Thermophysical properties of a H_2SO_4-H_2O binary system for a VHTR-assisted SI thermochemical cycle

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1. Introduction

The sulfur-iodine(SI) cycle and the Westinghouse sulfur hybrid cycle coupled to a very high temperature gas-cooled reactor(VHTR) are well known as a feasible technology to produce hydrogen.[1]

The concentration of the sulfuric acid solution and its decomposition are essential parts in both cycles.

In this paper, several thermophysical correlations for the H_2SO_4 and H_2O binary chemical system have been developed to apply to the dynamic analysis of a sulfuric acid concentrator. Based on the data in Perry's chemical engineers' hand book[2] and other experimental data[3, 4], not only the boiling point but also the latent heat of the sulfuric acid solution have been correlated as a function of the sulfuric acid concentration.

On the other hand, partial pressure equations of water, sulfuric acid, and sulfur trioxides have been obtained as functions of the sulfuric acid concentration and temperature, respectively. The equations introduced in our paper can be applied in the range of a 0 to 100% sulfuric acid concentration and until 3 MPa.

2. Thermophysical Properties

The SigmaPlot(Ver. 9.0) was used to develop the correlation equations and graph results. The best fitted equations were selected from the library of SigmaPlot(Ver. 9.0).

2.1 Boiling Point

In order to create a boiling point equation as a function of the total pressure and sulfuric acid concentration, the following equation was selected.

$$T_b = A + B \exp(C \log_{10} P) \quad (1)$$
$$A = a_1 x^3 + b_1 x^2 + c_1 x + d_1 \quad (2)$$
$$B = a_2 x^3 + b_2 x^2 + c_2 x + d_2 \quad (3)$$
$$C = a_3 x^3 + b_3 x^2 + c_3 x + d_3 \quad (4)$$

where T_b : boiling point(K)
P : total pressure(bar)
X : weight fraction
a_i, b_i, c_i, d_i : coefficients

By using the P-T data published in Perry's chemical engineer's hand book[1], the coefficients for eqs. (1)-(4) were determined as a follows.

Table 1. Coefficients in boiling point equation

Coefficient	wt% H_2SO_4 (10 ~ 98)	wt% H_2SO_4 (98.5 ~ 100)
a_1	-16.83	19639993.82
b_1	42.29	-58371430.06
c_1	-48.11	57825487.65
d_1	242.23	-19093861.03
a_2	546.80	-4398598.20
b_2	-453.67	12711928.43
c_2	189.69	-12237110.38
d_2	116.78	3924138.44
a_3	0.08	26895.60
b_3	-0.39	-79999.50
c_3	0.03	79313.18
d_3	0.51	-26209.12

2.2 Azeotrope

By using equation (1) and table (1), the boiling points as a function of the sulfuric acid concentration at the given total pressures can be drawn, and then we can establish the azeotrope points at $dT_b/dx = 0$. Table 2 shows a comparison of the calculated values to experimental values.

Table 2. Azeotropes of the H_2SO_4-H_2O system

Total pressure (mmHg)	Experimental (wt, % H_2SO_4)	Calculated (wt, % H_2SO_4)	RE(%)
100	98.790	98.745	0.046
200	98.704	98.711	0.010
300	98.645	98.694	0.041
400	98.597	98.685	0.081
500	98.557	98.677	0.115
600	98.524	98.670	0.144
650	98.509	98.666	0.156
700	98.495	98.663	0.171
750	98.482	98.663	0.184
800	98.469	98.658	0.192
850	98.457	98.657	0.203
900	98.446	98.656	0.213
950	98.436	98.653	0.220
1000	98.426	98.650	0.228

2.3 Latent Heat

The vaporization latent heat of the sulfuric acid solution was correlated with a sulfuric acid concentration by the following polynomial form.

$$L_v = 1364.93x^3 - 1226.46x^2 + 382.23x + 540.52 \quad (5)$$

Where, L_v : latent heat(cal/g)

x : H_2SO_4 weight fraction

Fig. 1 shows that the calculated values agree with the experimental data within a ±5% relative error.

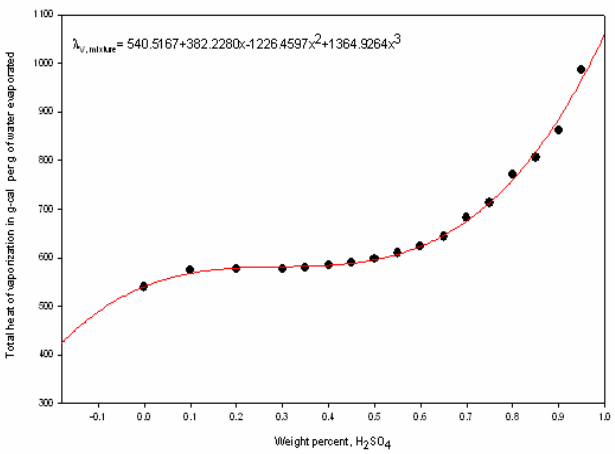

Fig. 1. Vaporization latent heat as a function of sulfuric acid concentration.

2.4 Partial Pressures of H_2O, H_2SO_4, and SO_3

The partial pressure of each compound in a H_2SO_4-H_2O system was reported in Perry's chemical engineers' hand book.[2] Based on this data, the correlation equation for the partial pressure of each compound has been obtained as follows.

$$\text{Log}_{10} p_i = A_i + B_i/T + C_i/T^2 \quad (6)$$

$$A_i = a_{i1} x^3 + b_{i1} x^2 + c_{i1} x + d_{i1} \quad (7)$$

$$B_i = a_{i2} x^3 + b_{i2} x^2 + c_{i2} x + d_{i2} \quad (8)$$

$$C_i = a_{i3} x^3 + b_{i3} x^2 + c_{i3} x + d_{i3} \quad (9)$$

Where p_i : partial pressure of i component(bar)

T : temperature(K)

subscript i=1: H_2O, 2:H_2SO_4, 3:SO_3

Table 2. Coefficients in partial pressure equation

Coefficient	H_2SO_4 wt. fraction (0.1 ~ 0.8)	H_2SO_4 wt. fraction (0.85 ~ 1)
a_{11}	-10.799	-4.43.5
b_{11}	-15.149	11105.8
c_{11}	-4.732	-10150.1
d_{11}	4.888	3091.96
a_{12}	8238.490	756055
b_{12}	-12356.600	-2130840
c_{12}	3869.240	1989900
d_{12}	-1569.430	-618436
a_{13}	-79287.2	-135190000
b_{13}	-1010110	381414000
c_{13}	3223960	-357427000
d_{13}	-2617210	111085000
a_{21}	31.666	540.247
b_{21}	-66.997	-1506.138
c_{21}	35.734	1394.101
d_{21}	3.253	-423.157
a_{22}	-16283.992	-384340.297
b_{22}	37689.985	1070172.953
c_{22}	-17333.649	-987107.436
d_{22}	-5449.468	298191.121
a_{23}	2077331.396	75724576.026
b_{23}	-4855012.753	-213488350.450
c_{23}	2793566.387	199869224.799
d_{23}	-415939.310	-62285697.275
a_{31}	34.816	4472.295
b_{31}	-73.363	-12305.921
c_{31}	37.657	11264.483
d_{31}	6.194	-3422.469
a_{32}	-17078.737	-1054957.067
b_{32}	41488.475	2966364.333
c_{32}	-18459.508	-2762554.915
d_{32}	-8981.487	846531.102
a_{33}	2928089.353	195340326.508
b_{33}	-6043040.412	-552130876.293
c_{33}	3148707.844	518209632.367
d_{33}	-277843.706	-161479604.936

3. Conclusion

The correlations of the boiling point, azeotrope, latent heat, total and partial pressures in a H_2SO_4-H_2O binary system have been obtained as a function of the sulfuric acid concentration.

The boiling point equation correlated with the total pressure and sulfuric acid concentration agrees with the data published in Perry's hand book within a ±5% relative error. The azeotropes estimated from the boiling point curves are almost the same as experimental data within a ±0.5% relative error.

Partial pressures of H_2O, SO_3, and H_2SO_4 are predicted within a 10% relative error. The error of the partial pressure value is increased by increasing the temperature and sulfuric acid concentration.

REFERENCES

[1]Brown LC, Besenbruch GE, Lentsch RD, Schultz KR, Funk JF, Pickard PS, Marshall AC, Showalter SK. High efficiency generation of hydrogen using nuclear power. 2003; GA-A24285.

[2]Robert Perry and Don W. Green, Perry's chemical engineers' hand book. 7th edition, McGraw Hill company Inc, 1999.

[3]Kunzler JE, Absolute sulfuric acid, a highly accurate primary standard. Analytical chemistry, Vol. 25, 100(1953).

[4]Gmitro and Vermeulen, Vapor pressures, normal boiling points, and latent heats of vaporization for aqueous solutions of H_2SO_4. Am. Inst. Chem. Engrs. J., Vol. 10, 741(1964).