

# Water Vapor Pressures of $\text{LiCl}\cdot 2\text{H}_2\text{O}$ -Saturated Solutions and $\text{C}_2\text{H}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ - $\text{C}_2\text{H}_2\text{O}_4$ Mixtures

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## ABSTRACT

This paper is pertaining to the preparations of  $\text{H}_2\text{O}$ - $\text{H}_2$  gas mixtures with very small  $\text{H}_2\text{O}/\text{H}_2$  ratios: the water vapor pressures of  $\text{LiCl}\cdot 2\text{H}_2\text{O}$ -saturated solutions and  $\text{C}_2\text{H}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ - $\text{C}_2\text{H}_2\text{O}_4$  mixtures were determined at temperatures lower than ambient temperature.

## 1. INTRODUCTION

High temperature metallurgical experiments often require  $\text{H}_2$ - $\text{H}_2\text{O}$  gas mixtures for controlling oxygen partial pressures. A classical technique to meet this requirement is based upon bubbling  $\text{H}_2$  or  $\text{Ar}$ - $\text{H}_2$  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.*,  $6.03 \times 10^{-3}$  atm. This water bath temperature of 273 K corresponds to equilibrium oxygen partial pressure of  $6.52 \times 10^{-17}$  atm at 1473 K for example. During a course of thermochemical studies conducted at the authors' laboratory, it became necessary to prepare much lower  $P_{\text{O}_2}$  through  $\text{H}_2\text{O}$ - $\text{H}_2$  gas mixtures. Following to Gokcen /1/, by using water saturated with hydrated lithium chloride,  $\text{LiCl}\cdot 2\text{H}_2\text{O}$ , rather than pure water, it would be possible to prepare such  $\text{H}_2\text{O}$ - $\text{H}_2$  gas mixtures of very small  $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$  ratios. The  $P_{\text{H}_2\text{O}}$  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  $T < 291.5\text{K}$  the hydrated lithium chloride in equilibrium with water is  $\text{LiCl}\cdot 2\text{H}_2\text{O}$  rather than  $\text{LiCl}\cdot \text{H}_2\text{O}$  /2/.

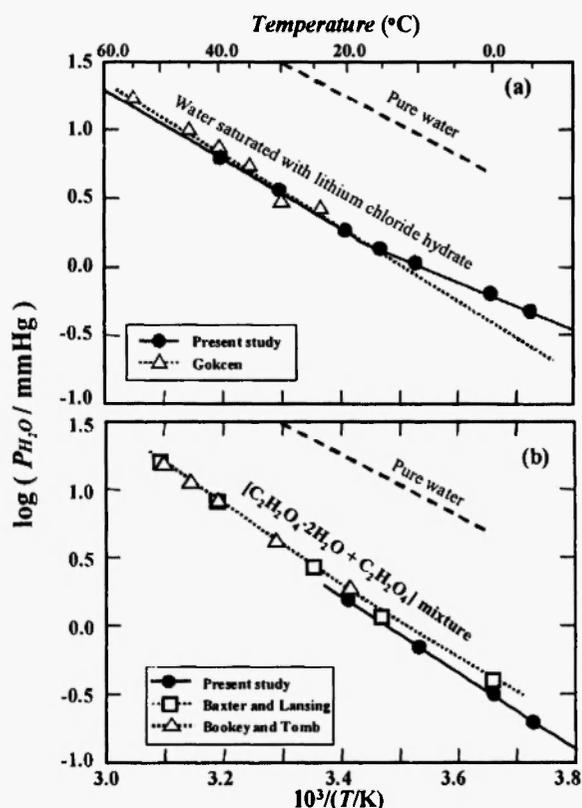


Fig. 1: Relation between water vapor pressure and reciprocal temperature. (a)  $\text{LiCl}\cdot 2\text{H}_2\text{O}$ - or  $\text{LiCl}\cdot \text{H}_2\text{O}$ -saturated water. (b)  $\text{C}_2\text{H}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ - $\text{C}_2\text{H}_2\text{O}_4$  mixture.

An alternative technique to obtain very small  $P_{\text{H}_2\text{O}}/P_{\text{H}_2}$  ratios would be passing hydrogen through a column containing a mixture of oxalic acid dihydrate,  $\text{C}_2\text{H}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ , and anhydrous oxalic acid,  $\text{C}_2\text{H}_2\text{O}_4$ . 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  $\text{LiCl}\cdot 2\text{H}_2\text{O}$ -saturated solutions and  $\text{C}_2\text{H}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ - $\text{C}_2\text{H}_2\text{O}_4$  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  $\text{LiCl}\cdot 2\text{H}_2\text{O}$ -saturated solution or  $\text{C}_2\text{H}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ - $\text{C}_2\text{H}_2\text{O}_4$  mixture. About 1,000 cc of the solution was contained in two bottles, while the  $\text{C}_2\text{H}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ - $\text{C}_2\text{H}_2\text{O}_4$  mixture, consisting of four parts  $\text{C}_2\text{H}_2\text{O}_4\cdot 2\text{H}_2\text{O}$  and one part  $\text{C}_2\text{H}_2\text{O}_4$  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  $\pm 0.01\text{K}$ . Argon- $\text{H}_2$ (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- $\text{H}_2$ (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  $P_{\text{H}_2\text{O}}$  values for  $\text{LiCl}\cdot 2\text{H}_2\text{O}$ -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  $\text{C}_2\text{H}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ - $\text{C}_2\text{H}_2\text{O}_4$  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  $P_{\text{H}_2\text{O}}$  values were 5 to 15% greater than those given in Figure 1(b).

By using the least squares method, the present data for  $\text{LiCl}\cdot 2\text{H}_2\text{O}$ -saturated water were given as:

$$\log (P_{\text{H}_2\text{O}}/\text{mmHg}) = 6.24 - 1,760/(T/\text{K}) \pm 0.03, \quad (1)$$

at  $T < 291.5\text{K}$  (18.5°C)

$$\log (P_{\text{H}_2\text{O}}/\text{mmHg}) = 8.82 - 2,510/(T/\text{K}) \pm 0.03, \quad (2)$$

at  $T > 291.5\text{K}$  (18.5°C)

For  $\text{C}_2\text{H}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ - $\text{C}_2\text{H}_2\text{O}_4$  mixtures, we obtained:

$$\log (P_{\text{H}_2\text{O}}/\text{mmHg}) = 9.76 - 2,810/(T/\text{K}) \pm 0.04, \quad (3)$$

at  $T < 293\text{K}$  (20°C)

If Ar- $\text{H}_2$ (12%) mixture was passed through  $\text{C}_2\text{H}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ - $\text{C}_2\text{H}_2\text{O}_4$  mixtures kept at 273 K, then the corresponding oxygen partial pressures are about two orders lower than those attainable with the conventional technique.

## REFERENCES

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