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Articles

Vapor Pressure Determination of the KOH + K_2CrO_4 + H_2O System

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The evaporation crystallization of K_2CrO_4 from KOH aqueous solution is one of the key units of the chromate cleaner production process developed by the Chinese Academy of Sciences. The vapor pressure of the KOH + K_2CrO_4 + H_2O system was determined so as to optimize the evaporation operation. On the basis of the experimental results, the relationship between the vapor pressure and the temperature as well as the concentrations of KOH and K_2CrO_4 were determined as $\log(P/\text{kPa}) = 7.52 - 3.62 \times 10^{-2}(C_{\text{KOH}}/\text{mol·L}^{-1}) - 7.83 \times 10^{-2}(C_{\text{K}_2\text{CrO}_4}/\text{mol·L}^{-1}) - 2055.74\ \text{K}/T$ wherein C_{KOH} ranges from (0.8 to 10) mol·L^{-1}, $C_{\text{K}_2\text{CrO}_4}$ ranges from (0 to 2) mol·L^{-1}, and T ranges from (328.15 to 368.15) K.

Introduction

Vapor pressure is an important experimentally determined quantity and is imperative in calculating the sublimation and vaporization heat of the solution system. Vapor pressure data are also of vital importance in various scientific and technical fields such as electrical industries and vacuum metallurgy.[1]

Chromium compounds are essential to many industries including papermaking, high-quality alloy manufacturing, dyeing, pharmacy, catalysts, and rubber synthesizing.[2] However, serious environmental problems are involved in the traditional production process for chromium compounds due to the discharge of a large amount of chromium-containing residues after the high-temperature roasting reaction. A new green manufacturing process has recently been developed by the Institute of Process Engineering, Chinese Academy of Sciences.[3,4] As a cleaner chromate production process, the new process exhibits a promising prospect in remarkably improving the resources and energy utilization efficiency and achieving minimal emission of chromium-containing residue.[5] In the new process, achieving higher separation efficiency of the intermediate product K_2CrO_4 helps to reduce more environmental pollution at the source. It was found that evaporation crystallization is the most effective approach to separating K_2CrO_4 from the mixed aqueous solution of KOH and K_2CrO_4. Determining the vapor pressure data of the KOH + K_2CrO_4 + H_2O system becomes highly imperative in designing and optimizing separation operation.

Therefore, in this work, the vapor pressure of the KOH + K_2CrO_4 + H_2O system was experimentally studied in a large range of concentration from (328.15 to 368.15) K, and the relationship between the vapor pressure and the concentrations of KOH and K_2CrO_4 as well as the temperature were also investigated. These results are expected to provide the basis for designing and controlling the separation unit of K_2CrO_4 from KOH solution.

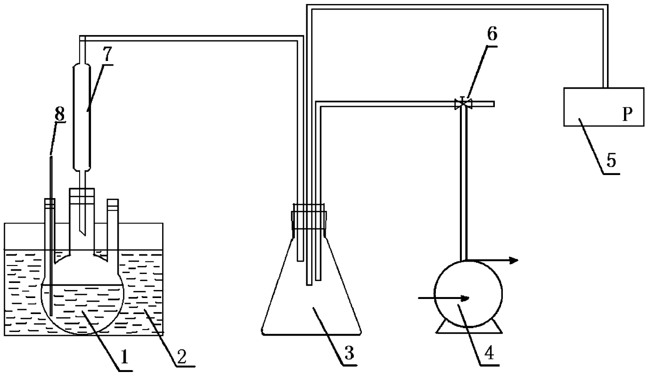

Figure 1. Experimental apparatus for measuring vapor pressures of the KOH + K_2CrO_4 + H_2O system: 1, three-necked bottle; 2, isothermal water bath; 3, buffer bottle; 4, vacuum pump; 5, mercury manometer; 6, three-way valve; 7, straight condensate tube; 8, thermoelectric couple.

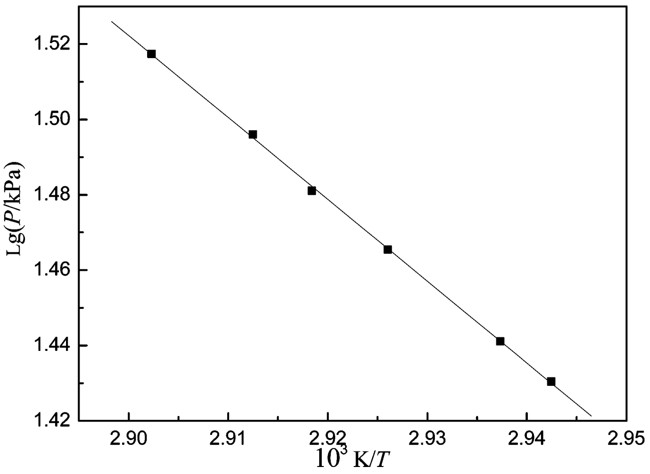

Figure 2. Relationship between measured vapor pressure and boiling point of pure water.

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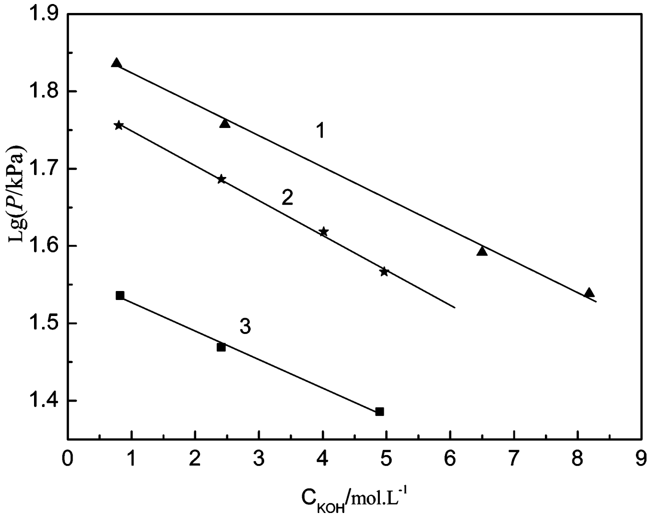

Figure 3. Plots of vapor pressure vs concentration of KOH. 1, $C_{K_2CrO_4} = 0.0525$ mol·L^{-1}, $T = 367.15$ K; 2, $C_{K_2CrO_4} = 0.2721$ mol·L^{-1}, $T = 360.15$ K; 3, $C_{K_2CrO_4} = 0.1062$ mol·L^{-1}, $T = 347.15$ K.

Table 1. Measured and Standard Values of Vapor Pressures for Pure Water

T/K	P/kPa measured value	P_{ref}/kPa standard value	$((P - P_{ref})/P) \times 100$ %
333.15	19.9	19.9	0
343.15	31.0	31.2	−0.65
353.15	46.9	47.4	−1.07
363.15	69.4	70.2	−1.15
368.15	83.7	84.6	−1.08
373.15	100.5	101.4	−0.90

Experimental Section

Reagents. The chemicals used were of analytical grade. The mass fraction purities of KOH are more than 0.82 and of K_2CrO_4 are more than 0.99. The former was manufactured by the Beijing Chemical Plant, and the latter was manufactured by Beijing Yili Fine Chemical Co., Ltd.

Apparatus. The boiling point method[6] was employed in this work to determine the saturated vapor pressure of the KOH + K_2CrO_4 + H_2O system. The experimental apparatus is shown in Figure 1.

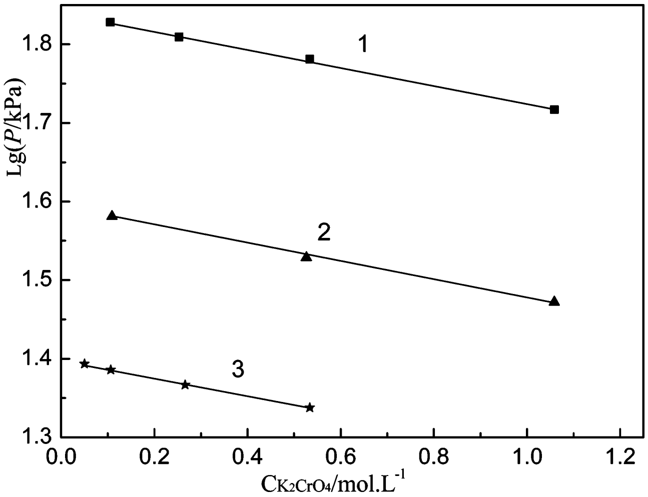

Figure 4. Plots of vapor pressure vs concentration of K_2CrO_4: 1, $C_{KOH} = 0.8397$ mol·L^{-1}, $T = 363.15$ K; 2, $C_{KOH} = 2.5558$ mol·L^{-1}, $T = 354.15$ K; 3, $C_{KOH} = 5.0024$ mol·L^{-1}, $T = 347.15$ K.

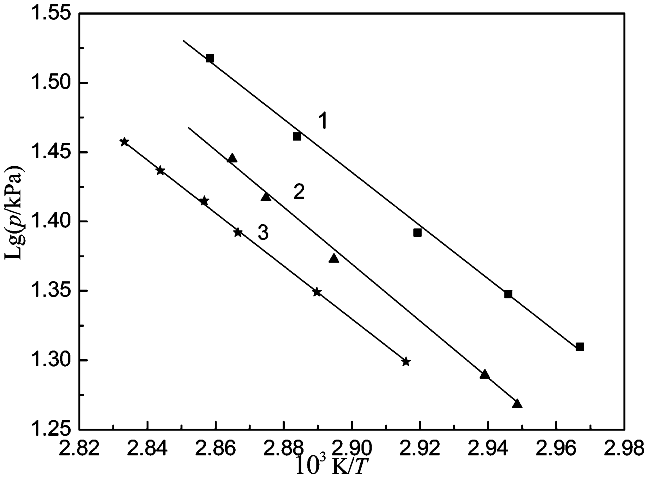

Figure 5. Plots of vapor pressure vs system temperature: 1, $C_{KOH} = 0.8397$ mol·L^{-1}, $C_{K_2CrO_4} = 1.0588$ mol·L^{-1}; 2, $C_{KOH} = 5.0024$ mol·L^{-1}, $C_{K_2CrO_4} = 0.2721$ mol·L^{-1}; 3, $C_{KOH} = 4.0896$ mol·L^{-1}, $C_{K_2CrO_4} = 0.1050$ mol·L^{-1}.

The investigated system was placed in a three-necked bottle that was submerged in an isothermal water bath. The temperature of the isothermal water bath was kept constant by using a thermostat with a precision of ± 0.02 K. In each experiment, the volume of the solution system was set between (500 and 600) mL, about (50 to 60) % of the volume of the bottle. The temperature inside the bottle was measured by a digital thermocouple with a Pt sensor whose precision is ± 0.01 K. This thermocouple was calibrated at the temperature range of (303.15 to 373.15) K. The pressure was measured by a mercury manometer, and the manometric readings were performed with a cathetometer to ± 0.5 mm. The estimated measurement uncertainties were 0.01 in mole fraction for the solution composition, 0.01 in K for the temperature, and ± 0.1 kPa for the pressure.

Table 2. Experimental Vapor Pressure Values of the Investigated Solutions

C_{KOH}	$C_{K_2CrO_4}$	P/kPa					
mol·L^{-1}	mol·L^{-1}	$T = 328.15$ K	$T = 336.15$ K	$T = 344.15$ K	$T = 352.15$ K	$T = 360.15$ K	$T = 368.15$ K
0.8397	0.1062	14.2	20.8	30.1	42.7	59.6	82.1
0.8397	0.2721	15.2	21.7	30.4	41.9	57.0	76.5
0.8397	0.5339	15.2	21.4	29.6	40.4	54.2	72.0
0.8397	1.0588	14.2	19.5	26.6	35.6	47.1	61.5
2.5558	0.0525	15.9	21.1	27.5	35.6	45.5	57.5
2.5558	0.1062	13.4	18.8	26.0	35.4	47.5	63.0
2.5558	0.5263	13.3	17.2	22.1	28.0	35.1	43.6
2.5558	1.0588	11.8	16.4	22.5	30.4	40.5	53.2
4.0896	0.1050	15.0	20.9	28.6	38.6	51.4	67.6
5.0024	0.0525	14.0	17.9	22.7	28.4	35.2	43.3
5.0024	0.1062	14.3	18.0	22.5	27.7	33.8	41.0
5.0024	0.2721	11.1	15.3	20.8	27.9	36.8	48.1
6.6286	0.0525	11.1	14.9	19.7	25.7	33.1	42.1
8.3981	0.0525	9.9	13.3	17.7	23.3	30.1	38.6

Procedures. The seal quality of system was checked first, making sure that the systematic pressure was vacuumized to (12 to 13) kPa and maintained for (15 to 20) min without obvious change. Then the solution with certain composition was put into the three-necked bottle, and the seal quality was checked for another time to make sure the system was sealed well. The system was vacuumized to a pressure of (13 to 27) kPa when the seal quality was good, then the three-way valve was shut off, and the water faucet was turned on to let water flow through the condensate tube. The solution was heated by using the water bath. Due to the refluxing of water vapor in the condensate tube, the concentration of the solution in the bottle was kept invariable. Owing to the bulky buffer bottle, the system pressure was not to fluctuate during the evaporation process. When the boiling state appeared to be stable for about 15 min, the corresponding temperature and pressure were recorded.

The three-way valve was turned on slowly to achieve an increase in the system pressure of (1.3 to 2.7) kPa, and another boiling point was measured. In this way, boiling points of the system were measured at pressure intervals of (1.3 to 2.7) kPa. The KOH and K_2CrO_4 concentrations of the solution were analyzed by using an ICP-OES (Optimal 5300DV, Perkin-Elmer Instruments).

Results. Vapor pressures of pure water were first measured to determine the reliability of the apparatus and method. Figure 2 illustrates the results. By mathematical treating, the dependence of vapor pressure on temperature was determined as

$$\log(P/\text{kPa}) = 7.84 - 2179.57\ \text{K}/T \tag{1}$$

The comparison of the measured values and standard values of vapor pressures for pure water is shown in Table 1. The standard values were given in ref 7:

$$\ln(p/p_c) = (T_c/T)(\alpha_1\tau + \alpha_2\tau^{1.5} + \alpha_3\tau^3 + \alpha_4\tau^{3.5} + \alpha_5\tau^4 + \alpha_6\tau^{7.5}) \tag{2}$$

where $\tau = 1 - T/T_c$, and values of T_c, p_c, and coefficients α_1 through α_6 were listed in ref 7.

It can be seen from Table 1 that the maximum deviation of the measured value and the standard value is 1.15 %. This indicated the credibility of the experimental apparatus and method.

For the KOH + K_2CrO_4 + H_2O system, the obtained vapor pressures are listed in Table 2. The plots of vapor pressure as a function of the concentration of KOH, the concentration of K_2CrO_4, and the system temperature are shown respectively in Figures 3 to 5. From Figures 3 to 5, it can be seen that the dependence of the vapor pressure on the system temperature, the concentration of KOH, and the concentration of K_2CrO_4 are almost linear.

The experimental data were mathematically disposed according to the relationship given by Li et al.[8] Through monadic linear regression, the dependence of the vapor pressure (P) on the system temperature (T), KOH concentration (C_{KOH}), and K_2CrO_4 concentration ($C_{\text{K}_2\text{CrO}_4}$) are expressed as

$$\log(P/\text{kPa}) = 7.52 - 3.62 \times 10^{-2}(C_{\text{KOH}}/\text{mol}\cdot\text{L}^{-1}) - 7.83 \times 10^{-2}(C_{\text{K}_2\text{CrO}_4}/\text{mol}\cdot\text{L}^{-1}) - 2055.74\ \text{K}/T \tag{3}$$

wherein C_{KOH} ranges from (0.8 to 10) mol·L^{-1}, $C_{\text{K}_2\text{CrO}_4}$ ranges from (0 to 2) mol·L^{-1}, and T ranges from (328.15 to 368.15) K.

Conclusions

For the KOH + K_2CrO_4 + H_2O system, by regressing the experimental data obtained, the relationship between the vapor pressure and the system temperature, concentrations of KOH and K_2CrO_4 were expressed as eq 3 in which the concentration of KOH ranges from (0.8 to 10) mol·L^{-1}, the concentration of K_2CrO_4 ranges from (0 to 2) mol·L^{-1}, and the system temperature ranges from (328.15 to 368.15) K.

Literature Cited

(1) Nesmeyanov, A. N. In *Vapor Pressure of the Chemical Elements*; Gary, R., Ed.; Elsevier: Amsterdam, 1963.
(2) Cheng, S. W.; Ding, J.; Yang, C. R. *Chromate Production Process*; Chemical Industry Press: Beijing, 1998.
(3) Chen, J. Y.; Zhang, Y.; Lu, K. Y.; Gong, Q.; Zhu, G. C. Studies on environmentally friendly leaching processes in China. *Chin. J. Chem. Eng.* **2001**, *9*, 5−11.
(4) Zhang, Y.; et al. Green chemistry and new revolution of chromic salts industry. *Prog. Chem.* **1998**, *10*, 172−178.
(5) Zheng, S. L.; Zhang, Y.; Li, Z. H. A cleaner production process of K_2CrO_4. Chinese Patent 01141683.1, 2001-10-08.
(6) Crockford, H. D. *Laboratory Manual of Physical Chemistry*; People's Education Press: Beijing, 1980.
(7) Palmer, D. A.; Roberto, Fernandez-Prini; Harvey, A. H. *Aqueous Systems at Elevated Temperatures and Pressures*: *Physical Chemistry in Water*, *Steam and Hydrothermal Solutions*; Elsevier Academic Press: Amsterdam, 2004.
(8) Li, H.; et al. *Studies on Fundamental Theory and New Technology on Alkaline Decomposition Process Tungsten Concentrates*; Central South University Press: Changsha, China, 1997.

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