Research Article

Vapor Pressure of Saturated Aqueous Solutions of Potassium Sulfate from 310 K to 345 K

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Received 29 June 2011; Accepted 11 September 2011

Academic Editor: Angelo Lucia

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The experimental evaluation of the vapor pressure of saturated aqueous solutions of potassium sulfate was carried out in the range of temperatures 310 K ≤ T ≤ 345 K. The experimental data were used to determine the corresponding values of the water activity in such solutions. The analytical expressions as a function of temperature of both, vapor pressure and water activity, were obtained from the correlation of the experimental results. The vapor pressure expression was also extrapolated to a different temperature range in order to make a comparison with the results obtained by other authors.

1. Introduction

The dependence on temperature of the vapor pressure of saturated aqueous solutions has been already determined for most of the inorganic salts, particularly halides, sulfates, and nitrates [1–3]. However, for the case of potassium sulfate the available information is surprisingly scarce and restricted to the temperature range 273 K ≤ T ≤ 323 K [4–7] plus one evaluation at 374 K [8]. On this context, the present work studied experimentally the vapor pressure of saturated aqueous solutions of potassium sulfate from 310 K to 345 K and evaluated from these data the dependence of the water activity on temperature. For this purpose, an isothermal static apparatus has been constructed and the reliability of the methodology employed was verified through the determination of the vapor pressure of pure water.

2. Experimental Section

2.1. Equipment. The apparatus used for the vapor pressure measurements, which is a modified version of the device employed by Kim et al. [9], is shown in Figure 1. It consists of a round-bottom flask (A) of 125 cm³ which contains the solution to be evaluated. It is connected to a U-tube mercury manometer (F) and to a vacuum pump (H) through the valve (G). The flask, the manometer, and the connecting tubes are immersed in an isothermal water bath (B), which temperature is controlled by a Lauda Thermostat UB20 Ultra (E), thermostated to within ±0.01 K. To ensure the uniformity of the bath temperature, a recirculation pump (D) was used with a flow rate of 4 dm³ min⁻¹. Moreover, a magnetic stirrer (C) was used in order to ensure the highest mass transfer rate between the liquid and vapor phases and also the temperature uniformity inside the equilibration flask. The temperature was measured by a digital thermometer Lauda R46, with a Pt resistance of 100 Ω which precision is ±0.01 K. The pressure was measured by an open U-tube mercury manometer and the manometric readings were made with a cathetometer to ±0.1 mm (±0.015 kPa). The reading performed at the temperature of each experiment was corrected according to the thermal expansion coefficient of mercury [10] and referred to 273.15 K. The atmospheric pressure was measured by a calibrated barometer.

2.2. Reagents. Potassium sulfate was analytical grade reagent manufactured by Merck and was used in the experiments without further purifications. The solutions were prepared with ultra-pure water (PureLab, Elga LabWater). Solid K₂SO₄ and the saturated solutions were degassed at room
temperature into a vacuum oven previously to be put into the equilibration flask.

2.3 Procedures. In each experiment, a volume of approximately 80 cm$^3$ of the saturated solution of potassium sulfate at room temperature was put into the flask (A) together with an amount of solid K$_2$SO$_4$ high enough to ensure the saturation condition at the temperature of the experiment, and a magnetic bar. Then the system was vacuumized through the valve (G) during two hours, with a vigorous and continuous agitation of the solution, ensuring that the boiling point is reached. This process produces the complete displacement of air by water vapor. After this stage, valve (G) is closed and the water bath (B) begins to be heated through the thermostat (E) and the recirculation pump (D). The solution is continually agitated to facilitate that the system could reach the equilibrium state, which is verified through the invariance of the manometric pressure. The presence of solid salt is also verified in order to ensure the saturation of the solution. In these conditions, the values of the temperature ($T$) and the vapor pressure ($P_w$) are obtained. The same procedure is used to verify the correct proper functioning of the equipment through the evaluation of the dependence of the vapor pressure of pure water on temperature.

Table 1: Measured and standard values of vapor pressure of pure water and relative deviation.

| $T$/K   | $P_w$/kPa | $P_w^{(a)}/$kPa | ($\Delta P_w/P_w^{(a)}/100$) |
|---------|-----------|-----------------|---------------------------|
| 308.10  | 5.62      | 5.612           | $-0.140$                  |
| 313.35  | 7.46      | 7.465           | 0.067                     |
| 318.70  | 9.87      | 9.870           | 0.000                     |
| 323.2   | 12.38     | 12.382          | 0.016                     |
| 327.95  | 15.63     | 15.612          | $-0.120$                  |
| 327.95  | 15.61     | 15.612          | 0.013                     |
| 333.35  | 20.13     | 20.132          | 0.010                     |
| 333.65  | 20.40     | 20.413          | 0.064                     |
| 337.55  | 24.38     | 24.378          | $-0.008$                  |
| 338.00  | 24.87     | 24.875          | 0.020                     |
| 338.05  | 24.93     | 24.931          | 0.004                     |
| 338.25  | 25.15     | 25.155          | 0.020                     |
| 343.80  | 32.06     | 32.089          | 0.090                     |
| 348.45  | 39.12     | 39.083          | $-0.094$                  |
| 348.50  | 39.16     | 39.164          | 0.010                     |
| 353.25  | 47.61     | 47.607          | $-0.008$                  |
| 353.45  | 48.00     | 47.994          | $-0.012$                  |

(a)[11].

3. Results

3.1. Vapor Pressure of Pure Water. Before the evaluation of the vapor pressure of the saturated aqueous solution of K$_2$SO$_4$ at different temperatures, the dependence of the vapor pressure of pure water on temperature was measured in order to verify the adequate operation of the apparatus, through the comparison of the results obtained with values reported in the literature [8]. Table 1 shows the values of the vapor pressure of pure water ($P_w^{(exp)}$) measured in the range $307 \leq T \leq 353$ K. The corresponding values obtained from the correlation proposed by Wagner and Prüß [11] ($P_w^{(ref)}$) are also illustrated. It can be appreciated that the average value of the relative deviation, evaluated as ($P_w^{(exp)} - P_w^{(ref)}/P_w^{(ref)}$), is 0.04%, while the highest value is 0.14%. These results demonstrate the correct functioning of the experimental device and the applied methodology.

3.2. Vapor Pressure of K$_2$SO$_4$-Saturated Solutions. Table 2 illustrates the values of the vapor pressure of saturated solutions of K$_2$SO$_4$ ($P_w$) measured at different temperatures. The relationship between ln$P_w$ and the inverse of temperature is shown in Figure 2. These experimental values were correlated employing the equation proposed by Apelblat and Korin [12], through the use of nonlinear least squares regression, and the resulting expression was as follows:

$$\ln(P_w/\text{kPa}) = 23.22469 - \frac{5293.806}{(T/\text{K})} - 0.75463 \ln(T/\text{K}).$$

(1)

This analytical dependence is illustrated in Figure 2 (continuous line). The quality of the correlation can be appreciated.
3.3. Water Activity in the $\text{K}_2\text{SO}_4$ Results obtained from the literature (the results of [4–7]).

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The quality of the water activity correlation can be appreciated by the average value of the relative deviation, which is 0.147%. The regression line was extrapolated to lower values of temperature in order to be compared with experimental results obtained from the literature (the results of [4–7]).

3.3. Water Activity in the $\text{K}_2\text{SO}_4$-Saturated Solutions. From the experimental values of the vapor pressure of saturated solutions of $\text{K}_2\text{SO}_4$ given in Table 2, the corresponding values of the water activity can be evaluated. In order to perform this calculation, it is proposed that the deviation from the ideal behavior of the vapor pressure can be appropriately described by the virial equation of state, considering only the second virial coefficient $B(T)$. In this case, the logarithm of the water activity can be evaluated from the following expression [13]:

$$\ln a_w = \ln \frac{P_w(T)}{P_w^0} + \frac{P_w(T) - P_w^0(T)}{RT} [B_w(T) - v_w^0(T)],$$

where $P_w(T)$ is the vapor pressure of saturated solutions of $\text{K}_2\text{SO}_4$, values given in Table 2. The values of the vapor pressure of pure water $P_w^0(T)$ were calculated from the equation proposed by Wagner and Prüß [11]. The second virial coefficient for water vapor $B_w(T)$ was evaluated with the equation proposed by Harvey and Lemmon [14]. Finally, the molar volume of liquid water $v_w^0(T)$ was calculated from the relationship between water density and temperature given by Kell [15]. The values of the water activity for the saturated solutions of $\text{K}_2\text{SO}_4$ evaluated experimentally are given in Table 2. The correlation of these values leads to the following equation:

$$\ln a_w = -10.2654 - \frac{579.361}{T} - 1.4607 \ln(T/K).$$

Figure 3 shows the experimental values (symbols) and the continuous line is the corresponding simulation with (3). It can be observed that this equation describes accurately the water activity of saturated solutions of potassium sulfate in the temperature range $310 \text{ K} \leq T \leq 345 \text{ K}$. The quality of the water activity correlation can be appreciated by the average value of the relative deviation, which is equal to 0.028%.

4. Discussion

The experimental evaluation of the vapor pressure of saturated aqueous solutions of potassium sulfate was carried out in the range of temperatures $310 \text{ K} \leq T \leq 345 \text{ K}$. In this range the solid phase corresponds to the anhydrous salt [16]. From the correlation of the experimental results, the corresponding analytical dependence was derived, which is given by (1). The results obtained were compared with the vapor pressure data reported by Leopold and Johnston [4], Foote et al. [5], and Adams and Merz [6]. There were also included vapor pressure values obtained from dew point measurements evaluated by Wexler and Hasegawa [7]. These data, which correspond to the temperature range $280 \text{ K} \leq T \leq 323 \text{ K}$, are included in Figure 2. To carry out the comparison, the dependence given in (1), obtained from the correlation of the ours experimental results, was extrapolated up to $280 \text{ K}$. There can be observed in Figure 2 a good agreement between the extrapolation of the correlation (continuous line) and the values of the vapor pressure
obtained from the literature [4–8], except those reported by Foote et al. These results are lower than those of the other authors in the low temperature range, being the corresponding slope of the dependence \( \ln P \) versus \( T \) significantly greater. The origin of this different behavior is unknown but could probably be due to same kind of systematic error in the experimental determination of pressure. Furthermore, when the evaluation of the vapor pressure of the saturated solution at 374.15 K, the unique result shown by Berkeley [8], is carried out by extrapolation with (1), the value \( P_w = 99.97 \) kPa is obtained. As the experimental value is \( P_w = 100.34 \) kPa, the relative deviation is 0.4%. This result shows an adequate agreement with the scarce data available for the vapor pressure of the saturated solution of potassium sulfate.

5. Conclusions

The experimental evaluation of the vapor pressure of saturated aqueous solutions of potassium sulfate was carried out in the range of temperatures \( 310 \) K \( \leq T \leq 345 \) K, which was not evaluated previously. The values of the water activity in such solutions were also determined. In both cases, the analytical dependences on temperature were obtained from the correlation of the experimental results, which accurately describe the behavior of these properties in such solution.

Acknowledgments

This work was supported by ANPCyT (PICT 541) and CONICET (PIP 1556), Argentina. M. O. Maggiolo thanks the scholarship granted by the Universidad Nacional del Litoral (Argentina).

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