Equilibrium evaporation of trace polonium from liquid lead–bismuth eutectic at high temperature

B. Gonzalez Prieto [a,b], J. Van den Bosch [a], J.A. Martens [b], J. Neuhausen [c], A. Aerts [a,*]

[a] SCK•CEN (Belgian Nuclear Research Centre), Boeretang 200, 2400 Mol, Belgium
[b] Centre for Surface Chemistry and Catalysis, KU Leuven, Kasteelpark Arenberg 23, 3001 Heverlee, Belgium
[c] Laboratory for Radio- and Environmental Chemistry, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland

HIGHLIGHTS

- We studied evaporation of trace polonium from liquid lead–bismuth eutectic.
- Our methods for Po are validated through analysis of LBE evaporation.
- At low concentration Po evaporates from LBE according to Henry's law.
- New Henry constant-temperature correlations for Po in LBE are presented.
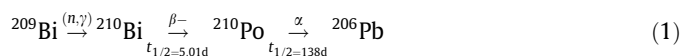
ARTICLE INFO

ABSTRACT

The evaporation of Po from its dilute solution in liquid lead–bismuth eutectic (LBE) was determined between 700 and 1000 °C in Ar/5%H$_2$ by the transpiration method. Concurrent measurements of the evaporation of LBE could be well reproduced by calculations using literature data, confirming conditions of equilibrium and convective vapor transport in our transpiration method experiments. This allowed to model the Po evaporation data and extract accurate temperature correlations for the Henry constant for Po dissolved in LBE at two different Po concentrations. Extrapolations of the new correlations were in excellent agreement with existing data at lower temperature.

1. Introduction

Quantitative data of the equilibrium vapor pressure of Po over its dilute solution in liquid lead–bismuth eutectic (LBE, 44.5 wt.% Pb 55.5 wt.% Bi) are essential for the design and safety evaluation of innovative spallation targets [1,2] and accelerator driven nuclear systems (ADS) in which LBE is used as target or coolant [3–5]. Most physicochemical properties of LBE are favorable for the operation and safety of such nuclear systems. Notable are a melting point of *ca.* 125 °C, which allows reactor/target operation at low temperature resulting in reduced corrosion rates and easier maintenance, and a high boiling temperature (1670 °C) which increases safety by eliminating pressurization and boiling problems [6]. A concern with the use of LBE is the production of polonium. ^{210}Po is formed by neutron capture with bismuth in the LBE and subsequent β decay of ^{210}Bi according to the following nuclear reaction chain:

$$^{209}\text{Bi} \overset{(n,\gamma)}{\longrightarrow} {}^{210}\text{Bi} \underset{t_{1/2}=5.01\text{d}}{\overset{\beta-}{\longrightarrow}} {}^{210}\text{Po} \underset{t_{1/2}=138\text{d}}{\overset{\alpha}{\longrightarrow}} {}^{206}\text{Pb} \qquad (1)$$

Typical maximal mole fractions $x_{\text{Po(lbe)}}$ of ^{210}Po encountered in spallation targets and ADS are of the order of 1×10^{-6} [6].

Several research groups reported measurements of the equilibrium vapor pressure of Po over its dilute solution in LBE, at different temperatures. Most frequently, evaporation in inert or mildly reducing atmosphere (in presence of maximum 7% hydrogen gas) was studied [7–9]. Such atmospheres are foreseen as cover gas in spallation and ADS facilities.

Two research groups used the so-called transpiration method to determine Po evaporation [8,9]. This is a dynamic method in which the vapors emanating from the liquid metal sample are transported away by a flowing carrier gas. The evaporated amount of Po is quantified by activity measurement of condensed vapors or by determination of the activity change of the sample. With the transpiration method, it is important to ensure that the experimental conditions are such that the carrier gas is saturated with vapors and convective vapor transport is dominant. Under these conditions, quantitative vapor pressure data can be derived by application of simple models [10,11].

In the present contribution, we use the transpiration method to simultaneously study LBE evaporation and Po evaporation from dilute solution in LBE, in mildly reducing atmosphere, Ar/5%H$_2$. LBE evaporation data were interpreted with standard evaporation

* Corresponding author. Tel.: +32 14 338018.
  E-mail address: aertsl@sckcen.be (A. Aerts).

models for pure components and compared with literature values which allowed us to validate our methods. Po evaporation data were consistently analyzed by a new model that takes into account depletion of solute during the experimental run, assuming Henry law behavior. Temperature correlations between 600 and 1000 °C for the Henry constant of Po in LBE in Ar/5%H$_2$ were determined at initial ^{210}Po mole fractions of 2×10^{-12} and 1×10^{-10}. As a result, a set of new, accurate Po vapor pressure data under previously unexplored conditions is provided.

2. Materials and methods

Two series of cylindrical LBE samples of 5 mm diameter and 13 mm height with a mass of *ca.* 2.7 g were irradiated in channel Y4 of the BR-1 reactor at SCK-CEN for 8 h in a thermal neutron flux of 3.5×10^{15} m^{-2} s^{-1}. After irradiation the samples were stored in a lead container for *ca.* 1 month to allow for decay of ^{210}Bi to ^{210}Po. The specific activity of ^{210}Po after 1 month of cooling was about 20 kBq/g, corresponding to a mole fraction of 10^{-10}. LBE samples with lower ^{210}Po mole fraction of *ca.* 10^{-12} were prepared by diluting a piece of irradiated sample with inactive LBE fragments. Active and inactive pieces were molten together and homogenized by heating to 600 °C during 30 min under a flow of 1 l/min of Ar/ 5%H$_2$. The activity of ^{210}Po in the diluted samples was *ca.* 500 Bq/g.

The transpiration setup used for evaporation experiments with LBE and Po is shown in Fig. 1.

Carrier gas flow rates were controlled by mass flow controllers (Bronkhorst). Carrier gases used were Ar (Air products, 99.9997%) or Ar/5%H$_2$ (Air Products, Ar 94.99 ± 0.02%, H$_2$ 5.0 ± 0.5%). The carrier gases were further purified before entering the evaporation section by a Ni-based filter operating at room temperature (SAES Pure Gas). The purifier was connected via 6 mm stainless steel and perfluoroalkoxy tubing to a quartz tube (inner diameter 13 mm) in which the sample was heated. A leak-tight connection with the quartz tube was accomplished by a stainless steel flange with a quartz counterflange attached to the quartz tube, sealed with a Viton O-ring. After each sample loading, the system was flushed during 15 min with a flow of 1 l/min of Ar/5%H$_2$. The sample section of the quartz tube was heated by a tubular furnace (Carbolite Type 301). LBE samples were loaded in a quartz boat, on quartz tissue to avoid sticking of the LBE to the boat. Quartz insertions were placed before and after the sample boat to reduce diffusive vapor transport. To prevent Po from escaping the setup an activated charcoal (Sigma–Aldrich) filter and a washing bottle

filled with silicon oil were installed downstream from the quartz tube. At the exhaust of the setup a paper filter allowed to check for contamination.

The temperature of the gas along the furnace length was measured by a 1 mm K-type thermocouple. Accurate knowledge of the temperature at the sample position was needed because the vapor pressure strongly depends on it.

3. Experimental

Before each evaporation experiment, ^{210}Po-doped LBE samples were homogenized by heating to 600 °C during 30 min while flushing with 1 l/min Ar/5%H$_2$. Samples were then cooled and unloaded. Subsequently, the samples were cleaned with acetone, and a small flake (*ca.* 100 mg) was removed and weighed (Sartorius CPA1245 balance) for the determination of the initial Po content by liquid scintillation counting (LSC) analysis. The flake was dissolved in 7 ml 1 M HNO$_3$(aq) and a volume of 2 ml of this solution was poured into a polyethylene LSC vial and mixed with 18 ml of scintillation cocktail (Zinsser Analytic Aquasafe 500Plus). Each sample was counted for 90 min in a Packard TriCarb 2100TR LSC instrument. Evaporation experiments at temperatures between 633 and 971 °C were performed in a flow of 100 ml/min Ar/5%H$_2$. Experiment time was 1 h. After each run at a given temperature, the weight loss of LBE was determined and the concentration of Po remaining in the sample was determined by LSC. The latter value was subtracted from the initial Po concentration to calculate the release. The one standard deviation uncertainty on the Po release values was estimated from the error resulting from sample weighing, the sampling of liquids, and the counting error of the LSC measurement. Individual errors were combined using standard error propagation rules. Two series of tests were carried out with samples with respectively initial Po mole fractions of 2×10^{-12} and 10^{-10}.

4. Results and discussion

4.1. LBE evaporation

It is generally assumed [12,13], but was not directly demonstrated experimentally, that the vapor above LBE consists of monoatomic Pb(g) and Bi(g) and diatomic Bi$_2$(g) molecules. Under conditions of saturation of the carrier gas and vapor transport by convection, the weight loss of the LBE sample during evaporation is given by [12]:

$$\Delta m_{lbe} = m_{lbe}(0) - m_{lbe}(t)$$
$$= \frac{\dot{V}t}{RT}\left(M_{Pb(g)}p_{Pb(g)} + M_{Bi(g)}p_{Bi(g)} + M_{Bi_2(g)}p_{Bi_2(g)}\right) \qquad (2)$$

where t is the experiment time [s], $\dot{V}$ is the carrier gas flow rate [m^3 s^{-1}], R is the ideal gas constant [J mol^{-1} K^{-1}] and T is the temperature [K]. The factors M and p are, respectively, the molecular weights [g mol^{-1}] and equilibrium partial pressures [Pa] of the vapor species.

The experimental weight loss of LBE (Δm_{lbe}) at different temperatures is shown in Fig. 2. To evaluate the accuracy of these experimental results, a comparison was made with the expected weight loss using Eq. (2) and literature data. To this end, we used two approaches. In the first, the equilibrium partial pressures of vapor constituents above LBE (Pb(g), Bi(g) and Bi$_2$(g), see Eq. (2)) were calculated following the procedure recommended in a review by Morita et al. [13] (detailed calculations are available as Supplementary information). In the second approach, the experimentally determined correlation for the vapor pressure of LBE in the range 450–750 °C by Ohno et al. [12] was used as a starting point. Com-
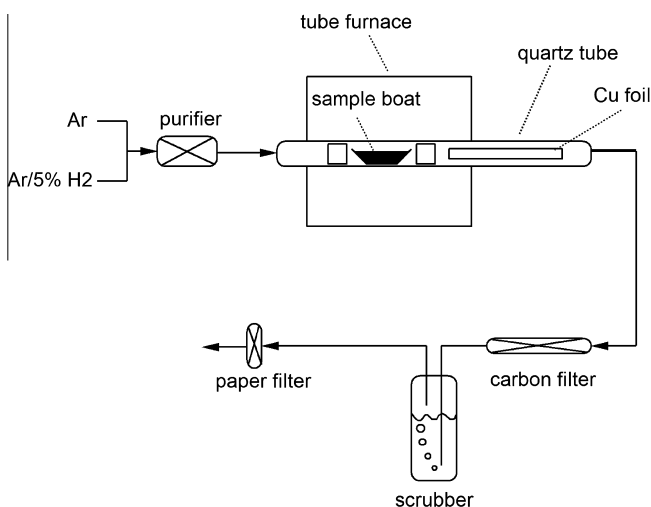

Fig. 1. Transpiration setup used for evaporation studies.