EXPERIMENTAL DETERMINATION OF
VAPOR PRESSURES OF KCl

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SYNOPSIS

The vapor pressures of KCl are measured in the temperature range of 873 to 1250K using transpiration technique. In the system, the variation of vapor pressure of solid KCl with temperature is determined as lnP(atm) = -14477.868/T - 10.45 ln T + 80.53 and that of liquid KCl as lnP(atm) = 326265.24/T + 283.41 ln T - 2286.24. The melting point and the boiling point of KCl were determined as 1047K and 1445K, respectively.

INTRODUCTION

Several investigations were made on the determination of vapor pressures and thermodynamic relationships of the KCl\(^{(1-3)}\). The work of Fiock and Rodebush\(^{(4)}\) on KCl did not clearly delineate the boundaries of the phase region. The plateau vapor pressures were not thoroughly defined and were considerably displaced in pressure compared to those from the work of Kangro and Wieking\(^{(5)}\). These latter authors concentrated their studies primarily from 1133 to 1263K in the pressure range of 2.5 to 25 mmHg. No data were determined to outline the regions of primary solid phase. Also the establishment of the plateau vapor pressure was rather limited in scope. In neither work was a treatment conducted of Gibbs energy of solutions of potassium compound in the single-phase regions and the integral thermodynamic quantities of mixing throughout the system. Therefore, an experimental study is undertaken to determine the complete equilibrium relationships and thermodynamic data for the KCl system, and a KCl equilibrium diagram is constructed.

EXPERIMENTAL

There are several methods that are widely used in the measurement of vapor pressures, such as dynamic method\(^{(6)}\), static method\(^{(7,8)}\) and other general methods\(^{(9,10)}\). In this study, the transpiration technique (or gas-saturation method)\(^{(11)}\) is employed for determining the vapor pressures of KCl in one component system. A measured volume of inert gas is saturated by passing it through the liquid at a definite temperature. The quantity of liquid vaporized is obtained from the loss in weight of the liquid, or by removal of the vapor from the gas stream.
in weighed absorbing tubes. Assuming Dalton's law of partial pressures and the ideal-gas law, the partial pressure of the vapor, \( p \), is calculated by the formula

\[
P = \frac{g}{Mv}RT
\]  

[1]

where \( R \) = gas constant, \( T \) = absolute temperature, and \( v \) = total volume of gas (including inert gas vapor) containing \( g \) grams of vapor of molecular weight \( M \). When both components of a solution, however, are volatile, it is necessary to have a suitable physical and chemical methods for analyzing the condensed vapor.

The overall view of the experimental set-up is shown in Figure 1. It consists of passing a stream of inert carrier gas at a known rate over a condensed sample of interest. The flow rate is maintained such that equilibrium saturation is established between the condensed and vapor phases. The carrier gas stream is saturated with the vapor from the sample and transported from the reaction chamber downstream to a condenser system. The vapor pressure is then calculated by using the following relationship for partial pressure:

\[
P_i = \frac{m_i}{m_t + m_f}P_T
\]  

[2]

where \( m_i \) is the moles of vapor species \( i \), \( m_t \) is the total moles of vapor species, \( m_f \) is moles of carrier gas, \( p_i \) is the partial pressure of vapor species \( i \) and \( P_T \) is the total pressure in the system.

The purified salts are loaded into high purity graphite sample boats under the protective atmosphere of a dry box and then transferred to the transpiration apparatus in an atmosphere of dry argon gas. The pure chloride salts are used as reference salts. Several sample boats such as silica, nickel and iron were unsuccessful as a container material. The furnaces are preheated to the desired set temperature and the sample carrier tube inserted into the reactor tube under a flow of the carrier gas. The temperature of the melt is measured using the Pt-13%Rh+Pt thermocouple. After the predetermined equilibration time of 4 hours, the sample boat is withdrawn and cooled to the room temperature under the argon gas. The condenser assembly is removed and the deposited material is dissolved in the striping solution. The striping solution is then analyzed by Ion Chromatograph. X-ray analysis of the condensed material is also made to identify the vapor species present in the gas phase.

RESULTS AND DISCUSSION

Vapor pressure of KCl

The vapor pressures of pure KCl are determined in the temperature range of 873 to 1300K. The results are presented in Figure 2. The experimentally determined values of vapor pressure of KCl (broken lines) are in very good agreement with the Kangro et al.'s data. 
Thermodynamic consideration

In the thermodynamic consideration, the Clausius-Clapeyron equation

\[ d \ln P = \frac{\Delta H}{RT^2} \, dT \]  \[3\]

can be employed. When \( \Delta C_p \) for the evaporation or sublimation is not zero, but independent of temperature, \( \Delta H_T \) is given as

\[ \Delta H_T = \Delta H_{298} + \Delta C_p \, (T - 298) = (\Delta H_{298} - 298 \, \Delta C_p) + \Delta C_p \, T \]  \[4\]

in which case integration of Eq. (3) gives

\[ \ln P = \frac{298 \, \Delta C_p - \Delta H_{298}}{R} \frac{1}{T} + \frac{\Delta C_p}{R} \ln T + \text{constant} \]  \[5\]

which is normally expressed in the form

\[ \ln P = \frac{A}{T} + B \ln T + C \]  \[6\]

Where \( A, B \) and \( C \) are constants. They can be calculated by selecting the experimental data of vapor pressures at different temperatures. In this study, the vapor pressure of solid potassium chloride with temperature is determined as

\[ \ln P(\text{atm}) = -14477.868 \frac{1}{T} - 10.45 \ln T + 80.35 \]  \[7\]

and the vapor pressure of liquid potassium chloride with temperature is determined as

\[ \ln P(\text{atm}) = \frac{326265.24}{T} + 283.41 \ln T - 2286.24 \]  \[8\]

Liquid-vapor and solid-vapor equilibria

The normal boiling temperature \( T_b \) of KCl can be defined as that temperature at which the vapor pressure of the liquid equals 1 atm. Therefore, from the liquid-vapor equilibrium equation (6),

\[ \ln P(\text{atm}) = 0 \text{ at } T = T_b \]

Thus
where $AH_f$ is the enthalpy of fusion, and $AV_f$ is the volume change. The volume of one mole of KCl (solid) is 37.57 cm$^3$, and the volume of one mole of KCl (liquid) is 45.94 cm$^3$\(^{(13)}\). Consequently:

$$\Delta V_f = V_l - V_s = 8.367 \text{ cm}^3/\text{mol} \quad [12]$$

In order to operate in compatible units, the volume change must be expressed in cal/mol atm. One cal/atm. represents 41.3 cm$^3$; therefore:

$$\Delta V_f = \frac{8.367}{41.3} = 0.2026 \text{ cal/mol.atm.} \quad [13]$$

and thus:

$$\frac{dP}{dT} = \frac{6251}{1045 \times 0.2026} = 29.52 \text{ atm/K} \quad [14]$$
This means that a container with KCl at 1°C will have to resist a pressure of 30 atmospheres.

Figure 3 represents the solid-liquid, solid-vapor and liquid-vapor equilibria in the vicinity of the triple point. From the figure, we can see that the lines OA, OB, and OC divide KCl into three distinct areas within each of which only one phase is stable. Within these areas the pressure exerted on the phase and the temperature of the phase can be independently varied without upsetting the one-phase equilibrium.

**Gibbs energy and properties of the phase**

The total Gibbs energy of phase change in the pure KCl system can be calculated by the equation

\[
\Delta G^0_{\text{phase change}} = R \, T \, \ln P_{e, \text{KCl}} \tag{15}
\]

where \( P_{e, \text{KCl}} \) is the equilibrium partial pressure of KCl. The relationship between Gibbs energy of phase change and the temperature is shown in Figure 4. From the figure, there is a Gibbs energy surface such as this for each phase - the vapor phase, the liquid phase, and one solid phase in KCl system. They intersect each other, and that portion of each surface which is lowest of all surfaces in the region gives the T-P range in which the corresponding phase is stable. It also shows that the KCl system has one possible solid phase.

**CONCLUSIONS**

From this thermodynamic study, the following conclusions can be made:

1. The vapor pressure of KCl measured in this study increased lightly from 0.83 to 1.80 mmHg at low temperature range (873 - 1023K); but at high temperature range (1180 - 1250K), it increased sharply from 4.79 to 11.10 mmHg.

2. The vapor pressure of solid potassium chloride with temperature is determined as \( \ln P(\text{atm}) = -14477.87/T - 10.45 \ln T + 80.53 \); and the vapor pressure of liquid potassium chloride with temperature is determined as \( \ln P(\text{atm}) = 326265.24/T + 283.41 \ln T - 2286.2 \) in KCl system.

3. From the equilibrium diagram of KCl, the melting point is determined as 1047K and boiling point is determined as 1445K at 1 atm.

4. A free energy surface of KCl is determined by the relationship between free energy of phase change with temperature and vapor pressure.

**ACKNOWLEDGEMENTS**

The authors are pleased to acknowledge the financial support of this research by Gas Research Institute and Arthur D. Little, Inc. U.S.A.. Thanks are also due to Drs. A. Lingras and S. Malhotra for their useful criticism and suggestions.
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Figure 1: Transpiration experimental setup
Figure 2. Vapor pressure of KCl as a function of temperature
Figure 3: Schematic representation of part of KCl phase diagram
Figure 4: The relationship of $G - P - T$ for KCl at 873 to 1250 K