

The X-ray diffraction lines observed with the solid solution containing 25 moles per cent MgO heated at 1,400° for 100 h are given in Table 1.

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Mass Spectrometric Investigation of Barium Iodide and Caesium Iodide Vaporizations

A MASS spectrometer (radius, 3 in. 45° sector) was used to examine Knudsen cell effusates¹. Cylindrical graphite cells had orifice-to-evaporant surface area ratios of approximately 0.03 and were heated by conduction from a resistance furnace and by radiation from a grid above the furnace. The grid was necessary for maintaining axial temperature uniformity in the absence of radiation shielding². Temperature was measured with a thermocouple attached to the cell base. A movable defining slit between the grid and water-cooled ion-source base made background correction of the ion signals possible; an electron multiplier followed the collector slit. Ionizing electron energies ranged from 7 to 20 eV. Repellers were kept at block potential and spectra were magnetically scanned. Vapour-pressure data (ion signals) were taken at random with respect to temperature; isotopic corrections of ion signals were made when necessary. Each experiment involved a fresh sample.

In some cases, cells contained the salt with a reference metal in a separate reservoir to prevent direct contact between their condensed phases. These metals served as vapour-pressure standards by simultaneous vaporization with the salt. The presence of both salt and reference vapours in cells showed low-level interaction, as may be seen in the spectra given here. However, vaporization enthalpies for the salts were unchanged within experimental error. This was established by comparing experiments involving the presence and absence of reference metals. The dissociation enthalpies obtained for reference metal dimers, which are reported here, agree reasonably well with published values. This also implies that salt-reference interactions were negligible.

Vaporization enthalpies with corresponding standard deviations were obtained by applying the least-squares method to experimental vapour-pressure data (ion-signal, absolute-temperature product: reciprocal absolute temperature). Monatomic reference-metal vapour pressures were taken from Stull and Sinke³. Ionization cross-sections were approximated (the relative value of 50.3 was used for Bi(g))⁴ and multiplier efficiencies were estimated⁵. In calculating free energies from experimentally determined pressures, an uncertainty in pressure of a factor of three was used.

Barium iodide was prepared in the laboratory and metallic silver was used as the reference. With silver present, major ions in order of importance were BaI⁺, BaI₂⁺, Ag⁺, Ba⁺, AgI⁺, and Ag₂⁺. For three experiments (28 points over 1,019°–1,278° K), the Ba⁺ : BaI⁺ : BaI₂⁺

ratio was constant within 7 per cent. With Hg⁺ as the standard, appearance potentials of these ions were 12.8, 9.6, and 8.1 (±1) eV, respectively. Spectra showed no evidence of barium iodide polymers. The vaporization of Ba(g), BaI(g), and BaI₂(g) from barium iodide would be expected to yield substantially different enthalpies. It is concluded that Ba⁺ and BaI⁺ resulted from dissociative or fragmentary processes in the ion source and that the important vaporization was BaI₂(l) = BaI₂(g). With reference to 1,150° K, ΔH°, ΔF°, and ΔS° were 54 ± 4 kcal mole⁻¹, 28 ± 4 kcal mole⁻¹, and 23 ± 6 e.u., respectively. These values compared reasonably well with published estimates⁶.

Commercial, single-crystal caesium iodide was used with metallic bismuth as the reference. With bismuth present, major ions in order of importance were Cs⁺, CsI⁺, Cs₂I⁺, Bi₂⁺, Bi⁺, and BiI⁺. With reference to Hg⁺, appearance potentials of Cs⁺, CsI⁺ and Cs₂I⁺ were 7.3, 7.3, and 10.7 (±1) eV, respectively. Signals attributed to Cs₂I₂⁺ and Cs₃I₂⁺ were noted, but were too small for meaningful measurements. No evidence of polymers higher than the trimer was observed. Although Cs⁺ evidently resulted from a precursor other than Cs(g), a decision about the gaseous precursors of Cs⁺ and CsI⁺ is difficult. The Cs⁺ : CsI⁺ : Cs₂I⁺ ratio was constant over the temperature-interval. Mass spectrometric investigations with other alkali metal halides show that the MX(g) species is predominant⁷, except in the case of lithium iodide⁸. For this work, it is assumed that Cs⁺ and CsI⁺ resulted entirely from CsI(g) and that Cs₂I⁺ resulted entirely from Cs₂I₂(g). The temperature interval was 705°–882° K (3 experiments, 20 points). With reference to 794° K, ΔH°, ΔF°, and ΔS°, for vaporization of CsI(g) from CsI(s), were 39 ± 2, 19 ± 3, and 25 ± 5 (units as foregoing). For vaporization of Cs₂I₂(g) from 2 CsI(s), these values were 40 ± 1, 26 ± 3, and 18 ± 4. These data compare well with reported estimates⁹.

The results also yielded the dissociation enthalpies (Table 1), which are compared with literature values:

Species	D ⁰ (eV), Present study	T (°K)	D ⁰ (eV), Literature	T (°K)	Ref.
Ag ₂	2.1 ± 0.2	0	1.8 ± 0.3	0	10
Bi ₂	1.8 ± 0.2	0	2.0	0	10
			1.7	0	11
Cs ₂ I ₂	1.7 ± 0.3	794	1.35 ± 0.004	787	12

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