SHORT COMMUNICATIONS

RECRYSTALLIZATION OF LEAD OXIDE FROM MOLTEN LEAD*

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During an investigation of the surface tension of liquid lead by means of a sessile drop technique, small transparent yellow crystals were observed to form on the solidified surface after heating at 750 °C in an argon atmosphere. X-Ray crystallographic analysis, using a 9 cm Guinier camera, confirmed the tetragonal structure and lattice dimensions of yellow lead oxide. It seemed probable that the oxide had been formed from small amounts of oxygen in the cylinder argon used in these experiments. A more systematic study of this crystallization process was subsequently carried out in vacuo, using weighed additions of A.R. lead oxide. This note describes the recrystallization process observed.

Pure lead specimens (99.999 %; supplied by the Metallurgy Department, University of Melbourne) consisting of 3.5 by 6.5 mm cylindrical pellets, were placed on specially prepared high density uranium dioxide plaques (UO$_2$), and a weighed amount of A.R. lead oxide placed on the pellet. The assembly was inserted into an induction heated tube furnace which was then evacuated and heated to 750 °C. Photographs of the profile of the sessile drop were taken at different temperatures and time intervals. After each run, the plaque and lead surface were examined microscopically (×300) and photomicrographs were taken when necessary.

The process of solution of lead oxide was accompanied by random motion of the particles over the surface of the lead drop, in much the same manner as small particles of camphor move on a water surface. This effect was observed to occur for lead sulphide, lead selenide, and lead telluride also, although in these cases formation of surface crystals did not occur, a result probably associated with greater solubility in the lead. Plate 1 shows three photographs (Figs. 1–3) of the solution process with lead oxide, the motion of the particles producing a blurred image in Figure 2, for which a 60 sec exposure was used. The lowest temperature at which appreciable solution was observed lies in the range 500 to 530 °C for each of the four solutes.

The rate of cooling has some influence on the formation of the crystals. Plate 1, Figure 4, is a photomicrograph of a rapidly cooled sample, and it will be noted that the lead oxide crystal is irregular in shape and appears to have been formed by growth from a crack in the initially formed lead "crust". Plate 1, Figure 5, on the other hand, shows some of the more regular lead oxide crystals produced by the slower cooling obtained in a furnace of larger heat capacity. These crystals were coloured red (probably an interference colour).

* Manuscript received March 4, 1959.
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The approximate maximum solubility of lead oxide in lead at 750 °C was estimated to be 0.019 molal (0.42 wt.%), which was inferred from the surface tension v. concentration isotherm (Bradhurst and Buchanan 1959, unpublished data), which showed maximum depression at this concentration. The value obtained by Richardson and Webb* was somewhat smaller (saturation at an interpolated value of 0.012 molal).

This work was supported by a grant from the Australian Atomic Energy Commission and forms part of a programme of work on the surface chemistry of liquid metal systems.

ACID–BASE EQUILIBRIA IN ACETIC ACID AT ELEVATED TEMPERATURES†

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A number of acid-base equilibrium constants in acetic acid at 25 °C have been determined by Lemaire and Lucas (1951), Smith and Elliott (1953), and Kolthoff and Bruckenstein (1956) using spectrophotometric measurements. Kolthoff and Bruckenstein (1956) have also determined the indicator constant for p-naphtholbenzeno with p-toluenesulphonic and hydrochloric acids in the temperature range 18–33 °C. From a consideration of these results and those of Jolly (1952) on the heat of neutralization of perchloric acid and sodium acetate, Kolthoff and Bruckenstein (1956) conclude that the heats of reaction between acids and bases in acetic acid are of the order of 5 to 7 kcal mole⁻¹ and are very little affected by the strength of the acid or the base, that is,

$$
B + H^+X^- \rightleftharpoons BH^+X^-,
$$

5 to 7 kcal mole⁻¹.

The equilibrium constant for the reaction between perchloric acid and the base, water, has been determined at 25 °C by Lemaire and Lucas (1951), Smith and Elliott (1953), and Kolthoff and Bruckenstein (1956) while that for acetamide has been determined by Lemaire and Lucas (1951). However, the values for these constants were required at 105 °C, which is well outside the temperature range used by Kolthoff and Bruckenstein (1956), and any extrapolation to 105 °C using their estimated heat of reaction would give only approximate values for the equilibrium constants.

Smith and Elliott (1953) and Kolthoff and Bruckenstein (1956) for most of their work used p-naphtholbenzeno. At 25 °C the acid form of this indicator is green and has absorption maxima at 464 and 625 m. At 105 °C or on heating

† Manuscript received February 2, 1959.
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