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JAN 78 D G ROBERTSON, J R JARRELL
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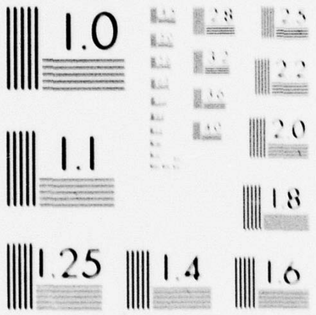

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BOILING POINTS OF SOLUTIONS OF SULFURIC ACID-WATER-AMMONIUM SULFATE OF VARIOUS COMPOSITIONS AT SEVERAL REDUCED PRESSURES.

⑩ DUDLEY G. ROBERTSON
JAMES R. JARRELL

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ARLCD-TR-77055	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) BOILING POINTS OF SOLUTIONS OF SULFURIC ACID-WATER-AMMONIUM SULFATE OF VARIOUS COMPOSITIONS AT SEVERAL REDUCED PRESSURES		5. TYPE OF REPORT & PERIOD COVERED Final
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Dudley G. Robertson James R. Jarrell		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Propellants Analysis Section, Propellants Div Feltman Research Laboratory Picatinny Arsenal, Dover, NJ 07801		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS US Army ARRADCOM ATTN: DRDAR-TSS Dover, NJ 07801		12. REPORT DATE JANUARY 1978
		13. NUMBER OF PAGES 16
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) Energetic Materials Division, LCWSL US Army ARRADCOM Dover, NJ 07801		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release, distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Boiling points
Dilute sulfuric acid/ammonium sulfate solutions
Sulfuric acid/water solutions
Boiling temperatures at reduced pressures

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Boiling point data are presented for sulfuric acid-water-ammonium sulfate solutions of various compositions at reduced pressures. The apparatus used and experimental conditions are described. The observed boiling points are compared to values drawn from reference literature wherever possible. The variation in boiling temperature was found to be a linear function of pressure described by the equation: $\log P = A - B\ (1/T)$. The constants A and B were calculated for each of the solutions tested.

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INTRODUCTION

Design studies for a Nitroguanidine Plant planned for construction at Sunflower AAP, required boiling point data for various mixtures of sulfuric acid and water, both with and without added ammonium sulfate, at several reduced pressures such as would be encountered in the sulfuric acid concentrator subsystem. This report presents the required data generated in a laboratory study.

EXPERIMENTAL

The apparatus consisted of a three-necked flask of 100 ml capacity. A short, water-cooled condenser attached to the center opening allowed boiling under total reflux. A thermometer was positioned in one opening so that the bulb would be well immersed in the liquid. The third opening served as a filling port and was stoppered during a run. Heat was supplied by a small heating mantle. A line from the top of the reflux condenser led to a cold trap (maintained at dry-ice temperature) and thence to an open-end manometer. The open end of the manometer was connected to a vacuum pump and to a needle valve serving as a bleed valve. The cold trap would both protect the pump and indicate the removal of any appreciable amount of solvent during the run. By manipulation of the bleed valve, any desired pressure could be set on the manometer.

Solutions were made up in 1000 gm batches to the acid/acid + water ratios of 25, 50, 65 and 80 (W/W). Sufficient ammonium sulfate by weight was added to portions of each stock solution to give salt concentrations of 5%, 10%, 15%, and 20%. Portions of each finished solution were analyzed for sulfuric acid.

A typical run was made by introducing into the boiling flask sufficient liquid to immerse the thermometer bulb (50-60 ml). A few boiling chips were added and the system closed. Pressure was reduced to the lowest point in the range to be covered (20 mm Hg) and exactly adjusted by means of the bleed. The heating mantle was energized and the system was allowed to come to a boil. When the thermometer showed that a stable temperature had been attained the temperature was recorded and observed again after 3 to 5 minutes. If it did not change during this interval, the observed temperature was recorded as the boiling point. If the temperature did change, it was monitored at 3-minute intervals until it was observed to remain constant. The pressure was then set to the next higher value and the process was repeated. The pressure range covered was

20 mm to 160 mm in most cases. At the conclusion of a run the system was allowed to come to ambient pressure and temperature, and the boiling flask removed and emptied, its contents being reserved. After being cleaned and dried, the apparatus was reassembled, refilled with the next sample, and the process repeated. At the end of each run the cold trap was examined for the presence of condensate, and the solutions whose boiling points had been determined were analyzed again for percent sulfuric acid. It was found that no condensate was collected and that the percentage of sulfuric acid in solution did not change during the run.

RESULTS AND DISCUSSION

The first tests were made on distilled, deionized water in order to compare observed temperatures with those derived from the referenced literature. Gross error due to the functioning of the apparatus would be made apparent and corrections made if possible. Table 1 compares our results to those taken from the Handbook of Chemistry and Physics (Ref 1). Observed values were plotted against literature values and the best straight line calculated by the method of least squares. This line was observed to have a slope of 1.023 and an intercept virtually equal to 0. (Exact correspondence would have given a slope of 1.000.) It was decided that any attempt to apply a correction factor would probably introduce a worse error and therefore no correction was attempted. The discrepancies apparent in Table 1 occur at random and are best ignored.

The next group of samples was the sulfuric acid-water solutions. Here too, the literature values were available for comparison. In 1925, Greenewalt (Ref 2) summarized the experimental data then available. His results have been tabulated by Perry (Ref 3) in the Chemical Engineer's Handbook. Later tables have been computed by Gmitro and Vermeulen (Ref 4) which agree in the main with Greenewalt's data.

Greenewalt found that equilibrium vapor pressure of sulfuric acid-water solutions obeyed the equation:

$$\log P = A - B/T \qquad (1)$$

Where P = pressure in mm Hg,

T = absolute temperature.

and A & B are constants for any given composition. This equation is derived from the Clausius-Clapeyron equation in which:

$$B = \frac{L}{2.303R} \qquad (2)$$

where L is the total heat of vaporization and R is the gas constant. Equation (2) will apply rigorously only to pure liquids on the assumption that the vapor behaves as an ideal gas. Greenewalt assumed that at reduced pressures this would be the case and calculated values for the constants A and B in Equation (1) for compositions from 0 to 95% H_2SO_4. He estimated that the maximum error in these values would be ± 2% from 0°C to the boiling point. Whether exact values of enthalpy can be derived from the experimental value of B is debatable. With this caveat in mind, we proceeded to calculate the constants A and B from our experimental results. Comparison with Greenewalt's values is presented in Table 2. Boiling point temperatures calculated from Greenewalt's data are compared to our experimental values in Table 3.

A word on the method of calculation of the constants A and B is in order. Equation (1) describes a straight line with slope equal to (-B) and an intercept (A) on the y axis. The method of least squares is the standard curve-fitting technique for such a plot. However, the usual simultaneous equations assume that the X values are exact and any error will be in the Y direction. Our experimental technique causes exactly the reverse to be true. The pressure was set exactly and any error would be in the temperature or X direction. Rabinowicz (Ref 5) discusses this problem at length in an elementary text on the treatment of experimental data. The least squares equations used in our calculations are drawn from his model.

The last series of experiments concerned the acid-water solutions with added ammonium sulfate. The behavior of these solutions continued to fit Equation (1) and values of the constants A and B were calculated as before. Tables 4, 5, 6, and 7 list the data for 5%, 10%, 15%, and 20% ammonium nitrate, respectively.

CONCLUSIONS

An examination of the tables shows that the boiling point is much more strongly affected by the percentage of sulfuric acid than by the percentage of dissolved salt. Boiling points decline sharply with decreasing sulfuric acid concentration in spite of increasing salt content. However, the presence of ammonium sulfate will increase the boing point of a solution if the sulfuric acid content is roughly constant. This is shown by comparison of a 65% sulfuric acid solution with no added salt; and, a 64% sulfuric acid solution with 20% added salt. It is also apparent from the tables that any plot of boiling point vs solution composition at constant pressure will not be linear. These plots illustrate general tendencies and may be used for interpolative purposes. Extrapolation beyond the limits of such a curve, however, may give misleading information.

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Table 1

Boiling points of water at various reduced pressures

P (mm Hg)	Observed Temp (°C)	Literature Temp (°C) (Ref 1)
27.5	27.0	27.5
35.0	31.8	31.7
45.0	38.0	36.2
55.0	42.0	39.9
65.0	43.0	43.1
80.0	47.3	47.1
100.0	51.7	51.6
120.0	56.0	55.4
140.0	59.9	58.6
150.0	60.5	60.1
160.0	64.0	61.5

Table 2

Parameters of vapor pressure equation log P = A - B (1/T)

	Observed		Greenewalt (Ref 2)	
% H_2SO_4	A	B	A	B
0	8.819	2221	8.916	2260
25	9.425	2450	Not given	
50	9.520	2607	8.832	2357
65	8.916	2558	8.853	2533
80	8.970	2944	9.293	3040

Table 3

Boiling points of sulfuric acid-water solutions at various reduced pressures

	25% H_2SO_4		50% H_2SO_4		65% H_2SO_4		80% H_2SO_4	
P (mm)	$t_{(obs)}$	$t_{(lit)}$	$t_{(obs)}$	$t_{(lit)}$	$t_{(obs)}$	$t_{(lit)}$	$t_{(obs)}$	$t_{(lit)}$
20	29.0	25.5	45.5	39.8	64.0	62.3	111.5	107.2
40	39.0	37.4	54.0	52.9	75.5	76.2	125.5	122.1
60	47.1	45.3	63.0	61.0	84.0	84.9	135.8	131.4
80	52.5	50.8	69.0	67.0	90.0	91.3	143.0	138.2
100	57.0	55.3	74.0	71.8	97.5	96.5	149.3	143.7
120	60.0	59.2	77.0	75.9	103.0	101.2	154.3	148.3
140	63.0	62.5	80.5	79.4	104.7	105.0	159.0	152.2
160	67.0	65.5	84.0	82.5	108.0	107.8		

$t_{(lit)}$ values are calculated from data in Ref 3, Tables 3-18.

Table 4

Boiling points of sulfuric acid-water solutions with 25% added salt at reduced pressures

Acid ratio		25	50	65	80
% H_2SO_4 (w/w)		23.75	47.50	61.75	76.0
	A	8.558	8.511	8.849	8.105
	B	2171	2254	2527	2543
P (mm)		t (°C)	t (°C)	t (°C)	t (°C)
20		22.5	39.0	62.0	99.0
40		40.0	53.5	75.0	119.0
60		47.0	62.1	84.5	130.0
80		53.5	68.2	90.0	138.5
100		58.0	73.0	96.0	144.0
120		61.9	77.5	100.0	149.0
140		65.0	80.5	104.0	152.0
160		(68.5)	84.0	107.5	156.5

Notes:

1. The following notes apply to Tables 4, 5, 6, and 7.
2. "Acid Ratio" is the ratio: $\dfrac{\text{gm } H_2SO_4}{\text{gm } H_2SO_4 + \text{gm } H_2O}$
3. A and B are the usual constants in the equation: $\log P = A - B(1/T)$ (Where T is absolute temperature).
4. Values in parenthesis were calculated using this equation and the listed constants.

Table 5

Boiling points of sulfuric acid-water solutions with 10% added salt at reduced pressures

Acid ratio		25	50	65	80
% H_2SO_4 (w/w)		22.50	45.00	58.50	72.0
	A	8.945	8.841	8.407	8.783
	B	2298	2361	2349	2777
P (mm)		t (°C)	t (°C)	t (°C)	t (°C)
20			40.0	56.0	97.9
30		34.5			
40			53.0	73.0	113.0
50		44.0			
60			61.0	83.0	124.0
70		50.2			
80			67.0	88.4	131.0
90		56.0			
100			72.0	93.5	136.5
110		60.0			
120			76.0	98.0	141.1
130		63.1			
140			79.0	101.7	145.0
150		66.0			
160			83.0	104.2	148.5

Table 6

Boiling points of sulfuric acid-water solutions with 15% added salt at reduced pressures

Acid ratio	25	50	65	80
% H_2SO_4 (w/w)	21.25	42.50	55.25	68.0
A	8.676	8.680	8.435	8.580
B	2211	2306	2343	2718
P (mm)	t (°C)	t (°C)	t (°C)	t (°C)
20	(26.6)	39.0	54.0	100.5
40	39.0	53.0	71.0	115.5
60	47.5	61.5	80.0	127.0
80	54.0	67.0	86.0	134.0
100	58.0	72.0	91.0	140.0
120	62.0	76.0	95.3	145.0
140	65.5	79.5	99.0	149.2
160	68.0	83.0	102.0	153.0

Table 7

Boiling points of sulfuric acid-water solutions with 20% added salt at reduced pressures

Acid ratio		25	50	65	80
% H_2SO_4 (w/w)		20.0	40.0	52.0	64.0
	A	8.687	8.654	8.803	8.704
	B	2219	2289	2455	2669
P (mm)		t (°C)	t (°C)	t (°C)	t (°C)
20		(27.3)	38.0	(54.1)	87.1
40		40.0	51.5	67.5	103.0
60		48.0	60.0	76.5	112.5
80		54.0	66.0	83.0	119.0
100		58.5	71.0	88.0	125.0
120		63.0	75.0	92.0	130.0
140		66.0	78.5	95.0	134.0
160		69.0	81.5	99.0	137.0

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