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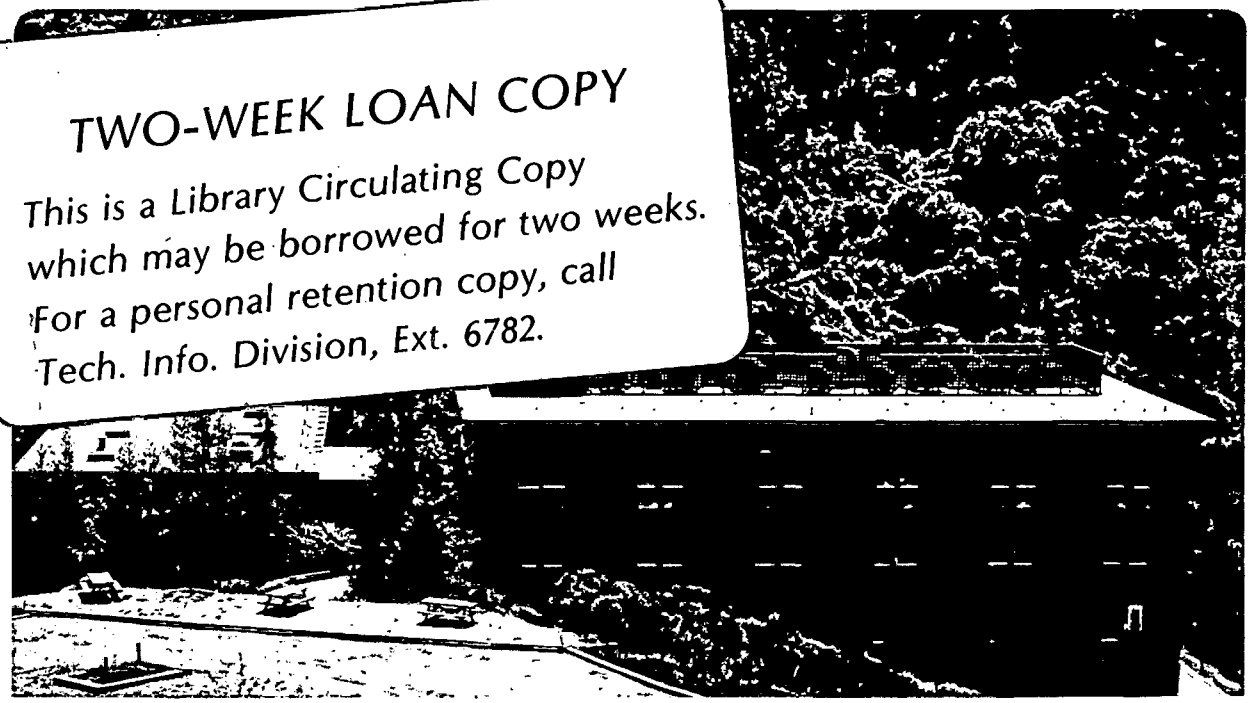
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Estimation of Activity Coefficients in
Concentrated Sulfite-Sulfate Solutions

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Abstract

The extended Debye-Hückel theory of Pitzer and coworkers is used to estimate geometric mean-ion activity coefficients in complex electrolyte solutions at 25-55°C. By using Pitzer's equations with ion-pair parameters estimated in this paper one can calculate activity coefficients up to high ionic strengths in aqueous mixtures containing any combination of the following ions: 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 $\text{S}_2\text{O}_5^{2-}$. 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.

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1. *Introduction*

One of the major elements of the 1977 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 report describes the first part of an effort to describe the thermodynamic properties of the chemicals present during operation of CaO/CaCO_3 scrubbers.

This first part 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^{--} , $\text{S}_2\text{O}_5^{--}$) 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 a relatively straightforward matter 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.

2. *Requirements for activity coefficient estimations*

If one is to estimate activity coefficients in multicomponent, aqueous electrolyte solutions at the concentrations and ionic strengths encountered in technology, one needs:

(1) A formulation which represents the activity coefficients of simple pure electrolytes adequately up to molalities m of 1-5 M . This means that, considering a virial expansion for a 1-1 electrolyte,

$$\ln \gamma_{MX} = f^Y + m B_{MX}^Y + m^2 C_{MX}^Y \quad (1)$$

(a) the series must converge and (b) the ionic strength dependence of the parameters f^Y , B_{MX}^Y and C_{MX}^Y must be known.

(2) The formulation should be one which can be readily extended to mixtures of different types (*i.e.*, 1-1, 2-1, 1-2, 2-2, 3-1, *etc.*) of electrolytes. This means that: (a) the equations for mixtures should contain few (preferably no) parameters additional to those for the individual positive-negative ion pairs which make up the solution. If additional parameters are introduced for mixtures they should be small corrections, not major contributors. In addition, (b) the leading term f^Y in Eq. (1) should be the same for all ion pairs at a given ionic strength and thus should be represented as a single analytical function of ionic strength. This function, of course, should reduce to the correct Debye-Hückel behavior in very dilute solution. Similarly, (c) the ionic strength dependence of the virial coefficients B_{MX}^Y and C_{MX}^Y should be expressed in one, relatively simple analytical form -- in order to facilitate computations, minimize the number of empirical parameters, and allow estimation of unmeasured parameters.

(3) Finally, to treat complex chemical mixtures, one needs a basis for estimation of those ion-pair parameters which have not been

measured. (a) One hopes that any estimates which must be made will have both a physical and an empirical basis. (b) It is highly desirable that the theoretical formulation be one such that the final calculated activity coefficients are relatively insensitive to the potential errors in the estimated quantities.

The above are formidable requirements which have posed a challenge to physical chemistry and molecular theory during the half century which has elapsed since 1923 when Debye and Hückel [1] provided proper limits for the behavior of electrolyte solutions at very low concentrations. In the present work, we make use of a formulation developed during the past few years by Pitzer and coworkers [2-4] 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.

3. *Summary of Pitzer formulation.*

We now briefly review the salient features of Pitzer's theory in order to clarify the basis of the approximations and estimations made in the present work. The treatment starts from a generalized virial expansion for the total excess Gibbs energy of a solution containing n_w kilograms of solvent (water) and n_i, n_j, \dots moles of solute ion i, j, \dots

$$\frac{G^{xs}}{RT} = n_w f + \frac{1}{n_w} \sum_{ij} \lambda_{ij} n_i n_j + \frac{1}{n_w^2} \sum_{ijk} \mu_{ijk} n_i n_j n_k \quad (2)$$

The activity coefficient γ_i of ion i is given by

$$\begin{aligned} \ln \gamma_i &= \frac{1}{RT} \frac{\partial G^{xs}}{\partial n_i} \\ &= \frac{z_i^2}{2} f' + 2 \sum_j m_j \lambda_{ij} + \sum_{jk} m_j m_k \left(\frac{z_i^2}{2} \lambda'_{jk} + 3\mu_{ijk} \right) \end{aligned} \quad (3)$$

where $f' = \partial f / \partial I$, $\lambda'_{ij} = \partial \lambda_{ij} / \partial I$, and $m_i = n_i / n_w$. The geometric mean ion activity coefficient of ion-pair $M_{\nu_M}^{z_M} X_{\nu_X}^{z_X}$ is

$$\ln \gamma_{MX} = \frac{\nu_M}{\nu} \ln \gamma_M + \frac{\nu_X}{\nu} \ln \gamma_X \quad (4)$$

where $\nu = \nu_M + \nu_X$.

The virial coefficients λ_{ij} and λ_{ijk} which appear in eqs. (2) and (3) are not measurable individually but only in certain combinations. Thus, practical expressions for the activity coefficients of pure electrolytes are written in terms of:

$$B_{MX} = \lambda_{MX} + \left| \frac{z_X}{2z_M} \right| \lambda_{MM} + \left| \frac{z_M}{2z_X} \right| \lambda_{XX} \quad (5)$$

$$B'_{MX} = \lambda'_{MX} + \left| \frac{z_X}{2z_M} \right| \lambda'_{MM} + \left| \frac{z_M}{2z_X} \right| \lambda'_{XX} \quad (6)$$

$$C_{MX} = \frac{z}{2 |z_M z_X|^{3/2}} \left[\left| \frac{z_X}{z_M} \right|^{1/2} \mu_{MMX} + \left| \frac{z_M}{z_X} \right|^{1/2} \mu_{MXX} \right] \quad (7)$$

For mixtures, Pitzer and Kim [4] introduce the additional parameter

$$\Theta_{MN} = \lambda_{MN} - \left| \frac{z_N}{2z_M} \right| \lambda_{MM} - \left| \frac{z_M}{2z_N} \right| \lambda_{NN} \quad (8)$$

which gives the deviation in the second virial coefficient λ_{MN} for ions M and N of the same sign from the average for M-M and N-N interactions. Because λ_{MM} is small compared to λ_{ML} , (λ is determined mainly by short range interactions and ions of like sign, which repel, are seldom close together), one expects Θ_{MN} to be small. Pitzer and Kim [4] find this to be true with $|\Theta_{MN}| < 0.1$ and only having a significant effect, >5%, on $\ln \gamma$ 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 [4] also introduce parameters Θ'_{MN} and ψ_{MNX} , the latter being the difference between μ_{MNX} and the average of μ_{MMX} and μ_{NNX} , but these terms are even smaller than Θ and are not significant at the level of approximation appropriate to the estimates presented here [5].

The expression for the mean ion activity coefficient of ion-pair M-X in a mixture of cations (c) and anions (a) becomes [4]:

$$\begin{aligned} \ln \gamma_{MX} &= |z_M z_X| f^Y \\ &+ \frac{2v_M}{v} \sum_a m_a \left[B_{Ma} + (\sum m_z) C_{Ma} + \frac{v_X}{v_M} \Theta_{Xa} \right] \\ &+ \frac{2v_X}{v} \sum_c m_c \left[B_{cX} + (\sum m_z) C_{cX} + \frac{v_M}{v_X} \Theta_{Mc} \right] \\ &+ \sum_c \sum_a m_c m_a \left[|z_M z_X| B'_{ca} + 2 \frac{v_M z_M}{v} C_{ca} \right] \end{aligned} \quad (9)$$

where $(\sum mz) = \sum_c m_c z_c = \sum_a m_a |z_a|$ and $f^Y = \frac{1}{2} f'$. Note that Eq. (9) reduces to Eq. (1) for a single 1-1 electrolyte when one makes the substitutions $B^Y = 2B + IB'$ and $C^Y = 3|z_M z_X|^{\frac{1}{2}} C$.

By a combination of examination of recent theoretical developments and empirical testing, Pitzer [2] has arrived at relatively simple expressions for the ionic strength dependence of f^Y and of B . The ionic strength dependence of $B' = dB/dI$ is determined by that of B . The ionic strength dependence of the higher-order corrections, C and Θ , is neglected as it is not of practical significance.

The Debye-Hückel term f^Y is chosen so that it depends only upon ionic strength. It represents the long-range effects of coulomb forces and also, in rigorous developments, includes a "hard core" repulsion [2] which depends upon ion size. However, as noted above, for practical computations one wants a formulation which is the same for all ions so one is reduced to an approximate expression. Statistical mechanics yield an expression of the form [3]:

$$f^Y = - A_\phi \left[\frac{I^{\frac{1}{2}}}{1+\rho I^{\frac{1}{2}}} + \frac{2}{\rho} \ln (1+\rho I^{\frac{1}{2}}) \right] \quad (10)$$

where I is the ionic strength

$$I = \frac{1}{2} \sum_i m_i z_i^2 \quad (11)$$

and ρ is related to the hard-core diameter a [$\rho = 6 A_\phi (DkT/e^2)a$]: empirically, it has been determined [3] that a suitable choice is $\rho = 1.2$. A_ϕ is the Debye-Hückel constant for the osmotic coefficient,

$\frac{1}{3} (2\pi N_A d_w/1000)^{1/2} (e^2/DkT)^{3/2}$. At temperatures in the range 0-55°C, A_ϕ is computed from the relation:

$$A_\phi = 0.377_{95} + 4.684 \times 10^{-4} t + 3.74 \times 10^{-6} t^2 \quad (12)$$

where $t = T-273.15$ is the Celsius temperature. This equation is that which appears as Eq. (A1) in ref. [6], adjusted to yield $A_\phi = 0.392$ at 25°C. The latter value was used to determine the ion-pair parameters listed in Table 1 and described below [7,8] and it is necessary to use that same value of A_ϕ when working with those parameters.

The second virial coefficients depend upon short-range pairwise interactions. For these, Pitzer, partly on empirical grounds [3], chooses a form similar but not identical to that suggested by statistical mechanics:

$$B_{MX} = \beta_{MX}^{(0)} + \frac{2\beta_{MX}^{(1)}}{\alpha_1^2 I} \left[1 - (1+\alpha_1 I^{1/2}) e^{-\alpha_1 I^{1/2}} \right] + \frac{2\beta_{MX}^{(2)}}{\alpha_2^2 I} \left[1 - (1+\alpha_2 I^{1/2}) e^{-\alpha_2 I^{1/2}} \right] \quad (13)$$

$$B'_{MX} = \frac{2\beta_{MX}^{(1)}}{\alpha_1^2 I^2} \left[-1 + (1+\alpha_1 I^{1/2} + \frac{1}{2} \alpha_1^2 I) e^{-\alpha_1 I^{1/2}} \right] + \frac{2\beta_{MX}^{(2)}}{\alpha_2^2 I^2} \left[-1 + (1+\alpha_2 I^{1/2} + \frac{1}{2} \alpha_2^2 I) e^{-\alpha_2 I^{1/2}} \right] \quad (14)$$

At this point, note also that

$$C_{MX}^{\phi} = \frac{C_{MX}^{\phi}}{2|z_M z_X|^{1/2}} \quad (15)$$

Silvester and Pitzer [9] 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° 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 $\beta^{(1)}$).

Equations (9)-(15) allow one to calculate mean-ion activity coefficients of single electrolytes or mixtures up to high ionic strengths. The only temperature-dependent quantity which changes significantly over the range $0-55^{\circ}\text{C}$ 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 large number of electrolytes by Pitzer and coworkers [4,7,8]. The values for the ion pairs of interest in the present context appear in Table 1 (ion-pair parameters) and Table 2 (interaction coefficients). A computer program has been written to calculate $\ln\gamma_{MX}$, and also osmotic coefficients ϕ (see ref. 4) from these data. The program calculates values at 25°C and at other, user-selected temperatures in the range $0-55^{\circ}\text{C}$. The program is listed in the appendix.

4. *Basis for estimates of ion-pair parameters.*

Estimation of activity coefficients does not require estimation of anywhere near the number of parameters suggested by the preceding paragraph. First of all, Pitzer and Mayorga [7,8] fit experimental data by choosing α_1 and α_2 to be constant for broad classes of electrolytes. Thus, for all 1-1, 1-2, 2-1, 1-3, 3-1, 1-4 and 1-5 electrolytes, $\alpha_1 = 2$ and the terms in α_2 and $\beta^{(2)}$ in Eqs. (13) and (14) are neglected (*i.e.*, $\beta^{(2)} = 0$). For all 2-2 electrolytes, $\alpha_1 = 1.4$ and $\alpha_2 = 12.0$. Secondly, as noted above, the third virial coefficients C^ϕ and interaction coefficients Θ are small and can be neglected with little error (<10% error in γ). These points are illustrated in Tables 1 and 2 and documented at length in the original papers [3,4,7,8].

This leaves two parameters to estimate: $\beta^{(0)}$ and $\beta^{(1)}$. (For 2-2 electrolytes one must also estimate $\beta^{(2)}$.) These parameters depend upon short-range interactions. However, the derivation of Eqs. (12) and (13) [ref. 3] shows that $\beta^{(1)}$ is relatively more important than $\beta^{(0)}$ at low ionic strengths where interactions between ions of unlike charge dominate: Thus, $\beta^{(1)}$ is determined primarily by interactions between ions of unlike charge, while $\beta^{(0)}$ also includes to a degree, contributions from short-range interactions between ions of like charge. Because both $\beta^{(0)}$ and $\beta^{(1)}$ are determined by the same general properties of the ions and solvent one anticipates [3,7] that they will follow generally parallel trends. In addition, one anticipates [3] that $\beta^{(1)}$ will be relatively much larger (by roughly a factor

of 4) for 2-1 electrolytes than for 1-1 electrolytes. Pitzer and Mayorga [7] have plotted $\beta^{(0)}$ vs. $\beta^{(1)}$ for different types of electrolytes and these plots may be used to estimate $\beta^{(1)}$ from $\beta^{(0)}$ (or *vice-versa*).

At this point, the problem of estimating activity coefficients has been reduced to one of estimating $\beta^{(0)}$. Furthermore, probably because the ionic strength dependence of $\ln \gamma$ is inherent in the form of Eqs. (9)-(15), it appears that $\beta^{(0)}$ 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 $\beta^{(0)}$ 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 the parameters are based on experiments on pure electrolytes [10].

As discussed above, and in more detail by Pitzer [3,7], the value of $\beta^{(0)}$ for a given ion-pair is determined primarily by short-range forces between the oppositely charged ions. The values of $\beta^{(0)}$ correlate [7] with the effect of the ions on the structure of liquid water, in the sense discussed extensively by Frank [11]. 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, $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{H}^+ > \text{Na}^+ > \text{K}^+$, the latter being intermediate in character. The most "structure-breaking" anions are large and only singly charged: the sequence goes approximately from $\text{OH}^- < \text{F}^- < \text{SO}_4^{2-} < \text{Cl}^- < \text{Br}^- < \text{I}^- < \text{ClO}_4^-$ with perchlorate

being an extreme "structure-breaker" [7]. These trends are the basis of the estimated parameters in Table 3 which are discussed in detail in the next section.

5. *Description of estimates*

K. S. Pitzer [12] estimated the Na-HCO₃ and K-HCO₃ values by using available data to estimate $\beta^{(0)} + \beta^{(1)}$, then using Fig. 2 of [7] to divide this into $\beta^{(0)}$ and $\beta^{(1)}$.

The value of $\beta^{(0)}$ for K-ClO₄ is estimated assuming that $\beta^{(0)}$ for K-ClO₄ is intermediate between that of K-ClO₃ (Table 1) and K-I (Table 4) to the same degree that $\beta^{(0)}$ for Na-ClO₄ (Table 1) is intermediate between that for Na-ClO₃ (Table 1) and Na-I (Table 4). This choice is based upon Na⁺ and K⁺ being intermediate "structure-makers" while ClO₃⁻, ClO₄⁻, and I⁻ are all "structure-breakers." $\beta^{(1)}$ is then estimated from $\beta^{(0)}$ using Fig. 2 of ref. [7].

The values of $\beta^{(0)}$ for Mg-(HCO₃)₂ and Ca-(HCO₃)₂ are based upon those for Mg-(ClO₄)₂ and Ca-(ClO₄)₂, respectively, in Table 1. This choice is based upon HCO₃⁻, like ClO₄⁻, being a strong "structure-breaker" while Mg²⁺ and Ca²⁺ are strong "structure-makers." Also, the approximate values for Na-HCO₃ and K-HCO₃ (Table 3) are very close to those for Na-ClO₄ (Table 1) and K-ClO₄ (Table 3), respectively. Values of $\beta^{(1)}$ are then estimated from $\beta^{(0)}$ values using the correlation in Fig. 4 of [7]. The parameters estimated for Mg-(HCO₃)₂ and Ca-(HCO₃)₂ are almost identical to

those estimated for Mg-ClO₃ and Ca-ClO₃ (Table 3) from the corresponding iodides.

The estimates for Mg-(ClO₃)₂ and Ca-(ClO₃)₂ are based upon the structure-breaking sequence Br⁻ < I⁻ < ClO₄⁻. It seems reasonable that ClO₃⁻ might have slightly less tendency to act as a "structure-breaker" than ClO₄⁻, so β⁽⁰⁾ and β⁽¹⁾ values for the chlorates are taken to be equal to those for the corresponding iodide or perchlorate, whichever is less. As expected, the β values for Mg are somewhat larger than those for Ca because of the enhanced "structure-making" tendency of Mg²⁺.

The bisulfate ion, HSO₃⁻, pair parameters for Na⁺, K⁺, Mg²⁺, and Ca²⁺ are taken equal to those for chlorates, ClO₃⁻, assuming these anions are of approximately equal size and have about the same effect on the structure of water. The Na-ClO₃ and K-ClO₃ values (Table 1) are based upon experiment, but for Mg and Ca this approximation corresponds to basing the bisulfate values on those of the iodides and perchlorates.

The sulfite ion, SO₃²⁻, parameters are based upon the "structure-breaking" sequence F⁻ < SO₄²⁻ < Cl⁻. One might expect SO₃²⁻ to be slightly less of a "structure-breaker" than SO₄²⁻ since it is smaller. The β⁽⁰⁾ and β⁽¹⁾ values for Na₂-SO₃ and K₂-SO₃ are taken to be half-way between those for the corresponding fluoride and sulfate. For Mg-SO₃ and Ca-SO₃, β⁽⁰⁾, β⁽¹⁾, and β⁽²⁾ are all taken to be 10% below (for β⁽²⁾, this is 10% more negative) those values for the corresponding sulfates [8].

For Mg-CO₃ and Ca-CO₃, it is assumed that CO₃²⁻ is a bit less of a "structure-breaker" than SO₃²⁻, so the experimental SO₄²⁻ parameters are lowered by 20% to estimate values for the carbonates. The values for K₂-CO₃ are estimated by lowering $\beta^{(0)} + \beta^{(1)}$ for Na₂CO₃ by an amount equal to the difference in this sum for Na₂-SO₄ and K₂-SO₄. The sum is apportioned into $\beta^{(0)}$ and $\beta^{(1)}$ in a fashion intermediate between that division for Na₂CO₃ and the general trends for 2-1 electrolytes summarized in Fig. 4 of [7].

The estimates for the disulfites are more arbitrary (and, one anticipates, considerably more uncertain) than those listed above. In the absence of further information, these are based upon the assumption that S₂O₅⁼ deviates from SO₄⁼ in its effect on the structure of water in the opposite direction from SO₃⁼ and also upon the trends in $\beta^{(0)}$ values [7] for Na₂SO₄, Na₂S₂O₃, Na(CH₃CO₂), and Na₂[CH₂(CO₂)₂]. The $\beta^{(0)}$ values for Na₂S₂O₅ and K₂S₂O₅ are obtained by adding 0.05 to the $\beta^{(0)}$ values for Na₂SO₄ and K₂SO₄; $\beta^{(1)}$ is then estimated from $\beta^{(0)}$. Parameters for MgS₂O₅ and CaS₂O₅ are obtained by a 10% increase in $\beta^{(0)}$, $\beta^{(1)}$, and $\beta^{(2)}$ for the corresponding sulfates.

6. *Some calculated results*

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 Ca²⁺ and SO₄²⁻ activities in flue gas

desulfurization analyses. Finally, we show the behavior (in neutral solution) of various ion-pair activity coefficients as NaCl is added to the solution.

Table 5 illustrates 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/CaCO₃ coal scrubbers and correspond to these in 1977 pilot-plant test run No. 5 of the Environmental Protection Agency Industrial Environmental Research Laboratory [13]. This run was one of the runs at highest total ionic strength in the test sequence.

The second part of Table 5 shows the Mg-SO₃ and Ca-SO₃ 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-SO₃ parameters have been uniformly increased by 20% over those of the base estimates. This corresponds to assuming that SO₃²⁻ is more, rather than less, of a structure-breaker than is SO₄²⁻, and to estimating the MgSO₃ parameters as 10% higher than those of Mg-SO₄, rather than 10% lower. This change probably is an upper limit to the potential errors in the Mg-SO₃ parameters and is about the same as the change in those parameters which would be caused by a 25° change in temperature [9]. The alternative Ca-SO₃ parameters correspond to taking a "typical" value of -40 for $\beta^{(2)}$, rather than an "extreme" value of -61.3. In contrast to the alternative Mg-SO₃ estimates, the alternative Ca-SO₃ estimates are probably just as

reasonable as the base estimates for Ca-SO_3 . The only other ion-pair parameters which have been estimated (as opposed to being based upon experiment) for the solution shown in Table 5 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 5 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, γ_{\pm} of Mg-SO_3 and of CaSO_3 changes by 12-13%. The effect of the parameter changes on γ_{\pm} of Ca-SO_4 is well below 1%, and is truly insignificant. The last column shows that raising the temperature from 25° to 50°C lowers γ_{\pm} by 13%.

The data in Table 5 lend confidence to two essential features 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 other than the pair whose activity coefficient is being calculated. Thus, it appears that $\gamma_{\pm}(\text{CaSO}_4)$ 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 all parameters are known [10]. (2) Changes in γ_{\pm} arising from changes in the estimated parameters are small compared to changes due to the temperature dependence of A_{ϕ} . Thus, over moderate temperature ranges, the temperature dependence of γ_{\pm} is adequately represented without considering the temperature dependencies of $\beta^{(0)}$ and $\beta^{(1)}$.

Table 6 compares the activity coefficients of Ca^{2+} and SO_4^{2-} calculated using Pitzer's equations with those calculated in the Bechtel Modified Radian Equilibrium Program [14], a widely used computer code for modelling of flue gas desulfurization units. In that program,

$$\ln \gamma_i = 3 A_\phi z_i \left\{ -I^{1/2} / [1 + 50.29 (DT)^{-1/2} a_i I^{1/2}] + B_i I \right\} \quad (16)$$

where: for Ca^{2+} , $a = 4.5$ and $B = 0.1$; for SO_4^{2-} , $a = 3.0$ and $B = 0$; and for SO_3^{2-} , $a = 4.5$ and $B = 0$. Since that code calculates individual ion activity coefficients, it is not appropriate to compare calculated activities of Ca^{2+} and SO_4^{2-} directly, but their product $a_2 = a_{\text{Ca}^{2+}} a_{\text{SO}_4^{2-}}$ can be compared. The different run numbers in Table 6 correspond to various pilot-plant test runs made at the Environmental Protection Agency Laboratory in North Carolina in 1977 [13]. 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 5. The present values for a_2 in all runs are about 25% higher than those calculated by the Radian program, and just as important, show rather different behavior with changes in ionic strength and mixture composition. 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 5.

The reason for the differences between the present computations and those using the Radian program when the mixture composition varies is illustrated in Figs. 1 and 2. Activity coefficients in the Radian program, eq. (16), depend only upon ionic strength and thus, at a given ionic strength, are independent of the chemical composition of the solution. The present treatment, in contrast, sums over pairwise interactions for all ions present and so the activity coefficient of a given ion pair depends markedly upon the nature of the other ions in the solution.

Figure 1 shows the variation of γ_{\pm} for 0.01 M Ca-SO₄ at 50°C as the ionic strength is increased (a) by adding MgSO₄ and (b) by adding NaCl. It can be seen that addition of MgSO₄ causes $\gamma_{\pm}(\text{CaSO}_4)$ to decrease markedly, following essentially the same curve as the hypothetical addition of CaSO₄ beyond the saturation limit. This is not surprising considering that MgSO₄ and CaSO₄ have a common anion and rather similar cations. The decrease in γ_{\pm} with addition of MgSO₄ is sufficiently rapid that it balances the increase in the activity of CaSO₄ resulting from the addition of sulfate. The product $a_2 = \gamma_{\pm}^2 \cdot m_{\text{Ca}^{2+}} \cdot m_{\text{SO}_4^{2-}}$ remains almost constant, and below the solubility product limit [10] of CaSO₄ over the entire range of ionic strength from I = 0.1 to I = 5 M. Figure 1 shows that addition of NaCl lowers the activity coefficient of CaSO₄ considerably less than does addition of MgSO₄. Added NaCl has only a small effect at ionic strengths above 1.5 M.

The computations for Fig. 1 are based upon experimentally derived 25°C ion-pair and interaction coefficients taken from the literature (cf. Tables 1 and 2). Comparing Pitzer's theory with the Radian program [14], at $I = 1 \text{ M}$ the Radian program yields a value of $\gamma_{\pm} (\text{CaSO}_4)$ which is a factor of 1.8 higher than is obtained from Pitzer's theory and parameters for $\gamma_{\pm} (\text{CaSO}_4)$ in the presence of MgSO_4 . The deviation between the two calculations is even larger for ionic strengths above this value. The Radian values increase above $I = 2 \text{ M}$ while the Pitzer values for added MgSO_4 (or hypothetical, pure CaSO_4) continue to decrease slowly. Thus, the classical Debye-Hückel treatment used in that program would lead one to expect that CaSO_4 will precipitate upon addition of MgSO_4 . Above $I = 1 \text{ M}$ the Radian program also deviates from the results computed for $\gamma_{\pm} (\text{CaSO}_4)$ upon addition of NaCl .

Figure 2 shows similar curves for CaSO_3 . For CaSO_3 , the present computations are based upon parameters estimated in this paper. The activity coefficients estimated for CaSO_3 are about 5-15% below those for CaSO_4 at equal concentrations but otherwise the pattern of Figs. 1 and 2 is very similar. Again, the decrease in $\gamma_{\pm} (\text{CaSO}_3)$ upon adding MgSO_3 is sufficiently large that the activity of CaSO_3 remains below the solubility product limit of CaSO_3 as MgSO_3 is added. In contrast to the present computations, in the Radian program $\gamma_{\pm} (\text{CaSO}_3)$ is about 50% above $\gamma_{\pm} (\text{CaSO}_4)$ because $\gamma(\text{SO}_3^{-2})$ in that program is about twice $\gamma(\text{SO}_4^{2-})$. Thus, the Radian program values for $\gamma_{\pm} (\text{CaSO}_3)$ are a

factor of 2-10 larger than the present estimates. This factor exceeds the uncertainty of the present estimates by an order of magnitude. Again, the Radian values increase above $I = 2$ while the present values of γ_{\pm} (CaSO_3) for CaSO_3 plus MgSO_3 continue to decrease slowly as the ionic strength increases. Just as with CaSO_4 , the present estimates and the Radian estimates leads to opposing expectations for the effect of added MgSO_3 upon the solubility of CaSO_3 .

Figures 1 and 2 show that there are marked differences in γ_{\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 γ_{\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 \underline{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 report has been concerned solely with neutral solutions of strong electrolytes. The next task is to add weak acid interactions which can probably be treated adequately at the present

level of approximations by treating the ion-pair interactions solely by an ionization equilibrium constant.

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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	.1775	2.0	.2945	---	---	.0008	Ref. (7), Table I
H-ClO ₄	.1747	2.0	.2931	---	---	.00819	Ref. (7), Table I
Na-Cl	.0765	2.0	.2664	---	---	.00127	Ref. (7), Table I
Na-ClO ₃	.0249	2.0	.2455	---	---	.0004	Ref. (7), Table I
Na-ClO ₄	.0554	2.0	.2755	---	---	-.00118	Ref. (7), Table I
K-Cl	.0484	2.0	.2122	---	---	-.00084	Ref. (7), Table I
K-ClO ₃	-.0960	2.0	.2481	---	---	---	Ref. (7), Table I
Mg-Cl ₂	.3524	2.0	1.6815	---	---	.00519	Ref. (7), Table VI
Mg-(ClO ₄) ₂	.4961	2.0	2.0085	---	---	.00958	Ref. (7), Table VI
Ca-Cl ₂	.3159	2.0	1.614	---	---	-.00034	Ref. (7), Table VI
Ca-(ClO ₄) ₂	.4511	2.0	1.7565	---	---	-.0050	Ref. (7), Table VI
Na ₂ -CO ₃	.1898	2.0	.846	---	---	-.04803	Ref. (7), Table VI
Na ₂ -SO ₄	.0196	2.0	1.113	---	---	.0057	Ref. (4), p. 5705
K ₂ -SO ₄	.0500	2.0	.7793	---	---	---	Ref. (7), Table VI
H-HSO ₄	.2103	2.0	.4711	---	---	---	Ref. (6), Table I
H-SO ₄	.0027	2.0	---	---	---	.0416	Ref. (6), Table I
Ca-SO ₄	.2000	1.4	2.65	12.0	-55.7	---	Ref. (8), Table I
Mg-SO ₄	.2210	1.4	3.343	12.0	-37.23	.0250	Ref. (8), Table I

Table 2. Interaction coefficients from literature.

Ion-pairs	θ	Ref.
$\theta(\text{H}^+, \text{Na}^+)$.036	Ref. (4), Table I
$\theta(\text{H}^+, \text{K}^+)$.005	Ref. (4), Table I
$\theta(\text{Na}^+, \text{K}^+)$	-.012	Ref. (4), Table I
$\theta(\text{Mg}^{2+}, \text{Ca}^{2+})$.010	Ref. (4), Table I
$\theta(\text{K}^+, \text{Ca}^{2+})$	-.040	Ref. (4), Table I
$\theta(\text{Cl}^-, \text{SO}_4^{2-})$	-.020	Ref. (15), Table IV

Table 3. Estimated ion-pair parameters.

Ion-Pair	$\beta^{(0)}$	α_1	$\beta^{(1)}$	α_2	$\beta^{(2)}$	c^ϕ	Ref.
Na-HSO ₄	.0554	2.0	.2755	---	---	-.00118	Ref. (6), p. 4935
Na-HCO ₃	.040	2.0	.20	---	---	---	Ref. (12)
K-HCO ₃	.0	2.0	.10	---	---	---	Ref. (12)
K-ClO ₄	-.040	2.0	.08	---	---	---	This work
Mg-(HCO ₃) ₂	.490	2.0	1.90	---	---	---	This work
Ca-(HCO ₃) ₂	.440	2.0	1.70	---	---	---	This work
Mg-(ClO ₃) ₂	.490	2.0	1.804	---	---	---	This work
Ca-(ClO ₃) ₂	.438	2.0	1.76	---	---	---	This work
Na-HSO ₃	.0249	2.0	.2455	---	---	.0004	This work
K-HSO ₃	-.096	2.0	.2481	---	---	---	This work
Mg-(HSO ₃) ₂	.490	2.0	1.804	---	---	---	This work
Ca-(HSO ₃) ₂	.438	2.0	1.76	---	---	---	This work
Na ₂ -SO ₃	.021	2.0	.66	---	---	---	This work
K ₂ -SO ₃	.065	2.0	.49	---	---	---	This work
Mg-SO ₃	.200	1.4	3.00	12.0	-41.0	---	This work
Ca-SO ₃	.180	1.4	2.38	12.0	-61.3	---	This work
K ₂ -CO ₃	.075	2.0	.66	---	---	---	This work
Mg-CO ₃	.180	1.4	2.70	12.0	-46.0	---	This work
Ca-CO ₃	.160	1.4	2.10	12.0	-69.0	---	This work
Na ₂ S ₂ O ₅	.07	2.0	.9	---	---	---	This work
K ₂ S ₂ O ₅	.10	2.0	1.1	---	---	---	This work
MgS ₂ O ₅	.24	1.4	3.7	12.0	-34.0	---	This work
CaS ₂ O ₅	.22	1.4	3.0	12.0	-50.0	---	This work

Table 4. Additional literature ion-pair parameters used as basis for estimation.

Ion-pair	$\beta^{(0)}$	α_1	$\beta^{(1)}$	Ref.
Na-OH	.0864	2.0	.253	Ref. (7), Table I
Na-F	.0215	2.0	.2107	Ref. (7), Table I
Na-Br	.0973	2.0	.2791	Ref. (7), Table I
Na-I	.1195	2.0	.3439	Ref. (7), Table I
K-OH	.1298	2.0	.320	Ref. (7), Table I
K-F	.0809	2.0	.2021	Ref. (7), Table I
K-Br	.0569	2.0	.2212	Ref. (7), Table I
K-I	.0746	2.0	.2517	Ref. (7), Table I
Mg-Br ₂	.4327	2.0	1.682	Ref. (7), Table VI
Mg-I ₂	.4902	2.0	1.804	Ref. (7), Table VI
Ca-Br ₂	.3816	2.0	1.613	Ref. (7), Table VI
Ca-I ₂	.4379	2.0	1.806	Ref. (7), Table VI
Na ₂ -S ₂ O ₃	.0662	2.0	1.276	Ref. (7), Table VI
Na ₂ - [CH ₂ (CO ₂) ₂]	.1395	2.0	.4313	Ref. (7), Table VII
Na-(CH ₂ CO ₂)	.1426	2.0	.3237	Ref. (7), Table II

Table 5. Effect of changing estimated parameters compared to effect of temperature.

<i>Concentrations</i>	$[Mg^{2+}] = .304$	$[Cl^-] = .1988$
<i>(molality):</i>	$[Ca^{2+}] = .014$	$[CO_3^{2-}] = .0026$
		$[SO_4^{2-}] = .184$
<i>Ionic Strength:</i>	$I = 1.173$	$[SO_3^{2-}] = .032$

Estimated parameters:

Ion-pair	$\beta^{(0)}$	α_1	$\beta^{(1)}$	α_2	$\beta^{(2)}$	Estimate
Mg-SO ₃	.20	1.4	3.00	12.0	-41.0	M
Mg-SO ₃	.24	1.4	3.00	12.0	-33.0	MA
Ca-SO ₃	.18	1.4	2.38	12.0	-61.3	C
Ca-SO ₃	.18	1.4	2.38	12.0	-40.0	CA

Activity coefficients calculated with different parameters:

<i>Temperature:</i>	25°	25°	25°	25°	50°C
<i>Parameters:</i>	M,C	MA,C	M,CA	MA,CA	M,C
$\gamma_{\pm} (CaSO_4)$.0918	.0912	.0925	.0919	.0799
$\gamma_{\pm} (MgSO_3)$.0975	.1096	.0978	.1100	.0848
$\gamma_{\pm} (CaSO_3)$.0805	.0961	.0874	.0972	.0752

Table 6. 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	.025	.076	.610	2.08×10 ⁻⁵	2.37×10 ⁻⁵
2	.032	.023	.265	1.66×10 ⁻⁵	2.29×10 ⁻⁵
5	.014	.184	1.173	1.50×10 ⁻⁵	1.65×10 ⁻⁵
					(1.62, 1.67, 1.65)
9	.0032	.070	.495	2.08×10 ⁻⁶	3.44×10 ⁻⁶
17	.086	.0094	.327	1.53×10 ⁻⁵	1.93×10 ⁻⁵
19	.073	.0016	.228	3.10×10 ⁻⁶	3.79×10 ⁻⁶

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

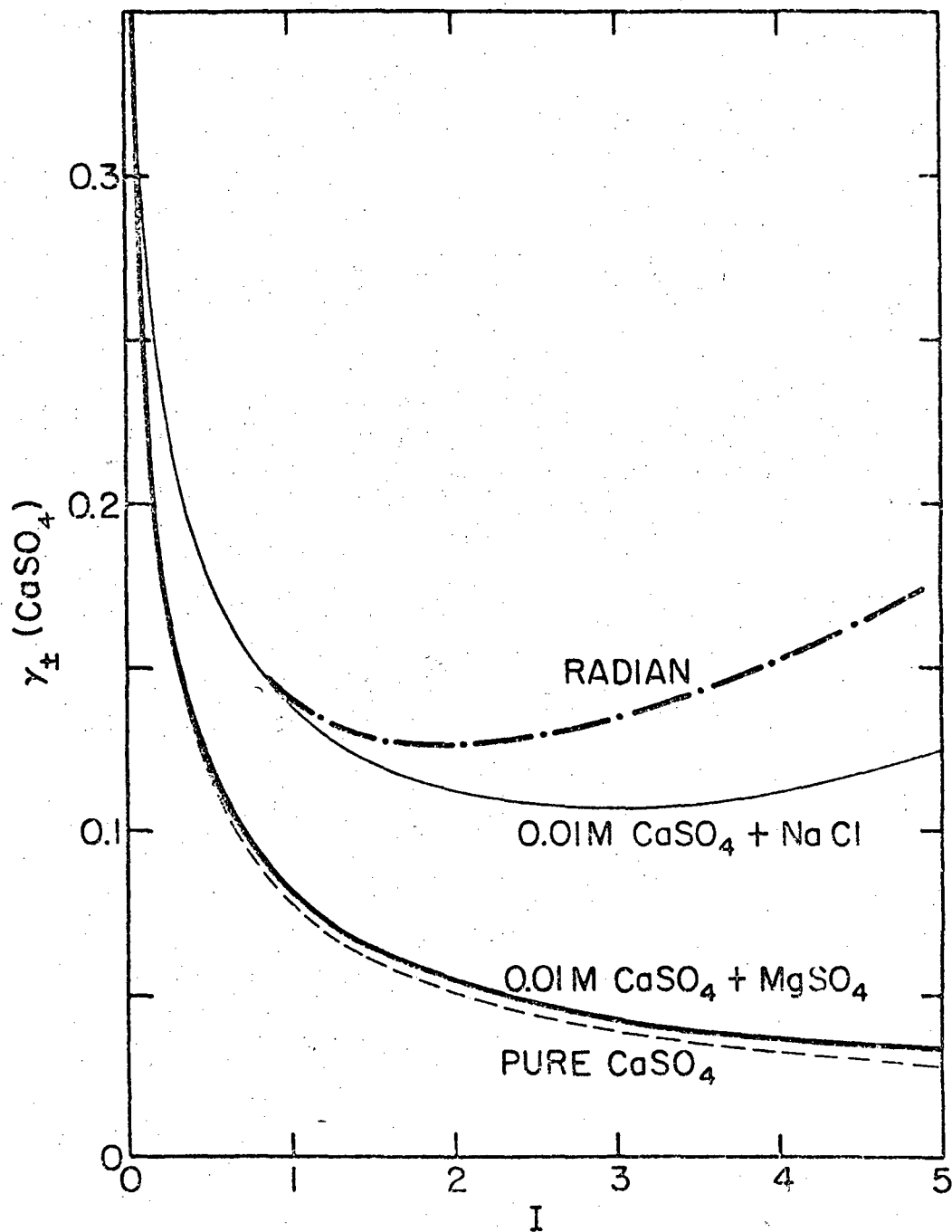


Fig. 1. Mean ion activity coefficient of CaSO_4 at 50°C as a function of ionic strength. The lower three curves are computed using Pitzer's equations and parameters. The upper curve corresponds to $[\gamma(\text{Ca}^{2+}) \cdot \gamma(\text{SO}_4^{2-})]^{1/2}$ from the Bechtel modified Radian equilibrium computer program [ref. 14].

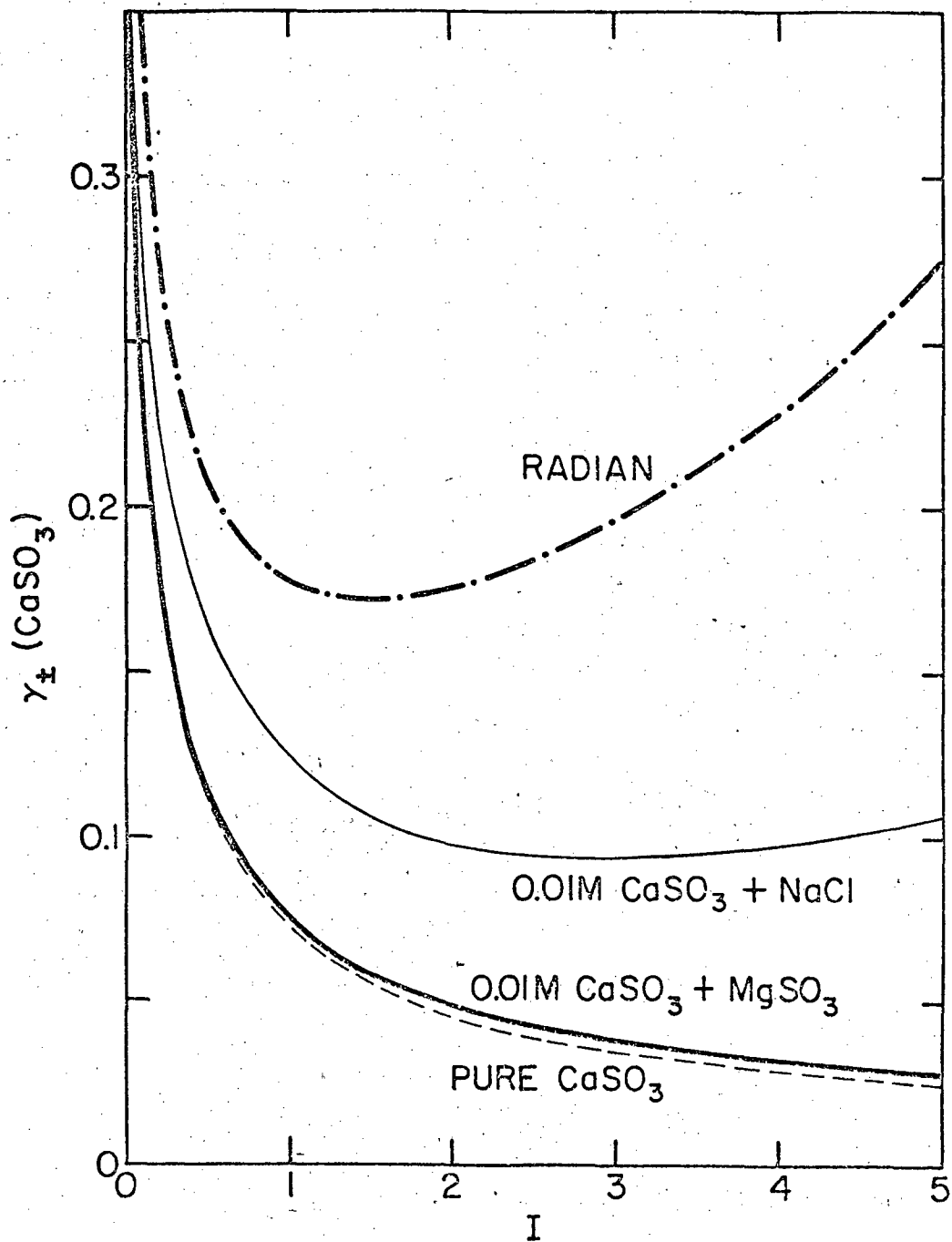


Fig. 2. Mean ion activity coefficient of CaSO_3 at 50°C as a function of ionic strength. The lower three curves are computed using Pitzer's equations and parameters estimated in this paper. The upper curve is $[\gamma(\text{Ca}^{2+}) \cdot \gamma(\text{SO}_3^{2-})]^{1/2}$ from the Bechtel modified Radian equilibrium computer program [ref. 14].

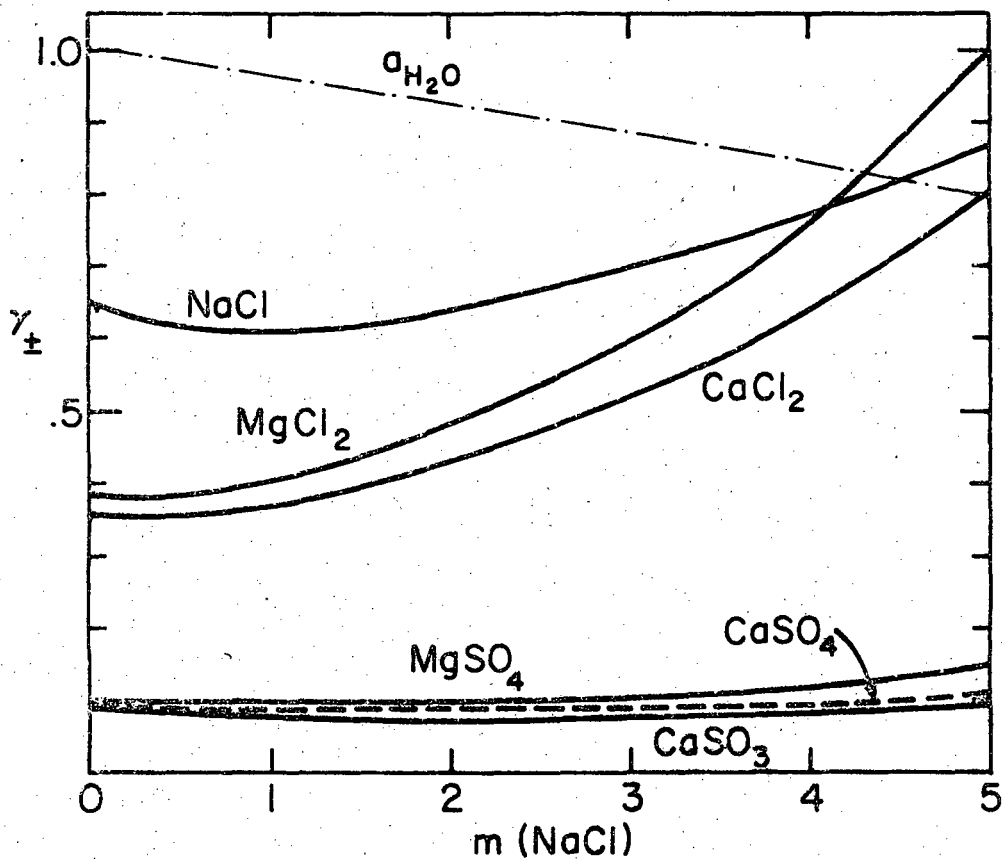


Fig. 3. Effect of addition of NaCl on mean ionic activity coefficients in a hypothetical, nearly saturated, sulfite-sulfate solution at 50°C. Ion concentrations: Mg^{2+} , 0.2; Ca^{2+} , 0.02; K^{+} , 0.01; SO_4^{2-} , 0.17; SO_3^{2-} , 0.04; HSO_3^{-} , 0.02; HCO_3^{-} , 0.01 M. Initial ionic strength: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

```
PROGRAM GAMMA01(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
C*****
C
C          GAMMA
C          G. M. ROSENBLATT
C          LAWRENCE BERKELEY LABORATORY
C          AUGUST, 1979
C*****
C          PROGRAM TO CALCULATE ACTIVITY COEFFICIENTS OF PURE AND MIXED
C          ELECTROLYTES USING METHODS DEVELOPED BY K. S. PITZER, JA(S 96,
C          5701 (1974) AND OTHER PAPERS IN THE SERIES
C*****
C          DIMENSION CONCM(5), CONCL(10), BETA0(5,10), ALPHA1(5,10),
C          1BETA1(5,10), ALPHA2(5,10), BETA2(5,10), CPHI(5,10), ZM(5), ZL(10),
C          2IPAIR(5,10), MCA(10), LCA(10), CONC(17), IONM(5), IONL(10),
C          3THEM(5,5), THEL(10,10), B(5,10), BP(5,10), C(5,10), ICOM(8),
C          4GAM(17,10,5), NIPAIR(10), PHI(17,5), TEMP(5),STG(17)
C          DATA THEL /100*0.0/THEM /25*0.0/TEMP(1)/ 25.0/
C
C          READ 810,( IONM(M),ZM(M) ,M=1,5)
C          READ 810,( IONL(L),ZL(L) ,L=1,10)
C          LIST OF IONS TO BE CONSIDERED. UPTO 5 + IONS (M). UPTO 10 - IONS
C          (L). THIS LIST ESTABLISHES A NUMEERING SCHEME WHICH MUST BE
C          FOLLOWED IN THE REST OF THE INPUT DATA. FIRST 9 SPACES FOR SYMBOL.
C          LAST SPACE FOR ABSOLUTE MAGNITUDE OF CHARGE.
C
C          CALL DATE(ITODAY)
C
C          100 READ 800,NOPROB, (MCA(I),LCA(I) ,I=1,10),(TEMP(J),J=2,5)
C          NOPROB IS USER-ASSIGNED PROBLEM NUMBER. IF 0 PROGRAM WILL STOP.
C          MCA, LCA SPECIFY ION PAIRS FOR WHICH ACTIVITY COEFFICIENTS ARE TO
C          CALCULATED. FIRST PAIR MC1-LC1 WILL HAVE NORMALITY VARIED OVER
C          RANGE SPECIFIED ON CONC CARD.
C          TEMP(J) ARE OPTIONAL TEMPERATURES ADDITIONAL TO 25 DEG
C
C          IF(NOPROB) 999,999,101
C
C          101 READ 811,ICOM
C          WRITE COMMENTS DESCRIBING PROBLEM ON THIS CARD
C
C          PRINT 900,ITODAY, NOPROB, ICOM
C
C          READ 801,(CONCM(M),M=1,5), CONC(1), (CONCL(L),L=1,10)
C          MOLALITIES OF ALL IONS EXCEPT SALT MC1-LC1 WHOSE CONCENTFATION
C          WILL BE VARIED. MANY DIFFERENT PROBLEMS CAN BE RUN CHANGING ONLY
C          THIS CARD AND THE NOPROB AND ICOM CARDS.
C
C          READ 801,(CONC(NC),NC=2,17)
C          CONC CARD. NORMALITY VALUES FOR SALT MC1-LC1
C
C          READ 803,NOBETA, NOTHEM, NOTHEL
C          NOBETA IS NUMBER OF ION PAIRS FOR WHICH BETA, ETC. VALUES ARE
C          LISTED ON INPUT CARDS.
C          NOTHEM AND NOTHEL ARE NUMBER OF THETA INTERACTION COEFFICIENTS
C          FOR + AND - IONS WHICH ARE LISTED ON INPUT CARDS.
C
C          IF(NOBETA.EQ.0) GO TO 103
C          PRINT 901
C          DO 102 I=1,NOBETA
C
```

```
      READ 802,M, L, IREF, BETA0(M,L), ALPHA1(M,L), BETA1(M,L),
1ALPHA2(M,L), BETA2(M,L), CPHI(M,L), IPAIR(M,L)
C      ION PAIR DATA FOR PITZER EQUATIONS. IONS M AND L ARE SPECIFIED AS
C      DESIGNATED IN LEADING INPUT CARDS. IREF IS SPACE TO LIST SOURCE
C      OF DATA.
102 PRINT 902,IPAIR(M,L), IONM(M), ZM(M), IONL(L), ZL(L), M, L,
1BETA0(M,L), ALPHA1(M,L), BETA1(M,L), ALPHA2(M,L), BETA2(M,L),
2CPHI(M,L), IREF
C      PRINTOUT SHOWS INPUT DATA AND ALLOWS CHECK ON ION NUMBERING.
103 PRINT 903
      IF(NOTHEM.EQ.0) GO TO 110
      DO 105 I=1,NOTHEM
C
C      INTERACTION TERMS THETA. FIRST FOR +, THEN FOR - IONS.
      READ 804,M1, M2, IREF, THEM(M1,M2), NAME
C
      THEM(M2,M1)=THEM(M1,M2)
105 PRINT 904, NAME, IONM(M1), ZM(M1), IONM(M2), ZM(M2), M1, M2,
1M2,M1,THEM(M1,M2), IREF
110 IF(NOTHEL.EQ.0) GO TO 120
      DO 115 I=1,NOTHEL
      READ 804,L1, L2, IREF, THEL(L1,L2), NAME
      THEL(L2,L1)=THEL(L1,L2)
115 PRINT 904, NAME, IONL(L1), ZL(L1), IONL(L2), ZL(L2),L1, L2,
1L2,L1,THEL(L1,L2), IREF
120 CONTINUE
C      LOOP TO VARY CONCENTRATION OF SALT MC1-LC1. FIRST CALCULATION IS
C      AT CONCENTRATIONS OF MC1 AND LC1 ON MOLALITY CARDS. SUCCEEDING
C      CALCULATIONS ADD NORMALITIES ON CONC CARD TO THOSE INITIAL VALUES
      NC=1
      MC1=MCA(1)
      LC1=LCA(1)
      CONCMC=CONCM(MC1)
      CONCLC=CONCL(LC1)
      GO TO 155
151 IF((CONC(NC).EQ.0.0) GO TO 500
      IF(((ZM(MC1)-ZL(LC1)).NE.0.0) GO TO 153
      CONCM(MC1)=CONC(NC) + CONCMC
      CONCL(LC1)=CONC(NC) + CONCLC
      GO TO 155
153 CONCM(MC1)=CONC(NC)*ZL(LC1)+CONCMC
      CONCL(LC1)=CONC(NC)*ZM(MC1)+CONCLC
155 NC0=NC-1
      PRINT 906,NC0,IPAIR(MC1,LC1),CONC(NC)
C      CALCULATE IONIC STRENGTH, STGTH
      SUMC=0.0
      SUMCZ=0.0
      STGTH=0.0
      DO 205 M=1,5
      L=M+5
      PRINT 907, IONM(M),ZM(M),CONCM(M),IONL(M),ZL(M),CONCL(M),
1IONL(L),ZL(L),CONCL(L)
      SUMC=SUMC+CONCM(M)
      SUMCZ=SUMCZ+CONCM(M)*ZM(M)
C      SUMCZ IS SUM OF CONC(M)*Z(M)
205 STGTH =STGTH+CONCM(M)*ZM(M)*ZM(M)
      CHECK=SUMCZ
      DO 210 L=1,10
      SUMC=SUMC+CONCL(L)
      CHECK=CHECK-(CONCL(L)*ZL(L))
210 STGTH=STGTH+CONCL(L)*ZL(L)*ZL(L)
```

```
C      CHECK ELECTRICAL NEUTRALITY. DOES SUM(CONC(M)*Z(M))=SUM(CONC(L)*
C      Z(L)). IF NOT, STOP.
      CHECK=ABS(CHECK)
      IF(CHECK.GT.0.00001) GO TO 998
      STGTH=0.5*STGTH
      STG(NC)=STGTH
      SQSTG=STGTH**0.5
      PRINT 908, STGTH
C      CALCULATE DEBYE-HUCKEL FACTORS. FPHI AND FGAM
C      APhi FROM PITZER II AND IV FOR CONSISTENCY WITH ION PAIR DATA
      APhi=0.392
      RHO=1.2
      FSTG=1.0+RHO*SQSTG
C      FPHI GIVEN BY EQ(5) OF PITZER IV.
      FPHI=-APhi*SQSTG/FSTG
C      FGAM GIVEN BY EQ(12) OF PITZER IV.
      FGAM=FPHI-APhi*(2/RHO)*ALOG(FSTG)
      IF(STGTH.EQ.0.0) GO TO 365
C      CALCULATE SECOND AND THIRD VIRIAL CIEFFICIENTS BPHI, BML, BPML,
C      AND CML
      PRINT 914
      TPhi=0.0
      SUMM=0.0
      DO 350 M=1,5
      IF(CONCM(M).NE.0.0) GO TO 303
      DO 302 I=1,10
302  IF(M.EQ.MCA(I)) GO TO 306
      GO TO 350
303  DO 305 M1=1,5
      IF(CONCM(M1).EQ.0.0) GO TO 305
      SUMM=SUMM+CONCM(M)*CONCM(M1)*THEM(M,M1)
305  CONTINUE
306  DO 349 L=1,10
      IF(CONCL(L).NE.0.0) GO TO 308
      DO 307 I=1,10
307  IF(L.EQ.LCA(I)) GO TO 308
      GO TO 349
308  IF(LEGVAR(BETA0(M,L))) 997,309,997
C      LEGVAR IS A CDC FUNCTION WHICH IS 0 WHEN VARIABLE HAS ASIGNED
C      DEFINITE VALUE
309  BPHI=BETA0(M,L)
      BML=BETA0(M,L)
      BPML=0.0
      ALPHA=ALPHA1(M,L)
      ALPH2=ALPHA2(M,L)
      BETA=BETA1(M,L)
310  A1ST=ALPHA*SQSTG
      A2ST=(A1ST**2)/2.0
      EAST=EXP(-A1ST)
      TB=1.0+A1ST
      TBP=TB+A2ST
      TB=1.0-(TB*EAST)
      TBP=-1.0+(TBP*EAST)
C      BPHI GIVEN BY EQ(6) OR EQ(10) OF PITZER IV.
      BPHI=BPHI+(BETA*EAST)
C      B(M,L) GIVEN BY EQ(13) OF PITZER IV.
      BML=BML+(BETA*TB/A2ST)
C      B-PRIME GIVEN BY EQ(14) OF PITZER IV.
      BPML=BPML+(BETA*TBP/(A2ST*STGTH))
      IF(ALPH2.EQ.0.0) GO TO 345
      ALPHA=ALPH2
      ALPH2=0.0
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BETA=BETA2(M,L)
GO TO 310
345 B(M,L)=BML
BP(M,L)=BPML
BGAM=BML+BPFI
ZTERM=(ZM(M)*ZL(L))**0.5
CML=CPhi(M,L)/ZTERM
TPHI=TPHI+CONCM(M)*CONCL(L)*(BPFI+SUMCZ*CML)
C(M,L) GIVEN JUST UNDERNEATH EQ(14) OF PITZER IV.
C(M,L)=0.5*CML
PRINT 909, IPAIR(M,L), M, L, BETA0(M,L), BPFI, BGAM, BML, BPML, C(M,L)
349 CONTINUE
350 CONTINUE
C CALCULATE OSMOTIC COEFFICIENT PHI1. EQ(11) OF PITZER IV.
SUML=0.0
DO 360 L=1,10
IF(CONCL(L).EQ.0.0) GO TO 360
DO 359 L1=1,10
IF(CONCL(L1).EQ.0.0) GO TO 359
SUML=SUML+CONCL(L)*CONCL(L1)*THEL(L,L1)
359 CONTINUE
360 CONTINUE
TPHI1 = SUMM+SUML
C LOOP TO VARY TEMPERATURE. ONLY APhi IS T DEPENDENT
365 IT=1
IF(STGTH.EQ.0.0) PHI(1,IT) = 0.0
IF(STGTH.EQ.0.0) GO TO 385
GO TO 380
370 T=TEMP(IT)
IF(T.EQ.0.0) GO TO 490
IF(STGTH.EQ.0.0) PHI(1,IT) = 0.0
IF(STGTH.EQ.0.0) GO TO 385
APHIO=APHI
C APhi GIVEN BY EQ. (A1) OF PITZER VII CORRECTED TO .392 AT 25 C
APHI= 0.37795+ (4.684E-4)*T + (3.74E-6)*T*T
RATIO=APHI/APHIO
FPhi=FPhi*RATIO
FGAM=FGAM*RATIO
380 PHI1=2.0*(STGTH*FPhi+TPHI)+ TPhi1
PHI(NC,IT)=PHI1/SUMC
385 PRINT 911,TEMP(IT), FGAM, PHI(NC,IT)
PRINT 913
C CALCULATE ACTIVITY COEFFICIENTS. EQ(15) OF PITZER IV.
NP=1
400 MC=MCA(NP)
IF(MC) 460,460,402
402 LC=LCA(NP)
IF(ZM(MC).NE.ZL(LC)) GO TO 404
VMC=1.0
VLC=1.0
GO TO 406
404 VMC=ZL(LC)
VLC=ZM(MC)
406 VTOT=VMC+VLC
SUML=0.0
SUMM=0.0
SUMML=0.0
IF(STGTH.EQ.0.0) GO TO 451
SUM OVER ANIONS (L)
DO 420 L=1,10
IF(CONCL(L).EQ.0.0) GO TO 420
TERM=B(MC,L)+SUMCZ*C(MC,L)+(VLC/VMC)*THEL(LC,L)
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SUML=SUML+CONCL(L)*TERM
420 CONTINUE
SUML=2.0*VMC*SUML/VTOT
C   SUM OVER CATIONS (M)
DO 450 M=1,5
IF(CONCM(M).EQ.0.0) GO TO 450
TERM=B(M,LC)+SUMCZ*C(M,LC)+(VMC/VLC)*THEM(MC,M)
SUMM=SUMM+CONCM(M)*TERM
C   DOUBLE SUM
DO 449 L=1,10
IF(CONCL(L).EQ.0.0) GO TO 449
TERM=ZM(MC)*ZL(LC)*BP(M,L) + 2.0*VMC*ZM(MC)*C(M,L)/VTOT
SUMML=SUMML+CONCM(M)*CONCL(L)*TERM
449 CONTINUE
450 CONTINUE
451 DHP=ZM(MC)*ZL(LC)*FGAM
SUMM=2.0*VLC*SUMM/VTOT
GAML=DHP+SUML+SUMM+ SUMML
C   GAML IS LN GAMMA(M,L)
NIPAIR(NP) = IPAIR(MC,LC)
GAM(NC,NP,IT) = EXP(GAML)
C   GAM IS GAMMA(M,L)
CON=((CONCM(MC)**VMC)*CONCL(LC)**VLC)**(1.0/VTOT)
C   CON IS MEAN ION MOLALITY
ACT = GAM(NC,NP,IT)*CON
C   ACT IS MEAN ION ACTIVITY
ACT2=ACT**VTOT
C   ACT2 IS ACTIVITY OF SOLUTE M-L, A2
PRINT 912, IPAIR(MC,LC), MC, LC, CONCM(MC), CONCL(LC), GAML,
1GAM(NC,NP,IT), CON, ACT, ACT2
NP=NP+1
IF(NP-10) 400,400,460
460 IT=1+IT
IF(IT-5) 370,370,490
490 NC=1+NC
ITM=IT-1
NPM=NP-1
IF(NC-17) 151,151,500
500 IF(NC.LT.4) GO TO 100
NCM=NC-1
CONCM(MC1) = CONCMC
CONCL(LC1) = CONCLC
PRINT 905,ITODAY, NOPROB, ICOM
DO 510 M=1,5
L=M+5
510 PRINT 907, IONM(M), ZM(M), CONCM(M), IONL(M), ZL(M), CONCL(M),
1IONL(L), ZL(L), CONCL(L)
PRINT 915, IPAIR(MC1,LC1), (NIPAIR(NP), NP=1, NPM)
DO 525 IT=1, ITM
PRINT 917, TEMP(IT)
DO 520 NC=1, NCM
NC0=NC-1
PHI1=1.0+PHI(NC,IT)
520 PRINT 916, NC0, CONC(NC), STG(NC), PHI1, (GAM(NC,NP,IT), NP=1, NPM)
525 CONTINUE
GO TO 100
997 PRINT 989, M, L, IONM(M), ZM(M), IONL(L), ZL(L)
GO TO 100
998 PRINT 990, CHECK
999 STOP
C   INSERT BLANK CARD AT END OF DATA TO STOP PROGRAM.
800 FORMAT(I4, 6X, 20I2, 4F5.0 )
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801 FORMAT(16F5.5)
302 FORMAT(2I2, A6, 6F10.0, A10)
303 FORMAT(3I2)
804 FORMAT(2I2, A6, F10.0, A10)
810 FORMAT(8(A9,F1.0))
811 FORMAT(8A10)
900 FCRMAT(1H1,A10, 2X, *ACTIVITIES OF ELECTROLYTES PROBLEM NO. *,
1I4 /13X, 8A10/*OION-PAIR PARAMETERS WHICH DIFFER FROM PRECEDING PR
2OBLEM*)
901 FORMAT(3X, *ION PAIR*, 25X, *M-L*, 12X,
1*BETA(0)*, 4X, *ALPHA1*, 8X,*BETA(1)*, 4X, *ALPHA2*, 8X,
2*BETA(2)*, 11X, *CPHI*, 4X, *REF*)
902 FORMAT(1X, A10, A9, F2.0, A9, F2.0, I4, 1H-, I2, F18.4, F10.1,
1F15.4, F10.1, F15.4, F15.5, 3X, A6)
903 FORMAT(*OINTERACTION PARAMETERS WHICH DIFFER FROM PRECEDING PROBL
1EM*)
904 FORMAT(1X, A10, A9, F2.0, A9, F2.0, 4X, *THETA(*, I2, 1H,, I2,
1*) = THETA(*, I2, 1H,, I2, *) =*F6.3, 10X, A6)
905 FORMAT(1H1, A10, 2X, *PROBLEM NO.*, I4, 10X, *SUMMARY OF CALCULATE
1D ACTIVITY COEFFICIENTS* / 13X, 8A10, /
2*O INITIAL ION CONCENTRATIONS (MOLALITY)*)
906 FORMAT(1H0/1H0/1X,I2,2X,*ION CONCENTRATIONS (MOLALITY) (MOLALITY*
1, 1X, A10, 1H=, F7.4, 1H))
907 FORMAT(25X,A9, F2.0, F11.4,5X, 2(5X,A9,F2.0,F11.4))
908 FORMAT(1H0,4X,*IONIC STRENGTH =*, F8.3)
909 FORMAT(30X,A10,4X,I2,1H-,I2, 4F13.4, E13.4, F13.4)
911 FORMAT(1H0, 4X, *T(DEG C) =*, F5.1/ 5X, *F(GAMMA) =*, F8.4/
1 EX, *PHI - 1 =*, F8.4)
912 FORMAT(3X, A10, 4X, I2, 1H-, I2, 6F15.4, E15.4)
913 FCRMAT(1H0, 4X, *ION PAIR*, 5X, *M-L*, 9X,
1 *CONC(M)*, 8X, *CONC(L)*, 7X, *LN GAMMA*, 8X, *GAMMA+-*, 5X,
2*MOLALITY+-*, 10X, *A+-*, 12X, *A2*)
914 FORMAT(31X , *ION PAIR*, 6X, *M-L*,
17X, *BETA(0)*,9X, *BPHI*, 7X, *BGAMMA*, 10X, *B*, 11X, *BF*,12X,
2*C*)
915 FORMAT(1H0, *CONCENTRATION IONIC*, 7X, *PHI*, 4X, *GAMMA+-*/
16X, A10, *STRENGTH*, 11X, 9A10)
916 FORMAT(1X, I2, F10.4, F9.3, F11.4, 9F10.4, F7.4)
917 FORMAT(*OT(DEG C) =*, F5.1)
989 FORMAT(1H0, *DATA MISSING FOR ION PAIR*, I2, 1H., I2, 4X, A9, F2.0
1, A9, F2.0)
990 FORMAT(* ELECTRICAL NEUTRALITY VIOLATED. CHECK =*, F8.5)
END

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