R & D NOTES

Aqueous Sodium Sulfite, Bisulfite and Sulfate Equilibria

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There is considerable interest in double alkali scrubbing of power plant flue gas for removal of sulfur dioxide. In this process, the flue gas is to be scrubbed with an aqueous solution of sodium sulfite, bisulfite, and sulfate in an inner loop, and in an outer loop scrubbing liquid is regenerated (bisulfite is converted to sulfite) and calcium sulfite and sulfate are removed by the addition of either or both limestone and lime. Sulfate is formed because of oxidation.

In the scrubber design, it is frequently necessary to know the equilibrium sulfur dioxide partial pressure over the solution and the liquid composition with the following specified: temperature, total pressure (slightly above atmospheric), sodium ion concentration, total dissolved sulfur dioxide concentration (sulfurous acid, sulfite, and bisulfite), carbon dioxide partial pressure, and sulfate ion concentration. This note describes a computationally feasible method for calculation of the compositions with the above input and a realistic set of equilibria.

The scrubbing part of the process, for the elimination of scaling with improved reliability, operates unsaturated with respect to both solid calcium sulfite and sulfate. Hence, the calcium equilibria has not been considered, and its concentration is low enough so it does not affect other dissolved components. Also, with negligible amounts of calcium and magnesium sulfates, the presence of ion pairs can be neglected in the formulation of the equilibria (Bromley, 1973). The equilibria considered are

$$SO_2(g) + H_2O \rightleftharpoons H_2SO_3 \qquad (1)$$

$$H_2SO_3 \rightleftharpoons H^+ + HSO_3^- \qquad (2)$$

$$HSO_3^- \rightleftharpoons H^+ + SO_3^{--} \qquad (3)$$

$$CO_2(g) + H_2O \rightleftharpoons H_2CO_3 \qquad (4)$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad (5)$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{--} \qquad (6)$$

$$H_2O \rightleftharpoons H^+ + OH^- \qquad (7)$$

and the corresponding equilibrium expressions are

$$a_1/p_{SO_2} a_{11} = K_1 \qquad (8)$$

$$a_2 a_3/a_1 = K_2 \qquad (9)$$

$$a_2 a_4/a_3 = K_3 \qquad (10)$$

$$a_5/(p_{CO_2} a_{11}) = K_4 \qquad (11)$$

$$a_2 a_6/a_5 = K_5 \qquad (12)$$

$$a_2 a_7/a_6 = K_6 \qquad (13)$$

$$a_2 a_8/a_{11} = K_7 \qquad (14)$$

Because of the concentration levels encountered, the equilibria must be formulated in terms of activities rather than molalities. The subscripts on the equilibrium constants refer to the reaction numbers. The electroneutrality equation for the ions considered is

$$m_2 + m_{10} = m_3 + 2m_4 + m_6 + 2m_7 + m_8 + 2m_9 \qquad (15)$$

The activities, molalities, and activity coefficients are related by

$$a_i = \gamma_i m_i \quad i = 1, \ldots 10 \qquad (16)$$

Bromley (1973) has developed a method for calculating the activity coefficients of ions of strong electrolytes in aqueous solutions of high ionic strength. This method is suitable where ionic strengths are greater than 0.1 M and can be extended to multicomponent systems by considering the dissolved species as forming a complex salt. The routines available in the open literature are valid to an ionic strength of 0.1 M. For the components considered, the expressions reduce to

$$\log \gamma_i = \frac{-AI^{1/2}}{1 + I^{1/2}} + \left[\frac{0.12 + 1.2B}{(1 + 0.75I)^2} + B\right] [2.25(m_4 + m_7 + m_9)] + \left[\frac{0.06 + 0.6B}{(1 + 1.5I)^2} + B\right] [m_3 + m_6 + m_8] \quad i = 2 \text{ and } 10 \qquad (17)$$

$$\log \gamma_i = \frac{-AI^{1/2}}{1 + I^{1/2}} + \left[\frac{0.06 + 0.6B}{(1 + 1.5I)^2} + B\right] [m_2 + m_{10}] \quad i = 3, 6, 8 \qquad (18)$$

$$\log \gamma_i = \frac{-4AI^{1/2}}{1 + I^{1/2}} + \left[\frac{0.12 + 1.2B}{(1 + 0.75I)^2} + B\right] [2.25(m_2 + m_{10})] \quad i = 4, 7, 9 \qquad (19)$$

and for the uncharged species (Lowell et al., 1970)

$$\log \gamma_i = 0.076I \quad i = 1 \text{ and } 5 \qquad (20)$$

The B value can be evaluated by treating the individual salts as forming a complex salt (Bromley, 1973).

$$B = 4[2.25B_{Na_2SO_3} m_4 m_{10} + 2.25B_{Na_2SO_4} m_9 m_{10} + 2.25B_{Na_2CO_3} m_7 m_{10} + B_{NaHSO_3} m_3 m_{10} + B_{NaHCO_3} m_6 m_{10} + B_{NaOH} m_8 m_{10}]/ (m_3 + m_4 + m_6 + m_7 + m_8 + m_9 + m_{10}) (m_3 + 4m_4 + m_6 + 4m_7 + m_8 + 4m_9 + m_{10}) \qquad (21)$$

The B values for the individual salts are: −0.0204 for Na_2SO_4, 0.0089 for Na_2CO_3, 0.048 for NaOH (Bromley, 1973), −0.0374 for $NaHSO_3$, −0.0282 for Na_2SO_3 (both calculated from mean activity coefficient data of Morgan, 1960), and −0.0125 for $NaHCO_3$ (calculated from mean activity data of Han and Bernardin, 1958). Since the first term in Equations (17), (18), or (19) is dominant, the only temperature dependence of the activity coefficient considered was in the Debye-Hückel constant A.

The ionic strength I can be calculated from

Table 1. Computational Results at 125°F, Carbon Dioxide Partial Pressure of 0.1 Atm and 1 Atm Total Pressure

Specified molalities			Calculated molalities								
Na^+	SO_4^{--}	Total dissolved SO_2	H_2SO_3	H^+	HSO_3^-	SO_3^{--}	H_2CO_3	HCO_3^-	CO_3^{--}	OH^-	p_{SO_2}, Atm
1.1	0.5	0.005	2.820E-10	4.425E-08	3.204E-04	4.644E-03	1.296E-03	8.559E-02	2.166E-03	5.458E-06	7.323E-10
		0.010	7.358E-10	5.056E-08	7.324E-04	9.300E-03	1.335E-03	7.723E-02	1.712E-03	4.925E-06	1.913E-09
		0.020	2.073E-09	6.128E-08	1.709E-03	1.799E-02	1.333E-03	6.387E-02	1.174E-03	4.073E-06	5.391E-09
1.1	0.6	0.005	3.258E-03	1.017E-01	1.742E-03	1.199E-08	1.254E-03	3.898E-08	4.683E-16	2.486E-12	8.743E-03
		0.010	6.546E-03	1.035E-01	3.454E-03	2.345E-08	1.252E-03	3.840E-08	4.552E-16	2.449E-12	1.759E-02
		0.020	1.323E-02	1.068E-01	6.774E-03	4.463E-08	1.251E-03	3.724E-08	4.285E-16	2.375E-12	3.557E-02
1.2	0.6	0.005	3.866E-04	4.579E-03	4.613E-03	7.081E-07	1.252E-03	8.683E-07	2.328E-13	5.538E-11	1.039E-03
		0.010	1.310E-03	8.238E-03	8.689E-03	7.414E-07	1.293E-03	4.984E-07	7.426E-14	3.178E-11	3.521E-03
		0.020	4.078E-03	1.405E-02	1.592E-02	7.997E-07	1.292E-03	2.930E-07	2.570E-14	1.869E-11	1.098E-02
0.8	0.4	0.005	4.894E-04	4.555E-03	4.510E-03	5.192E-07	1.425E-03	7.634E-07	1.535E-13	4.869E-11	1.181E-03
		0.010	1.729E-03	8.816E-03	8.270E-03	4.943E-07	1.424E-03	3.957E-07	4.130E-14	2.523E-11	4.177E-03
		0.020	5.163E-03	1.473E-02	1.484E-02	5.332E-07	1.422E-03	2.375E-07	1.490E-14	1.515E-11	1.249E-02

$$I = \tfrac{1}{2}(m_2 + m_3 + 4m_4 + m_6 + 4m_7 + m_8 + 4m_9 + m_{10}) \quad (22)$$

The activity of water is close to unity and has been approximated as the water mole fraction (Han and Bernardin, 1958).

$$a_{11} = 55.5 \Big/ \sum_{i=1}^{10} (m + 55.5) \quad (23)$$

This approximation has been checked with experimental activities of water in sodium sulfate solutions, Pearce and Eckstrom (1937), and agrees to within 1% for sodium sulfate molalities of 1.0 or less. For most designs being considered, sodium sulfate is the dominant dissolved specie.

Equations (9) and (10) can be combined with the expression for total dissolved sulfur dioxide

$$m_1 + m_3 + m_4 = S \quad (24)$$

to give an expression for the bisulfite molality in terms of the activity coefficients, equilibrium constants, total dissolved sulfur dioxide molality, and sulfite molality.

$$m_3 = -\frac{\gamma_1 \gamma_4 m_4 K_2}{2 \gamma_3^2 K_3} + \frac{1}{2 \gamma_3^2 K_3} \sqrt{\gamma_1 \gamma_4 m_4 K_2 (\gamma_1 \gamma_4 m_4 K_2 + 4\gamma_3^2 K_3 (S - m_4))} \quad (25)$$

The remaining molalities can be calculated sequentially.

$$m_2 = \frac{\gamma_3 m_3 K_3}{\gamma_2 \gamma_4 m_4} \quad (26)$$

$$m_1 = \frac{\gamma_2 m_2 \gamma_3 m_3}{\gamma_1 K_2} \quad (27)$$

$$m_6 = \frac{P_{CO_2} K_4 a_{11} K_5}{\gamma_2 m_2 \gamma_6} \quad (28)$$

$$m_7 = \frac{K_6 \gamma_6 m_6}{\gamma_2 m_2 \gamma_7} \quad (29)$$

$$m_8 = \frac{K_7 a_{11}}{\gamma_2 m_2 \gamma_8} \quad (30)$$

The square of the deviation from electroneutrality is

$$f = (m_2 - m_3 - 2m_4 - m_6 - 2m_7 - m_8 - 2m_9 + m_{10})^2 \quad (31)$$

Computational experience indicates this function is unimodal. A Fibonacci search on the sulfite molality in the range

$$0 < m_4 < S \quad (32)$$

has been used with Equations (25) through (32) to determine the liquid compositions yielding electroneutrality. Several numerical methods have been used, but a Fibonacci search has been found to be the most reliable. This method of solution has the following advantages which the usual linearization methods generally do not have: the computer programming is simple; little machine time is required; the algorithm always converges.

The computational algorithm consists of the following steps:

1. With temperature specified calculate the equilibrium constants and the Debye-Hückel constant A. Expressions for the equilibrium constants as a function of temperature have been developed by Lowell et al. (1970) or can be calculated from tabulated thermodynamic properties (Wagman et al., 1968, 1969; Parker et al., 1971).
2. Set the unspecified molalities equal to zero.
3. Calculate the B factor from Equation (21), the ionic strength from Equation (22), and the water activity from Equation (23).
4. Calculate the activity coefficients.
5. Calculate the liquid molalities by performing a Fibonacci search on the sulfite molality [Equations (11) and (25) through (31)].
6. Repeat steps 3 through 5 until constants molalities are obtained.
7. Calculate sulfur dioxide partial pressure from equation (8).

Some computed results are shown in Table 1.

NOTATION

A = Debye-Hückel constant = 0.511 $kg^{1/2}$ $mol^{-1/2}$ at 25°C
a = activity
B = constant, dependent upon the dissolved species
f = square of deviation from electroneutrality, (gm moles/kg of solvent)^2
I = ionic strength
K = equilibrium constant, subscripts refer to the reaction numbers
m = molality, g moles/kg of water
p = partial pressure, atm

S = total dissolved sulfur dioxide (sulfurous acid, sulfite, and bisulfite), g moles/kg of water

Greek Letters

γ = activity coefficients

Component Subscripts

1 = sulfurous acid
2 = hydrogen ion
3 = bisulfite
4 = sulfite
5 = carbonic acid
6 = bicarbonate
7 = carbonate
8 = hydroxide
9 = sulfate
10 = sodium ion
11 = water

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Decoupling Control

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In a recent communication, Waller (1974) discusses the decoupling control of the transfer matrix or P-structure process model. As noted earlier (Changlai and Ward, 1972), the decoupling and primary feedback control roles for this particular process model cannot be separated. For this reason, there are an infinite number of decoupling choices, each resulting in different dynamic responses for the decoupled subsystems. A specified subsystem response can be approached only through a trial-and-error application of the diagonalization condition (Kavanagh, 1958; Freeman, 1957; Bollinger and Lamb, 1965). It may be difficult to even find a realizable design. There have been a number of attempts to provide straightforward control design for this terminal model by approximate methods.

PSEUDO-DECOUPLING

In an attempt to separate the decoupling and feedback roles, Waller proposes a simple feedforward decoupling logic, illustrated in the matrix structures of Figure 1. The diagonalization condition is applied to the matrix product $T = GD$. This decoupling implies that the pseudo-inputs m will not interactively affect the outputs y. However, the process intercoupling between the actual manipulative inputs u and the outputs y has not been eliminated. An additional difficulty is the effective design of the diagonal feedback control matrix P operating on pseudo-inputs rather than the process inputs since each p control element affects all of the u process inputs.

This pseudo-decoupling control logic is illustrated for a two-variable example in the signal flow diagram of Figure 2a, which corresponds to the block diagram (Figure 2) of the cited reference. The control structure in Figure 2a is that found in the feedback control of the transfer matrix model, as illustrated in Figure 2b. The variable v is used here to represent either a setpoint or disturbance input. Even though the setpoint enters the loop after y, this simplification is adequate for illustration since the control elements are actuated by the error.

DESIGN APPROACHES

Waller discusses two design classes for his proposed control structure. In the first, an arbitrary diagonal form

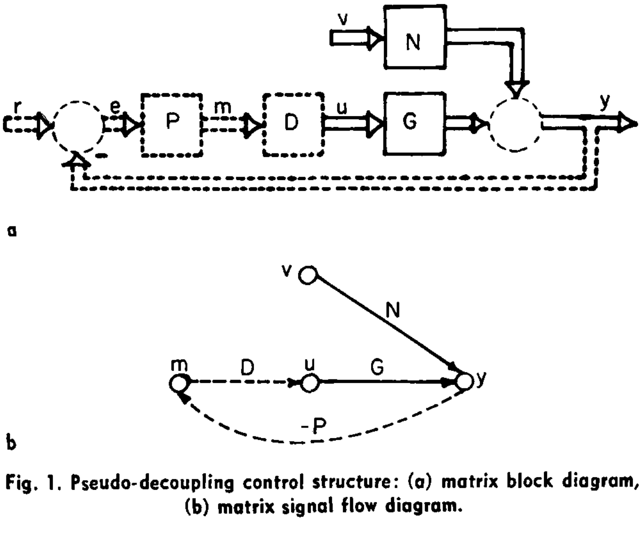

Fig. 1. Pseudo-decoupling control structure: (a) matrix block diagram, (b) matrix signal flow diagram.

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