Water Vapor Pressures of $LiCl\bullet 2H_2O$-Saturated Solutions and $C_2H_2O_4\bullet 2H_2O$-$C_2H_2O_4$ Mixtures

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ABSTRACT

This paper is pertaining to the preparations of H_2O-H_2 gas mixtures with very small H_2O/H_2 ratios: the water vapor pressures of $LiCl\bullet 2H_2O$-saturated solutions and $C_2H_2O_4\bullet 2H_2O$-$C_2H_2O_4$ mixtures were determined at temperatures lower than ambient temperature.

1. INTRODUCTION

High temperature metallurgical experiments often require H_2-H_2O gas mixtures for controlling oxygen partial pressures. A classical technique to meet this requirement is based upon bubbling H_2 or Ar-H_2 gas mixture into distilled water kept at a constant temperature. Needless to say, the water vapor pressures obtainable with such technique are to be greater than those at 273 K (0 °C), *i.e.*, 6.03×10^{-3} atm. This water bath temperature of 273 K corresponds to equilibrium oxygen partial pressure of 6.52×10^{-17} atm at 1473 K for example. During a course of thermochemical studies conducted at the authors' laboratory, it became necessary to prepare much lower P_{O_2} through H_2O-H_2 gas mixtures. Following to Gokcen /1/, by using water saturated with hydrated lithium chloride, $LiCl\bullet H_2O$, rather than pure water, it would be possible to prepare such H_2O-H_2 gas mixtures of very small P_{H_2O}/P_{H_2} ratios. The P_{H_2O} values reported by Gokcen, which are given in Figure 1(a), however, cannot be extrapolated to temperatures lower than 291.5 K (18.5°C), because at $T < 291.5$K the hydrated lithium chloride in equilibrium with water is $LiCl\bullet 2H_2O$ rather than $LiCl\bullet H_2O$ /2/.

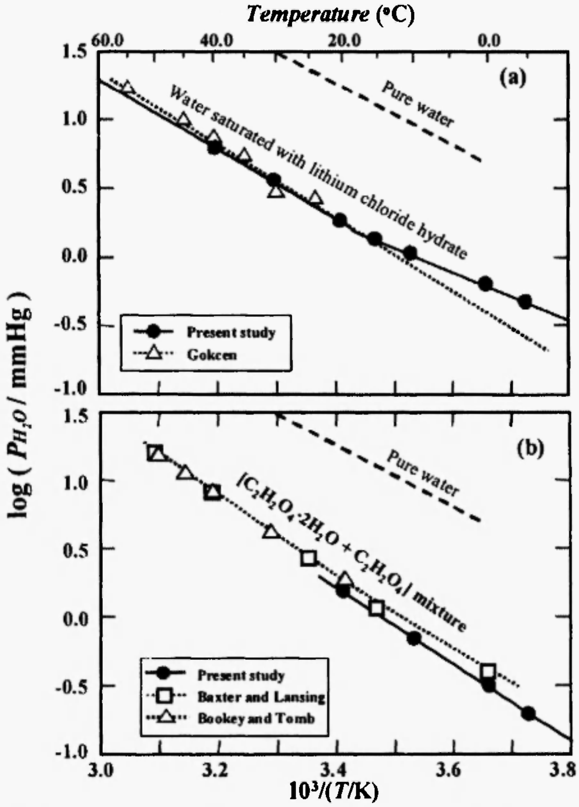

Fig. 1: Relation between water vapor pressure and reciprocal temperature. (a) $LiCl\bullet 2H_2O$- or $LiCl\bullet H_2O$-saturated water. (b) $C_2H_2O_4\bullet 2H_2O$-$C_2H_2O_4$ mixture.

An alternative technique to obtain very small PH_2O/PH_2 ratios would be passing hydrogen through a column containing a mixture of oxalic acid dihydrate, $C_2H_2O_4 \bullet 2H_2O$, and anhydrous oxalic acid, $C_2H_2O_4$. The water vapor pressures of such mixtures were determined by Baxter and Lansing/3/, and Bookey and Tombs/4/, as shown in Figure 1(b). At the time of their measurements, *i.e.*, 1920 and 1952, respectively, it would be very difficult to maintain water bath temperatures lower than the ambience with a satisfactory accuracy, resulting in that reexaminations would be required. The present study is aimed at measuring the water vapor pressures of $LiCl \bullet 2H_2O$-saturated solutions and $C_2H_2O_4 \bullet 2H_2O$-$C_2H_2O_4$ mixtures at temperatures lower than 293K (20°C).

2. EXPERIMENTAL

A stirred bath of about 32 liters of ethylene glycol-water solution was contained in an electronic thermostat, through which bath temperatures could be maintained down to 268K. The bath contained either $LiCl \bullet 2H_2O$-saturated solution or $C_2H_2O_4 \bullet 2H_2O$-$C_2H_2O_4$ mixture. About 1,000 cc of the solution was contained in two bottles, while the $C_2H_2O_4 \bullet 2H_2O$-$C_2H_2O_4$ mixture, consisting of four parts $C_2H_2O_4 \bullet 2H_2O$ and one part $C_2H_2O_4$ in weight, was placed within a glass tube of 16 mm i.d. and 380 mm in length together with glass beads. Temperatures of the thermostat were measured by a standard thermometer and controlled to ±0.01K. Argon-H_2(12%) gas mixtures were admitted into such mediums at flow rates between 50 and 150 cc/min through a copper tube placed within the thermostat bath. This copper tube of 6 mm i.d. and 2,500 mm in length was essential to ensure that there would be negligible temperature gradient between gas flow and the thermostat bath.

The purification train for Ar-H_2(12%) gas mixture consisted of silica gel and three towers of phosphorous pentoxide. After leaving the thermostat, the gas flow entered two U-type weighing tubes containing magnesium perchlorate in order to collect water vapor for 90 to 800 minutes, depending upon the thermostat temperatures, until weight increase exceeded 20 mg. Water vapor pressures thus determined were independent of flow rates between 50 and 150 cc/min.

3. RESULTS AND DISCUSSION

The present PH_2O values for $LiCl \bullet 2H_2O$-saturated water are shown in Figure 1(a). As shown in this figure, it is evident that extrapolation of the data by Gokcen /1/ to lower temperatures would result in significant errors. For $C_2H_2O_4 \bullet 2H_2O$-$C_2H_2O_4$ mixtures, as shown in Figure 1(b), the present data were lower than those by Baxter and Lansing /2/, and Bookey and Tombs /4/. This disagreement would be due to temperature gradient between gas flow and thermostat bath in their experiments. With respect to this, it is noted that if water vapor pressure measurements in this study were made without the copper tube of 2,500 mm in length, then the observed PH_2O values were 5 to 15% greater than those given in Figure 1(b).

By using the least squares method, the present data for $LiCl \bullet 2H_2O$-saturated water were given as:

$$\log (P_{H_2O}/mmHg) = 6.24 - 1{,}760/(T/\mathrm{K}) \pm 0.03, \quad \text{at } T < 291.5\mathrm{K}\ (18.5^\circ\mathrm{C}) \qquad (1)$$

$$\log (P_{H_2O}/mmHg) = 8.82 - 2{,}510/(T/\mathrm{K}) \pm 0.03, \quad \text{at } T > 291.5\mathrm{K}\ (18.5^\circ\mathrm{C}) \qquad (2)$$

For $C_2H_2O_4 \bullet 2H_2O$-$C_2H_2O_4$ mixtures, we obtained:

$$\log (P_{H_2O}/\mathrm{mmHg}) = 9.76 - 2{,}810/(T/\mathrm{K}) \pm 0.04, \quad \text{at } T < 293\ \mathrm{K}\ (20^\circ\mathrm{C}) \qquad (3)$$

If Ar-H_2(12%) mixture was passed through $C_2H_2O_4 \bullet 2H_2O$-$C_2H_2O_4$ mixtures kept at 273 K, then the corresponding oxygen partial pressures are about two orders lower than those attainable with the conventional technique.

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