

Vapor Pressures of SO_2 and NH_3 over $(\text{NH}_4)_2\text{SO}_3-(\text{NH}_4)_2\text{S}_2\text{O}_5$ Solutions Containing $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_2\text{SO}_4$

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Statistically designed experiments were used to study the vapor pressures of both SO_2 and NH_3 over ammonium sulfite-bisulfite solutions containing diammonium phosphate and ammonium sulfate. Vapor pressures were measured by using ultraviolet (UV) spectrophotometry. The following predictive equations were developed from the data using nonlinear regression: P_{SO_2} (mmHg) = $10^{(5.73-(2333.31/T))} \{2S - C + 1.42[(\text{NH}_4)_2\text{SO}_4] + 1.09[(\text{NH}_4)_2\text{HPO}_4]\}^2 / [C - S - 1.42[(\text{NH}_4)_2\text{SO}_4] - 1.09[(\text{NH}_4)_2\text{HPO}_4]$, P_{NH_3} (mmHg) = $10^{(13.02-(4794.77/T))} C \{C - S - 1.23[(\text{NH}_4)_2\text{SO}_4] - 2.27[(\text{NH}_4)_2\text{HPO}_4]\} / [2S - C + 1.23[(\text{NH}_4)_2\text{SO}_4] + 2.27[(\text{NH}_4)_2\text{HPO}_4]$, where C , S , $[(\text{NH}_4)_2\text{SO}_4]$, and $[(\text{NH}_4)_2\text{HPO}_4]$ are in mol/(100 mol of water); C and S are the total NH_3 and sulfite-sulfur concentrations, respectively. These equations should be useful for calculating partial pressures of SO_2 and NH_3 over ammonium sulfite-bisulfite solutions containing $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$.

Introduction

The vapor pressures of SO_2 and NH_3 over ammonium sulfite-bisulfite solutions containing diammonium phosphate and ammonium sulfate were measured. Sulfur dioxide and NH_3 vapor pressures, P_{SO_2} and P_{NH_3} , over pure ammonium sulfite-bisulfite solutions have been measured by Johnstone (1) and Berdianskaya et al. (2). Both gave equations for predicting the partial pressures of SO_2 and NH_3 as functions of C , $S:C$, and T , where C and S are the total ammonia and sulfite-sulfur concentrations of the solution in mol/(100 mol of water) and T is the absolute temperature. In later publications Chertkov and Dobromyslova (3) and Trutneva and Chertkov (4) presented data showing the effect that ammonium sulfate alone and both ammonium sulfate and ammonium dihydrogen phosphate have on SO_2 vapor pressure in the ammonium sulfite-bisulfite system, but they did not study the vapor pressure of NH_3 .

Moldabekov et al. (5) determined the partial pressure of SO_2 over ammonium bisulfite solutions containing a mixture of mono- and diammonium phosphates. They did not measure the partial pressure of NH_3 because it was very low. Solubilities in the systems $\text{NH}_3-\text{SO}_2-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ and $\text{NH}_3-\text{SO}_2-\text{SO}_3-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ (6) also have been studied.

Experimental Section

In the work presented here, a 2^4 factorial design was used to determine the effects of CA, $S:\text{CA}$, $[(\text{NH}_4)_2\text{HPO}_4]$, and $[(\text{NH}_4)_2\text{SO}_4]$ on the vapor pressures of SO_2 and NH_3 over ammonium sulfite-bisulfite solutions. CA is the ammonia concentration in mol/(100 mol of water) and does not include the ammonia from $(\text{NH}_4)_2\text{HPO}_4$ or $(\text{NH}_4)_2\text{SO}_4$, that is, $\text{CA} = C - 2[(\text{NH}_4)_2\text{HPO}_4] - 2[(\text{NH}_4)_2\text{SO}_4]$. The experimental design is shown in Table I. The effect of temperature was determined by running most of the experiments in Table I at three different temperatures (37.5, 47.5, and 57.5 °C).

Sample solutions were prepared by using freshly boiled deaerated water, $(\text{NH}_4)_2\text{S}_2\text{O}_5$, $(\text{NH}_4)_2\text{SO}_3$, $(\text{NH}_4)_2\text{HPO}_4$, and $(\text{NH}_4)_2\text{SO}_4$. The $(\text{NH}_4)_2\text{SO}_3$ and $(\text{NH}_4)_2\text{S}_2\text{O}_5$ were prepared in the

Table I. Experimental Design

factor	CA ^{a,b}	S:CA ^c	$[(\text{NH}_4)_2\text{-HPO}_4]^a$	$[(\text{NH}_4)_2\text{-SO}_4]^a$
(-) level	7.93	0.60	0.1883	0.4090
(0) level	10.900	0.70	0.3765	0.5453
(+) level	13.87	0.80	0.5648	0.6817
Experiments				
test no.	CA	S:C	$[(\text{NH}_4)_2\text{-HPO}_4]$	$[(\text{NH}_4)_2\text{-SO}_4]$
1	-	--	--	--
2	+	-	--	--
3	-	+	--	--
4	+	+	--	--
5	-	-	+	--
6	+	-	+	--
7	--	+	+	--
8	+	+	+	--
9	-	-	-	+
10	+	-	-	+
11	-	+	-	+
12	+	+	-	+
13	-	-	+	+
14	+	-	+	+
15	-	+	+	+
16	+	+	+	+
17	0	0	0	0
18	-2 ^d	0	0	0

^a Units: mol/(100 mol of water). ^b CA = $C - 2[(\text{NH}_4)_2\text{-HPO}_4] - 2[(\text{NH}_4)_2\text{SO}_4]$. ^c S = concentration of sulfite S in mol/(100 mol of water). ^d 2 level of CA = 4.95.

laboratory; the $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_2\text{SO}_4$ were reagent grade. Each sample solution was analyzed for S_T (total sulfur), $\text{SO}_2\text{-S}$, P_2O_5 , and N_T (total nitrogen). Partial pressures of SO_2 and NH_3 were measured by using a dynamic method similar to that used by Johnstone (1). The method is described below.

A stream of oxygen-free nitrogen, flowing at approximately 20 cm³/min, was passed through four gas scrubbing bottles connected in series and filled with the sample solution. The entire sample train was immersed in a constant-temperature bath. As the nitrogen passed through the sample train, it became saturated with SO_2 , NH_3 , and water vapor and was equilibrated with the sample solution by the time it reached the fourth bottle. After leaving the fourth bottle, the equilibrated gas was passed through water-jacketed glass tubing to the UV cell of a Cary 17 spectrophotometer, where it was analyzed for SO_2 and NH_3 . In order to ensure that no condensation occurred after the gas left the fourth bottle, we maintained both the water-jacketed glass tubing and the cell compartment of the Cary 17 at 70 °C. Pressure inside the UV cell was measured with a red oil manometer. After the last vapor pressure measurement, the sample solution in the fourth bottle was analyzed for S_T , $\text{SO}_2\text{-S}$, P_2O_5 , and N_T to ensure that it had not been depleted during the experiment. Accuracy of the vapor pressure apparatus was verified by checking the vapor pressure of water at the three specified temperatures.

The concentrations of SO_2 and NH_3 were determined from the UV absorbance of the gas at nine different wavelengths between 210 and 190 nm; SO_2 peaks occurred at four of these wavelengths, NH_3 peaks occurred at four, and both an SO_2 and

Table II. Vapor Pressure Data

expt no.	soln composition				T, °C	vapor pressure, mmHg				soln pH
	CA ^{a,b}	S:CA	[$(\text{NH}_4)_2^-$] HPO ₄ ^a	[$(\text{NH}_4)_2^-$] SO ₄ ^a		P _{SO₂}	P _{SO₂} (calcd) ^c	P _{NH₃}	P _{NH₃} (calcd) ^d	
1a	8.0450	0.6052	0.1910	0.4519	57.5	0.0175	0.0206	1.029	0.7758	6.92
1b	8.0450	0.6052	0.1910	0.4519	57.5	0.0256	0.0206	1.032	0.7758	6.92
2a	13.1940	0.6234	0.1883	0.5719	37.5	0.0000	0.0229	0.0942	0.1071	6.65
2b	13.1940	0.6234	0.1883	0.5719	37.5	0.0141	0.0229	0.1192	0.1071	6.65
2c	13.1940	0.6234	0.1883	0.5719	47.5	0.0067	0.0393	0.3316	0.3243	6.60
2d	13.1940	0.6234	0.1883	0.5719	47.5	0.0451	0.0393	0.3658	0.3243	6.60
2e	13.1940	0.6234	0.1883	0.5719	57.5	0.0673	0.0652	1.031	0.9188	6.60
2f	13.1940	0.6234	0.1883	0.5719	57.5	0.0531	0.0652	0.9909	0.9188	6.60
3a	7.1064	0.8364	0.1913	0.6628	37.5	0.1472	0.1713	0.0261	0.0129	6.00
3b	7.1064	0.8364	0.1913	0.6628	37.5	0.1277	0.1713	0.0160	0.0129	6.00
3c	7.1064	0.8364	0.1913	0.6628	47.5	0.2446	0.2937	0.0444	0.0390	6.35
3d	7.1064	0.8364	0.1913	0.6628	47.5	0.2274	0.2937	0.0651	0.0390	6.35
3e	7.1064	0.8364	0.1913	0.6628	57.5	0.3865	0.4875	0.1459	0.1105	6.25
3f	7.1064	0.8364	0.1913	0.6628	57.5	0.3701	0.4875	0.0409	0.1105	6.25
4a	13.9858	0.7972	0.1956	0.4661	37.5	0.2736	0.3110	0.0259	0.0234	5.75
4b	13.9858	0.7972	0.1956	0.4661	37.5	0.2948	0.3110	0.0270	0.0234	5.75
4c	13.9858	0.7972	0.1956	0.4661	47.5	0.4293	0.5334	0.0327	0.0708	5.80
4d	13.9858	0.7972	0.1956	0.4661	47.5	0.4952	0.5334	0.0499	0.0708	5.80
4e	13.9858	0.7972	0.1956	0.4661	57.5	0.9903	0.8854	0.2259	0.2006	5.75
4f	13.9858	0.7972	0.1956	0.4661	57.5	0.8410	0.8854	0.1693	0.2006	5.75
5a	8.2027	0.5749	0.5056	0.3789	37.5	0.0000	0.0012	0.1379	0.1320	6.88
5b	8.2027	0.5749	0.5056	0.3789	37.5	0.0000	0.0012	0.1374	0.1320	6.88
5c	8.2027	0.5749	0.5056	0.3789	47.5	0.0000	0.0020	0.4047	0.4000	6.75
5d	8.2027	0.5749	0.5056	0.3789	47.5	0.0147	0.0020	0.4118	0.4000	6.75
5e	8.2027	0.5749	0.5056	0.3789	57.5	0.0139	0.0034	1.132	1.133	6.85
5f	8.2027	0.5749	0.5056	0.3789	57.5	0.0161	0.0034	1.191	1.133	6.85
6a	14.1200	0.5863	0.5684	0.4353	37.5	0.0042	0.0069	0.1590	0.1678	6.77
6b	14.1200	0.5863	0.5684	0.4353	37.5	0.0011	0.0069	0.1599	0.1678	6.77
6c	14.1200	0.5863	0.5684	0.4353	47.5	0.0019	0.0119	0.4822	0.5084	6.65
6d	14.1200	0.5863	0.5684	0.4353	47.5	0.0078	0.0119	0.4863	0.5084	6.65
6e	14.1200	0.5863	0.5684	0.4353	57.5	0.0211	0.0197	1.346	1.440	6.84
6f	14.1200	0.5863	0.5684	0.4353	57.5	0.0325	0.0197	1.354	1.440	6.84
7a	7.7775	0.8239	0.5699	0.4245	37.5	0.1147	0.1412	0.0114	0.0121	6.10
7b	7.7775	0.8239	0.5699	0.4245	37.5	0.1164	0.1412	0.0125	0.0121	6.10
7c	7.7775	0.8239	0.5699	0.4245	47.5	0.1887	0.2421	0.0220	0.0366	6.40
7d	7.7775	0.8239	0.5699	0.4245	47.5	0.1930	0.2421	0.0324	0.0366	6.40
7e	7.7775	0.8239	0.5699	0.4245	57.5	0.3469	0.4018	0.1480	0.1036	6.30
7f	7.7775	0.8239	0.5699	0.4245	57.5	0.3331	0.4018	0.1567	0.1036	6.30
8a	14.1218	0.8044	0.5803	0.4889	37.5	0.2773	0.2800	0.0277	0.0225	5.70
8b	14.1218	0.8044	0.5803	0.4889	37.5	0.2880	0.2800	0.0415	0.0225	5.70
8c	14.1218	0.8044	0.5803	0.4889	47.5	0.4742	0.4801	0.0840	0.0683	5.75
8d	14.1218	0.8044	0.5803	0.4889	47.5	0.4790	0.4801	0.0959	0.0683	5.75
8e	14.1218	0.8044	0.5803	0.4889	57.5	0.7463	0.7969	0.1719	0.1935	5.80
8f	14.1218	0.8044	0.5803	0.4889	57.5	0.8053	0.7969	0.2193	0.1935	5.80
9a	7.8243	0.5971	0.1885	0.6685	37.5	0.0011	0.0041	0.1106	0.1274	6.81
9b	7.8243	0.5971	0.1885	0.6685	47.5	0.0007	0.0071	0.3499	0.3860	6.59
9c	7.8243	0.5971	0.1885	0.6685	57.5	0.0130	0.0117	1.010	1.093	6.55
9d	7.8243	0.5971	0.1885	0.6685	57.5	0.0099	0.0117	0.9918	1.093	6.55
10a	12.8959	0.6070	0.1814	0.4752	37.5	0.0000	0.0161	0.1040	0.1219	6.75
10b	12.8959	0.6070	0.1814	0.4752	37.5	0.0000	0.0161	0.1067	0.1219	6.75
10c	12.8959	0.6070	0.1814	0.4752	47.5	0.0019	0.0277	0.3450	0.3693	6.80
10d	12.8959	0.6070	0.1814	0.4752	47.5	0.0063	0.0277	0.3676	0.3693	6.80
10e	12.8959	0.6070	0.1814	0.4752	57.5	0.0267	0.0459	0.9671	1.046	6.75
10f	12.8959	0.6070	0.1814	0.4752	57.5	0.0328	0.0459	0.9390	1.046	6.75
11a	7.8874	0.8086	0.1899	0.7125	37.5	0.1506	0.1446	0.0138	0.0173	6.04
11b	7.8874	0.8086	0.1899	0.7125	37.5	0.1530	0.1446	0.0138	0.0173	6.04
11c	7.8874	0.8086	0.1899	0.7125	47.5	0.2523	0.2480	0.0229	0.0525	5.74
11d	7.8874	0.8086	0.1899	0.7125	57.5	0.3726	0.4117	0.0323	0.1488	5.82
12a	13.0760	0.8215	0.1881	1.0608	37.5	0.3405	0.3077	0.0382	0.0246	5.85
12b	13.0760	0.8215	0.1881	1.0608	37.5	0.3417	0.3077	0.0195	0.0246	5.85
12c	13.0760	0.8215	0.1881	1.0608	47.5	0.5828	0.5278	0.0773	0.0745	5.85
12d	13.0760	0.8215	0.1881	1.0608	47.5	0.5566	0.5278	0.0734	0.0745	5.85
12e	13.0760	0.8215	0.1881	1.0608	57.5	0.8425	0.8760	0.2052	0.2111	5.88
12f	13.0760	0.8215	0.1881	1.0608	57.5	0.9785	0.8760	0.2052	0.2111	5.88
13a	8.0198	0.5896	0.5682	0.6498	37.5	0.0097	0.0012	0.1395	0.1363	6.65
13b	8.0198	0.5896	0.5682	0.6498	37.5	0.0015	0.0012	0.1291	0.1363	6.65
13c	8.0198	0.5896	0.5682	0.6498	47.5	0.0024	0.0020	0.4021	0.4130	6.68
13d	8.0198	0.5896	0.5682	0.6498	47.5	0.0026	0.0020	0.3812	0.4130	6.68
13e	8.0198	0.5896	0.5682	0.6498	57.5	0.0330	0.0033	1.106	1.170	6.70
13f	8.0198	0.5896	0.5682	0.6498	57.5	0.0319	0.0033	1.257	1.170	6.70
14a	14.0525	0.6052	0.5679	0.7811	37.5	0.0112	0.0100	0.1706	0.1561	6.90
14b	14.0525	0.6052	0.5679	0.7811	37.5	0.0059	0.0100	0.1683	0.1561	6.90
14c	14.0525	0.6052	0.5679	0.7811	47.5	0.0598	0.0172	0.5485	0.4727	6.95
14d	14.0525	0.6052	0.5679	0.7811	47.5	0.0314	0.0172	0.5052	0.4727	6.95
14e	14.0525	0.6052	0.5679	0.7811	57.5	0.0633	0.0285	1.458	1.339	6.82

Table II (Continued)

expt no.	soln composition				$T, ^\circ\text{C}$	vapor pressure, mmHg			
	CA ^{a,b}	S:CA	$[(\text{NH}_4)_2\text{HPO}_4]^a$	$[(\text{NH}_4)_2\text{SO}_4]^a$		P_{SO_2} (calcd) ^c	P_{NH_3} (calcd) ^d	soln pH	
14f	14.0525	0.6052	0.5679	0.7811	57.5	0.0633	0.0285	1.242	1.339
14g	14.0525	0.6052	0.5679	0.7811	57.5	0.0494	0.0285	1.325	1.339
15a	7.7289	0.8144	0.5664	0.7234	37.5	0.1516	0.1073	0.0126	0.0166
15b	7.7289	0.8144	0.5664	0.7234	47.5	0.2231	0.1841	0.0145	0.0503
15c	7.7289	0.8144	0.5664	0.7234	47.5	0.2565	0.1841	0.0360	0.0503
15d	7.7289	0.8144	0.5664	0.7234	57.5	0.3825	0.3056	0.0775	0.1424
15e	7.7289	0.8144	0.5664	0.7234	57.5	0.3825	0.3056	0.0955	0.1424
16a	13.7930	0.8132	0.5692	0.6497	37.5	0.3206	0.2853	0.0309	0.0223
16b	13.7930	0.8132	0.5692	0.6497	37.5	0.3283	0.2853	0.0197	0.0223
16c	13.7930	0.8132	0.5692	0.6497	47.5	0.5268	0.4893	0.0554	0.0675
16d	13.7930	0.8132	0.5692	0.6497	47.5	0.5472	0.4893	0.0782	0.0675
16e	13.7930	0.8132	0.5692	0.6497	57.5	0.8599	0.8121	0.1696	0.1913
16f	13.7930	0.8132	0.5692	0.6497	57.5	0.8476	0.8121	0.1477	0.1913
17a	10.2754	0.7215	0.3782	0.7304	37.5	0.0671	0.0652	0.0405	0.0395
17b	10.2754	0.7215	0.3782	0.7304	37.5	0.0619	0.0652	0.0392	0.0395
17c	10.2754	0.7215	0.3782	0.7304	47.5	0.1052	0.1118	0.1119	0.1197
17d	10.2754	0.7215	0.3782	0.7304	47.5	0.0980	0.1118	0.1119	0.1197
17e	10.2754	0.7215	0.3782	0.7304	57.5	0.1656	0.1855	0.3335	0.3391
17f	10.2754	0.7215	0.3782	0.7304	57.5	0.1727	0.1855	0.3324	0.3391
18a	4.6995	0.7420	0.3827	0.7500	37.5	0.0158	0.0184	0.0345	0.0255
18b	4.6995	0.7420	0.3827	0.7500	37.5	0.0228	0.0184	0.0385	0.0255
18c	4.6995	0.7420	0.3827	0.7500	47.5	0.0229	0.0316	0.1068	0.0772
18d	4.6995	0.7420	0.3827	0.7500	47.5	0.0225	0.0316	0.0932	0.0772
18e	4.6995	0.7420	0.3827	0.7500	57.5	0.0257	0.0524	0.2842	0.2186
18f	4.6995	0.7420	0.3827	0.7500	57.5	0.0380	0.0524	0.3216	0.2186

^a Units: mol/(100 mol of water). ^b CA = C - 2[$(\text{NH}_4)_2\text{HPO}_4$] - 2[$(\text{NH}_4)_2\text{SO}_4$]. ^c Equation 4. ^d Equation 5.

NH₃ peak occurred at one. The absorbances of SO₂ and NH₃ obey Beer's law, and they are related to concentrations by the following equations:

$$A(i)_{\text{SO}_2} = \epsilon(i)_{\text{SO}_2} b P_{\text{SO}_2} \quad (1)$$

$$A(i)_{\text{NH}_3} = \epsilon(i)_{\text{NH}_3} b P_{\text{NH}_3} \quad (2)$$

where $A(i)_{\text{SO}_2}$ and $A(i)_{\text{NH}_3}$ are the component absorbances at wavelength i ; $\epsilon(i)_{\text{SO}_2}$ and $\epsilon(i)_{\text{NH}_3}$ are the absorptivities at the same wavelength; b is the cell path length; and P_{SO_2} and P_{NH_3} are the concentrations of SO₂ and NH₃, respectively. The total absorbance of the gas mixture is the algebraic sum of the absorbances of the components, that is

$$A(i)_T = \epsilon(i)_{\text{SO}_2} b P_{\text{SO}_2} + \epsilon(i)_{\text{NH}_3} b P_{\text{NH}_3} \quad (3)$$

The values of ϵ_{SO_2} and ϵ_{NH_3} were determined by using SO₂ and NH₃ calibration gas. The total absorbance of the equilibrated vapor from the test solution was measured by repeatedly scanning from 210 to 190 nm until the spectra were duplicated within the error of the instrument. The concentrations of SO₂ and NH₃ were determined by iteration using the five SO₂ peaks for SO₂ and the five NH₃ peaks for NH₃. The peaks were weighted according to their height.

Results and Discussion

The experimental data are shown in Table II. Most of the measurements on each solution were made twice at three different temperatures (37.5, 47.5, and 57.5 °C). Predictive equations for P_{SO_2} and P_{NH_3} were obtained by fitting the data to the following models using nonlinear regression to determine the values of the parameters A , B , m , and n :

$$P_{\text{SO}_2} = 10^{(A_{\text{SO}_2} + (B_{\text{SO}_2}/T))} \{2S - C + m_{\text{SO}_2}[(\text{NH}_4)_2\text{SO}_4] + n_{\text{SO}_2}[(\text{NH}_4)_2\text{HPO}_4]\}^2 / \{C - S - m_{\text{SO}_2}[(\text{NH}_4)_2\text{SO}_4] - n_{\text{SO}_2}[(\text{NH}_4)_2\text{HPO}_4]\} \quad (4)$$

$$P_{\text{NH}_3} = 10^{(A_{\text{NH}_3} + (B_{\text{NH}_3}/T))} \{C - S - m_{\text{NH}_3}[(\text{NH}_4)_2\text{SO}_4] - n_{\text{NH}_3}[(\text{NH}_4)_2\text{HPO}_4]\} / \{2S - C + m_{\text{NH}_3}[(\text{NH}_4)_2\text{SO}_4] + n_{\text{NH}_3}[(\text{NH}_4)_2\text{HPO}_4]\} \quad (5)$$

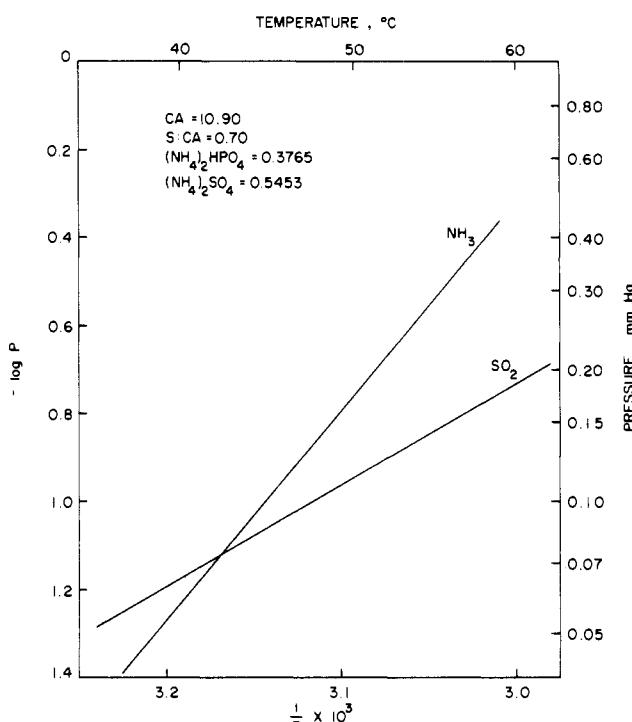
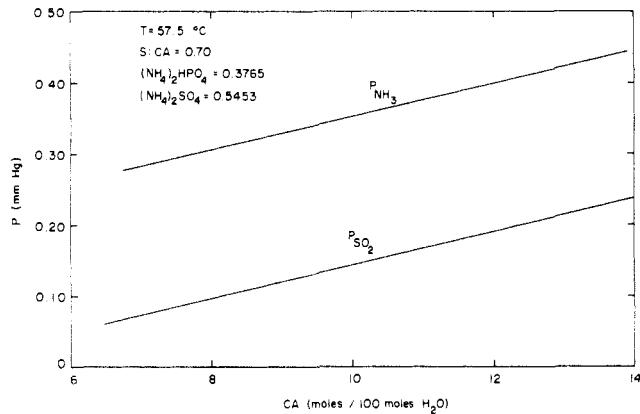
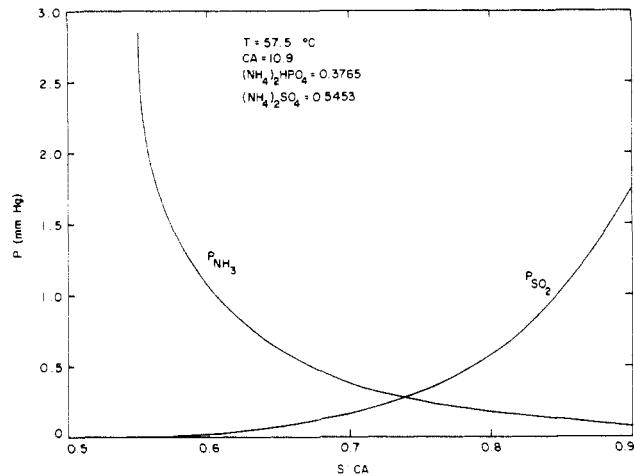


Figure 1. Effect of temperature on P_{SO_2} and P_{NH_3} .

These equations are simply expansions of Johnstone's (1) model for solutions in which a strong acid is present. The parameters A and B are the intercept and the slope, respectively, for the temperature effect and m and n are empirical constants which correct the vapor pressures for the presence of $(\text{NH}_4)_2\text{SO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$; P_{SO_2} and P_{NH_3} are in mmHg; and C , S , $[(\text{NH}_4)_2\text{SO}_4]$, and $[(\text{NH}_4)_2\text{HPO}_4]$ are in mol/(100 mol of water). Values of the parameters for P_{SO_2} and P_{NH_3} are given in Table III. The values of the A and B parameters for the temperature effect agree closely with those obtained by Johnstone (1). Calculation of the heats of vaporization (ΔH_v) from the B parameters gives average values of 10 677 and 21 940

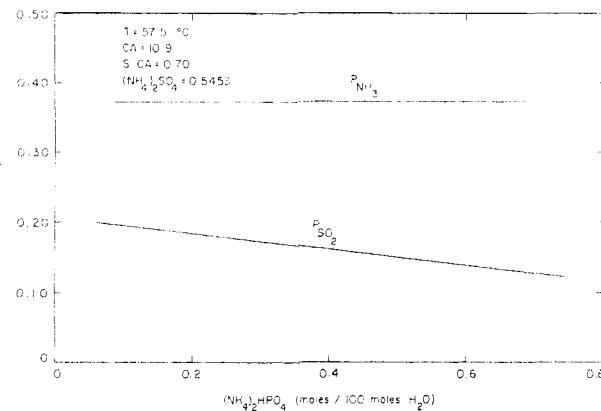
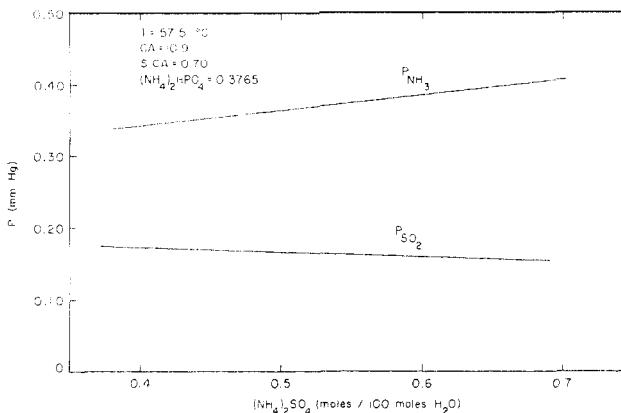
Table III. Values of Parameters for P_{SO_2} and P_{NH_3} Equations

parameter	P_{SO_2}	P_{NH_3}
A	5.73 ± 0.26	13.02 ± 0.45
B	-2333.31 ± 84.33	-4794.77 ± 148.94
m	1.42 ± 0.07	1.23 ± 0.06
n	1.09 ± 0.10	2.27 ± 0.07
R^2 , model	0.98	0.98
standard error, mmHg	0.04	0.06

Figure 2. Effect of CA on P_{SO_2} and P_{NH_3} .Figure 3. Effect of S:CA on P_{SO_2} and P_{NH_3} .

cal/mol for SO_2 and NH_3 , respectively.

The projected effects of T , CA, S:CA, $[(NH_4)_2HPO_4]$, and $[(NH_4)_2SO_4]$ are shown in Figures 1–5. As expected, T , CA, and S:CA had a much larger effect over the range studied than $[(NH_4)_2HPO_4]$ or $[(NH_4)_2SO_4]$. Increasing T and CA increases the vapor pressure of both SO_2 and NH_3 ; increasing S:CA increases P_{SO_2} but decreases P_{NH_3} . The vapor pressure of SO_2 decreases with increasing $(NH_4)_2HPO_4$ concentration. Increasing the $(NH_4)_2HPO_4$ concentration had very little effect on the vapor pressure of NH_3 . Our data show that addition of $(NH_4)_2SO_4$ increases P_{NH_3} and decreases P_{SO_2} . This is contrary to Chertkov and Dobromyslova's data (3) which showed that

Figure 4. Effect of $[(NH_4)_2HPO_4]$ on P_{SO_2} and P_{NH_3} .Figure 5. Effect of $[(NH_4)_2SO_4]$ on P_{SO_2} and P_{NH_3} .

increasing $(NH_4)_2SO_4$ concentration increases P_{SO_2} . Chertkov and Dobromyslova did not study the effect of $[(NH_4)_2SO_4]$ on P_{NH_3} .

We think that our data are an improvement over those obtained previously (1–5) because our experiments were statistically designed and determined the effect of $[(NH_4)_2HPO_4]$ and $[(NH_4)_2SO_4]$ on both P_{SO_2} and P_{NH_3} . Our models should be useful for calculating scrubbing parameters for NH_3 – SO_2 scrubbing systems containing $(NH_4)_2HPO_4$ and $(NH_4)_2SO_4$.

Registry No. SO_2 , 7446-09-5; NH_3 , 7664-41-7; $(NH_4)_2SO_3$, 10196-04-0; $(NH_4)HSO_3$, 10192-30-0; $(NH_4)_2HPO_4$, 7783-28-0; $(NH_4)_2SO_4$, 7783-20-2.

Literature Cited

- Johnstone, H. F. *Ind. Eng. Chem.* 1935, 27, 587.
- Berdianskaya, R. A.; Golyand, S. M.; Chertkov, B. A. *Zh. Prikl. Khim. (Leningrad)* 1959, 32, 1930.
- Chertkov, B. A.; Dobromyslova, N. S. *Zh. Prikl. Khim. (Leningrad)* 1984, 37, 1718.
- Trutneva, N. V.; Chertkov, B. A. *Tr.—Nauchno-Issled. Inst. Udobr. Insectofungit. im Prof. Ya. V. Samoilova* 1970, 111.
- Moldabekov, Sh.; Salybaev, A.; Seitmagzai, A. *Khim. Tekhnol. Silik.* 1974, 307.
- Gautney, J.; Frazier, A. W.; Kim, Y. K.; Hatfield, J. D. *J. Chem. Eng. Data* 1980, 25, 154.

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