

complex with EDTA. With HEDTA only a mono- and an unprotonated complex seem to exist while the existence of a protonated NTA complex is rather doubtful. Table 1 demonstrates a striking difference in reactivity between the unprotonated and the two protonated Fe(II)-EDTA complexes. This may be due to an equilibrium between sexa- and quinquadentate bound ligand, the former being less reactive, as the reaction involves the breaking of a metal-carboxylate bond.

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A Method for Solubility Measurements in a Two Phase Liquid System

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Solubility measurements at high temperatures in molten systems where the solubility changes with temperature is often very difficult to perform. A common method is to freeze the equilibrium by a rapid quench and then analyse the solidified phases. Great care must be exercised, however, in order to obtain the true values as the composition of the melt usually changes very rapidly during quenching. This is particularly the case in those metal/molten salt systems where the metal has a high vapour pressure and the molten salt phase a relatively low heat conductivity. A further complication is the fact that these salts normally supercool very easily.

If a two phase equilibrium mixture of a metal-metal salt system is rapidly quenched from a high temperature the metal dissolved in the salt phase will precipitate out of that phase and to some extent join the metal phase. This is, e.g., the case in the Ca-CaCl₂ system where the metal is much lighter than the salt and consequently floats on top of the latter. This system exhibits a large miscibility gap that closes at 1338°C.¹ Experiments in this system have shown that a mixture of metal and salt with an overall composition in the two phase region after equilibration at 1100°C in a closed iron crucible changes its salt phase composition due to precipitation of metal from the salt solution even during a very rapid quench in brine. Subsequent chemical analysis of the phases from the quenched sample did therefore not give the true high temperature equilibrium values but instead it was found that the solubility figure for the metal varied depending on the quenching rate and from which part of the salt phase the sample was taken.

If mass transfer between the two phases in some way could be prevented after equilibrium was reached true values of the solubility of the metal could be obtained by analysing the whole of the salt phase.

This was obviously impossible for the whole of the salt phase but could be achieved for part of it if it were contained in a separate compartment. To achieve this the following double crucible method was developed and was found to work satisfactorily. See Fig. 1.

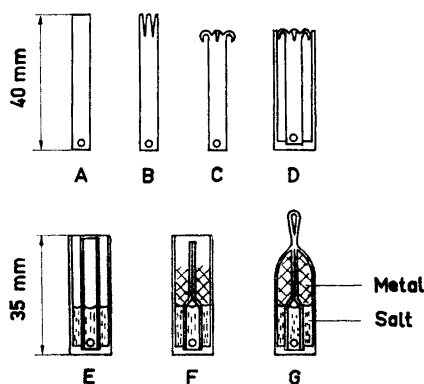


Fig. 1. Crucible for solubility experiment. Inner tube 5 mm O.D., 4 mm I.D. Holes 1.5 mm. Outer crucible part 12 mm O.D., 11 mm I.D. Bottom 2.5 mm.

The sequence (A to G) in which this crucible was assembled and filled will be clear from the figure. The crucibles which were of pure iron consisted of a thin inner tube that fitted tightly into a shallow hole drilled into the bottom of the outer crucible part. Two 1.5 mm holes were drilled through the wall of the inner tube so that when it was in place, the holes were just above the floor of the outer crucible part. The upper end of the tube was cut into three portions which were bent round to press on the wall of the outer crucible part. This served to hold the inner tube in place during loading and premelting of the salt. The inner tube as well as the space between it and the crucible wall, were filled with salt and the

salt premelted. As the solidified salt kept the inner tube in position the bent portions on its top could now be cut off and the tube above the salt was then pressed together with a pair of pliers. The outer compartment around the tube was now loaded with calcium metal and the crucible mechanically closed and spotwelded. During equilibration the metal would first saturate the outer salt phase and then start to diffuse into the inner crucible through the holes in its wall. After sufficient time this part of the salt phase would also become saturated with the metal. The crucible was then quenched and the metal precipitated from the salt in the inner tube was trapped in this part of the crucible. The quenching medium was a 10 per cent lithium chloride water solution which gives a very high quenching rate.³ After quenching the inner tube was removed and its outer surface cleaned in a dry-box. The whole content of the inner tube was then analysed for excess calcium.

The required equilibrium time at a given temperature was established by finding the minimum time for reaching constant metal composition. The results obtained with this method showed very good agreement with data from DTA measurements on the same system. The results will be published shortly.

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