Calculation of Supersaturation Ratios of Flue Gas Scrubbing Slurries

C. P. KERR

Tennessee Technological University
Cookeville, Tennessee

In the lime and limestone wet scrubbing processes for flue gas desulfurization, the scaling tendency of these processes is primarily dependent upon the calcium sulfite and calcium sulfate supersaturation ratios. These ratios are determined by first analyzing experimentally the composition of the liquid portion of the slurry: molalities of dissolved sulfur dioxide, sulfate, carbon dioxide, chloride, sodium and potassium, calcium, magnesium, and *p*H. The activities of the components are then calculated from the appropriate equilibrium expressions and the above experimental quantities. Finally, the supersaturation ratios can be calculated. Because of the large number of dissolved components, twenty-eight, the calculation of the activities of the dissolved components is rather tedious, especially if linearization methods are used. This note describes a computationally simple method for performing this task by using a Hooke-Jeeves search (1961). A discussion of the Hooke-Jeeves search can also be found in Beveridge and Schechter (1970).

The equilibria present in the liquid have been determined by Lowell et al. (1970) and are shown in Table 1. Potassium has been included as sodium. These equilibria can be expressed mathematically in terms of a temperature dependent equilibrium constant K as

$$\frac{a_B a_C}{a_A} = K \tag{1}$$

with activities related to molalities through the activity coefficients

$$a = \gamma m \tag{2}$$

Expressions for the equilibrium constants for this system have been tabulated by Lowell et al. (1970) and are presented in Table 2. The equilibrium constants can also be calculated from tabulated thermodynamic properties.

The measured molalities are related to the individual molalities through the following mass balance expressions:

$$m_{SO_2} = m_3 + m_4 + m_5 + m_{13} + m_{19} \tag{3}$$

$$m_{SO_4} = m_6 + m_7 + m_{14} + m_{20} + m_{25} \tag{4}$$

$$m_{CO_2} = m_8 + m_9 + m_{10} + m_{15} + m_{16} + m_{21} + m_{22} + m_{26} + m_{27} \tag{5}$$

$$m_{Ca} = m_{11} + m_{12} + m_{13} + m_{14} + m_{15} + m_{16} \tag{6}$$

$$m_{Mg} = m_{17} + m_{18} + m_{19} + m_{20} + m_{21} + m_{22} \tag{7}$$

These equations can be used to define the following artificial function:

$$\begin{aligned} y = {} & (m_{SO_2} - m_3 - m_4 - m_5 - m_{13} - m_{19})^2 \\ & + (m_{SO_4} - m_6 - m_7 - m_{14} - m_{20} - m_{25})^2 \\ & + (m_{CO_2} - m_8 - m_9 - m_{10} - m_{15} - m_{16} \\ & \quad - m_{21} - m_{22} - m_{26} - m_{27})^2 \\ & + (m_{Ca} - m_{11} - m_{12} - m_{13} - m_{14} - m_{15} - m_{16})^2 \\ & + (m_{Mg} - m_{17} - m_{18} - m_{19} - m_{20} - m_{21} - m_{22})^2 \end{aligned} \tag{8}$$

The search variables chosen to zero the above function are the molalities of bisulfite, bicarbonate, calcium, magnesium, and sulfate ions. With this choice of search variables, the calculation of the remaining molalities at any point on the search surface can be easily performed sequentially by using the equilibrium expressions written for the reactions shown in Table 1 and the calculated activity coefficients. The calculation sequence is the same as the order in which the equations appear in Table 1: first, hydroxide molality from the equilibrium constant for water dissociation, the water activity, *p*H, and the hydroxide activity coefficient; second, the sulfite molality from the bisulfite dissociation constant, *p*H, the search value of bisulfite molality, and activity coefficients of sulfite and bisulfite; third, sulfurous acid molality from its dissociation constant, *p*H, the search value of bisulfite molality, and activity coefficients of bisulfite and sulfurous acid; fourth, the bisulfate molality from its dissociation constant, *p*H, the search value of sulfate molality, and activity coefficients of bisulfate and sulfate. By continuing through Table 1 in this manner, the remainder of the molalities can be obtained for a given search point. The artificial function y is evaluated, and a new search point is located by using the Hooke-Jeeves search method. On the first cycle of the search, the sodium ion molality is taken as the total dissolved sodium molality. As the search progresses past the first cycle, the molality of the sodium ion is obtained more precisely by subtracting the sodium ion pair molalities obtained during the previous cycle. At the end of the search, generally when y falls below 10^{-8}, the calcium sulfate supersaturation ratio can be found by dividing the product of calcium and sulfate ion activities by the solubility product. The calcium sulfite supersaturation ratio is calculated in the same fashion. A check of the reliability of the measured compositions of the liquid

Table 1. Equilibria Present in Flue Gas Scrubbing Slurries for the Lime or Limestone Processes

$H_2O \rightleftharpoons H^+ + OH^-$	(1)	$HSO_3^- \rightleftharpoons H^+ + SO_3^{--}$	(2)
$H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$	(3)	$HSO_4^- \rightleftharpoons H^+ + SO_4^{--}$	(4)
$HCO_3^- \rightleftharpoons H^+ + CO_3^{--}$	(5)	$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$	(6)
$CaOH^+ \rightleftharpoons Ca^{++} + OH^-$	(7)	$CaSO_3^0 \rightleftharpoons Ca^{++} + SO_3^{--}$	(8)
$CaSO_4^0 \rightleftharpoons Ca^{++} + SO_4^{--}$	(9)	$CaCO_3^0 \rightleftharpoons Ca^{++} + CO_3^{--}$	(10)
$CaHCO_3^+ \rightleftharpoons Ca^{++} + HCO_3^-$	(11)	$MgOH^+ \rightleftharpoons Mg^{++} + OH^-$	(12)
$MgSO_3^0 \rightleftharpoons Mg^{++} + SO_3^{--}$	(13)	$MgSO_4^0 \rightleftharpoons Mg^{++} + SO_4^{--}$	(14)
$MgCO_3^0 \rightleftharpoons Mg^{++} + CO_3^{--}$	(15)	$MgHCO_3^+ \rightleftharpoons Mg^{++} + HCO_3^-$	(16)
$NaOH^0 \rightleftharpoons Na^+ + OH^-$	(17)	$NaSO_4^- \rightleftharpoons Na^+ + SO_4^{--}$	(18)
$NaCO_3^- \rightleftharpoons Na^+ + CO_3^{--}$	(19)	$NaHCO_3^0 \rightleftharpoons Na^+ + HCO_3^-$	(20)
$CaSO_4 \cdot 2H_2O \rightleftharpoons Ca^{++} + SO_4^{--} + 2H_2O$	(21)	$CaSO_3 \cdot \frac{1}{2}H_2O \rightleftharpoons Ca^{++} + SO_3^{--} + \frac{1}{2}H_2O$	(22)

TABLE 2. EXPRESSIONS FOR EQUILIBRIUM CONSTANTS FROM LOWELL ET AL. (1970)

$$\log K = -B/T - C \log T - DT + E$$

Reaction	B	C	D	E
1	4.4710E 03	0.0000	1.7060E-02	6.0875E 00
2	−6.3384E 02	0.0000	0.0000	−9.3320E 00
3	−8.4367E 02	0.0000	0.0000	−4.7171E 00
4	4.7514E 02	0.0000	1.8222E-02	5.0435E 00
5	2.9024E 03	0.0000	2.3790E-02	6.4980E 00
6	3.4047E 03	0.0000	3.2786E-02	1.4843E 01
7	−2.7300E 02	0.0000	0.0000	−2.2900E 00
8	−5.0480E 02	0.0000	0.0000	−5.0910E 00
9	2.5721E 03	2.3150E 01	0.0000	6.3600E 01
10	−4.7548E 02	0.0000	0.0000	−4.7954E 00
11	−3.0185E 02	0.0000	0.0000	−2.2720E 00
12	−5.1799E 02	0.0000	0 0000	−4.3223E 00
13	−4.3250E 02	0.0000	0.0000	−4.3715E 00
14	−1.0579E 03	0.0000	0.0000	−5.7950E 00
15	−5.0480E 02	0.0000	0.0000	−5.0910E 00
16	−2.3508E 02	0.0000	0.0000	−1.7470E 00
17	0.0000	0.0000	0.0000	5.7000E-01
18	−2.4100E 02	0.0000	0.0000	−1.5290E 00
19	−3.0341E 02	0.0000	0.0000	−2.2852E 00
20	0.0000	0.0000	0.0000	2.5000E-01
21	4.9440E 03	3.7745E 01	0.0000	1.0536E 02
22	0.0000	0.0000	0.0000	−7.0757E 00

portion of the slurry can be obtained by calculating the ionic charge imbalance.

The activity coefficients of the charged components, which are required each time the function y is evaluated during the search, can be calculated by using the method of Bromley (1973). This method is suitable up to ionic strengths of 6 M. For this application, the ionic strength is less than 0.2 M. These expressions, where calcium chloride is the predominant dissolved component, are

$$\log\gamma_i = \frac{-AI^{1/2}}{1 + I^{1/2}} + \left[\frac{0.1169}{(1 + 1.5I)^2} + 0.0948\right] m_{28}$$

$$\text{for} \quad i = 1,\ 11,\ 16,\ 17,\ 22,\ 24 \qquad (9)$$

$$\log\gamma_i = \frac{-AI^{1/2}}{1 + I^{1/2}} + 2.25\left[\frac{0.2338}{(1 + 0.75I)^2} + 0.0948\right] m_{12}$$

$$\text{for} \quad i = 2,\ 3,\ 6,\ 8,\ 25,\ 26,\ 28 \qquad (10)$$

$$\log\gamma_i = \frac{-4AI^{1/2}}{1 + I^{1/2}} + 4.0\left[\frac{0.4675}{(1 + 0.375I)^2} + 0.0948\right] m_{12}$$

$$\text{for} \quad i = 4,\ 7,\ 9 \qquad (11)$$

$$\log\gamma_i = \frac{-4AI^{1/2}}{1 + I^{1/2}} + 2.25\left[\frac{0.2338}{(1 + 0.75I)^2} + 0.0948\right] m_{28}$$

$$\text{for} \quad i = 12,\ 18 \qquad (12)$$

For the uncharged components, the expression of Lowell et al. (1970) was used:

$$\log\gamma_i = 0.076I$$

$$\text{for} \quad i = 5,\ 10,\ 13,\ 14,\ 15,\ 19,\ 20,\ 21,\ 23,\ 27 \qquad (13)$$

The value of ionic strength used in the above expressions was obtained from the molalities from the previous search point. The activity of water was taken as the water mole fraction (Han and Bernardin, 1958).

The starting values of the search variables were taken as half the molality of that dissolved component. The search step size was 0.01 of the molality of the dissolved component. The computer execution time for a case is about 0.06 min.; the program size is 2145 words (Xerox Data Systems Sigma 5). An example case with compositions of the liquid portion of the slurry determined by Epstein et al. (1974) is shown in Table 3.

TABLE 3. EXAMPLE CALCULATION

Measured quantities

Component	Gram moles per liter
Sulfur dioxide	0.2500E-02
Carbon dioxide	0.333E-02
Calcium	0.499E-01
Magnesium	0.904E-02
Sodium and potassium	0.217E-02
Sulfate	0.1353E-01
Chloride	0.8460E-01

$pH = 5.9$

Temperature = 298°K

Calculated quantities

Component	Molality	Component	Molality
H^+	0.1701E-05	$CaCO_3^0$	0.5493E-06
OH^-	0.1040E-07	$CaHCO_3^+$	0.2360E-03
HSO_3^-	0.1061E-02	$MgOH^+$	0.9805E-08
SO_3^{--}	0.1246E-03	Mg^{++}	0.8028E-02
H_2SO_3	0.2521E-32	$MgSO_3^0$	0.7731E-04
HSO_4^-	0.3529E-06	$MgSO_4^0$	0.9098E-03
SO_4^{--}	0.6942E-02	$MgCO_3^0$	0.1623E-06
HCO_3^-	0.9927E-03	$MgHCO_3^+$	0.2214E-04
CO_3^{--}	0.8726E-07	$NaOH^0$	0.3293E-11
H_2CO_3	0.2084E-02	Na^+	0.2145E-02
$CaOH^+$	0.3221E-08	$NaSO_4^-$	0.2441E-04
Ca^{++}	0.4279E-01	$NaCO_3^-$	0.1080E-08
$CaSO_3^0$	0.1235E-02	$NaHCO_3^0$	0.6566E-06
$CaSO_4^0$	0.5622E-02	Ionic charge Imbalance	0.3227E-02

Calcium sulfite supersaturation ratio = 1.132

Calcium sulfate supersaturation ratio = 1.182

NOTATION

A = Debye-Huckel constant = 0.511 $kg^{1/2}$ $mole^{-1/2}$ at 25°C

B, C, D, E = constants in expressions for equilibrium constants

I = ionic strength

K = equilibrium constant

a = activity

m = molality, g moles/kg of water

y = squares of molality imbalance, (g moles/kg of water)^2

γ = activity coefficients

Component subscripts

Ca = total calcium

CO_2 = total carbon dioxide

Mg = total magnesium

SO_2 = total dissolved sulfur dioxide

SO_4 = total dissolved sulfate

1 = H^+

2 = OH^-

3 = HSO_3^-

4 = SO_3^{--}

5 = $H_2SO_3^0$

6 = HSO_4^-

7 = SO_4^{--}

8 = HCO_3^-

9 = CO_3^{--}

10 $= H_2CO_3$
11 $= CaOH^+$
12 $= Ca^{++}$
13 $= CaSO_3^0$
14 $= CaSO_4^0$
15 $= CaCO_3^0$
16 $= CaHCO_3^+$
17 $= MgOH^+$
18 $= Mg^{++}$
19 $= MgSO_3^0$
20 $= MgSO_4^0$
21 $= MgCO_3^0$
22 $= MgHCO_3^+$
23 $= NaOH^0$
24 $= Na^+$
25 $= NaSO_4^-$
26 $= NaCO_3^-$
27 $= NaHCO_3^0$
28 $= Cl^-$

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Long Range Attractive Forces for Hydrogen-Light Hydrocarbon Pairs

HSUAN TIEN, THOMAS NENNER, and J. B. FENN

Department of Engineering and Applied Science
Yale University, New Haven, Connecticut 06520

Some of the pathways which connect the macroscopic properties of gaseous systems with the dynamics of binary encounters between their constituent molecules have been traveled frequently in both directions. Even so, there remain unknown stretches along the most familiar trails, and prospective routes for most polyatomic molecular systems have not been traversed in even one direction. Not long ago, Chu, Chappelear, and Kobayashi (1975) analyzed experimental data on diffusivity, viscosity, and second virial coefficients for binary mixtures of hydrogen with methane, ethane, propane, and *n*-butane. By a fitting procedure they determined best values of the molecular interaction parameters ϵ/k and σ for specifying both a Lennard-Jones (12-6) potential and a modified Buckingham (Exp-6) potential. For the third parameter (repulsive steepness) of the latter they assumed a value of 12. They then computed the transport and virial properties from these potentials for a number of specific conditions and found good agreement between the calculated and experimental values, usually less than 1% difference. They concluded that in most cases the Exp-6 potential provided somewhat more accurate predictions than the L-J (12-6) potential.

We have been determining absolute values of total cross sections for the scattering of molecular beams of argon atoms by a variety of aliphatic hydrocarbon molecules. By the so-called Schiff-Landau-Lifshitz (1956, 1959) approximation it is possible to determine from the total cross section Q_t the Van der Waals coefficient C_6 of the inverse sixth power term which describes the long range attractive force in practically all realistic potential models for nonpolar molecules. We thought it would be interesting to compare C_6 values obtained from molecular beam scattering experiments with those which could be inferred from the potentials which CCK arrived at from transport and virial properties. Accordingly, we measured total cross sections for the scattering of a hydrogen beam by methane, ethane, propane, and *n*-butane.

The apparatus and procedure are described in detail elsewhere (Nenner et al., 1975). It will suffice here to outline the essential features of the method. Hydrogen at 298°K and 133 kN/m^2 (1 000 torr) is expanded through a sonic orifice 0.1 mm in diameter to form a supersonic free jet in a chamber maintained at 1.33 N/m^2 (10^{-2} torr). A molecular beam is extracted from the core of the jet through a conical brass skimmer into a collimating chamber maintained at 133 μN/m^2 (10^{-6} torr) and then through a collimating slit into a test chamber maintained at about 13 μN/m^2 (10^{-7} torr). In this test chamber the beam molecules pass successively through a second collimating slit, a scattering box, and then into an ionization gauge detector. The detector signal measures the beam intensity I_o when the scattering box is empty and I when there is target gas in the box. The density n_s of target molecules is determined by measurement of box pressure with a capacitance manometer (MKS Baratron 90-M-XR). The attenuation of the beam is described by the Beer's law relation

$$I/I_o = e^{-Qn_sL} \qquad (1)$$

where L is the path length over which scattering occurs and Q is the scattering cross section. The angular resolution of our apparatus is high enough [0.77×10^{-3} rad by the Kusch (1964) criterion] and the velocity spread in the beam molecules is narrow enough so that by applying small corrections (von Busch, 1966; Berkling et al., 1962) we could convert our measured Q's into absolute total cross sections Q_t's. Absolute values of the Ar-Ar total cross section determined in our apparatus are within 2% of the best previous experimental values (Rothe and Neynaber, 1965; Swedenburg, 1972). Consequently, we believe that the hydrogen-hydrocarbon values reported here are similarly accurate. It is noteworthy that the apparatus is controlled by a PDP 11/40 minicomputer which provides on line processing of the data. Each reported cross section is in effect the average of forty-eight independent measurements of I, I_o, and n_s. The standard deviation ranges from 0.6 to 1.5%.

From absolute values of Q_t the Van der Waals coefficient C_6 can be obtained by means of the Schiff-Landau-Lifshitz approximation (1956, 1959) which, for our pres-