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An improved high temperature cryoscopic technique

H. B. BELL† and C. R. MASSON‡
† Department of Metallurgy, Royal College of Science and Technology, Glasgow
‡ Atlantic Regional Laboratory, National Research Council Halifax, N. S., Canada
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Abstract. A simple technique is described for determining accurately the melting points of materials in which nucleation can be induced by seeding. The technique may be used also for measuring the depression of freezing points with high precision.

In determining accurately the melting points of several inorganic materials, difficulty was experienced occasionally in applying the well-known method of thermal arrests. Well-defined arrests often were not found, due to supercooling of the melts. The effect became more pronounced the higher the purity of the materials under investigation. With one compound, calcium fluoride of purity 99·95%, the method failed entirely due to this cause. Satisfactory arrests were never obtained with this material despite numerous attempts to promote nucleation by agitating the melts during cooling.

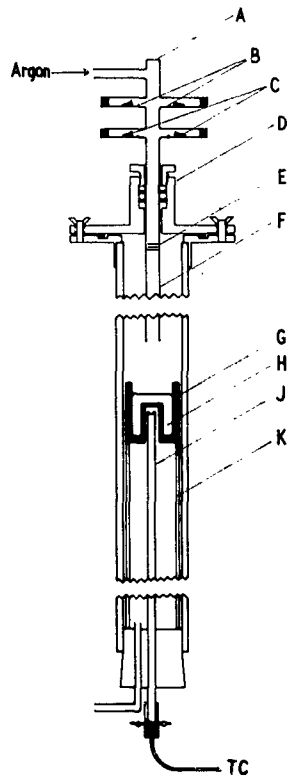
A simple technique overcomes this difficulty and also provides a procedure of high accuracy for determining the melting points of substances in which nucleation can be induced by seeding. In addition, it provides a method for measuring with high precision the depression of the freezing point due to the addition of other substances.

The temperature, as indicated by a thermocouple in close contact with the melt, is recorded as a cooling curve and is allowed to 'line out' at approximately 1–2 degc below the expected melting point. A small seed of the pure crystalline material is then introduced. The abrupt rise in temperature which occurs is followed by a long, well-defined 'plateau' which indicates the liquidus temperature with high precision.

The arrangement adopted for seeding calcium fluoride melts in an atmosphere of argon is illustrated in the figure. The salt is held in a spectrographically pure graphite crucible 1 in. in diameter and 1·25 in. deep, the temperature being monitored by a Pt–Pt/13% Rh thermocouple arranged as shown.

Seeds B of weight 1–10 mg were introduced by moving the soft iron slugs C with a magnet. Their progress on falling was observed through window A. By loading sufficient seeds initially, many determinations could be made with the same melt. The same procedure was followed when controlled amounts of impurities were introduced for cryoscopic measurements, so that successive determinations could be performed with the same thermocouple and under identical conditions.

The reproducibility of results obtained by this technique in the range 1200–1420°C was found to be better than 0·5 degc, which was the limit of precision of the potentiometric recorder employed. The melting point of calcium fluoride, as measured by a thermocouple which had been calibrated previously at the gold point, was 1419 (±1)°C,



Apparatus for cryoscopic measurements with calcium fluoride. A, window; B, seeds of CaF_2, or weighed quantities of other material; C, soft iron slugs; D, adjustable (Wilson) seal; E, graded seal; F, quartz tubing; G, graphite crucible; H, melt; J, twin-bored ceramic tubing; K, alumina pedestal; TC, thermocouple.

which is in good agreement with the value of 1418 (±1)°C reported by Naylor (1945) and by Baak (1954).

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