An Investigation of Thermodynamic Activity in Multicomponent Alkali-Metal Liquids by a New Variant of the Effusion Method

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A new variant of the effusion method for measuring the Gibbs energy (thermodynamic activity) in alkali-metal multicomponent coolants is proposed. It was developed for the pressure range intermediate between the Knudsen's and the hydrodynamic efflux modes.

The activity is determined using the partial pressures of the components by the effusion method with a measurement of atomic beam intensity. As oxygen inevitably reacts with a molten alkali metal, the effusion hole cannot be made in advance. Therefore, the effusive hole is machined directly in the vacuum chamber by an electron-ray pulse (the electron linear accelerator was located inside the chamber) after the cell acquired the working temperature. Then the cell is transferred by a remote-controlled drive to under the cryogenic condenser, which is cooled by liquid nitrogen. Spectrochemical analysis gives the condensate composition, and, because it is equivalent to the vapor composition in the atomic beam, one can determine the partial intensity and pressure for each component, and, correspondingly, the activity.

The pressure range is intermediate between the Knudsen’s and the hydrodynamic efflux modes. A detailed analysis shows that it is possible to operate outside of the range where the Hertz-Knudsen equation applies. A general expression for the effusion method is obtained and the Hertz-Knudsen equation is a particular case of this general expression. The general form of the physical relationships persists, but there are essential numerical differences.

In addition, developing the effusion method for alkali-metal alloys at pressures outside of the Hertz-Knudsen equation applicability range fills a gap between the methods for examining the saturation pressures: manometric methods ($P > 100$ Pa) and methods based on the Hertz-Knudsen equation ($P < 1$ Pa).