Bubble Point Pressure of the Solutions of $H_2SiF_6 + H_2O$ and $H_2SiF_6 + CO(NH_2)_2 + H_2O$ from 323 K to 353 K

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The isobaric method was used to determine the bubble point pressure of the solutions of H_2SiF_6 (1) + H_2O (mass fraction, $w_1 = 0.003$ to 0.006) and H_2SiF_6 (1) + $CO(NH_2)_2$ (2) + H_2O ($w_1 = 0.003$ to 0.006, $w_2 = 0.004$, 0.012, and 0.020) from 323 K to 353 K. The experimental results indicated that the relationship between bubble point pressure P_v and the temperature T can be fitted as the following equation: $\log(P_v/\mathrm{kPa}) = A + B/(T/\mathrm{K})$.

Introduction

The reaction between phosphate rock and sulfuric acid is the most important one in the phosphoric acid and compound fertilizer production. During the reaction, more than 40 % of the fluorine in the phosphate rock is emitted in gas form, and it causes some environmental problems. A new process was proposed by Peudpiece[1] in 1994 and has been given much attention in China.[2,3] In the process, urea−sulfuric acid is used to decompose phosphate rock, Under appropriate process conditions, fluorine emission rate was decreased to a mass fraction of between (3 and 7) % of the total fluorine content, which resulted in an improved operation environment and economized fluorine absorption cost. The authors studied the fluorine emission law[4] on the two-stage fluorine absorption apparatus with a fluorine ionic selective electrode and found that the action of urea was the most important factor for the fluorine emission rate. To evaluate the effect of urea, discuss the low-fluorine emission mechanism, and give some foundational data for the design of the new process, the bubble point pressure of the fluorosilicic acid solution was studied in the presence of urea. There is no bubble point pressure data on the $H_2SiF_6 + CO(NH_2)_2 + H_2O$ solution up to now.

In the $H_2SiF_6 + H_2O$ system, the following reactions occurred:

$$6HF + SiO_2 = H_2SiF_6 + 2H_2O \tag{1}$$

$$2H_2SiF_6 + SiO_2 = 3SiF_4 + 2H_2O \tag{2}$$

$$H_2SiF_6 = SiF_4 + 2HF \tag{3}$$

Due to the complex equilibrium relationship, it was difficult to measure the partial pressure of the different components. The bubble point pressures of the mixtures at temperatures from 323 K to 353 K were measured in this work.

Experimental Section

Chemicals. Fluorosilicic acid, AR grade, mass content of H_2SiF_6 of (30 to 32) %, was manufactured by Tianjin Kemio Chemical Co., China. Urea ($CO(NH_2)_2$), AR grade, purity of 99.99 %, was manufactured by Tianjin Kemio Chemical Co., China.

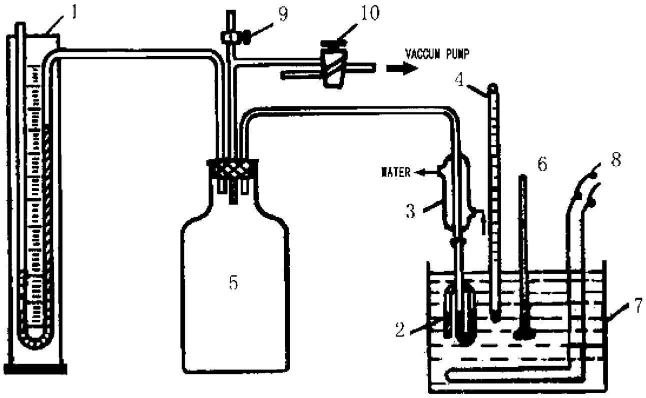

Figure 1. Experimental apparatus for determining bubble point pressure of fluorosilicic acid solution: 1, U-shapes manometer; 2, isobaric tube; 3, condensing system; 4, precise thermometer; 5, surge bottle; 6, agitator; 7, glass thermostat; 8, electric calorifier; 9, two-way cock; 10, three-way cock.

Apparatus and Instrument. The bubble point pressure of the fluorosilicic acid solution was measured by the apparatus (shown in Figure 1).[5] The bubble point pressure was measured according to the following steps. First, the measured solution (urea, fluorosilicic acid, or the mixture of the above) was filled into the dried isobaric tube. The isobaric tube was composed of three parallel vertical tubes and was placed in the thermostat. After checking the airtightness of the apparatus, the bubble point pressure could be measured. The vacuum pump was turned on, the system pressure was reduced, and the solution in the tube was boiled. When the air in the tube was effluent completely, the vacuum pump was turned off, and the three-way cock was adjusted to keep the surface level of solution in the two tubes on the right side of the isobaric tube the same and had no variety within 2 min; then the height value on the U shape manometer was recorded. The room temperature and atmosphere pressure were recorded precisely too. The thermostat temperature and the concentration of the solution were altered to measure as the above steps. The temperature range of the glass thermostat was from (273.15 to 373.15) K, uncertainty was ± 0.1 K; measured precise thermometers ranged from (323 to 373) K, with an uncertainty of ± 0.1 K. The mini-scale of the U shape manometer of mercury was 0.5 mm, so the uncertainty of the bubble point pressure was 0.067 kPa.

Test of Apparatus. To ensure proper operation of the apparatus, the saturated vapor pressure of $CO(NH_2)_2$ (1) + H_2O

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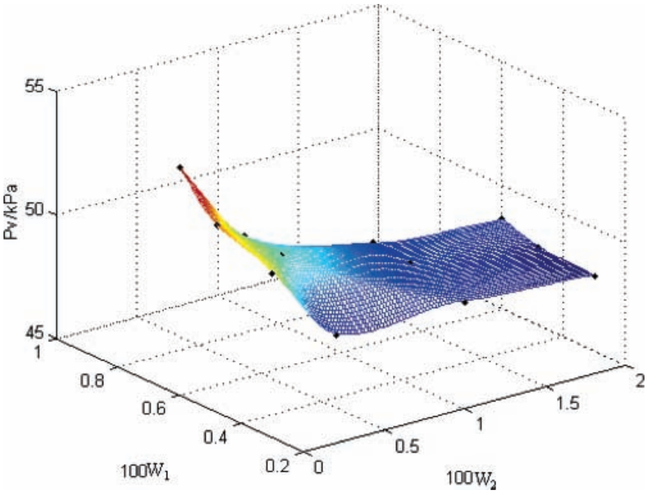

Figure 2. Bubble point pressure, P_v, of H_2SiF_6 (1) + CO $(NH_2)_2$ (2) + H_2O (100 w_1 = 0.3, 0. 48, 0. 6; 100 w_2 = 0. 4, 1.2, 2.0) at T = 353 K.

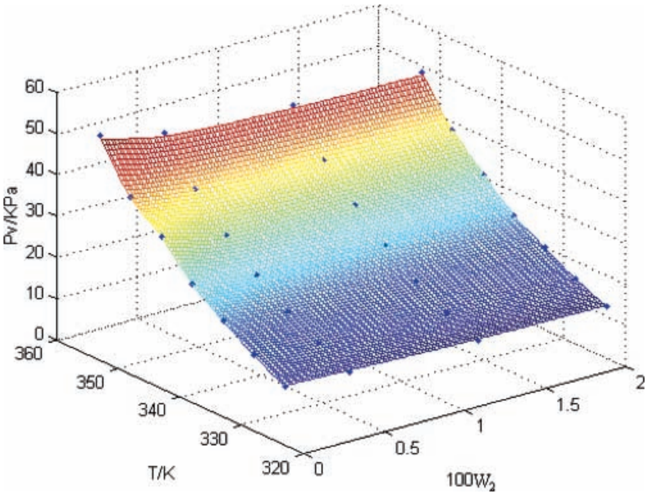

Figure 3. Bubble point pressure, P_v, of H_2SiF_6 (1) + CO $(NH_2)_2$ (2) + H_2O (100 w_1 = 0. 6; 100 w_2 = 0. 4, 1.2, 2.0) from T = 323 K to 353 K.

Table 1. Vapor Pressure of $CO(NH_2)_2$ (1) + H_2O (Mass Fraction, w_1 = 0.20) between Measure Values P_v and Literature Values P_v^* from 323 K to 353 K[a]

T/K	P_v/kPa	P_{H_2O}/kPa[6]	$P_v^* = \alpha P_{H_2O}$/kPa[7]	δ/%
323	11.84	12.33	11.71	1.11
328	15.03	15.73	14.94	0.60
333	19.01	19.92	18.92	0.48
338	23.79	25.00	23.75	0.17
343	29.90	31.16	29.60	1.01
348	37.34	38.54	36.61	1.99
353	46.11	47.34	44.97	2.52

[a] α = {vapor pressure of $CO(NH_2)_2$ (1) + H_2O (mass fraction w_1 = 0.20)}/vapor pressure of pure water. P_{H_2O}, vapor pressure of water.

(mass faction, $w_1 = 0.20$) solution was measured and compared with the reported values in the literature.[6] The measured values and the derivations (δ/%) are listed in Table 1. The values in Table 1 indicate that the measuring values agreed with the reported values, with a maximum deviation of 2.52%.

Results and Discussion

Bubble Point Pressure of H_2SiF_6 (1) + H_2O from 323 K to 353 K. Experiments were done with the H_2SiF_6 (1) + H_2O (2) system, in which w_1 was from 0.003 to 0.006. The results are given in Table 2. If we treated each mixture as a "pure fluid", a Clausius−Clapeyron relationship would exist between the bubble point pressure of fluorisilicic acid P_v and temperature T. That is, log P_v and the inverse temperature were regressed as follows:

$$\log(P_v/\text{kPa}) = A + B/(T/\text{K}) \tag{4}$$

Table 2. Bubble Point Pressures, P_v, of H_2SiF_6 (1) + H_2O from T = 323 K to 353 K

	P_v/kPa		
T/K	$w_1 = 0.003$	$w_1 = 0.0048$	$w_1 = 0.006$
323	13.40	13.65	14.11
328	16.32	16.84	18.36
333	21.37	21.89	23.14
338	26.42	27.20	28.72
343	35.45	36.23	36.69
348	40.49	41.55	42.80
353	51.65	52.57	54.23
	$\log(P_v/\text{kPa}) = A + B/(T/\text{K})$		
A	8.10	8.09	7.94
B	−2254.73	−2249.2	−2191.98
SD	0.014	0.013	0.009

Table 3. Bubble Point Pressures, P_v/kPa, of H_2SiF_6 (1) + CO $(NH_2)_2$ (2) + H_2O (w_1 = 0.003, 0.0048, 0.006; w_2 = 0.004, 0.012, 0.020) from T = 323 K to 353 K

	P_v/kPa		
T/K	$w_1 = 0.003$, $w_2 = 0.004$	$w_1 = 0.0048$, $w_2 = 0.004$	$w_1 = 0.006$, $w_2 = 0.004$
323	13.36	13.48	13.58
328	15.75	16.41	17.03
333	20.80	21.19	21.28
338	25.31	26.50	26.60
343	31.69	32.35	32.97
348	38.60	40.58	40.68
353	48.43	50.68	50.77
	$\log(P_v/\text{kPa}) = A + B/(T/\text{K})$		
A	7.77	7.92	7.85
B	−2149.18	−2194.85	−2169.9
SD	0.0107	0.0073	0.0038

	P_v/kPa		
T/K	$w_1 = 0.003$, $w_2 = 0.012$	$w_1 = 0.0048$, $w_2 = 0.012$	$w_1 = 0.006$, $w_2 = 0.012$
323	12.43	12.52	12.69
328	15.62	15.71	15.87
333	19.87	19.96	20.12
338	24.12	24.74	25.44
343	30.76	31.11	31.81
348	38.55	39.08	39.25
353	48.38	48.91	49.08
	$\log(P_v/\text{kPa}) = A + B/(T/\text{K})$		
A	8.01	8.05	8.03
B	−2235.36	−2247.82	−2238.44
SD	0.0077	0.0055	0.0035

	P_v/kPa		
T/K	$w_1 = 0.003$, $w_2 = 0.020$	$w_1 = 0.0048$, $w_2 = 0.020$	$w_1 = 0.006$, $w_2 = 0.020$
323	11.99	12.32	12.43
328	15.18	15.78	15.62
333	19.43	19.50	19.87
338	23.94	24.54	24.12
343	30.58	31.18	30.76
348	37.93	38.36	38.03
353	48.03	48.19	48.63
	$\log(P_v/\text{kPa}) = A + B/(T/\text{K})$		
A	8.14	8.03	7.95
B	−2281.12	−2241.6	−2216.21
SD	0.0055	0.0053	0.0072

Bubble Point Pressure of H_2SiF_6 (1) + $CO(NH_2)_2$ (2) + H_2O from 323 K to 353 K. In the system of H_2SiF_6 (1) + CO-

$(NH_2)_2$ (2) + H_2O ($w_1 = 0.003, 0.0048, 0.006$; $w_2 = 0.004, 0.012, 0.020$), the bubble point pressures of the solutions were measured and are listed in Table 3.

In Table 2 and Table 3, SD represents the standard deviation. In the regression analysis, we could see that SD < 0.014 showed good reliability of correlation. When $CO(NH_2)_2$ was added in, the bubble point pressure of the $H_2SiF_6 + CO(NH_2)_2 + H_2O$ solution become greater with temperature and the concentration of H_2SiF_6 solution, the effect of $CO(NH_2)_2$ on the bubble point pressure of $H_2SiF_6 + CO(NH_2)_2 + H_2O$ solution can be seen in Figure 2 and Figure 3.[8]

Conclusions

When urea was added in, the bubble point pressure of the fluorinesilicic acid solution increases with the increase of temperature and the composition of fluorinesilicic acid. The analysis of XRD on the product indicated that a new complex $[CO(NH_2)_2H]_2SiF_6$ was formed in the reaction system[2]. There was an O···H···O bond in the complexation between $CO(NH_2)_2$ and H_2SiF_6, which decreased the decomposition reaction rate of H_2SiF_6 and resulted in the low fluorine emission rate.

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