

in solution, the solution would be expected to be colored, and the evaporation of solvent should yield a mixture because of the statistical recombination of the dissociation products and also because of the reaction of the free radicals with atmospheric oxygen. When this experiment was carried out with each compound, no color was observed even at the boiling point of the solution and no change in melting point of the solid was observed. In addition, an electron-spin resonance experiment carried out by Mr. T. H. Brown and Dr. J. A. Weil of this Laboratory failed to detect the presence of free radicals in either saturated benzene solution or hot naphthalene solution. This evidence of the absence of dissociation is consistent with the conclusions of Gilman and Wu in regard to these compounds.¹⁷ Stuart-Briegleb models show that the three aryl groups must be arranged in the form of a propeller in order to allow a reduction of the C-Si-C bond angle by 7.5° and at the same time prevent dissociation of the Si-Si linkage.

According to equation 5 $\tan \theta$ is dependent only on the ratio of μ_I^2 and μ_{II}^2 and not on the absolute magnitude of either. As a result the absolute magnitude of the induced polarization is of small consequence in the evaluation of the Si-Si-C bond angle. Since the moment of I and II can be considered equal within the experimental error, and any induced polarization which may not have been accounted for in the use of R_D to calculate the moments may also be considered to be the same for both compounds, the error introduced by the approximation is within the probable error assigned to the value of the bond angle.

Calculation of Group Moments.—Calculation of the aryl-silicon group moments is more approximate because of the uncertainty in the absolute values of the dipole moments. Furthermore, in III the extent of the distortion of the bond angles is

(17) H. Gilman and T. C. Wu, *THIS JOURNAL*, **75**, 3762 (1953).

uncertain, but is presumably less than in I and II because of the smaller size of the methyl group as compared to the phenyl. As an approximation, however, tetrahedral symmetry is assumed and the moment of III is expressed by the equation

$$\mu_{III} = \mu_p \pm \mu_m \quad (6)$$

where μ_m is the CH₃-Si bond moment, estimated by Altshuller and Rosenblum⁷ to be 0.2×10^{-18} with direction Si⁺--CH₃. When (6) is solved simultaneously with (1) and (2), or (3) and (4), the following results are obtained: For case A, using the - sign in (6), $\mu_p = 0.84 \times 10^{-18}$ with direction Si⁺--phenyl, and $\mu_t = 0.25 \times 10^{-18}$ with direction Si⁺-*p*-tolyl. For case B, using the + sign in (6), $\mu_p = 0.44 \times 10^{-18}$ with direction Si⁻+phenyl, and $\mu_t = 0.15 \times 10^{-18}$ with Si⁻-*p*-tolyl.

The result for case A is more reasonable than that for case B because of the fact that the phenyl group is more electronegative than the methyl group,¹⁸ which, in turn, is more electronegative than silicon. However, the effect of adding a *p*-methyl group to the phenyl ring should be to decrease μ_p by about¹⁷ $0.3-0.4 \times 10^{-18}$ instead of 0.6×10^{-18} as obtained above. The source of this discrepancy may lie in the uncertainty of the induced polarization as previously discussed or in the considerable uncertainty of the Si⁺--CH₃ moment, or in both. Indeed, reduction of all three moments by 50% would yield the values $\mu_p = 0.5 \times 10^{-18}$ and $\mu_t = 0.2 \times 10^{-18}$, which give the correct difference, but there is no justification for this calculation. The possibility remains that μ_p and μ_t alter each other's value when both are on the same silicon atom, but this effect cannot be treated quantitatively.

On the basis of the foregoing discussion the following maximum group moment magnitudes and their directions may be assigned: phenyl⁻+Si = 0.84×10^{-18} and *p*-tolyl⁻+Si = 0.25×10^{-18} .

PRINCETON, NEW JERSEY

(18) C. P. Smyth, ref. 14, p. 253.

[CONTRIBUTION FROM THE MINERAL BENEFICIATION LABORATORY, COLUMBIA UNIVERSITY]

Thermal Analysis of the Ferrous Chloride-Potassium Chloride System^{1a}

BY HARRY L. PINCH^{1b} AND JACK M. HIRSHON^{1c}

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The phase diagram for the system FeCl₂-KCl is presented. Two intermediate compounds exist: KFeCl₃ with a congruent melting point of 399° and K₂FeCl₄ with an incongruent melting point of 380°. There is a eutectic formed between K₂FeCl₄ and KFeCl₃ at 38.2 mole % FeCl₂ and another between KFeCl₃ and pure FeCl₂ at 54.2 mole % FeCl₂. There are also two solid-solid transitions.

The system FeCl₂-KCl was studied as part of the fused-salt program of this Laboratory. The solid-liquid phase diagram has been obtained, and the results of our investigation are reported.

Experimental Procedure

Reagents.—Anhydrous FeCl₂ was prepared from Fisher "Certified" reagent, FeCl₂·4H₂O. The hydrated FeCl₂

was heated to 400-500° in a dried HCl stream for several hours. The heating was continued for an hour after the last traces of water had disappeared from a cooled condenser in the exit gas stream. Analysis of the anhydrous salt showed that it was 99.95% FeCl₂.

The KCl was Fisher "Certified" reagent which was vacuum dried while molten. The cooled salt was crushed within a dry-box and then re-dried for several hours at 110° before use in sample preparation.

Preparation of Samples.—The two salts were weighed into Vycor test-tubes. All transferring operations were carried out in the dry-box. The samples were not pre-fused but were stirred well when molten. The samples ranged in weight from 15 to 25 g. After a determination the samples were dissolved and analyzed. In general, the compositions

(1) (a) The work reported herewith was performed under contract AT (49-1)-621 between the Atomic Energy Commission and Columbia University. Reproduction in whole or part is permitted for any purpose of the United States Government. (b) RCA Laboratories, Princeton, N. J. (c) Lansdale Tube Co., Lansdale, Penna.

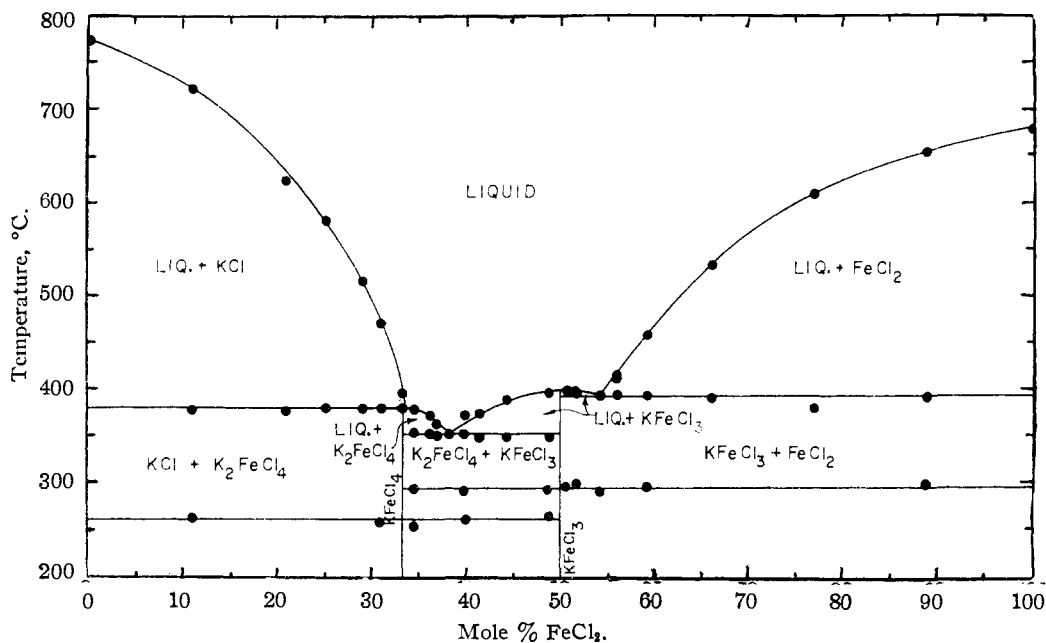


Fig. 1.—Solid-liquid phase diagram of the system FeCl_2 - KCl .

calculated from the analytical results agreed with the prepared compositions.

Thermal Analysis.—The cooling-curve data were obtained by two measurement techniques. One method employed a chromel-alumel thermocouple with a fixed temperature reference at the ice point. The other used differential thermal analysis with the sample block as the reference temperature. In the first case the data were plotted as a time-temperature curve on a 10 mv. Leeds and Northrup Speedomax recorder. A type K-2 potentiometer was used to balance the output from the thermocouple in 10-mv. steps, and the difference voltage was recorded. The recorder was standardized at regular time intervals and checked against the potentiometer when transitions were observed on the cooling curves. The thermocouple was checked against the melting points of zinc (419.5°) and aluminum (660.1°). Simultaneously, the output of the differential thermocouple system was plotted against time on a (+0.25)–0–(–0.25) mv. Brown Elektronik recorder. The differential system enabled certain of the liquidus points and solid–solid transitions to be found more readily. The rate of cooling was to be found more readily. The rate of cooling was about $2.5^\circ/\text{min}$. A manual stirring system was provided. Throughout each determination the entire furnace core was swept with a stream of dried pure nitrogen.

Results

The complete phase diagram is shown in Fig. 1. There are two intermediate compounds, K_2FeCl_4 and KFeCl_3 . The former melts incongruently at

$380 \pm 1^\circ$ and the latter melts congruently at $399 \pm 1^\circ$.

The region between 0 and 33.3 mole % FeCl_2 represents equilibrium between KCl and K_2FeCl_4 . The descending KCl -solubility curve intersects the K_2FeCl_4 curve at 33.7 ± 0.3 mole % FeCl_2 . A eutectic is formed between K_2FeCl_4 and KFeCl_3 at 38.2 mole % FeCl_2 , and it melts at $351 \pm 1^\circ$. In addition, KFeCl_3 and pure FeCl_2 form a eutectic mixture at 54.2 mole % FeCl_2 . This eutectic melts at $393 \pm 1^\circ$. The melting point of pure FeCl_2 was determined to be $677 \pm 1^\circ$. The previously reported values are 670 – 674° and 677° .³

There are two solid–solid transitions. One occurs at $260 \pm 5^\circ$ and extends from 0 to 50 mole % FeCl_2 . The second occurs at $293 \pm 5^\circ$ and extends from 33.3 mole % FeCl_2 to pure FeCl_2 . The high uncertainty in the solid–solid transition temperatures probably is due to poor thermal contact between the thermocouple and the solidified salt.

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(2) "Handbook of Chemistry and Physics," Thirty-Fourth Edition, Chemical Rubber Publishing Co., Cleveland, Ohio, 1952, p. 511.

(3) K. K. Kelley, Bull. U. S. Bur. Mines, 1935, No. 383.