The Solubility of Chromium in Chromium(II) Chloride

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The depression of the freezing point of anhydrous $CrCl_2$ has been determined by DTA and solubility measurements. The melting point of pure $CrCl_2$ was found to be 822 ± 1 °C and the eutectic was obtained at 806 °C and 3.4 ± 0.1 mol % Cr. From the saturation solubility curve, a value of 57.0 kJ/mol for the heat of solution of Cr in $CrCl_2$ was determined.

An understanding of the solution process of metals in their molten salts is of great importance technologically as well as theoretically. Considerable efforts have been made to study various metal-metalhalide systems, the chlorides in particular, to determine the type of ionic species present in such systems. Of these, the solution of Cr in $CrCl_2$ has received very little attention so far. This system is, however, of considerable technological interest, e.g. in the process for chromizing iron from a salt melt. The only reported work on this system is that of Corbett, Clark and Munday.[1] These authors measured the depression of the freezing point of $CrCl_2$ by the addition of Cr and found this to be 6 °C at the eutectic composition. The melting point of pure $CrCl_2$, according to their work was 824 °C and the eutectic composition was given as $3-4$ mol % Cr. As a freezing point depression of 6 °C is incompatible with the existing models of solution of metals in their molten salts [2] and as the melting point of pure $CrCl_2$ has also been variously reported between 815 and 824 °C in literature, the present work was undertaken to clarify the uncertainties existing in this system.

EXPERIMENTAL

Materials. Electrolytic chromium with a purity of 99.99 wt % was used. The $CrCl_2$ was prepared by passing pure chlorine gas from a cylinder containing liquid chlorine over pieces of Cr metal in a quartz boat, kept in a quartz reaction tube and heated in a horizontal tube furnace to 900 °C. The chlorine was dried by conc. H_2SO_4 and P_2O_5. Approximately 20 g of the metal were used in each batch of the $CrCl_2$ synthesis and the reaction was normally complete in about 24 h. $CrCl_2$, condensed in the form of violet crystals in the colder parts of the furnace, was collected and stored in a closed glass vessel in a dry-box under an argon atmosphere. To avoid the absorption of moisture the $CrCl_2$ crystals thus prepared were handled only in the dry-box. This salt did not dissolve in water, which may be taken as an indication of high purity.

For the DTA measurements accurately known weights of $CrCl_2$ (approximately 400 mg) were transferred into thinwalled vycor tubes of 1 cm diameter in the dry-box. To this, proper proportions of Cr were added on top so that ultimately different ratios of $Cr/CrCl_2$ could be obtained. The volume above the Cr metal was closed by a tight-fitting quartz plunger tube and sealed under a vacuum of less than 10^{-3} Torr, by fusion in an oxy-hydrogen flame. The samples were pre-heated in a vertical furnace at 900 °C for 24 h to ensure that the formation of the dichloride and the solution of the metal in the fused dichloride were complete. Some of the samples were made to correspond to stoichiometric $CrCl_2$. To be sure of the purity of the $CrCl_2$ used for the preparation of the $CrCl_2$ some experiments were also carried out using resublimed $CrCl_2$. This procedure did, however, not alter the melting point of the pure $CrCl_2$.

DTA measurements. The DTA measurements were made in a Mettler Thermoanalyzer No. 59 with Pt/10 % Rh-Pt thermocouples. The reference was a vycor tube filled with crystalline quartz powder and sealed in the same way as the $Cr-CrCl_2$ capsules. The thermocouples were calibrated with pure aluminium and pure, dehydrated and pre-melted NaCl, sealed in vycor tubes under vacuum. The reference as well as the calibration capsules were nearly of the same dimension as the $CrCl_2$-Cr capsules. The quartz middle-range furnace supplied by

Mettler was used for heating the samples. The melting and freezing points could be accurately read with the aid of the five-fold magnification of the temperature scale provided in the thermo-analyzer.

Solubility measurements. Supplementing the DTA studies, the solubility of Cr in $CrCl_2$ was directly measured by equilibrating pieces of Cr metal of known weight with known amounts of $CrCl_2$ at fixed temperature and measuring the weight loss of Cr after equilibration. The samples were prepared in the same way as for DTA studies except that a large, single piece of chromium metal was used for each sample. The sample was kept inside a copper block and heated in a vertical tube furnace having a large constant temperature zone in the centre. The temperature was measured along the entire length of the sample by two Pt/10 % Rh-Pt thermocouples. The furnace was controlled by a Eurotherm thyristor regulator to ± 1 °C, with a Pt/10 % Rh-Pt thermocouple embedded very close to the furnace windings. The equilibration was carried out for 72 h with repeated shaking of the sample. The sample was cooled fast, broken and the chromium piece was re-covered. It was repeatedly boiled with distilled water, washed with pure alcohol, dried and the weight loss was determined.

RESULTS AND DISCUSSION

Twenty-five samples having compositions from 0 to 70 mol % chromium were studied by the DTA method. The composition corresponding to pure $CrCl_2$ gave identical melting and freezing points corresponding to 822 ± 1 °C. This is somewhat higher than the results of Shiloff,[3] Seifert and Klatyk [4] and Kühnl and Ernst [5] but is slightly lower than the value obtained by Corbett et al.[1] and Fischer and Gewehr,[6] as can be seen in Table 1. The value of 815 °C reported by Doerner [6] could possibly be low due to contamination of the chloride.

Table 1. Melting point of chromium(II) chloride.

Melting point °C	Stated accuracy °C	Ref.
824	± 1	1
820	± 3	3
820.5	± 1	4
820.5	± 1	5
815	—	6
816	—	7
824	± 2	8
822	± 1	This work

While it appeared that the true liquidus of $CrCl_2$ could be observed in the DTA measurements, in some samples with very low amounts of excess Cr (up to 1 mol %), the runs with higher chromium content indicated that the solution process was often incomplete. Heating of the samples in inverted position prior to the DTA experiments often improved the results but because the capsules could not be shaken in the DTA apparatus the solution process was so slow that the measured liquidus values could hardly be relied upon. In such runs, there was a first melting peak corresponding to the eutectic at 806 °C, followed closely by a larger peak. On cooling the freezing always started much earlier, often only 2 or 3 °C lower than that of pure $CrCl_2$. This was not the case with pure $CrCl_2$. This point was clarified by the thermal analysis of samples containing a very large excess of Cr (of the order of 70 mol %). In these cases, Cr pieces extended through the entire height of the melt and thus Cr was available for solution at all heights. In these instances, only the eutectic peak was observed during heating as well as cooling. The eutectic temperature of 806 °C, observed in the present work corresponds to a depression of the freezing point of 16 °C. The lower value of 6 °C observed
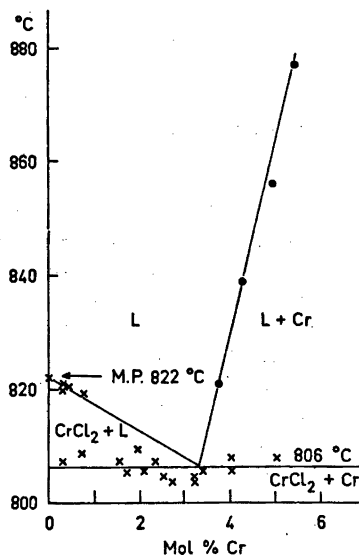

Fig. 1. The solubility of Cr in $CrCl_2$. ×, DTA; ●, Solubility measurements.

by Corbett et al.[1] can probably be explained on the basis of the slow rate of solution of chromium in $CrCl_2$ which might lead to non-equilibrium conditions. This appears to be a likely explanation particularly as the discrepancy in melting point of pure $CrCl_2$ between their work and this work is small and within the experimental error.

The eutectic composition was determined from an extrapolation of the saturation solubility curve which was established by solubility measurements. The results are summarized in Fig. 1, in which, however, the values obtained for samples with a Cr-content of more than 5 mol % are not shown. The intersection of the solubility line and the eutectic line gives the eutectic composition as 3.4 ± 0.1 mol % Cr which is within the range of 3 to 4 mol % Cr given by Corbett et al.

As the saturated salt melt is in equilibrium with pure solid chromium the heat of solution of chromium in the melt can be evaluated from the slope of the solubility curve. This gave a value of 57.0 kJ/mol.

The depression of the freezing point of $CrCl_2$ provides a means to estimate the number of foreign particles that enters the melt for each chromium atom added and will in this way give an indication of the mechanism by which the metal dissolves in the melt. In dilute solutions the two most likely models for dissolution of the metal as ions in its salt are the following:

$$Cr + Cr^{2+} \rightarrow Cr_2^{2+} \qquad (A)$$

$$Cr + Cr^{2+} \rightarrow 2\ Cr^+ \qquad (B)$$

Assuming Cr being insoluble in solid $CrCl_2$ these two models will give the following ideal Temkin activity for $CrCl_2$ expressed by the mol fraction x of $CrCl_2$.

$$a_{CrCl_2} = (2x - 1)/x \qquad (A)$$

$$a_{CrCl_2} = 2x - 1 \qquad (B)$$

ΔT can be computed from the equation

$$\Delta T = - \frac{RT_0 T}{\Delta H_f} \ln a_{CrCl_2}$$

where T_0 is the melting point in degree K of pure $CrCl_2$, T is the eutectic temperature, $\Delta T = T_0 - T$ and ΔH_f the heat of fusion. With

$\Delta H_f = 7.7 \pm 1.5$ kcal/mol[9] it is found that model A gives $\Delta T = 10.5$ K, while model B gives $\Delta T = 20.5$ K at the eutectic, which is much higher than the value suggested by Corbett et al.[1] Unfortunately, the uncertainty in ΔH_f is too large to permit a choice between the two models.

REFERENCES

1. Corbett, J. D., Clark, R. J. and Munday, T. F. J. Inorg. Nucl. Chem. 25 (1963) 1287.
2. Corbett, J. D., Chapter 6 in Fused Salts, Sundheim, B. R., Ed., McGraw, New York 1964, p. 341.
3. Shiloff, J. C. J. Phys. Chem. 64 (1960) 1566.
4. Seifert, H. J. and Klatyk, K. Z. Anorg. Allg. Chem. 334 (1964) 113.
5. Kühnl, H. and Ernst, W. Z. Anorg. Allg. Chem. 317 (1962) 84.
6. Doerner, H. A. Chemistry of the Anhydrous Chlorides of Chromium, U.S. Dep. of Interior, Bur. Mines, Tech. Paper 577 (1937).
7. Shkolnikov, S. N. Trans. Leningrad Polytech. Inst. 272 (1967) 30.
8. Fischer, W. and Gewehr, R. Z. Anorg. Allg. Chem. 222 (1935) 303.
9. Kubaschewski, O., Evans, E. Ll. and Alcock, C. B. Metallurgical Thermochemistry, 4th Ed., Pergamon Press, London 1967.