Experimental solubility values were not obtained close enough to $N \rightarrow 1$, however, to obtain independent estimates of heats of fusion. The heats of fusion used for calculation were 2.9 ± 0.5 (6) 2.00 (4) and 1.84 (9) kcal./mole for $GeBr_4$, $SiBr_4$ and $SiCl_4$ respectively. The heat of fusion for $GeCl_4$ was not available in the literature for comparison.

The $GeBr_4$-$SiBr_4$ melting point–composition curve shown in Figure 4 is seen to be bowed upward slightly above a linear curve between the melting points of the pure components, indicating that a continuous series of solid solutions are formed in this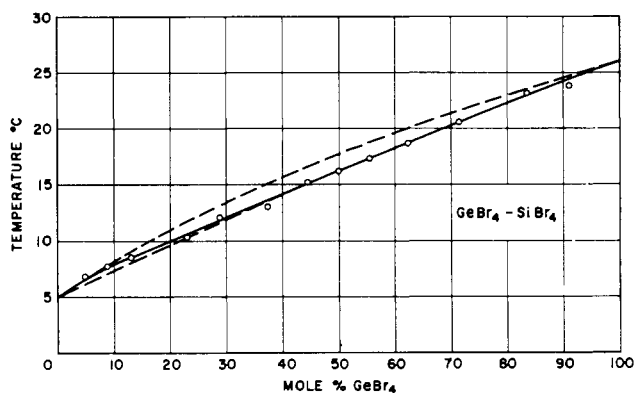 system. The ideal liquidus and solidus solid solution curves have been calculated (5) for this system and compared with the experimental liquidus curve in Figure 4.

ACKNOWLEDGMENT

Figure 4. Experimental liquidus curve for $GeBr_4$-$SiBr_4$ compared with calculated ideal liquidus and—solidus solid solution curves: – – –, ideal; ——, experimental

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Formation Constants of Copper and Nickel Chelates of RAPOX

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GRAVIMETRIC ESTIMATIONS of copper and nickel and their separation using RAPOX (resacetophenone oxime) is described earlier (1). The colorimetric study of these complexes and their solvent extraction using cyclohexanone is partly published (2, 3). The solvent extraction method was extended to prepare a carrier free source of Cu-64, 67 from neutron irradiated zinc (4). The solubility study of these complexes in different organic solvents immiscible with water is described recently (5).

The present communication is the extension of the study of RAPOX chelates and deals with the evaluation of the formation constant of copper and nickel complexes.

EXPERIMENTAL

MATERIALS. Resacetophenone oxime was synthesized from resorcinol and crystallized from ethanol (1).

Merck's extra pure copper sulphate was used. The standard solution when analyzed (1) for copper gave 3.75×10^{-2} mole of copper per liter.

Merck's extra pure quality nickel sulfate was utilized. The analysis of the standard solution for nickel (1) gave 4.378×10^{-2} mole of nickel per liter.

Cyclohexanone was purified and distilled (6, 7).

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Freshly crystallized potassium biphthalate and B.D.H. (AnalaR) Potassium dihydrogen phosphate were used for preparing various buffer solutions.

Instruments. Lumetron photoelectric colorimeter, 402E model with monochromatic filters, was used.

For pH determinations Leeds and Northrup pH meter, Cat. No. 7666, was employed.

EVALUATION OF FORMATION CONSTANT

When an n valent metal in an aqueous medium is shaken with a chelating agent in water immiscible organic solvent, the formation of the chelate may be represented (8) by the reaction:

$$M^{-n} + n HR \rightleftarrows MR_n + n H^- \tag{1}$$
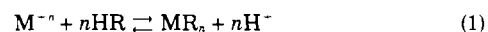
where HR stands for the chelating agent.

The over-all equilibrium constant then is given by:

$$K_M = \frac{[MR_n][H^-]^n}{[M^{-n}][HR]^n} \tag{2}$$

Substituting D for $[MR_n]/[M^{-n}]$

Formation constants of copper and nickel complexes of RAPOX have been determined by solvent extraction method using cyclohexanone. Experiments were carried out at various pH's of the aqueous solutions of these metals, simultaneously varying the amount of RAPOX in the organic phase. The experimental readings obtained for the distribution of these chelates when plotted against log of the excess reagent gave straight lines with slopes indicating the composition of the complexes in both the cases. Formation constants calculated from the intercepts of these lines on log D axis and from the normal equation of the formation of these chelates:

gave the value

and

$$M^{+n} + nHR \rightleftarrows MR_n + nH^+$$

$$K_{Cu} = 2.521 \times 10^{-4}$$

$$K_{Ni} = 5.446 \times 10^{-11}$$

$$K_M = D \frac{[H^-]^n}{[HR]^n} \qquad (3)$$

where D represents the distribution ratio for the metal expressed as the total concentration of the metal in the organic phase divided by the toatal concentration of the metal in the water phase.

It is indicated here that Equation 1 is an approximation and represents the resultant of several independent equilibria. A more rigorous and more accurate equation which takes into account the dissociation of the chelating agent and the chelate MR_n in the aqueous medium, the distribution of the former in both the phases and the presence of complexes like $MR^{+(n-1)}MR_2^{-(n-2)}\ldots MR_n^{-1}{}_{-1}$ in the aqueous medium is suggested by Irving (9).

Equations 2 and 3 involve the assumption that the concentration of the metal chelate (MR_n) in the aqueous phase is negligible compared to that of the metal ion (M^{+n}) as well as any intermediate stages in chelate formation.

It is emphasized here that in the present case when the complexes of RAPOX with copper and nickel are to be considered, concentration of the chelating agent RAPOX in the organic phase was very high in the pH range in which the experiments were accomplished. This led to the consequence that the aqueous phase contained practically negligible amount of RAPOX, so that any formation of the intermediate complexes of the reagent with metals could be taken as prevented. Equation 3, therefore, became applicable to the system under consideration here. A very similar relationship was employed by Kolthoff and Sandell (10) in respect of the extraction of zinc by dithizone.

Taking log of Equation 3,

$$\log K_M = \log D + n \log H - n \log HR$$

$$= \log D - n\, pH - n \log HR$$

$$\therefore \log D = n \log HR + \log K_M + n\, pH$$

$$= n \log HR + \log K'$$

where

$$\log K' = \log K_M + n\, pH$$

If values of log D are plotted against log HR a straight line is obtained. The slope, n of this straight line indicates the number of reagent molecules required to react with the metal, and hence, the composition of the complex. The intercept of the straight line of log D axis gives the value of log K'. Should the pH of the aqueous solution be known, one can calculate the value of log K_M is the formation constant of the chelate.

EXPERIMENTAL PROCEDURE

Two ml. of the standard copper solution were pipetted out into a glass stoppered centrifuge tube of about 30 ml. capacity. Eight ml. of the requisite buffer solution and 10 ml. of cyclohexanone containing RAPOX were then added. Several tubes containing the same amount of copper solution but various amounts of RAPOX in cyclohexanone were prepared. These were arranged horizontally in a wodden box fixed on the shaking machine in that same position.

The shaking was done in forward and backward direction. The assembly was maintained at 30° ± 1° C. in a therm-

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Table I. Evaluation of Formation Constant of Copper RAPOXimate Chelate

Copper sulphate solution: 4.5×10^{-3} mole per liter (for 1 to 8) and cuvette used, 0.995 cm. and 7.5×10^{-3} mole per liter (for 9 to 11) and cuvette used, 0.4975 cm.

Buffer: Potassium biphthalate; filter, 620M.   Temp. 30° C.

No.	RAPOX Added $M \times 10^2$	O.D., Cm.	Cu Extracted as CuR_2 Calculated from $\epsilon_{620} = 102.8$ $M \times 10^3$	D	Cu Remaining in Aqueous Phase $M \times 10^4$	Excess RAPOX in Org. Phase $M \times 10^2$	pH of the Aq. Phase	H^+, M	$K_{Cu} \times 10^4$
1	7.1984	0.07	0.6844	0.1794	38.156	7.0616	2.55	2.818×10^{-3}	2.858
2	9.5979	0.10	0.9777	0.2776	35.223	9.4024	2.55	2.818×10^{-3}	2.496
3	11.9974	0.14	1.3690	0.4373	31.310	11.7236	2.55	2.818×10^{-3}	2,529
4	0.5027	0.09	0.8798	0.2431	36.202	0.3267	4.00	1.0×10^{-4}	2.329
5	1.5081	0.29	2.835	1.7030	16.650	0.9411	4.00	1.0×10^{-4}	1.923
6	2.5135	0.41	4.009	8.1660	4.910	1.7117	4.00	1.0×10^{-4}	2.787
7	3.5189	0.44	4.302	21.730	1.980	2.6585	4.00	1.0×10^{-4}	3.075
8	4.5243	0.45	4.399	43.560	1.010	3.6445	4.00	1.0×10^{-4}	3.278
9	2.2497	0.32	6.256	5.029	12.44	0.9985	4.20	6.31×10^{-5}	2.008
10	2.9996	0.36	7.039	15.27	4.61	1.5918	4.20	6.31×10^{-5}	2.398
11	3.7495	0.37	7.235	27.30	2.65	2.3025	4.20	6.31×10^{-5}	2.050

Mean $K_{Cu} = 2.521 \times 10^{-4}$

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ostat. Shaking continued ten hours. Trial experiment had shown that equilibrium would be attained in this length of time. All experiments were carried out in duplicate.

After shaking, the tubes were centrifuged. The upper organic layer was then subjected to Lumetron examination using 620 M filter. From the optical density obtained, the amount of copper extracted was calculated from ϵ, the molar extinction coefficient at 620 M, and hence, the amount of RAPOX used up in chelate formation.

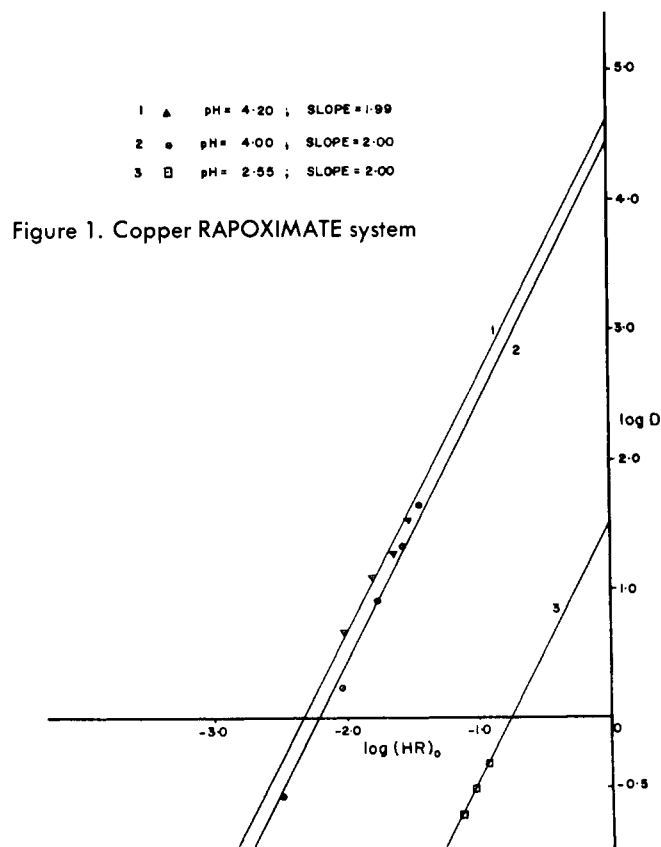The results so obtained are surveyed in Table I and represented in Figure 1.

Similar experiments were repeated for the extraction of nickel chelate except that the eight ml. of buffer were added last and the resulting mixture shaken immediately. The results obtained are surveyed in Table II and Figure 2.

The molar extinction coefficients in the case of copper and nickel respectively were ϵ_{620} = 102.8 and ϵ_{620} = 114.8 (5, 7).

DISCUSSION

The buffer solution added to the mixture of the maintenance of the pH also served to keep the ionic strength constant. Incidentally, it was superfluous to add any electrolyte for this purpose.
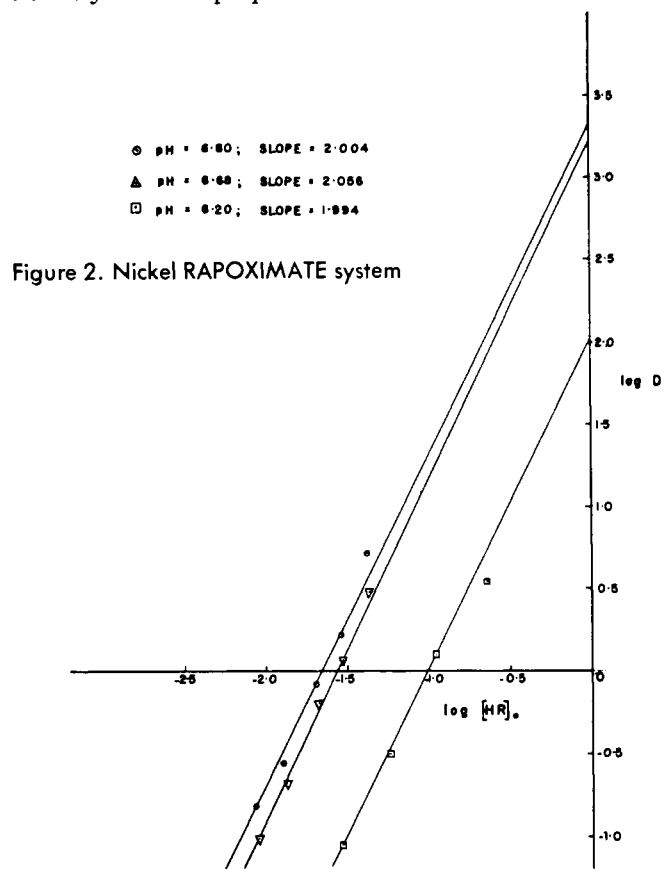

Figure 1. Copper RAPOXIMATE system

Figure 2. Nickel RAPOXIMATE system

Table II. Evaluation of Formation Constant of Nickel RAPOXimate Chelate

Nickel sulphate solution: 8.756×10^{-3} mole per liter (Expts. 1 to 4); cuvette used, 0.4975 cm. and 4.055×10^{-3} mole per liter (Expts. 5 to 14); cuvette used, 0.995 cm.

Filter, 620 M   Buffer: KH_2PO_4—NaOH   Temp. = 30° C.

No.	RAPOX Added $M \times 10^2$	O.D., Cm.	Nickel Extracted as NiR_2 Calcd. from ϵ_{620} = 114.8 $M \times 10^3$	Phase D	Nickel Remaining in Aqueous Phase $M \times 10^3$	Excess RAPOX $M \times 10^2$	pH	$H^- \times 10^7$, M	$K_{Ni} \times 10^{11}$
1	2.991	0.04	0.7004	0.08694	8.056	2.851	6.20	6.31	4.256
2	5.982	0.12	2.101	0.3157	6.655	5.562	6.20	6.31	4.061
3	11.964	0.28	4.904	1.2740	3.852	10.983	6.15	7.079	5.294
4	23.928	0.39	6.830	3.5460	1.926	22.562	6.10	7.943	4.496
5	0.9572	0.04	0.3502	0.09452	3.705	0.8872	6.70	1.995	4.780
6	1.4358	0.08	0.7004	0.2087	3.355	1.295	6.70	1.995	4.955
7	2.393	0.18	1.576	0.6357	2.479	2.078	6.70	1.995	5.860
8	3.3502	0.25	2.189	1.1730	1.866	2.912	6.65	2.239	6.933
9	4.7860	0.35	3.065	3.0960	0.990	4.173	6.65	2.239	8.915
10	0.9572	0.06	0.5254	0.1488	3.530	0.8521	6.85	1.413	4.092
11	1.4358	0.10	0.8756	0.2754	3.179	1.2607	6.80	1.585	4.350
12	2.393	0.21	1.839	0.8299	2.216	2.0252	6.80	1.585	5.083
13	3.3502	0.29	2.539	1.6740	1.516	2.842	6.80	1.585	5.207
14	4.7860	0.39	3.415	5.3350	0.640	4.103	6.80	1.585	7.960

Mean $K_{Ni} = 5.446 \times 10^{-11}$

Figure 1 shows the average slope of 2, indicating the composition of the copper complex as 1:2. A study of the same system made by Job's and Slope Ratio methods in a two phase system (2, 3, 7), and the composition of the complex in the solid state (7) indicate this composition is correct.

From Table I, the mean value of log K_{Cu} is found to be 2.521×10^{-4}. This is in agreement with that arrived at from the intercepts of the straight lines on log D axis in Figure 1.

Similar findings are recorded for nickel also. The value of log K_{Ni} surveyed from Table II and confirmed from the intercepts on log D axis (cf. Figure 2) is 5.446×10^{-11}.

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Thermodynamic Properties of HF

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An enthalpy-temperature diagram and an entropy-temperature diagram for anhydrous hydrogen fluoride (HF) were prepared by critical evaluation of published data for temperatures between $-40°$ and $240°$ C. and absolute pressures between two and 1000 lb. force/in². In the vapor phase HF molecules are strongly associated into polymeric forms; dissociation to the monomeric form is accompanied by large changes in enthalpy. Published information for some regions of the diagrams is inconsistent or discordant, and in places is entirely lacking.

THE THERMODYNAMIC properties of anhydrous hydrogen fluoride (HF), because of molecular association in both the liquid and vapor, cannot be calculated from generalized correlations for ordinary unassociated substances. Experimental data in the literature for some regions of interest are not available, and in other regions are conflicting or not self-consistent. This study was undertaken to make a critical review of the published literature, and to prepare a set of charts summarizing the best values of the thermodynamic properties. This work includes both an enthalpy and an entropy diagram. The pressure range is from 2 to 1000 lb. force/in.² absolute; the temperature range is from $-40°$ to $240°$ C.

The thermodynamic charts (Figures 1 and 2) were prepared from data in the published literature and have been deposited with the American Documentation Institute. It proved necessary to resolve conflicting data and to convert much information into a different form. This conversion revealed many inconsistencies in the published values. In addition, in a substantial part of the superheated-vapor region there is no published information whatever. Arbitrary techniques of smoothing and interpolation were used in preparing some parts of the diagrams. In all the calculations and in the tabulated data nonsignificant figures were carried to reduce the calculation errors. The final numbers were then rounded off. The sources of information and methods of calculating enthalpy and entropy for the several regions were done with the following procedures.

Saturated Liquid Line. Data for C_p of the saturated liquid were taken from Hu, White, and Johnston (7), and for C_V from Franck and Spalthoff (4). The data of Dahmlos and Jung (2) are inconsistent with those of others (4, 7) and were not used. Vapor-pressure data were taken from several sources, among which there was some disagreement. The charts are based on data from Simons (11) for temperatures below 10° C.; from Jarry and Davis (8) for temperatures between 10° and 112° C.; and from Franck and Spalthoff (4) for temperatures above 112° C.

The calculation of enthalpy and entropy from these data is not straightforward, and since the construction of the entire chart depends on the position assigned to the saturated liquid line, the calculation procedure is outlined in detail below.

The specific heat of the saturated liquid is defined by Lewis and Randall [(9), Equation 6-9]:

$$C_s = \lim_{\Delta T \to 0} \left(\frac{\Delta q}{\Delta T} \right)_s = \left(\frac{\partial H}{\partial T} \right)_s - V \left(\frac{\partial p}{\partial T} \right)_s \qquad (1)$$

Since

$$H = \phi(T, p),$$

$$dH = \left(\frac{\partial H}{\partial T} \right)_p dT + \left(\frac{\partial H}{\partial p} \right)_T dp$$