ζ^* = disturbance effect defined by Eq. 2
κ = Rynsdorp interaction measure
λ = Bristol-relative gain element
λ_o = steady-state value of λ
Λ_i = C_iG_{ii}
π = 3.14159. . .
τ = $\tau_{22} - \tau_{11}$
τ_{ij} = dead time in G_{ij}
ω_{ui} = single-loop ultimate frequency for loop i
ω_{uiI} = ultimate frequency for interacting control of loop i

Indices

i = 1, 2
j = 1, 2

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Estimation of Activity Coefficients in Concentrated Sulfite-Sulfate Solutions

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The electrolyte theory of Pitzer and coworkers is used to estimate geometric mean-ion activity coefficients in strong electrolyte solutions at 25-55°C. By using Pitzer's equations with ion-pair parameters estimated in this paper, one can calculate activity coefficients to moderately high ionic strengths in aqueous mixtures containing the following ions: Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, ClO_3^-, ClO_4^-, HCO_3^-, HSO_3^-, CO_3^{2-}, SO_4^{2-}, SO_3^{2-}, and $S_2O_5^{2-}$. Mixtures containing these ions are present in $CaO/CaSO_4$ flue gas desulfurization units and in laboratory experiments aimed at understanding the chemistry occurring in such units. The computed activity coefficients are relatively insensitive to the values of the estimated quantities. The basis of the estimates, as well as their effect on calculated activity coefficients, is discussed. It is concluded that activity coefficients are estimated with an accuracy of ±25% or better.

SCOPE

Optimizing the performance of $CaO/CaCO_3$ flue gas desulfurization scrubbers requires understanding of the chemistry occurring in these units and knowledge of the thermodynamic properties of the chemical species present. Because some of the chemistry, particularly the sulfur chemistry, is complex, experimental values for the thermodynamic properties of many of the species which may be present are not available and these properties have to be estimated. The present work describes estimates of the activity coefficients at 25°-55°C of the strong electrolytes, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, ClO_3^-, ClO_4^-, HCO_3^-, HSO_4^-, HSO_3^-, CO_3^{2-}, SO_4^{2-}, SO_3^{2-}, and $S_2O_5^{2-}$, present in

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operating $CaO/CaCO_3$ and other aqueous scrubbers, or in laboratory studies of their chemistry.

In the computer code for alkali scurbbers in current use, activities are calculated by combining association equilibria for strongly attractively-interacting ion-pairs with extended Debye-Hückel ion activity coefficients. The latter depend upon a parameter for the ion and upon the ionic strength of the solution but not upon the nature of the other ions present. When applied to moderately concentrated (ionic strength $I > 0.2$) complex mixtures the approach has well-recognized deficiencies.

More recent developments in the statistical mechanics of electrolyte solutions, which have been put into practical form by Pitzer and coworkers, sum over pairwise interactions for all ions present in the solution and thus enable one to calculate activity coefficients for ions in mixtures which reflect the differences in the degrees of interaction between various ions. Such calculations closely reproduce experiment even at high concentration. Pitzer's equations require parameters for all ion pairs present in the mixture. In this paper, the required parameters are estimated by empirical methods based upon a correlation between the parameters and the water "structure-making" or "breaking" tendencies of the ions. For this purpose, Pitzer's equations are truncated so as to have the minimum number of parameters consistent with the accuracy to which activity coefficients can be calculated from pure electrolyte and estimated parameters. The sensitivity of computed activity coefficients to potential errors in estimated parameters is examined.

CONCLUSIONS AND SIGNIFICANCE

Eqs. 1-7 and the ion-pair parameters summarized in Tables 1-3 allow one to calculate mean-ion activity coefficients $\gamma_\pm$ in complex, concentrated sulfite-sulfate electrolyte solutions with an accuracy estimated to be better than ±25% in the range 25-55°C. The accuracy of calculated activity coefficients is limited to about the same degree by uncertainties in the estimated parameters and by simplifications introduced in the theory in order to reduce the number of parameters to be estimated.

The empirical procedure used to estimate parameters, by interpolation or extrapolation from values for measured ion-pairs, is described in section 3. Estimations of this kind might be used to apply Pitzer's theory to other complex mixtures which contain ion pairs for which there are no experimental data. Because activity coefficients are determined to quite an extent by the form of Pitzer's equations and are not extremely sensitive to the exact values of parameters, ion-pair parameters have only to be estimated within a reasonable range.

Upon comparing the present Pitzer-theory calculations for typical scrubber solutions with the association-equilibrium, extended Debye-Hückel model in current use one sees differences which reflect the differences in concentration range and applicability to mixtures of the two approaches.

Regardless of the accuracy of the parameters estimated in this paper, Pitzer's formulation offers a satisfactory way to model strong electrolyte activity coefficients in concentrated and complex mixtures. When sufficient experimental data are available, calculations considerably more accurate than those in this paper can be made. Attaining high accuracy may require not only experimentally-based parameters but also that one employ third virial coefficients and additional mixing terms and include explicit temperature dependencies for the various parameters.

One of the major elements of the U.S. national energy plan is the increased use of coal as a fuel for utility and industrial boilers. Environmental requirements make it necessary to install flue gas desulfurization units on coal-fired burners. While existing flue gas desulfurization technology based upon $CaO/CaCO_3$ scrubbers has been shown to control SO_2 emissions, many aspects of the chemistry associated with successful operation of these units are incompletely understood. The present work is part of an effort to describe the thermodynamic properties of the chemicals present during operation of $CaO/CaCO_3$ or similar aqueous scrubbers.

This paper is concerned with an estimation of activity coefficients for the strong electrolytes (H^+, Na^+, K^+, Mg^{++}, Ca^{++}, Cl^-, ClO_3^-, ClO_4^-, HCO_3^-, HSO_4^-, HSO_3^-, $CO_3^=$, $SO_4^=$, $SO_3^=$, $S_2O_5^=$) present in operating flue gas desulfurization scrubbers or in laboratory studies aimed at clarifying the complex sulfur chemistry which may occur in these units. The initial effort is restricted to strong electrolytes at 25-55°C. It should be possible to extend the treatment to include dissociation constants of weak acids and solubility products of sparingly soluble electrolytes so that pH and solubility can be calculated.

To predict activity coefficients in multicomponent, aqueous electrolyte solutions at the concentrations and ionic strengths encountered in technology, one first requires a theoretical formulation which represents the activity coefficients of pure electrolytes adequately to molalities of 1-5 $\underline{M}$ and which can be readily extended to mixtures of different types (1-1, 2-1, etc.) of electrolytes. Extension to mixtures should add a minimal number of parameters to those describing pure electrolytes and added mixing parameters should be small contributors. One also needs a physical and/or empirical basis for estimation of unmeasured, pure-electrolyte parameters. Finally, calculated activity coefficients should be relatively insensitive to errors in estimated quantities.

These are formidable requirements. This work uses a formulation developed by Pitzer (1973, 1977) and Pitzer and Kim (1974) which appears to have the features desired. Pitzer's formulation, although in part empirical for simplicity and generality, has been guided by recent developments in the statistical mechanical treatment of electrolytes in solution. Because it is a convergent series, it lends itself to the compromises between theoretical complexity and obtainable accuracy which must be made when dealing with electrolytes for which there are no adequate data and for which parameters have to be estimated. Other useful procedures for estimating activity coefficients have been presented by Bromley (1973), Meissner (Meissner and Kusik, 1972; Meissner and Tester, 1972), and Gokcen (1979).

EQUATIONS USED

Based upon Pitzer and Kim (1974), the geometric mean-ion activity coefficient of ion-pair $M_{\nu_M}^{z_M} X_{\nu_X}^{z_X}$ (z is charge and ν is stoichiometric number) in a mixture of cations (c) and anions (a) is:

$$\ln\gamma_{MX} = |z_M z_X|\, f^\gamma$$

$$+ \frac{2\nu_M}{\nu} \sum_a m_a \left[B_{Ma} + (\Sigma mz) C_{Ma} + \frac{\nu_X}{\nu_M} \theta_{Xa} \right]$$

$$+ \frac{2\nu_X}{\nu} \sum_c m_c \left[B_{cX} + (\Sigma mz) C_{cX} + \frac{\nu_M}{\nu_X} \theta_{Mc} \right]$$

$$+ \sum_c \sum_a m_c m_a \left[|z_M z_X| \, B'_{ca} + 2 \frac{\nu_M z_M}{\nu} C_{ca} \right] \quad (1)$$

In this equation, γ in f^γ is a superscript label not a power, $\nu = \nu_M + \nu_X$, m represents molality, and $(\Sigma mz) = \Sigma_c m_c z_c = \Sigma_a m_a |z_a|$.

The quantities B, B', and C describe the thermodynamic properties of a pure electrolyte: B and B' represent measurable combinations of second virial coefficients, which arise from binary intersections, while C is related to third virial coefficients. The additional parameter θ introduced for mixtures gives the difference between the second virial coefficient for ions M and N of the same sign and the average second virial coefficient for M—M and N—N interactions. Because second virial coefficients are determined mainly by short range interactions, and ions of like sign, which repel, are seldom close together, θ_{MN} is expected to be small. Pitzer and Kim (1974) find $|\theta_{MN}| < 0.1$. θ has a significant effect, >5%, on $\ln\gamma$ only for systems involving mixing of singly-charged ions which differ greatly in their interaction with water (Cs^+ with H^+ or Li^+; OH^- with Cl^- or Br^-). Pitzer and Kim (1974) include further mixing parameters ψ_{MNX}, arising from differences in third virial coefficients, but these terms are smaller than θ and will be neglected at the present level of approximation. [Although neglect of ψ_{MNX} terms introduces negligible error in mixtures of 1-1 electrolytes (Holmes et al., 1979), it is one of the limiting features in treating unsymmetrical mixtures at high concentrations in the present work (Harvie and Weare, 1980). It is discussed later.]

By examination of recent theoretical developments and empirical testing, Pitzer (1973, 1977) obtained expressions for the ionic strength dependence of f^γ and of B. The ionic strength dependence of $B' = dB/dI$ is fixed by the analytical function for the ionic-strength dependence of B. The ionic strength dependence of the higher-order corrections, C and θ, is neglected as it is not of practical significance.

For the Debye- Hückel term f^γ, statistical mechanics yield an expression of the form (Pitzer, 1973):

$$f^\gamma = -A_\phi \left[\frac{I^{1/2}}{1 + \rho I^{1/2}} + \frac{2}{\rho} \ln (1 + \rho I^{1/2}) \right] \quad (2)$$

where I is the ionic strength,

$$I = \frac{1}{2} \sum_i m_i z_i^2 \quad (3)$$

and ρ is related to the ion-pair hard-core diameter. In order to have an expression which is the same for all ions, $\rho = 1.2$ is taken to be constant (Pitzer, 1973). In the range 0-55°C the Debye-Hückel constant for the osmotic coefficient, $A_\phi = 1/3\ (2\pi N_A d_w/1000)^{1/2} (e^2/DkT)^{3/2}$, is computed from:

$$A_\phi = 0.377_{95} + 4.684 \times 10^{-4}\, t + 3.74 \times 10^{-6}\, t^2 \quad (4)$$

where $t = T$-273.15 is the Celsius temperature. Eq. 4 is Eq. A1 of Pitzer, Roy, and Silvester (1977), adjusted to yield $A_\phi = 0.392$ at 25°C. The latter value was used by Pitzer and Mayorga (1973, 1974) to determine the ion-pair parameters listed in Table 1 and it is necessary to use that same value of A_ϕ when working with those parameters.

The second virial coefficients have an ionic strength dependence (Pitzer, 1973) similar but not identical to that suggested by statistical mechanics:

$$B_{MX} = \beta^{(0)}_{MX} + \frac{2\beta^{(1)}_{MX}}{\alpha_1^2 I} [1 - (1 + \alpha_1 I^{1/2}) e^{-\alpha_1 I^{1/2}}]$$

$$+ \frac{2\beta^{(2)}_{MX}}{\alpha_2^2 I} [1 - (1 + \alpha_2 I^{1/2}) e^{-\alpha_2 I^{1/2}}] \quad (5)$$

TABLE 1. ION-PAIR PARAMETERS FROM LITERATURE BASED UPON EXPERIMENTAL DATA

Ion-Pair	$\beta^{(0)}$	α_1	$\beta^{(1)}$	α_2	$\beta^{(2)}$	C^ϕ	Ref.
H-Cl	0.1775	2.0	0.2945	—	—	0.0008	a
H-ClO_4	0.1747	2.0	0.2931	—	—	0.00819	a
Na-Cl	0.0765	2.0	0.2664	—	—	0.00127	a
Na-ClO_3	0.0249	2.0	0.2455	—	—	0.0004	a
Na-ClO_4	0.0554	2.0	0.2755	—	—	−0.00118	a
Na-HCO_3	0.0277	2.0	0.0411	—	—	—	b
K-Cl	0.0484	2.0	0.2122	—	—	−0.00084	a
K-ClO_3	−0.0960	3.0	0.2481	—	—	—	a
Mg-Cl_2	0.3524	2.0	1.6815	—	—	0.00519	c
Mg-$(ClO_4)_2$	0.4961	2.0	2.0085	—	—	0.00958	c
Ca-Cl_2	0.3159	2.0	1.614	—	—	−0.00034	c
Ca-$(ClO_4)_2$	0.4511	2.0	1.7565	—	—	−0.0050	c
Na_2-CO_3	0.1898	2.0	0.846	—	—	−0.04803	c
Na_2-SO_4	0.0196	2.0	1.113	—	—	0.0057	d
K_2-SO_4	0.0500	2.0	0.7793	—	—	—	c
H-HSO_4	0.2103	2.0	0.4711	—	—	—	e
H-SO_4	0.0027	2.0	—	—	—	0.0416	e
Ca-SO_4	0.2000	1.4	2.65	12.0	−55.7	—	f
Mg-SO_4	0.2210	1.4	3.343	12.0	−37.23	0.0250	f

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a: Pitzer and Mayorga (1973), Table 1.
b: Pitzer and Peiper (1980).
c: Pitzer and Mayorga (1973), Table 5
d: Pitzer and Kim (1974), p. 5705.
e: Pitzer, Roy, and Silvester (1977), Table 1.
f: Pitzer and Mayorga (1974), Table 1.

$$B'_{MX} = \frac{2\beta^{(1)}_{MX}}{\alpha_1^2 I^2} \left[-1 + (1 + \alpha_1 I^{1/2} + \frac{1}{2} \alpha_1^2 I) e^{-\alpha_1 I^{1/2}} \right]$$

$$+ \frac{2\beta^{(2)}}{\alpha_2^2 I^2} \left[-1 + (1 + \alpha_2 I^{1/2} + \frac{1}{2} \alpha_2^2 I) e^{-\alpha_2 I^{1/2}}_{\;1} \right] \quad (6)$$

Also,

$$C_{MX} = \frac{C^\phi_{MX}}{2|z_M z_X|^{1/2}} \quad (7)$$

Silvester and Pitzer (1978) have examined the temperature dependencies of $\beta^{(0)}$, $\beta^{(1)}$, and C^ϕ. These are small; typical values for $d\beta^{(0)}/dT$ being about 10^{-3}. Thus, temperature changes of 25°C or so lead to no significant change in these parameters. (Later sections of this paper illustrate the relative insensitivity of calculated activity coefficients to moderate changes in $\beta^{(0)}$ and $\beta^{(1)}$.)

Eqs. 1-7 allow one to calculate mean-ion activity coefficients of single electrolytes or mixtures. (The computer program is listed by Rosenblatt, 1979). The only temperature-dependent quantity which changes significantly over the range 0-55°C is A_ϕ. To use these equations one needs values for the ion-pair parameters $\beta^{(0)}$, α_1, $\beta^{(1)}$, α_2, $\beta^{(2)}$, and C^ϕ and for the interaction coefficients θ. These parameters have been evaluated from experimental osmotic coefficient or activity coefficient data for a

TABLE 2. INTERACTION COEFFICIENTS FROM LITERATURE

Ion-Pair	θ	Ref.
$\theta(H^+, Na^+)$	0.036	a
$\theta(H^+, K^+)$	0.005	a
$\theta(Na^+, K^+)$	−0.012	a
$\theta(Mg^{2+}, Ca^{2+})$	0.010	a
$\theta(K^+, Ca^{2+})$	−0.040	a
$\theta(Cl^-, HCO_3^-)$	−0.030	b
$\theta(Cl^-, SO_4^{2-})$	0.020	c

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a: Pitzer and Kim (1974), Table 1.
b: Pitzer and Peiper (1980).
c: Downes and Pitzer (1976), Table 4.

TABLE 3. ESTIMATED ION-PAIR PARAMETERS

Ion-Pair	$\beta^{(0)}$	α_1	$\beta^{(1)}$	α_2	$\beta^{(2)}$	C^{ϕ}	Ref.
$Na\text{-}HSO_4$	0.0554	2.0	0.2755	—	—	−0.00118	a
$K\text{-}HCO_3$	−0.0005	2.0	−0.013	—	—	—	b
$K\text{-}ClO_4$	−0.040	2.0	0.08	—	—	—	c
$Mg\text{-}(HCO_3)_2$	0.490	2.0	1.90	—	—	—	c
$Ca\text{-}(HCO_3)_2$	0.440	2.0	1.70	—	—	—	c
$Mg\text{-}(ClO_3)_2$	0.490	2.0	1.804	—	—	—	c
$Ca(ClO_3)_2$	0.438	2.0	1.76	—	—	—	c
$Na\text{-}HSO_3$	0.0249	2.0	0.2455	—	—	0.0004	c
$K\text{-}HSO_3$	−0.096	2.0	0.2481	—	—	—	c
$Mg\text{-}(HSO_3)_2$	0.490	2.0	1.804	—	—	—	c
$Ca\text{-}(HSO_3)_2$	0.438	2.0	1.76	—	—	—	c
$Na_2\text{-}SO_3$	0.021	2.0	1.0	—	—	—	
$K_2\text{-}SO_3$	0.065	2.0	1.0	—	—	—	
$Mg\text{-}SO_3$	0.200	1.4	3.00	12.0	−41.0	—	c
$Ca\text{-}SO_3$	0.180	1.4	2.38	12.0	−61.3	—	c
$K_2\text{-}CO_3$	0.075	2.0	0.66	—	—	—	c
$Mg\text{-}CO_3$	0.180	1.4	2.70	12.0	−46.0	—	c
$Ca\text{-}CO_3$	0.160	1.4	2.10	12.0	−69.0	—	c
$Na_2S_2O_5$	0.07	2.0	0.9	—	—	—	c
$K_2S_2O_5$	0.10	2.0	1.1	—	—	—	c
MgS_2O_5	0.24	1.4	3.7	12.0	−34.0	—	c
CaS_2O_5	0.22	1.4	3.0	12.0	−50.0	—	c

a: Pitzer, Roy, and Silvester (1977), p. 4935. b: Pitzer and Peiper (1980) c: Rosenblatt (1979).

large number of electrolytes by Pitzer and Mayorga (1973, 1974) and Pitzer and Kim (1974). Values for ion pairs of interest in flue-gas desulfurization chemistry appear in Table 1 (ion-pair parameters) and Table 2 (interaction coefficients). Using these empirical parameters, as shown at length by Pitzer (Pitzer and Mayorga, 1973, 1974; Pitzer and Kim, 1974) and others (Khoo et al., 1977a, 1977b; Culberson et al., 1978; Macaskill and Bates, 1978; Macaskill et al., 1978; Holmes et al., 1979; Harvie and Weare, 1980), Eqs 1-7 reproduce experimental data for pure electrolytes and for mixtures usually to within better than 2% and in all cases to ±0-20%.

ESTIMATES OF ION-PAIR PARAMETERS

Estimation of activity coefficients does not require estimation of as many parameters as may be implied by the preceding paragraph. Pitzer and Mayorga (1973, 1974) fit experimental data for 1-1, 1-2, 2-1, 1-3, 3-1, 1-4 and 1-5 electrolytes by taking $\alpha_1 = 2$ and neglecting the terms in α_2 and $\beta^{(2)}$ in Eqs. 5 and 6 (i.e., setting $\beta^{(2)} = 0$). For all 2-2 electrolytes, they take $\alpha_1 = 1.4$ and $\alpha_2 = 12.0$. In addition, the third virial coefficients C^{ϕ} and interaction coefficients θ (and ψ) are small and can be neglected under most conditions with little error (<10% error in γ). These points are illustrated in Tables 1 and 2 and have been documented by Pitzer (1973; Pitzer and Mayorga, 1973, 1974; Pitzer and Kim, 1974) and others (Macaskill and Bates, 1978; Macaskill et al., 1978).

Two parameters remain to be estimated: $\beta^{(0)}$ and $\beta^{(1)}$. (For 2-2 electrolytes one must also estimate $\beta^{(2)}$.) These depend upon short-range interactions, $\beta^{(1)}$ being determined primarily by interactions between ions of unlike charge, while $\beta^{(0)}$ also includes contributions from interactions between ions of like charge (Pitzer, 1973; Pitzer and Mayorga, 1973; Gupta, 1979). Because $\beta^{(0)}$ and $\beta^{(1)}$ are determined by the same general properties of the ions and solvent they follow generally parallel trends. Also, $\beta^{(1)}$ is relatively much larger (by roughly a factor of 4) for 2-1 electrolytes than for 1-1 electrolytes (Pitzer, 1973). Pitzer and Mayorga (1973) plot $\beta^{(0)}$ vs. $\beta^{(1)}$ for different types of electrolytes and these plots may be used to approximate $\beta^{(1)}$ from $\beta^{(0)}$ (or vice versa). The values of $\beta^{(2)}$ (Pitzer and Mayorga, 1974) describe additional attractive interactions unique to bi-bivalent and more highly charged electrolytes at concentrations below 0.1 $\underline{M}$; the more negative is $\beta^{(2)}$, the greater is the additional association. The term in $\beta^{(2)}$ has only a small, constant effect on $\ln\gamma_{\pm}$ at concentrations above 0.1 $\underline{M}$.

Thus, the problem of estimating activity coefficients essentially reduces to one of estimating $\beta^{(0)}$. Furthermore, apparently because the ionic strength dependence of $\ln\gamma$ is inherent in the form of Eqs. 1-7, $\beta^{(0)}$ does not have to be estimated extremely accurately to yield useful estimates of activity coefficients. Calculations made during the course of this work indicate that changing $\beta^{(0)}$ and $\beta^{(1)}$ by 20% changes γ by 10-20%, not that much different from the worst-case deviations between theory and experiment in complex mixtures when all parameters are based on experiment (Culberson et al., 1978).

Values of $\beta^{(0)}$ and $\beta^{(1)}$ for a given ion-pair correlate (Pitzer and Mayorga, 1973) with the effect of the ions on the structure of liquid water, in the sense discussed extensively by Frank (1965 and other papers). The more dissimilar the ions are in this respect, the greater the values of $\beta^{(0)}$ and $\beta^{(1)}$. The most "structure-making" cations are small and multiply charged, $Mg^{2+} > Ca^{2+} > H^+ > Na^+ > K^+$, the latter being intermediate in character. The most "structure-breaking" anions are large and only singly charged: the sequence goes approximately from $OH^- < F^- < SO_4^{2-} < Cl^- < Br^- < I^- < ClO_4^-$ with perchlorate being an extreme "structure-breaker." These trends are the basis of the estimated parameters in Table 3. The $\beta^{(0)}$ values were estimated by interpolation and extrapolation of experimentally-based $\beta^{(0)}$ values for similar ion-pairs, i.e., ion-pairs close in the water structure-making sequence. The $\beta^{(1)}$ (and $\beta^{(2)}$) values were obtained by a combination of the comparison used to obtain $\beta^{(0)}$ and the overall $\beta^{(0)}$:$\beta^{(1)}$ trends plotted by Pitzer and Mayorga (1973). A detailed description of the individual estimates appears elsewhere (Rosenblatt, 1979). Two examples may suffice to describe the approach.

The value of $\beta^{(0)}$ for $K\text{-}ClO_4$ is taken to be intermediate between that of $K\text{-}ClO_3$ and $K\text{-}I$ to the same degree that $\beta^{(0)}$ for $Na\text{-}ClO_4$ is intermediate between that for $Na\text{-}ClO_3$ and $Na\text{-}I$. Both Na^+ and K^+ are intermediate "structure-makers" while ClO_3^-, ClO_4^-, and I^- are "structure-breakers."

Sulfite ion, SO_3^{2-}, parameters are based upon sulfate values and upon trends in the "structure-breaking" sequence $OH^- < F^- < SO_4^{2-} < Cl^- < Br^-$. One might expect SO_3^{2-} to be slightly less of a "structure-breaker" than SO_4^{2-} since it is smaller. For $Na_2\text{-}SO_3$, $\beta^{(0)}$ is taken to be 5% larger than for $Na_2\text{-}SO_4$ because the minimum in $\beta^{(0)}$ in the sequence OH^-, F^-, Cl^-, Br^- occurs with F^- and because $\beta^{(0)}$ for Na-F is only 10% above $\beta^{(0)}$ for $Na_2\text{-}SO_4$. For $K_2\text{-}SO_3$, $\beta^{(0)}$ is taken to be above $\beta^{(0)}$ for $K_2\text{-}SO_4$ by one-half the fractional amount $\beta^{(0)}$ for K-F is above K-Cl. Values

TABLE 4. EFFECT OF CHANGING ESTIMATED PARAMETERS COMPARED TO EFFECT OF TEMPERATURE

Concentrations (molality):	$[Mg^{2+}] = 0.304$	$[Cl^-] = 0.1988$
	$[Ca^{2+}] = 0.014$	$[CO_3^{2-}] = 0.0026$
		$[SO_4^{2-}] = 0.184$
Ionic Strength:	$I = 1.173$	$[SO_3^{2-}] = 0.032$

Estimated Parameters:

Ion-Pair	$\beta^{(0)}$	α_1	$\beta^{(1)}$	α_2	$\beta^{(2)}$	Estimate
Mg-SO_3	0.20	1.4	3.00	12.0	−41.0	*M*
Mg-SO_3	0.24	1.4	3.60	12.0	−33.0	*MA*
Ca-SO_3	0.18	1.4	2.38	12.0	−61.3	*C*
Ca-SO_3	0.18	1.4	2.38	12.0	−40.0	*CA*

Activity Coefficients Calculated with Different Parameters:

Temperature: Parameters:	25° *M,C*	25° *MA,C*	25° *M,CA*	25° *MA,CA*	50°C *M,C*
$\gamma_\pm$ ($CaSO_4$)	0.0918	0.0912	0.0925	0.0919	0.0799
$\gamma_\pm$ ($MgSO_3$)	0.0975	0.1096	0.0978	0.1100	0.0848
$\gamma_\pm$ ($CaSO_3$)	0.0865	0.0961	0.0874	0.0972	0.0752

of $\beta^{(1)}$ are estimated from $\beta^{(0)}$ by a compromise between the approximate general correlation of $\beta^{(0)}$ and $\beta^{(1)}$ (Pitzer and Mayorga, 1973, Figure 4) and $\beta^{(0)}$:$\beta^{(1)}$ in the corresponding sulfates. For Mg-SO_3 and Ca-SO_3, $\beta^{(0)}$, $\beta^{(1)}$, and $\beta^{(2)}$ are taken to be 10% below (for $\beta^{(2)}$, this is 10% more negative) the values for the corresponding sulfates.

SOME CALCULATED RESULTS AND DISCUSSION

In this section, we first examine the sensitivity of the calculated activity coefficients to changes in temperature and in the estimated parameters. We then compare some results with a widely used computer code for Ca^{2+} and SO_4^{2-} activities in flue gas desulfurization analyses. Finally, we illustrate the behavior (in neutral solution) of various ion-pair activity coefficients as NaCl is added to a hypothetical scrubber solution.

Table 4 shows the effect on calculated activity coefficients of changes in the estimated ion-pair parameters. It also illustrates the effect of a change in temperature. The initial concentrations (molality units) are typical of CaO/$CaCO_3$ coal scrubbers and correspond to these in 1977 pilot-plant test run No. 5 of the Environmental Protection Agency Industrial Environmental Research Laboratory (Borgwardt, 1978). This run was one of the runs at highest total ionic strength in the test sequence.

The second part of Table 4 shows the Mg-SO_3 and Ca-SO_3 ion-pair parameters which are in Table 3 (*M* and *C*, respectively), and also, alternative estimates (*MA* and *CA*) for these ion-pairs. The alternative Mg-SO_3 parameters have been uniformly increased by 20% over those of the base estimates. This corresponds to assuming that SO_3^{2-} is more, rather than less, of a structure-breaker than is SO_4^{2-}, and to estimating the $MgSO_3$ parameters as 10% higher than those of Mg-SO_4, rather than 10% lower. This change probably is an upper limit to the potential errors in the Mg-SO_3 parameters and is about the same as the change in those parameters which would be caused by a 25°C change in temperature. The alternative Ca-SO_3 parameters correspond to taking a "typical" value of −40 for $\beta^{(2)}$, rather than an "extreme" value of −61.3. In contrast to the base estimates and to available experimental evidence (Lowell et al., 1970), the alternative estimates of $\beta^{(2)}$ for Ca-SO_3 and Mg-SO_3 correspond to assuming that these metal-sulfites are less associated (ion-paired) then the corresponding metal-sulfates. The only other ion pair parameters which have been estimated (as opposed to being based upon experiment) for the solution shown in Table 4 are those for Mg-CO_3 and Ca-CO_3, and these are relatively unimportant because of the low concentration of carbonate ion.

The third part of Table 4 compares mean-ion activity coefficients for Ca-SO_4, Mg-SO_3, and Ca-SO_3 calculated using the base estimates and combinations of base and alternative estimates. At most, $\gamma_\pm$ of Mg-SO_3 and of $CaSO_3$ change by 12-13%. The effect of the parameter changes on $\gamma_\pm$ of Ca-SO_4 is below 1%, and is insignificant. The last column shows that raising the temperature from 25 to 50°C lowers $\gamma_\pm$ by 13%.

The data in Table 4 lend credence to two requirements of the present estimates. (1) The calculated activity coefficients are relatively insensitive to the estimated parameters used. This is particularly true for changes in the parameters of ion-pairs which do not share a common ion with the pair whose activity coefficient is being calculated. Thus, it appears that $\gamma_\pm$ ($CaSO_4$) can be calculated about as accurately (5-18%) in a mixture containing ions for which experimental ion-pair data are not available as in a mixture where the parameters in Eqs. 1-7 are all based upon experimental data (Culberson et al., 1978). (2) Changes in $\gamma_\pm$ arising from changes in the estimated parameters and from the temperature coefficients of the parameters are small compared to changes due to the temperature dependence of A_ϕ. Thus, over moderate temperature ranges, the temperature dependence of $\gamma_\pm$ is represented adequately without considering the temperature dependencies of $\beta^{(0)}$ and $\beta^{(1)}$.

Sensitivity calculations of the type illustrated in Table 4 suggest that the overall accuracy of the present estimates of $\gamma_\pm$ is better than ±25%. The accuracy of the estimated parameters appears comparable to the level of the theory in Eqs. 1-7. Calculations of higher accuracy than the present estimates require not only more accurate ion-pair parameters but also that one include theoretical terms neglected in the present calculations. This is illustrated by the recent work of Harvie and Weare (1980) who achieve high accuracy with Pitzer's theory. To match experimental solubility data in complex mixtures they found it important to include third virial coefficients *C* and mixing parameters ψ, as well as additional electrostatic mixing terms (Pitzer, 1975) which arise upon mixing ions of the same sign but different charge. Inclusion of these last terms may explain the increased accuracy achieved by Harvie and Weare (1980) over that of Culberson, Latham, and Bates (1978). In addition, one must include the temperature dependencies of the various parameters to achieve significantly greater accuracy at 50°C than the present estimates.

Table 5 compares activities of Ca^{2+} and SO_4^{2-} calculated using Pitzer's equations with those calculated in the Bechtel Modified Radian Equilibrium Program (Lowell et al., 1970; Epstein, 1975), a widely used computer code for modelling of flue gas desulfurization units. In that program (Lowell et al., 1970), specific interactions between oppositely charged ions are treated as formation of ion pairs, described by a chemical equilibrium constant, and the activity coefficients of the remaining "free" ions are described by classical, extended Debye-Hückel theory:

$$\ln \gamma_i' = 3A_\phi z_i^2\{-I'^{1/2}/\ [1 + 50.29(DT)^{-1/2}\, a_i I'^{1/2}] + B_i I'\} \qquad (8)$$

where the ionic strength I' is a sum over "free" ion molalities

TABLE 5. COMPARISON OF ACTIVITIES CALCULATED BY PRESENT PROGRAM AND RADIAN PROGRAM FOR COAL-SCRUBBER PILOT-PLANT-TEST SOLUTIONS AT 50°C

Run No.	$[Ca^{2+}]$	$[SO_4^{2-}]$	Ionic Strength	$a_2^{(Radian)}$	$a_2^{(This\ Work)}$
1	0.025	0.076	0.610	2.08×10^{-5}	2.37×10^{-5}
2	0.032	0.023	0.265	1.66×10^{-5}	2.29×10^{-5}
5	0.014	0.184	1.173	1.50×10^{-5}	1.65×10^{-5} (1.62, 1.67, 1.65)
9	0.0032	0.070	0.495	2.08×10^{-6}	3.44×10^{-6}
17	0.086	0.0094	0.327	1.53×10^{-5}	$1.93\times^{-5}$
19	0.073	0.0016	0.228	3.10×10^{-6}	3.79×10^{-6}

$a_2 = a_{Ca^{2+}} \cdot a_{SO_4^{2-}}$

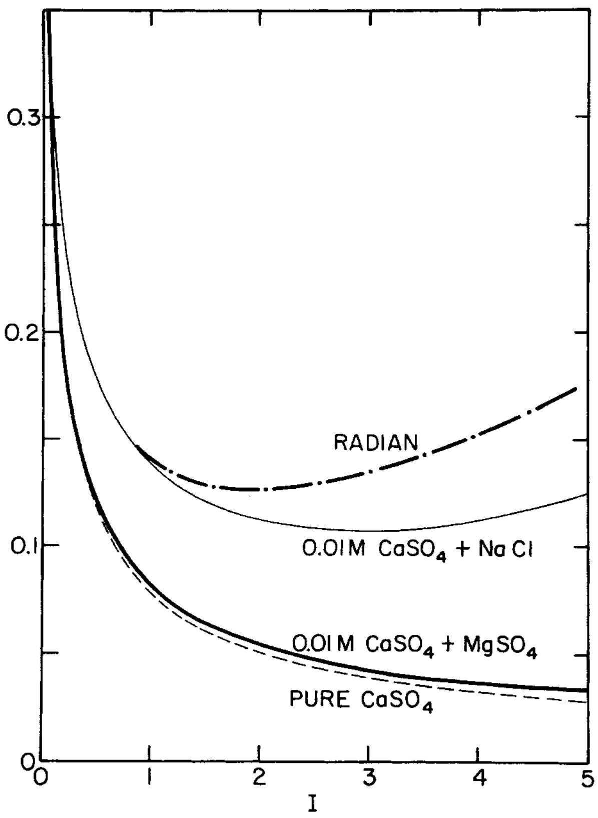

Figure 1. Mean ion activity coefficient of $CaSO_4$ at 50°C as a function of ionic strength. The lower three curves are computed using Pitzer's equation and parameters. The upper curve corresponds to $[\gamma(Ca^{2+}) \cdot \gamma(SO_4^{2-})]^{1/2}$ from the Bechtel modified Radian equilibrium computer program (Epstein, 1975).

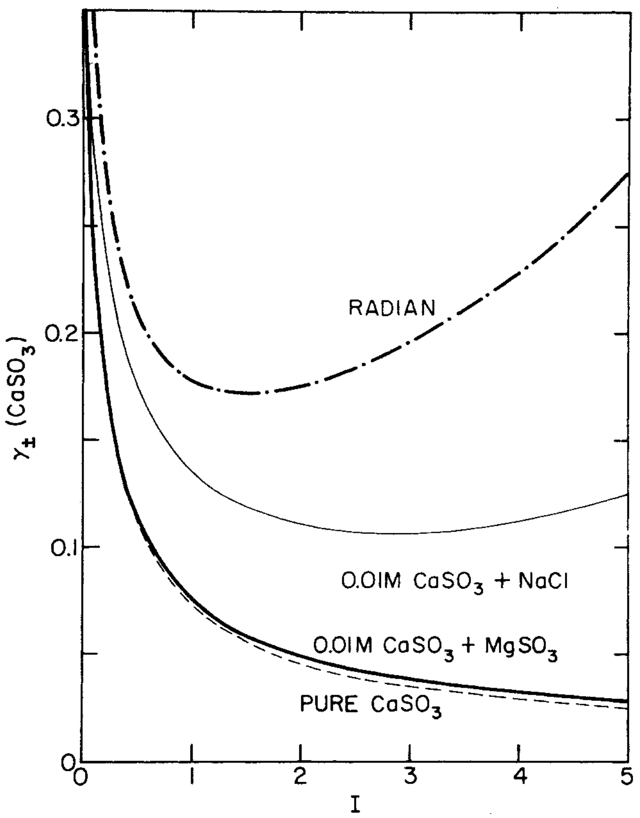

Figure 2. Mean ion activity coefficient of $CaSO_3$ at 50°C as a function of ionic strength. The lower three curves are computed using Pitzer's equations and parameters estimated in this paper. The upper curve is $[\gamma(Ca^{2+}) \cdot \gamma(SO_3^{2-})]^{1/2}$ from the Bechtel modified Radian equilibrium computer program (Epstein, 1975).

(reiteration is necessary to calculate I'). In the Bechtel-Radian program the ion coefficients (a_i, B_i) have the values Ca^{2+} (4.5, 0.1), SO_4^{2-} (3.0, 0), and SO_3^{2-} (4.5, 0). Since the code calculates individual ion quantities, it is not appropriate to compare calculated activities of Ca^{2+} and SO_4^{2-} directly with the present calculations, but the product $a_2 = a_{Ca^{2+}} a_{SO_4^{2-}}$ can be compared. The different run numbers in Table 5 correspond to various pilot-plant test runs made at the Environmental Protection Agency Laboratory in North Carolina in 1977 (Borgwardt, 1978). The ions present were Mg^{2+}, Ca^{2+}, Cl^-, CO_3^{2-}, SO_4^{2-}, and SO_3^{2-}. The runs chosen for comparison represent various extreme conditions, that is, runs with a relatively high or low concentration of one of the ions. Ion concentrations for run No. 5, which has high concentrations of Mg^{2+} and SO_4^{2-}, are shown at the top of Table 4. The present values for a_2 in all runs are about 25% higher than those from the Radian program, and just as important, show rather different behavior with changes in ionic strength and mixture compositions. The numbers in parentheses under the present results for run No. 5 correspond to the different pairs of estimates (*MA-C*, *M-CA*, *MA-CA*) shown in Table 4.

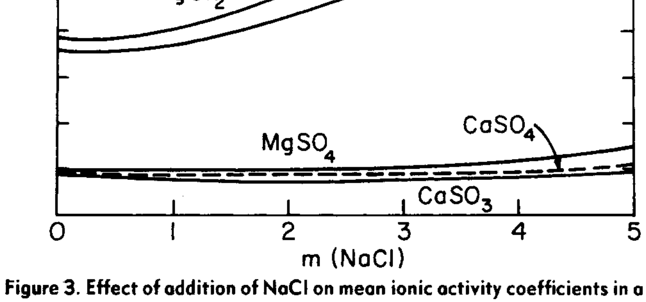

Figure 3. Effect of addition of NaCl on mean ionic activity coefficients in a hypothetical, nearly saturated, sulfite-sulfate solution at 50°C. Ion concentrations: Mg^{2+}, 0.2; Ca^{2+}, 0.02; K^+, 0.01; SO_4^{2-}, 0.17; SO_3^{2-}, 0.04; HSO_3^-, 0.02; HCO_3^-, 0.01 *M*. Initial ionic strength: 0.88 $\underline{M}$. The upper (dash-dot) line shows the activity of the solvent.

The reasons for the differences between the present computations and those using the Radian program when the mixture composition varies probably go back to the underlying theoretical foundations of the two approaches. Either association-equilibrium or virial expansion models can describe adequately moderately dilute solutions ($I < 0.2$) of pure electrolytes, e.g., 2-2, which associate strongly. However, association-equilibrium models and classical Debye-Hückel formulations have well-recognized deficiencies in mixtures and at higher concentrations. Ion activity coefficients calculated from Eq. 8 are independent of solution composition, depending solely upon ionic strength; activities depend upon solution composition by involving specific attractive interactions for oppositely charged ions. Along with the general limitations of extended Debye-Hückel activity coefficients at high concentrations, the approach neglects specific interactions between like-charged ions, which are known to be important even at quite low concentrations (Friedman, 1960; Wood and Smith, 1965).

A consequent difficulty in applying association-equilibrium models to general mixtures is that, while there are parameters additional to the Debye-Hückel ones which can be adjusted to fit a given salt mixture, accurate representation of different salt mixtures may require different values for what should be the same physical parameters (Yeatts and Marshall, 1972). Association-equilibrium models also have ambiguities concerning the ionic strength. In contrast, Pitzer's virial expansion sums over pairwise (and triple) interactions, attractive and repulsive, for *all* ions present, in a manner that allows coverage up to high concentration of the entire range between weakly interacting and quite strongly associated ion-pairs (Pitzer and Mayorga, 1974; Pitzer and Silvester, 1976; Pitzer et al., 1977).

Figure 1 shows the variation of $\gamma_\pm$ for 0.01 M Ca-SO_4 at 50°C as the ionic strength is increased: (a) by adding $MgSO_4$ and (b) by adding NaCl. Addition of $MgSO_4$ causes $\gamma_\pm(CaSO_4)$ to decrease markedly, following essentially the same curve as the hypothetical addition of $CaSO_4$ beyond the saturation limit. The decrease in $\gamma_\pm$ with addition of $MgSO_4$ is sufficiently rapid that the product $a_2 = \gamma_\pm^2 \cdot m_{Ca}{}^{2+} \cdot m_{SO_4}{}^{2-}$ remains almost constant, and below the solubility product limit (Culberson, et al., 1978) of $CaSO_4$ over the entire range of ionic strength from I = 0.1 to I = 5 $\underline{M}$. Addition of NaCl lowers the activity coefficient of CaSO, considerably less than does addition of $MgSO_4$ and has only a small effect at ionic strengths above 1.5 $\underline{M}$. The computations for Figure 1 are based upon experimentally derived 25°C ion-pair and interaction coefficients taken from the literature (cf. Tables 1 and 2). From the extensive prior work (Pitzer and Mayorga, 1973, 1974; Pitzer and Kim, 1974; Downes and Pitzer, 1976; Pitzer et al., 1977; Khoo et al., 1977a, b; Macaskill et al., 1978; Macaskill and Bates, 1978; Culberson et al., 1978; Holmes et al., 1979; Harvie and Weare, 1980) validating the theory and parameters, these curves should be at least within 20% of experiment.

The curve labelled Radian in Figure 1 corresponds to $\gamma_\pm = (\gamma_{Ca}{}^{2+} \cdot \gamma_{SO_4^{2-}})^{1/2}$ where $\gamma_{Ca}{}^{2+}$ and $\gamma_{SO_4^{2-}}$ are calculated from Eq. 8 and the Radian parameters. Because the ionic strength and activity of Ca-SO_4 in the Radian approach are modified by ion-pairing that curve is not exactly comparable to any of the others. However, it is approximately comparable to the added NaCl curve because the Radian program invokes no Cl^- ion-pairs and only a very weak Na-SO_4^- association. There are no differences between the added NaCl curve and the Eq. 8 values below I = 1 $\underline{M}$, but the Eq. 8 values become significantly higher than the Pitzer values at high ionic strength.

Figure 2 shows similar curves for $CaSO_3$ based upon parameters estimated in this paper. The activity coefficients estimated for $CaSO_3$ are up to 20% below those for $CaSO_4$ at equal concentrations but the pattern of Figures 1 and 2 is very similar. Again, the decrease in $\gamma_\pm(CaSO_3)$ upon adding $MgSO_3$ is sufficiently large that the activity of $CaSO_3$ is calculated to remain below the solubility product limit of $CaSO_3$ as $MgSO_3$ is added. Making an approximate comparison of the added-NaCl curve with $\gamma_\pm$ from Eq. 8, the Radian values are about a factor of two larger than the present estimates at ionic strengths above 1$\underline{M}$. This factor considerably exceeds the anticipated uncertainty of the present estimates and arises because, in contrast to the present computations, $\gamma(SO_3^{2-})$ in the Radian program is *larger* than $\gamma(SO_4^{2-})$ by about a factor of two.

Figures 1 and 2 show that there are marked differences in $\gamma_\pm$ for $CaSO_3$ and $CaSO_4$ when the ionic strength of the solution is raised by adding NaCl and when it is raised by adding $MgSO_3$ or $MgSO_4$. Figure 3 illustrates the changes in $\gamma_\pm$ which occur, for a complex solution already at quite high ionic strength, as the ionic strength is increased by adding a salt such as NaCl to the solution. The concentrations are such that $m(CaSO_4)$ is very near saturation. For the 2-2 electrolytes $CaSO_4$, $MgSO_4$, $CaSO_3$ and $MgSO_3$ there is little change, a slight drop followed by a slow rise. The values are quite small, about 0.1 After dropping slightly the activity coefficient of NaCl rises as NaCl is added. The activity coefficients of $CaCl_2$ and $MgCl_2$ rise quite sharply as Cl^- is added, going from values below 0.4 to values near 1.

The present paper has been concerned solely with neutral solutions of strong electrolytes. Weak acid interactions can probably be added adequately at the present level of approximation by treating the ion-pair interactions solely by an ionization equilibrium constant.

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NOTATION

A_ϕ = Debye-Hückel constant for osmotic coefficient = 0.392 (kg/mol)$^{1/2}$ at 25°C
a = ion hard-core diameter
a_2 = activity of ion-pair M-X
B = second virial coefficient
B' = $\partial B/\partial I$
C = third virial coefficient
D = dielectric constant of water
d_w = density of water
e = charge on electron
f^γ = Debye-Hückel term given by Eq. 2
I = ionic strength
k = Boltzmann constant
ln = natural logarithm
M = cation of interest
m = molality, i.e., mol/(kg of water)
N_A = Avogadro's number
T = absolute temperature, Kelvin
t = temperature, °C
X = anion of interest
z = ion charge
α_1, α_2 = parameters in Eqs. 5 and 6
$\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$ = parameters in Eqs. 5 and 6
γ = activity coefficient
ρ = size parameter in Eq. 2
θ = pairwise interaction deviation parameter for ions of same sign
ψ = three-body interaction deviation parameter
ν = stoichiometric number of ions in neutral ion-pair

Subscripts

a = any anion
c = any cation

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Diffusivity and Solubility of Carbondioxide in Diluted Polymer Solutions

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Diffusion coefficients of CO_2 in aqueous Newtonian solutions of polyvinyl alcohol and polyethylene glycol with molecular weights varying from 1500 to 100,000 were obtained from absorption rate measurements in a wetted-wall column and the CO_2 solubilities determined independently. The exponent A of the diffusivity-viscosity relation is found to be a strong function of the molecular weight of the applied polymer. The data suggest the following correlation:

$$(D/D_o) = (\mu/\mu_o)^{-3.7\sqrt{M_n/M_P}}$$

which indicates that the exponent may vary from 0.04 to 0.4 for the solutions studied.

SCOPE

Correlations which permit estimation of diffusion coefficients are of considerable importance in all calculations concerning interphase mass transfer phenomena. Special attention deserve such correlations which relate D with easily available or measurable physico-chemical quantities as for instance the viscosity. Hayduk and Cheng (1971) critically reviewed the diffusivity-viscosity relation:

$$D\mu^A = K_1 \qquad (1)$$

and concluded that the value of A depends on the diffusing substance only, but not on temperature, solvent molecular weight or molar volume. For large solute molecules diffusing in small solvent molecules the Stokes-Einstein relation with $A = 1$ results. For the other limiting case of small solute molecules in a solvent of large molecules Hiss and Cussler (1973) found an exponent of 2/3. However, experimental data show that A may vary from 0.5 to values above 1.

If a solute gas molecule diffuses in a diluted solution of a macro-molecule the situation is still more complicated. Experimental results (Astarita, 1965; Zandi and Turner, 1970; Wasan et al., 1972; Perez and Sandall, 1973; Mashelkar and Soylu, 1974) clearly indicate that diffusivities of small

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