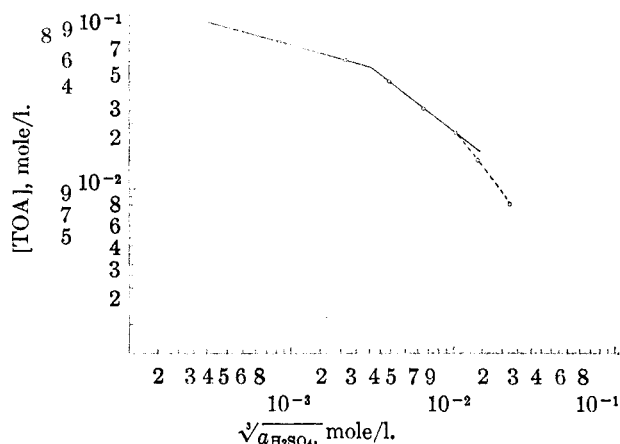
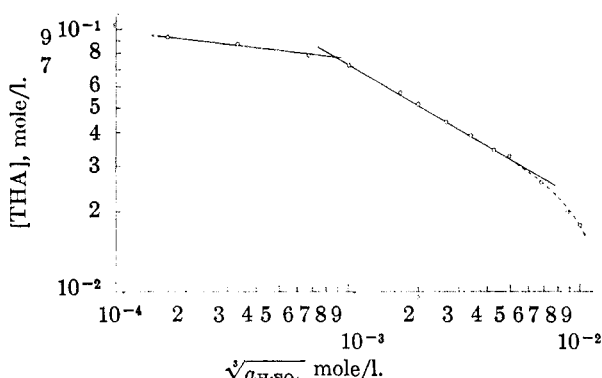


Fig. 1a.—Anion-exchange titration curve for THA in the presence of a salting-out agent (Na_2SO_4).

and $\log [\text{THA}]$, respectively, Figs. 2 and 2a are found. There is a qualitative agreement between both these figures but the straight lines obtained never correspond to a slope

$$\frac{d \log [\text{amine}]}{d \log a_{\text{H}_2\text{SO}_4}^{1/2}} = -3/2 \quad (5,5a)$$

which might be expected if equations 4 and 4a were followed. In the range of low acidities the slope obtained in Fig. 2 is found as

Fig. 2.—Free amine concentration [TOA] vs. $\sqrt{a_{\text{H}_2\text{SO}_4}}$.Fig. 2a.—Free amine concentration [THA] vs. $\sqrt{a_{\text{H}_2\text{SO}_4}}$.

$$\frac{d \log [\text{TOA}]}{d \log a^{1/2} \text{H}_2\text{SO}_4} = -1/3 \quad (6)$$

corresponding to an empirical constant

$$K_2 = a_{\text{H}_2\text{SO}_4} [\text{TOA}]^9 \quad (7)$$

with the numerical value

$$K_2 = 75 \times 10^{-21} (\text{mole/l.})^{12}$$

In the range of high acidities the slope is found to be equal to $-3/4$, according to an empirical constant

$$K_3 = a_{\text{H}_2\text{SO}_4} [\text{TOA}]^4 = 24 \times 10^{-14} (\text{mole/l.})^7 \quad (8)$$

In Fig. 2a the slope at low acidities is difficult to estimate and only can be given as

$$|1/12| < \frac{d \log [\text{THA}]}{d \log a^{1/2} \text{H}_2\text{SO}_4} < |1/8| \quad (6a)$$

or

$$K_2^a = a_{\text{H}_2\text{SO}_4} [\text{THA}]^n \quad (7a)$$

with $24 < n < 36$.

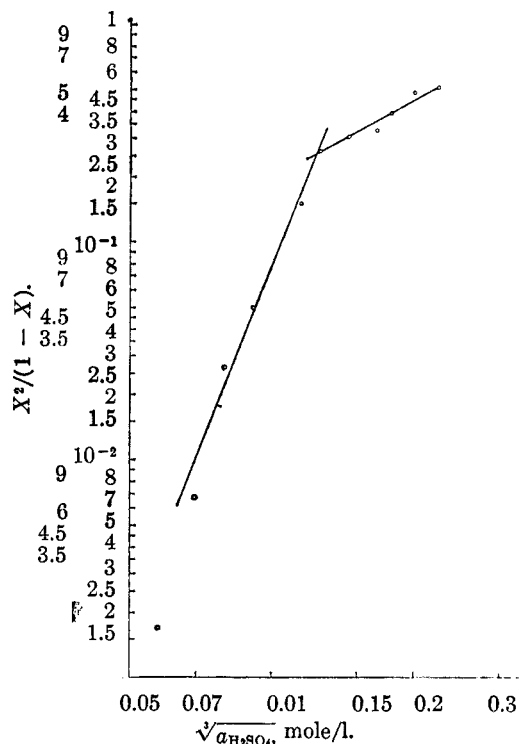
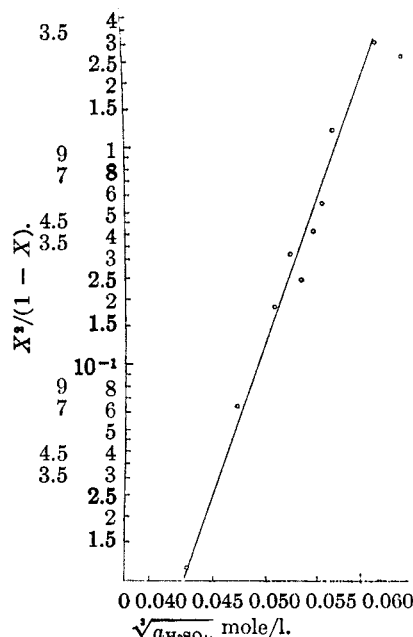
At high acidities it is found that the slope is equal to $-1/2$, or

$$K_3^a = a_{\text{H}_2\text{SO}_4} [\text{THA}]^6 \quad (8a)$$

with

$$K_3^a = 15 \times 10^{-9} (\text{mole/l.})^9$$

The changes in n in the formula $K_A = a_{\text{H}_2\text{SO}_4} [\text{amine}]^n$ take place at the activity at which the neutralization step in the titration curves (Fig. 1, 1a) starts. The readers attention might be drawn to the fact that the empirical formulas given in 7, 7a, 8 and 8a show a qualitative agreement with the results obtained from the distribution of H_2SO_4 be-

Fig. 3.— $X^2/(1 - X)$ vs. $\sqrt{a_{\text{H}_2\text{SO}_4}}$ for TOA.Fig. 3a.— $X^2/(1 - X)$ vs. $\sqrt{a_{\text{H}_2\text{SO}_4}}$ for THA.

tween water and a 0.100 M solution of TOA in benzene at 65° .⁴

The deviations from the Figs. 2 and 2a must be ascribed to the first formation of bisulfate. These deviations start at $[\text{THA}] < 0.030 M$ and at $[\text{TOA}] < 0.020 M$, in agreement with the greater basicity of THA, which was found previously.⁴ In the range of acidities where the equilibria mentioned under 2 and 2a are predominant another treatment must be chosen.

Allen⁶ already pointed out that it might be assumed that the normal amine sulfate and the amine bisulfate form a completely miscible ideal solution, which is analogous to the ideal solid solution of the components of a solid ion exchanger. In that case the activities of the resin species can be represented by their mole fraction X .

The equilibrium constants K and K_a of the equilibria 2 and 2a can be given as

$$K_x = \frac{X^2(\text{TOAH})\text{HSO}_4}{a_{\text{H}_2\text{SO}_4}X(\text{TOAH})_2\text{SO}_4} \quad (9)$$

with

$$X_{(\text{TOAH})\text{HSO}_4} = X = \frac{(\text{TOAH})\text{HSO}_4}{(\text{TOAH})\text{HSO}_4 + 2(\text{TOAH})_2\text{SO}_4} \quad (10)$$

and

$$X_{(\text{TOAH})_2\text{SO}_4} = 1 - X \quad (11)$$

and the same relations exist for THA.

Our K_x can be written now as

$$K_x = \frac{1}{a_{\text{H}_2\text{SO}_4}} \times \frac{X^2}{1 - X} \quad (9a)$$

Plotting $a^{1/2}_{\text{H}_2\text{SO}_4}$ vs. $X^2/(1 - X)$ for the TOA and the THA system, respectively, we find the Figs. 3 and 3a. There is again a qualitative agreement, but the form of the TOA Fig. 3 is somewhat more complicated, in agreement with the more complicated titration curve (Fig. 1). In Fig. 3 the part at low acidities corresponds to a slope

$$\frac{d \log \frac{X^2}{1 - X}}{d \log a^{1/2}_{\text{H}_2\text{SO}_4}} = 6 \quad (12)$$

in agreement with an empirical constant

$$K_4 = \frac{1}{a_{\text{H}_2\text{SO}_4}} \left(\frac{X^2}{1 - X} \right)^{1/2} \quad (13)$$

and

$$K_4 = 30.5 (\text{mole/l.})^{-3}$$

at high acidities we find a slope

$$\frac{d \log \frac{X^2}{1 - X}}{d \log a_{\text{H}_2\text{SO}_4}} = 1 \quad (14)$$

corresponding to

$$K_5 = \frac{1}{a_{\text{H}_2\text{SO}_4}} \left(\frac{X^2}{1 - X} \right)^3 \quad (15)$$

with the numerical value

$$K_5 = 11.4 (\text{mole/l.})^{-3}$$

In the THA case (Fig. 3a) only the slope 6 is found corresponding to

$$K_4^* = \frac{1}{a_{\text{H}_2\text{SO}_4}} \left(\frac{X^2}{1 - X} \right)^{1/2} \quad (13a)$$

with the numerical value

$$K_4^* = 5570 (\text{mole/l.})^{-3}$$

Discussion

From the experiments and the results described above no quantitative conclusions can be drawn. The relations obtained are only empirical and will certainly have no general thermodynamic validity.

The only conclusion which might be drawn is that the transition points in Fig. 2, 2a and 3 correspond to inflection points in the titration curves 1 and 1a. A surprising point of interest is furthermore the great difference in the processes underlying the distribution when benzene is replaced by kerosene as the solvent.

THE HEAT OF VAPORIZATION AND THE HEAT OF FUSION OF FERRIC CHLORIDE

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Pressures of $\text{Fe}_2\text{Cl}_6(\text{g})$ above solutions of FeCl_2 in $\text{Fe}_2\text{Cl}_6(\text{l})$ were measured in the range 300–470°. These data indicate that above liquid ferric chloride $\log P_{\text{Fe}_2\text{Cl}_6}(\text{mm.}) = 48.57 - 12.55 \log T - 6373/T$, where $\Delta H_{580.7}(\text{Fe}_2\text{Cl}_6 \text{ vap.}) = 14.6 \pm 0.5 \text{ kcal./mole Fe}_2\text{Cl}_6$, $\Delta S_{580.7}(\text{Fe}_2\text{Cl}_6 \text{ vap.}) = 24.8 \pm 1.0 \text{ e.u./mole Fe}_2\text{Cl}_6$. The boiling point is estimated to be 315°. The heat of fusion was measured by a drop calorimeter and found to be $\Delta H_{580.7}(\text{FeCl}_3 \text{ fusion}) = 9.0 \pm 0.4 \text{ kcal./mole FeCl}_3$.

Introduction

The currently accepted^{1a,b} value of the heat of vaporization, 12.04 kcal./mole Fe_2Cl_6 , at the accepted boiling point of liquid ferric chloride, 319°, derives from measurements by Stirnemann² of the total pressure within a closed bulb containing ferric chloride at temperatures up to 493°. This thermodynamic value was calculated without correcting the observed total pressures for the sig-

nificant partial pressure of Cl_2 present along with the $\text{Fe}_2\text{Cl}_6(\text{g})$ in the vapor space above the ferric chloride.³ The magnitude of the chlorine pressure correction to Stirnemann's data is discussed below, and the heat of vaporization of $\text{Fe}_2\text{Cl}_6(\text{l})$ is recalculated.

Experimental

Vapor Pressure.—Ferric chloride–ferrous chloride mixtures were contained in a ca. 13-cc. cylindrical Pyrex sample

(1) (a) "Selected Values of Chemical Thermodynamic Properties," Circular 500, National Bureau of Standards (1952); (b) O. Kubaschewski and E. Evans, "Metallurgical Thermochemistry," 2nd Ed., John Wiley and Sons, New York, N. Y., 1956.

(2) E. Stirnemann, *Neues Jahrb. Mineral. Geol. u. Paläontol.*, **52A**, 334 (1925).

(3) W. Kangro and E. Petersen, *Z. anorg. Chem.*, **261**, 157 (1950), corrected Stirnemann's pressures for Fe_2Cl_6 and for PCl_2 . The latter calculation, however, contained the assumption that $a_{\text{FeCl}_3} = 1$, which is invalid for Stirnemann's experiments above the FeCl_2 – FeCl_3 eutectic temperature because of the solubility of FeCl_3 in molten Fe_2Cl_6 . See H. Schäfer, *Z. anorg. u. allgem. Chem.*, **266**, 269 (1951).