Boiling Points and Ideal Solutions of Ruthenium and Osmium Tetraoxides

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Ruthenium and osmium tetraoxides have the same boiling point and dissolve each other to make ideal solutions, which suggests that the physical and chemical properties of these compounds are based mainly upon tetrahedrally co-ordinated oxygen atoms in the outer shell rather than the central metal ion of the molecule.

Although the reprocessing of nuclear fuels and the solidification of fission products are markedly disturbed by the presence of volatile radioactive ruthenium,[1] very little is known about ruthenium tetraoxide (RuO_4).

The boiling point of RuO_4 has never been determined directly, probably because it has been reported that RuO_4 is unstable and explosively decomposes at 106 or 108 °C.[2] The literature quotes widely different values, *e.g.* 40,[3] 100,[4] 133.4 ± 1 °C[5] for its boiling point.

Using a special boiling point determination apparatus (Figure 2)[6] for a small amount of sample, the boiling point of RuO_4 has been measured directly for the first time. To avoid induction of explosive decomposition of RuO_4 by the presence of trace amounts of organic substances, all inner parts of this apparatus which were to be in contact with RuO_4 were carefully cleaned[7] just prior to use by repeated washing. The sample of RuO_4 was freshly prepared and dried. The determined value: 129.6 ± 0.2 °C (corrected) was identical with the boiling point of osmium tetraoxide (OsO_4): 129.7 ± 0.2 °C (corrected), in spite of the factor of 1.54 difference in their molecular weights. Every mixture of RuO_4 and OsO_4

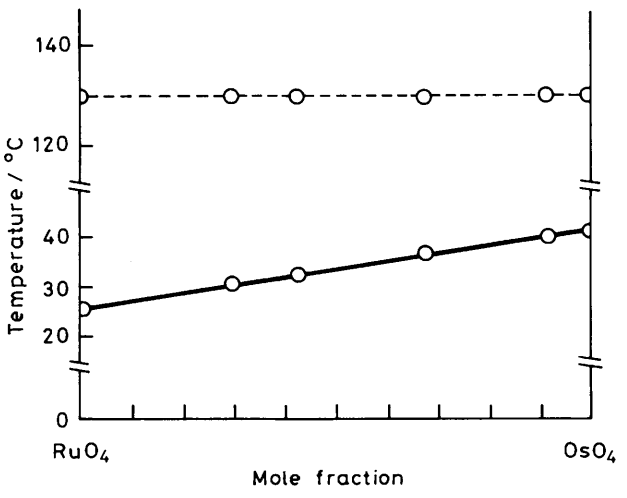

Figure 1. Boiling and melting point of the RuO_4–OsO_4 system. Boiling point, dashed line; and melting point, solid line.

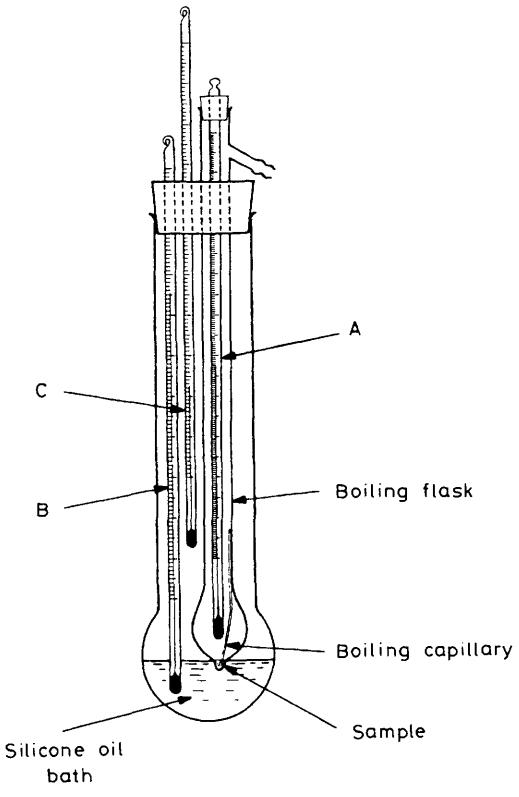

Figure 2. Boiling point determination apparatus for a mall amount of sample. A: Inner thermometer (calibrated to 0.1 °C); B, C: thermometers (calibrated to 1 °C).

showed practically the same boiling point as those of the component oxides.

A plot of the melting point determined using the capillary method *vs.* the mole fraction for the RuO_4–OsO_4 sytem gave a straight line. Figure 1 shows these data. Nisel'son *et al.*[8] presented a crystal–liquid equilibrium diagram for the OsO_4–RuO_4 system, indicating the system to be almost ideal. Their melting point data show values *ca.* 1 °C higher than the respective present values. The discrepancies may be due to differences in the quantity of sample used. The amount of sample used in the Niesel'sons measurement[9] was of the order of grams as compared with the order of milligrams in the present measurement.

In Nisel'son's results,[8] the deviation from ideality may also be ascribed to the use of the boiling point value of 133.4 ± 1 °C instead of the value of 129.6 ± 0.2 °C reported here for calculation of the molar volume of RuO_4 at its normal boiling point and relative volatility at normal pressure. Therefore, some of the deviation from ideal behaviour is as a result of their calculations. In view of the present results, together with the above considerations, undoubtedly RuO_4 and OsO_4 are ideal solutions.

The properties of these tetraoxides appear to be based mainly upon their tetrahedrally co-ordinated oxygen atoms in the outer shell of the molecule. Therefore in one sense, these tetraoxides may be regarded as chemical homologues of oxygen and ozone. This concept has lead the author to devise an improved method, which will be presented elsewhere, for treatment of fission products.[10]

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