THERMODYNAMIC ASPECTS OF MULTICOMPONENT

ELECTROLYTIC AEROSOLS

by

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For

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ABSTRACT

Considerable evidence exists for the presence of multicomponent aqueous electrolytic aerosols in the atmosphere. The size and chemical composition of these aerosols depend in large part on the interfacial equilibrium between the aerosol and surrounding gases, and correct description of condensation/evaporation on/from the particle requires knowledge of the thermodynamics at the interface.

Four models used for predicting the water activity and solute activity coefficients of electrolytic aerosols are examined in this study. The predictions of these models are compared to data of various electrolyte solutions, including data on $H_2SO_4-(NH_4)_2SO_4-H_2O$ and $(NH_4)_2SO_4-NH_4NO_3-H_2O$ systems. Particular emphasis is placed on model predictions for low water activities, which are important for aerosol modeling in arid regions.

Using the equilibrium chemistry for liquid phase oxidation of NO and NO_2, the characteristic parameters of a nitrate aerosol are predicted. In the final section, the size and chemical composition of an aerosol droplet exposed to SO_2, NO, NO_2, NH_3, H_2SO_4 and H_2O are predicted as a function of time. The gas phase oxidation of SO_2 to H_2SO_4 is included. For both cases, Bromley's model is used to predict the multicomponent thermodynamic data. The gas phase concentrations used are typical of those measured in the atmosphere.

CHAPTER 1

PROPERTIES OF SECONDARY AEROSOLS IN ARID REGIONS

Particulate matter is continuously generated and removed in air by different mechanisms. The physical and chemical properties of these particles are largely determined by the nature of the sources, both natural and anthropogenic, and the meteorology and the topography of the specific location.

Materials such as smoke and dust, directly emitted into the atmosphere in particulate form, are termed primary aerosols. On the other hand, particles generated in the atmosphere by gas-to-particle conversion are referred to as secondary aerosols. Formation from the gas phase tends to produce fine particles. Aerosols can be the cause of climatic changes and visibility degradation and may also be hazardous to human health. Such adverse effects associated with the aerosol behavior bear strong functionality to the size, concentration and chemical composition of these airborne particles. Therefore major efforts in urban aerosol studies are intended to gain a comprehensive understanding of the formation mechanisms, composition, growth rates and size distributions of the atmospheric aerosols.

Much work is done to measure and correlate the concentration of different elements and ionic species in urban atmospheric aerosols (Moyers, Ranweiler, Hopf and Korte, 1977; Gaarenstroom, Perone and Moyers, 1977; Sadasivan, 1980). These factor analysis techniques have been

instrumental in identifying the sources and interpreting gas to particle
conversion processes.

The chemical form of these species within the aerosol phase has
been a topic of investigation in recent years. Biggins and Harrison
(1979) identified specific chemical compounds like ammonium sulfate, lead
sulfate, sodium chloride and sodium sulfate in roadside aerosol samples.
High mass fraction of sulfates within the total aerosol mass was noted by
Tanner and Marlow (1977). These sulfates were found to be associated with
ammonium (NH_4^+) and hydrogen (H^+) ions. Hitchcock, Spiller and Wilson
(1980), Dzubay, Snyder, Reutter and Stevens (1979), Forrest, Garber and
Newman (1979) and Dawson (1978) have all identified and measured ionic
species, predominantly sulfate (SO_4^{-2}), ammonium (NH_4^+), nitrate (NO_3^-), hy-
drogen (H^+), chloride ($C\ell^-$), magnesium (Mg^{+2}) and sodium (Na^+) in atmo-
spheric aerosols. Metal chlorides were detected primarily in marine
aerosols (Hitchcock, Spiller and Wilson, 1980). Sadasivan (1980) proved
that only half the total sulfate in marine aerosols was from seasalt.

Oxides of nitrogen and sulfur may be oxidized to more stable
nitrate and sulfate species, respectively, either by gas phase photo-
chemical oxidation (Calvert, Bottenheim and Strausz, 1978; Altshuller,
1979; Sander and Seinfeld, 1976) or by liquid phase oxidation. Gas
phase oxidation results in the formation of sulfuric acid and nitric
acid molecules in vapor phase and these molecules subsequently condense
on the existing aerosol droplets or may cause the formation of new
particles by nucleation and growth (Yue, 1979). Both catalytic (Hegg
and Hobbs, 1978; Beilke and Gravenhorst, 1978) and non-catalytic (Hegg

and Hobbs, 1979) mechanisms have been proposed by different investigators to describe the liquid phase oxidation of sulfur dioxide. Relatively few workers have studied the liquid phase oxidation of oxides of nitrogen to nitrates (Peterson and Seinfeld, 1979; Orel and Seinfeld, 1977).

Though pH values of atmospheric aerosols reported by different workers (Hitchcock, Spiller and Wilson, 1980; Hegg and Hobbs, 1979) differ and range from 1 to 6, there is a general agreement that atmospheric sulfate aerosols are acidic in nature, and the bulk of the sulfate is partially or fully neutralized by ammonia (Charlson, Covert, Larson and Waggoner, 1978). Observations made by Kadowaki (1977) and Orel and Seinfeld (1977) agree in that the principal nitrate compound in coarse marine aerosols is sodium nitrate whereas submicron inland particles are dominated by ammonium nitrate.

All this experimental evidence leads us to conclude that secondary aerosols can be described chemically as multicomponent solutions of strong electrolytes. While inland aerosols are dominated by ammonium sulfate and ammonium nitrate, marine aerosols contain seasalts like sodium and magnesium chlorides in addition. Furthermore these aerosols are acidic in nature and contain small amounts of unneutralized sulfuric and nitric acids.

Ambient concentrations of ionic species in the arid southwestern U.S.A. have been measured by various workers (Moyers, Ranweiler, Hopf and Korte, 1977; Gaarenstroom, Perone and Moyers, 1977; Macias, Blumenthal, Anderson and Cantrell, 1980). Trijonis (1979) has analyzed 25 years of airport visibility data and 10 years of particulate data in the

southwest and concludes that historical decrease in visibility is caused by secondary aerosols dominated by sulfates and nitrates. The author (Trijonis, 1979) also notes that these secondary aerosols are formed in the accumulation size range (0.1-1.0 micron). Macias, Blumenthal, Anderson and Cantrell (1980) attribute as much as forty percent of the total scattering coefficient of light to ammonium sulfate.

Relative humidities in arid regions are low in general (can be less than ten percent) and undergo very wide variations. Henry and Hidy (1979) observed that sulfate variability was strongly correlated with relative humidity in regions where relative humidity fluctuated over a wide range of values. The mass fraction of water in a single aerosol droplet is directly related to the moisture content, i.e., relative humidity, of the surrounding air by phase equilibrium relationship. Low water vapor pressure of the surroundings will lead to relatively small concentration of water in the aerosol droplet which in turn implies higher concentrations of solutes, e.g., ammonium sulfate, ammonium nitrate, sulfuric acid and nitric acid.

Hygroscopic compounds like sulfuric acid exhibit monotonic growth curves, i.e., continuous absorption or desorption of water with changes in relative humidity. Binary salts like $(NH_4)_2SO_4$, NH_4HSO_4 and NH_4NO_3, extensively identified and measured in atmospheric aerosols, however, exhibit a step change behavior. These compounds suddenly absorb water when relative humidity exceeds a certain level and similarly suddenly release water when decreasing humidity falls below a certain level. These phenomena of sudden uptake and release of water are termed deliquescence and efflorescence, respectively. Corresponding relative

humidities are called deliquescence and efflorescence points. These two are not equal in general (Charlson, Covert, Larson and Waggoner, 1978; Tang, 1980). As the water activity of an aerosol droplet is directly related to the moisture content of the surrounding air by interfacial equilibrium relationships, separation of the solid phase may occur when the relative humidity reaches a value corresponding to the water activity of the saturated solution (Tang, 1976; Tang, 1980). Thus in contrast to multicomponent electrolytic aerosols in high humidity conditions, similar aerosols in arid regions exist at relatively high concentrations of solutes and under extreme conditions of humidities these aerosols may be saturated with or without the separation of solid phase.

It is possible to calculate the sizes and compositions of these multicomponent electrolytic aerosols if extensive multicomponent thermo-dynamic data are available. Such data are usually available for binary solutions only. Tang (1976, 1980) and Peterson and Seinfeld (1979) have stressed the need of adequate multicomponent thermodynamic information, at relatively high concentration of solutes, to accurately predict the sizes and compositions of atmospheric aerosols.

It is the purpose of this work, then, to find some accurate means of predicting multicomponent thermodynamic properties of electrolytic solutions. Further, we seek to prove the applicability of such a pro-cedure by comparisons with experimental data for multicomponent systems. The data to be compared will be for systems found to exist in the atmo-spheric aerosols or closely resembling them in terms of chemical proper-ties. Heavy emphasis is laid on predictions and comparisons at high

concentrations of solutes. Finally, the applicability of such an approach is illustrated for predicting the properties of atmospheric aerosols.

CHAPTER 2

THERMODYNAMIC CONCEPTS

There is considerable inconsistency in the notation used by
different authors in thermodynamic literature, and it is the purpose
of this chapter to establish a sound thermodynamic framework, free from
any inherent error or ambiguity. A brief review of common notation and
definitions is presented here and the physical significance of thermo-
dynamic parameters used in subsequent chapters is duly stressed.

Activity Coefficients of Electrolytes

For an ideal multicomponent phase, the chemical potential μ_i
of the ith component is given by

$$\mu_i = \mu_i^o + RT \ln x_i \qquad (1)$$

where x_i is the mole fraction of component i and μ_i^o its chemical
potential in some standard state.

Ideality of a solution implies the absence of any interactions
among the particles constituting it. The presence of long-range coulom-
bic interactions differentiates the solutions of electrolytes from those
of nonelectrolytes. For noneletrolytes, the long-range coulombic inter-
actions are nonexistent and the short-range interactions caused by
dipole-dipole or dispersion forces would become appreciable only for
small separation distances between the solute particles, i.e., when the
solute concentration is high. Though the coulombic interactions, due

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to their inverse proportionality to the interionic distance, would also decrease with the increasing separation distance (dilution), in general, for electrolytes the solute-solute interactions are stronger than those for nonelectrolytes. Moreover the solute-solvent interactions must also be strong for the formation of ions (Petrucci, 1971; Pass, 1973). Therefore for electrolytes, even in dilute solutions, we have a system of interacting constituents; ions with opposite charges and solvent molecules. Chemical potential changes for such a solution is obtained by using effective rather than true concentration in Eq. (1):

$$\mu_i - \mu_i^0 = RT\ln x_i f_i \tag{2}$$

where $x_i f_i$ is the "effective" concentration or the activity, a_i, of the component i and f_i is an empirical concentration correction factor called the activity coefficient of the component i, so that

$$a_i = x_i f_i \tag{3}$$

From Eqs. (1) and (2)

$$\left[\mu_i\right]_{Real} - \left[\mu_i\right]_{Ideal} = RT\ln f_i \tag{4}$$

The left hand side of Eq. (4) is the chemical potential change arising from the interactions (solute-solute and solute-solvent) in the solution, and activity coefficient, thus, is a measure of this change.

Activities and corresponding activity coefficients can be defined on three different scales of concentration measurement (Robinson and

Stokes, 1965):

Molal scale : $a(m) = \gamma m$

Molar scale : $a(c) = yc$

Mole fraction scale : $a(N) = fN$

where $a(m)$, $a(c)$ and $a(N)$ are activities on molal, molar and mole

fraction scales respectively, γ, y and f are corresponding activity

coefficients; m is the molality of solute in moles/kg of solvent,

c is molarity in moles/liter of solvent and N is mole-fraction (one

often uses x to denote the same quantity).

Standard State

The standard state for each scale is so chosen that the mean

ionic activity coefficient of the solute on that scale approaches unity

when the concentration is reduced to zero. This applies to every

temperature and pressure.

For solvent, the standard state is generally taken to be the pure

solvent at the temperature and pressure of the solution. A similar

standard state can not be chosen for solutes because most electrolytes

have very different physical and chemical properties in pure state.

For example some common electrolytes like ammonium sulfate, ammonium

nitrate and sodium chloride are solid and unionized at normal temperature

and pressure.

Mean Ionic Activity Coefficient

The activity coefficient of an individual ion, by definition,

is dependent upon the free energy changes when that species is added to

the solution. It would be impossible to measure such changes for an ionic species alone and the only quantity accessible to such measurements is the activity coefficient of an electrolyte as a whole, i.e., of at least two ionic species together. There is a need to conceptually relate the activity coefficient of an electrolyte in solution (experimentally measurable) to that of individual ionic species constituting it.

For an ionic solute yielding ν_1 cations and ν_2 anions on dissociation, the "mean ionic activity coefficient" is defined by:

$$\gamma_{\pm}^{\nu} = \gamma_1^{\nu_1} \gamma_2^{\nu_2} \tag{5}$$

where γ_1 and γ_2 are individual (ionic) activity coefficients and $\nu = \nu_1 + \nu_2$.

Geometric means are taken in the case of $\gamma_{\pm}$ because the effects of activity coefficient on free energy are multiplicative (Bockris and Reddy, 1970). For strong electrolytes the ionization is essentially complete and, even if it is not, it is conventional (Denbigh, 1971) to assume that $m_+ = \nu_+ m$ and $m_- = \nu_- m$. The activity coefficient, $\gamma_{\pm}$, thus estimated includes the effect of incomplete ionization or dissociation or any deviations from ideality.

Solvent Activity and Osmotic Coefficient

Activity of the solvent is defined by

$$\mu_A - \mu_A^O = RT \ln a_A \tag{6}$$

Also, we have

$$\mu_A = \mu_A^O(V) + RT \ln p_A \tag{7}$$

and

$$\mu_A^o = \mu_A^o(V) + RT\ln P_A \tag{8}$$

from the condition of vapor-liquid equilibrium for solution and pure solvent respectively. Here $\mu_A^o(V)$ is the chemical potential of the vapor in a standard state of solution temperature and one atmosphere pressure, p_A, is the solvent partial pressure over the solution and P_A its vapor pressure at the solution temperature.

From Eqs. (6), (7), and (8)

$$a_A = p_A/P_A \tag{9}$$

Vapor is assumed to be ideal so that fugacities can be replaced by the pressures.

Solvent activity is thus independent of concentration measurement scale.

The osmotic coefficient of the solvent is a logarithmic function of its activity. It is useful when the activity coefficient of the solvent differs from unity by a very small amount, making activity coefficient a poor indicator of deviations from ideality.

The "rational" osmotic coefficient, g, is defined by:

$$\ln a_A = g \ln N_A = -g \ln \left(1 + \frac{\nu m W_A}{1000} \right) \tag{10}$$

where a_A is the activity of the solvent and W_A is its molecular weight. On a molal scale, the osmotic coefficient is defined by:

$$\ln a_A = -\frac{\nu m W_A \phi}{1000} \tag{11}$$

The product νm (ν is the total moles of ions liberated by dissociation of one mole of solute and m is its molality) should be summed over all solutes for multicomponent solutions.

Mole Fraction

A conceptual difficulty arises when defining mole fractions of ionic solutes. It can be defined either as the ratio of total number of solute particles (ions) to the total number of ions plus molecules of solvent, or as the ratio of formula weights of solute to the total number of formula weights of solute ions plus solvent, i.e.,

$$N_B = \frac{\nu m}{\sum_i \nu m + 1000/W_A}$$

or,

$$N_B = \frac{m}{\sum_i \nu m + 1000/W_A}$$

The first definition is used throughout this work, although the relationship between the rational activity coefficient and the other representations is unaffected by this choice.

Ionic Strength and Ionic
Strength Fraction

The ionic strength is a measure of the electrical environment of ions in a solution. It is related to the concentrations as follows:

$$I = \frac{1}{2} \sum_i m_i Z_i^2 \tag{12}$$

where m_i is the concentration of the ith species and z_i is the formal charge on it. Summation is to be carried over all ionic species present in the solution.

Another very commonly used parameter is the ionic strength fraction, defined as

$$Y_B = \frac{I_B}{I} \tag{13}$$

where Y_B = ionic strength fraction of solute B

   I_B = ionic strength of solute B

and   I = total ionic strength.

The Gibbs-Duhem Equation

This equation restrains the manner in which the activity coefficients of the components may vary with temperature, pressure, and composition. Derived from the conditions of restraint on the partial molal quantities of a multicomponent solution, it can be written as (Smith and Van Ness, 1975):

$$-\frac{\Delta H}{RT^2} dT + \frac{\Delta V}{RT} dP = \sum_i x_i d\ln f_i \tag{14}$$

where T is the temperature, P the pressure and ΔH and ΔV are enthalpy and volume change of mixing, respectively. This equation must be satisfied for each phase of the system.

If we assume constant temperature and pressure, Eq. (14) simplifies to

$$\sum_i x_i d\ln f_i = 0 \tag{15}$$

While most activity and osmotic coefficient data are presented
on a molal scale, the Gibbs-Duhem equation, as evident, is written
employing "rational" thermodynamic quantities. For a solution contain-
ing more than one electrolyte, the two activity coefficients are related
by

$$f_\pm = \gamma_\pm (1 + 0.001 \, W_A \Sigma \nu m) \tag{16}$$

where

ν = number of moles of ions formed by the ionization of one
mole of solute

W_A = mulecular weight of the solute

m = moles of solute per kg of solvent

and $f_\pm$, $\gamma_\pm$ = mean rational and molal activity coefficients
respectively.

Notation convention of standard electrochemistry texts is used
in this work with one exception of x replacing N for mole fraction.

CHAPTER 3

EQUILIBRIUM ASPECTS OF AEROSOL GROWTH

As noted in the earlier chapter, it is widely accepted that
atmospheric aerosols are dominated by aqueous solutions of sulfates
(H_2SO_4, $(NH_4)_2SO_4$ etc.) and nitrates (HNO_3, NH_4NO_3 etc.) Any attempt
to study the formation and growth of such secondary aerosols from pri-
mary pollutant gases, in terms of characterization of size and composi-
tion, would require an understanding of both kinetic and equilibrium
steps involved in this process. In this chapter attention is focused
on equilibrium mechanisms, both phase and chemical, included in overall
aerosol growth model. Different methods to estimate the thermodynamic
parameters required to calculate chemical and phase equilibria are
elucidated.

The Interfacial Equilibrium

Solute Gases

Henry's law is assumed to hold and a linear relationship
exists between the concentration of an absorbed gas and its surface
pressure. This simplifying assumption will not introduce any error for
atmospheric chemistry problems because pollutant gases are present in
parts per million or parts per billion concentrations, ensuring
liquid phase concentrations small enough to justify the use of
Henry's law.

The Solvent

Aerosol particles composed of water soluble compounds undergo changes in both size and chemical composition as a consequence of exposure to gases and water vapor in the atmosphere. The changes which take place in aerosol size are dictated by the interfacial equilibrium for the solvent. Koehler (1936) used Raoult's law to describe this equilibrium, but such a relationship would hold only for very high humidities (i.e., $x_{water} \cong 1$). Moreover, the effect of curvature on surface pressure cannot be neglected for small particles (less than 1.0 μm), which dominate tropospheric aerosols and cause visibility degradation and adverse health effects. Two prime factors influencing the vapor-liquid equilibrium for water are discussed here.

The Kelvin Effect. This effect tends to increase the vapor pressure above a curved surface. It is represented for a binary system by

$$P_{ci} = P_{fi} \exp\left(\frac{2\sigma\overline{V_i}}{rRT} \left[1 + \frac{X_j}{\overline{V_i}} \frac{d\overline{V_i}}{dX_j} - \frac{3}{2} \frac{X_j}{\sigma} \frac{d\sigma}{dX_j}\right]\right) \qquad (17)$$

where

P_{ci} = vapor pressure of i over a droplet of radius r, atmospheres

P_{fi} = vapor pressure of i over a flat surface, atmospheres

σ = droplet surface tension, dyne/cm

$\overline{V_i}$ = partial molar volume of species i, liter/mole (liquid phase)

X_j = mole fraction of species j ($X_j = 1 - X_i$)

Suitable derivation of this relationship could be found in Nair and Vohra (1975).

If density and surface tension changes are independent of droplet composition, Eq. (17) is simplified to:

$$P_{ci} = P_{fi} \exp\left(\frac{2\sigma \overline{V_i}}{rRT}\right) \tag{18}$$

This assumption may hold good for dilute solutions of electrolytes. For aerosols containing organic compounds, even in trace concentrations, this may be a highly erroneous assumption due to surfactant properties of many organic compounds.

The Solute Effect. While the Kelvin effect accurately relates the surface pressure over a curved surface to that over a flat surface with identical composition, the solute effect accounts for the presence of solutes and establishes a relationship between the surface pressure of the solvent in pure state and in a solution of given composition by

$$P_{fi} = f_i x_i P_{sat_i} \tag{19}$$

where

P_{sat_i} = equilibrium saturation pressure of i over a flat

surface at tempterature T of solution

f_i = activity coefficient of i in the liquid phase.

Here the vapor phase is assumed to be an ideal gas.

For aqueous aerosols Eq. (19) can be written as

$$P_{fw} = a_w P_{sat_w} \tag{20}$$

Finally Eq. (20) can be substituted in Eq. (18) to obtain an expression that relates the surface pressure of water above a curved surface to conditions within the aerosol droplet:

$$p_w = a_w P_{sat_w} \exp\left(\frac{2\sigma\overline{V_i}}{rRT}\right) \tag{21}$$

Surface pressure, p_w, can be related to the relative humidity and hence it is possible to predict equilibrium size for a given relative humidity provided that water activity is known as a function of composition of the multicomponent electrolyte solution in the aerosol. The range of values over which water activity must be known (as a function of composition) typically lies between 1 (dilute solutions) and 0.1 or lower, depending on the fractional relative humidity of the surroundings.

The Chemical Equilibrium

Liquid phase oxidation of sulfur dioxide and oxides of nitrogen into sulfate and nitrate respectively and the subsequent neutralization of these compounds by atmospheric ammonia is commonly modeled as a series of equilibrium reaction steps and a rate controlling kinetic step (Scott and Hobbs, 1967; Orel and Seinfeld, 1977). Information on species activity coefficients is required in order to properly define these equilibrium conditions. This is particularly true for aerosols in arid environments, where aqueous electrolytic solutions must be sufficiently concentrated (therefore high ionic strengths) to remain in equilibrium with the low water vapor pressure of the surroundings.

While thermodynamic data are available for many binary aqueous electrolyte solutions over a reasonable range of solute concentrations,

extensive data on water activity and solute activity coefficients for multicomponent electrolytes are not available. It is necessary, therefore, to utilize a thermodynamic model to predict multicomponent water activities and species activity coefficients from available binary data.

Both solute-solute interactions and solute-solvent interactions affect the water activity and solute activity coefficients of multi-component electrolyte solutions. Many of the more comprehensive models (Reilly, Wood and Robinson, 1971; Pitzer, 1973; Scatchard, Rush and Johnson, 1970) consider the nonidealities of both these interactions. However, specification of interaction parameters for these models requires multicomponent data which are simply not available in general. While assumption of ideality for both solute-solute and solute-solvent interactions in electrolytic solutions would obviously lead to gross inaccuracies in the prediction of thermodynamic quantities, it may be possible to accurately characterize these quantities by correctly describing solute-solvent interactions while assuming ideal solute-solute interactions. Simply, this approach accounts for the nonidealities experienced in binary electrolytes between the solute and solvent, but neglects any additional interactions incurred by "combining" binary electrolytic solutions to form a multicomponent system. Models developed under this assumption require activity data for all binary pairs of solute-solvent type in the multicomponent system, but do not require any information on interactions between the solutes themselves. Intuitively this assumption would hold up best for dilute solutions, which for atmospheric aerosols implies high humidity conditions. The applicability

of such an assumption for concentrated electrolyte solutions (low humidities) remains to be shown. By utilizing models presently available to predict activity coefficients and water activities for multicomponent electrolytes, and comparing these predictions to the data available (usually ternary data at best), some confidence can be placed on the use of these models for atmospheric aerosols containing acids and ammonium sulfates and nitrates.

A comparative and comprehensive study of a number of models predicting water activities has been reported by Sangster and Lenzi (1974). They report on models of Reilly, Wood, and Robinson (1971), Robinson and Bower (1965), Meissner and Kusik (1973) and Zdanovskii, Stokes and Robinson (1936, 1966) (RWR, RB, MK and ZSR respectively). All these models neglect solute-solute interactions, and predict either water activity or osmotic coefficients for multicomponent electrolytes. Their results allow them to make the following observations:

1. There appears no obvious advantage in using the more complicated RWR and MK models over the RB and ZSR models.

2. MK does poorly for electrolytes of unequal charges (e.g., $MgSO_4$ and NaCl). The RWR model actually reduces to the MK model for electrolytes of same valence type.

3. For common-ion electrolytic solutions, RB holds a slight advantage over ZSR. Electrolyte solutions with no common ion are better represented by ZSR.

As mentioned earlier, a knowledge of species activity coefficients is imperative in solving equilibrium chemical reaction equations for the composition of an aerosol droplet. Some of the earlier workers (Scott and Hobbs, 1967; Beilke, Lamb, and Muller, 1975; Freiberg, 1976) have used concentrations rather than activities in their equilibrium calculations. This would restrict the application of such analysis to only ideal (hence $\gamma_{i,s} = 1$) solutions which in turn implies very low concentration of chemical species. Some recent studies (Peterson and Seinfeld, 1979, 1980; Beyak and Peterson, 1980) have significantly overcome this limitation by including activity coefficients in chemical equilibrium equations. These coefficients were computed from Davies approximation which is

$$\log_{10}\gamma_Z = -AZ^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right) \tag{22}$$

where

Z = ionic charge

A = 0.5085 mole$^{\frac{1}{2}}$-kg$^{-\frac{1}{2}}$ for water.

This equation is valid up to ionic strengths of 0.5 moles-kg^{-1}.

Davies approximation is an empirical modification of the well-known Debye-Huckel limiting law and assumes that the activity coefficients do not depend on the particular ionic species but only on their valence type. Moreover all these studies (Peterson and Seinfeld, 1979, 1980; Beyak and Peterson, 1980) predicted concentrations significantly higher than 0.5 moles-kg^{-1} and sometimes as high as 6.7 moles-kg^{-1}.

Some work has been done in recent years to predict the activity coefficients of electrolytes in multicomponent solutions of relatively high ionic strengths. Notable among them are Lietzke and Stoughton (1972), Meissner and Kusik (1972) and Bromley (1972, 1973). Lietzke and Stoughton propose a simple equation (hereafter referred to as LS(I)) for species activity coefficients that utilizes binary data for each electrolyte at the total ionic strength of the solution. Meissner and Kusik's formulation, derived from Bronsted's theory of specific ionic interactions, is more rigorous in that it utilizes the binary data of not only electrolytes present in the solution but of all possible electrolytes that can be formed by a combination of various cations and anions present in the solution. This takes into account all possible binary ionic interactions between the ions of unlike charges but does assume the interactions between ions with like charges to be negligibly small. Bromley (1973) has proved that the equations proposed by Meissner and Kusik (1972) involve an implicit assumption of equality of charges for all ions of like charge (i.e., all the negative ions have one charge and all the positive ions have the same or another charge) and proposed a similar but more involved equation. Seemingly two isolated problems of water activity estimation and solute activity coefficients prediction can be reduced to one by realizing that the calculation of water activity from models predicting solute activity coefficients is possible through the Gibbs-Duhem equation. It would be useful, therefore, to investigate models predicting activity coefficients of solutes, to estimate water activities using these predicted activity coefficients and the Gibbs-Duhem

equation, and to compare these results to available multicomponent data. We can also review the accuracy of two simple methods for predicting water activities, namely the ZSR model and another model proposed by Lietzke and Stoughton (1974) for the prediction of osmotic coefficients of multicomponent solutions (hereafter referred to as LS(II)). These models cannot provide us with estimates of solute activity coefficients, however.

Here we utilize the models of Lietzke and Stoughton (1972) and Bromley (1973) to predict the activity coefficient of each electrolyte in a multicomponent aqueous solution of electrolytes.

Lietzke and Stoughton Model

The Lietzke and Stoughton (1972) model (LS(I)) is written as:

$$\frac{1}{|z_i^+ z_i^-|} \log \gamma_i = \frac{1}{|z_i^+ z_i^-|} \log \gamma_i^o$$

$$+ \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{Y_j}{2} \left(\frac{1}{|z_j^+ z_j^-|} \log \gamma_j^o - \frac{1}{|z_i^+ z_i^-|} \log \gamma_i^o \right)$$

(23)

where z^+ and z^- represent the charges on the cation and anion respectively, γ_i is the mean ionic activity coefficient of the ith component in a mixture of n electrolytes with a common ion; superscript o implies activity coefficient values in binary state at the total ionic strength of the multicomponent solution and Y_j is the ionic strength fraction of jth component.

Many methods of activity coefficient prediction for multicomponent electrolyte solutions use the activity data of each component in the "pure" state (i.e., aqueous solution). Usually, the method of least squares is employed to correlate the functional dependence of the activity coefficient of each component in the pure state with its binary concentration in the ion-component treatment. This involves the determination of coefficients relating pure state activity coefficients to corresponding concentrations and later these coefficients are combined to predict the activity coefficient of each component in a multicomponent electrolyte solution. In contrast Eq. (23) uses the binary activity coefficient values of each electrolyte at the total ionic strength of the mixture directly.

For an aqueous solution of two electrolytes Eq. (23) simplifies to

$$\frac{1}{|z_1^+ z_1^-|} \log \gamma_1 = \frac{1}{|z_1^+ z_1^-|} \log \gamma_1^{\,o}$$

$$+ \frac{Y_2}{2} \left(\frac{1}{|z_2^+ z_2^-|} \log \gamma_2^{\,o} - \frac{1}{|z_1^+ z_1^-|} \log \gamma_1^{\,o} \right) \tag{24}$$

If all the ionic species were of the same valence type, the charges (i.e., z_1^+, z_2^+ etc.) would disappear from Eq. (24), and the resultant expression is similar to an equation proposed by Harned and Owen (1958) which follows from Guggenheim's treatment of the theory of specific ion interactions.

Although this model is purely empirical, its authors claim (Lietzke and Stoughton, 1972) their results for a number of ternary and quaternary solutions are consistent with values predicted with more elaborate ion-component models. In most cases, results of Eq. (23) agreed within a few percent of these more elaborate models. In this work, we go a step further. With Eq. (23) and the Gibbs-Duhem Eq. (15), water activities of multicomponent (in this case ternary) electrolyte solutions are estimated. These estimates are compared to available data, where available, and the applicability of this approach to atmospheric electrolytic aerosols is discussed.

For a ternary electrolyte solution, Eq. (15) can be rearranged and integrated to yield:

$$\int_a^b \partial \ln f_3 = \int_a^b - \left[\frac{x_1}{x_3} \left(\frac{\partial \ln f_1}{\partial x_1} \right)_{x_2} + \frac{x_2}{x_3} \left(\frac{\partial \ln f_2}{\partial x_1} \right)_{x_2} \right] \partial x_1 \qquad (25)$$

where, a and b are lower and upper limits of integration respectively and this operation (differentiation and subsequent integration) has to be carried out at constant mole fraction of component 2.

Two steps are involved in the estimation of water activities of a multicomponent electrolyte solution:

1. Computation of ternary activity coefficients of electrolytes from binary data and Eq. (23).

2. Numerical differentiation and integration to obtain water activities from Eq. (25).

We can therefore compare both calculated solute activity coefficients and water activities to experimental data for these parameters.

Bromley's Model

This model, proposed for ionic strengths up to 6, is given by:

$$\log \gamma_{12} = -\frac{A_{\gamma} |Z_1 Z_2| I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} + \frac{|Z_1 Z_2|}{Z_1 + Z_2} \left[\frac{F_1}{Z_1} + \frac{F_2}{Z_2} \right] \quad (26)$$

where

$$F_1 = Y_{21} \log\gamma_{12}^{O} + Y_{41} \log\gamma_{14}^{O} + Y_{61} \log\gamma_{16}^{O} + \ldots$$

$$+ \frac{A_{\gamma} I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} \left[Z_1 Z_2 Y_{21} + Z_1 Z_4 Y_{41} + Z_1 Z_6 Y_{61} \ldots \right] \quad (27)$$

and

$$F_2 = X_{12} \log \gamma_{12}^{O} + X_{32} \log \gamma_{32}^{O} + \ldots$$

$$+ \frac{A_{\gamma} I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} \left[Z_1 Z_2 X_{12} + Z_3 Z_2 X_{32} + \ldots \right] \quad (28)$$

with

$$Y_{21} = \frac{\bar{Z}_{12}^2 m_2}{I} = \left(\frac{Z_1 + Z_2}{2} \right)^2 \frac{m_2}{I} \quad (29)$$

and

$$X_{12} = \frac{\bar{Z}_{12}^2 m_1}{I} = \left(\frac{Z_1 + Z_2}{2} \right)^2 \frac{m_1}{I} \quad (30)$$

The cations are designated by the subscripts 1,3,5, etc. and anions by 2,4,6, etc. The terms Z_1 and Z_2 use absolute value of the charge irrespective of its sign.

For the prediction of properties of water, the author (Bromley, 1973) has treated the multicomponent electrolytic solution as a solution

of a single complex salt and defined an effective interaction parameter

B, as

$$B = -\frac{4\frac{4\Sigma\Sigma B_{ij} \bar{Z}_{ij}^2 \nu_i \nu_j}{\nu \sum_K \nu_K Z_K^2}}{\nu \sum_K \nu_K Z_K^2}$$

(31)

where i and j summations are to be carried over all cations and anions

respectively and

$$\nu = \sum_K \nu_K$$

Here K designates all ionic species and ν_K is the stoichiometric number
of ions of species K.

Bromley has tabulated B_{ij} values for a large number of electro-
lytes and these can be used to estimate the effective parameter "B",
which in turn is used in the osmotic coefficient expression for binary
solution:

$$1-\phi = 2.303A_\gamma |Z^+Z^-| \frac{I^{\frac{1}{2}}}{3} \sigma(\rho I^{\frac{1}{2}})$$

$$- 2.303(0.06 + 0.6B)|Z^+Z^-| \frac{I}{2} \psi(aI) - 2.303B \frac{I}{2}$$

(32)

where the functions σ and ψ are defined by

$$\sigma(\rho I^{\frac{1}{2}}) = \frac{3}{(\rho I^{\frac{1}{2}})^3} \left[1 + \rho I^{\frac{1}{2}} - \frac{1}{1 + \rho I^{\frac{1}{2}}} - 2 \ln (1+\rho I^{\frac{1}{2}})\right]$$

(33)

and

$$\psi(aI) = \frac{2}{aI} \left[\frac{1+2aI}{(1+aI)^2} - \frac{\ln(1+aI)}{aI}\right]$$

(34)

respectively and $\rho = 1.0$; $a = 1.5/|Z^+Z^-|$; $A_\gamma = 0.511 \text{ Kg}^{\frac{1}{2}} \text{ mole}^{-\frac{1}{2}}$ at $25°C$ and

$$|Z^+Z^-| = \frac{\Sigma \, \nu_K Z_K^2}{\Sigma \, \nu_K} \tag{35}$$

The author has successfully employed this method for estimating properties of seawater.

In the next section we employ these models to predict multi-component thermodynamic properties and compare the results to available data.

CHAPTER 4

MODEL PREDICTIONS AND COMPARISONS
WITH PUBLISHED DATA

Again, the purpose of this study is to determine which thermo-
dynamic model is most appropriate for describing chemical and inter-
facial equilibria for growing and reacting atmospheric electrolytic
aerosols, and to subsequently employ this model for aerosol growth
studies in low humidity environments. Here we compare the predictions
forwarded by the models previously discussed to data on selected aqueous
electrolyte solutions.

The prediction of solute activity coefficients is necessary in
aerosol growth calculations because of the ionic equilibrium dependence
on these coefficients. Knowledge of these activity coefficients be-
comes all the more important in an arid environment, where an aqueous
electrolytic solution must be sufficiently concentrated to remain in
equilibrium with the low water vapor pressure of its surroundings.
Previous work by Peterson and Seinfeld (1979, 1980) and Beyak and
Peterson (1980) has shown that the nonideality of equilibrium condi-
tions as represented by the solute activity coefficients must be in-
cluded.

Interfacial equilibrium of an aerosol droplet is strongly
dependent upon its water activity. Under low humidity conditions
equilibrium water contents of such aerosol droplets are small and thus

water activity is significantly less than one. It would range between 1 and 0.1 or lower depending upon relative humidity. Due to large departures from ideality (i.e., $a_w = 1$) water activity must not only be known accurately for correct description of interfacial equilibrium but must also be included in the chemical equilibrium equations.

Two types of comparisons have been made in the present work:

1. Comparisons of solute activity coefficient calculated from Eq. (23) and from Eq. (26) with published data.

2. Comparisons of water activities estimated from Eqs. (23) and (25) and from Eq. (32) with published data. For completeness, comparison is also made to the ZSR and LS(II) models.

The ZSR model, commonly used in previous aerosol growth calculations (Peterson and Seinfeld, 1980; Beyak and Peterson, 1980; Tang, 1976) is given by

$$1 = \sum_i \frac{m_i}{m_{bi}(a_w)} \tag{36}$$

where m_i is the molality of component i in the multicomponent solution and $m_{bi}(a_w)$ is the molality in the binary state at the desired water activity, a_w, of the multicomponent solution.

The LS(II) model predicts the osmotic coefficient, ϕ_m, of a multicomponent solution by

$$\phi_m = \frac{\sum_i \nu_i m_i \phi_i}{\sum_i \nu_i m_i} \tag{37}$$

where ν_i is the number of ions released by the complete dissociation of one molecule of component i, m_i is its molality, and ϕ_i is the osmotic coefficient of the binary solution of component i at the total ionic strength of the multicomponent solution.

Experimental measurements of γ_{HCl} for aqueous HCl-KCl solutions were made by Hawkins (1932) for relatively high ionic strengths of 3-4 moles Kg^{-1}. Comparison of these measurements to γ_{HCl} calculated from Eqs. (23) and (26) is presented in Fig. 1. Relative error is typically less than 5% for both Eq. (23) and Eq. (26) and the linearity noted by Hawkins between $\log \gamma_{HCl}$ and m_1 is evident. It should also be noted that Eq. (23) and Eq. (26) provide as good a comparison to the data as the more sophisticated ion-interaction model of Guggenheim (1955), as shown by Sengupta, Pal, and Chakravarti (1977).

Khoo, Lim and Chan (1979) have used cell EMF measurements to evaluate the acid activity coefficient, γ_{HBr}, for aqueous HBr-BaBr$_2$ solutions. They also calculated interaction parameters for use in Pitzer (1975) and Scatchard (1970) models, and used these models to estimate γ_{BaBr_2}. Figures 2 and 3 compare these measured and calculated values for activity coefficients to those predicted by Eq. (23) and by Eq. (26). Typical percentage errors in predicting γ_{HBr} and γ_{BaBr_2} from Eq. (23) are 5 and 7 percent respectively. Equation (26) is somewhat more accurate and error is never more than one percent. For both Eq. (23) and Eq. (26), at any given ionic strength, the error decreases with increasing ionic strength ratio.
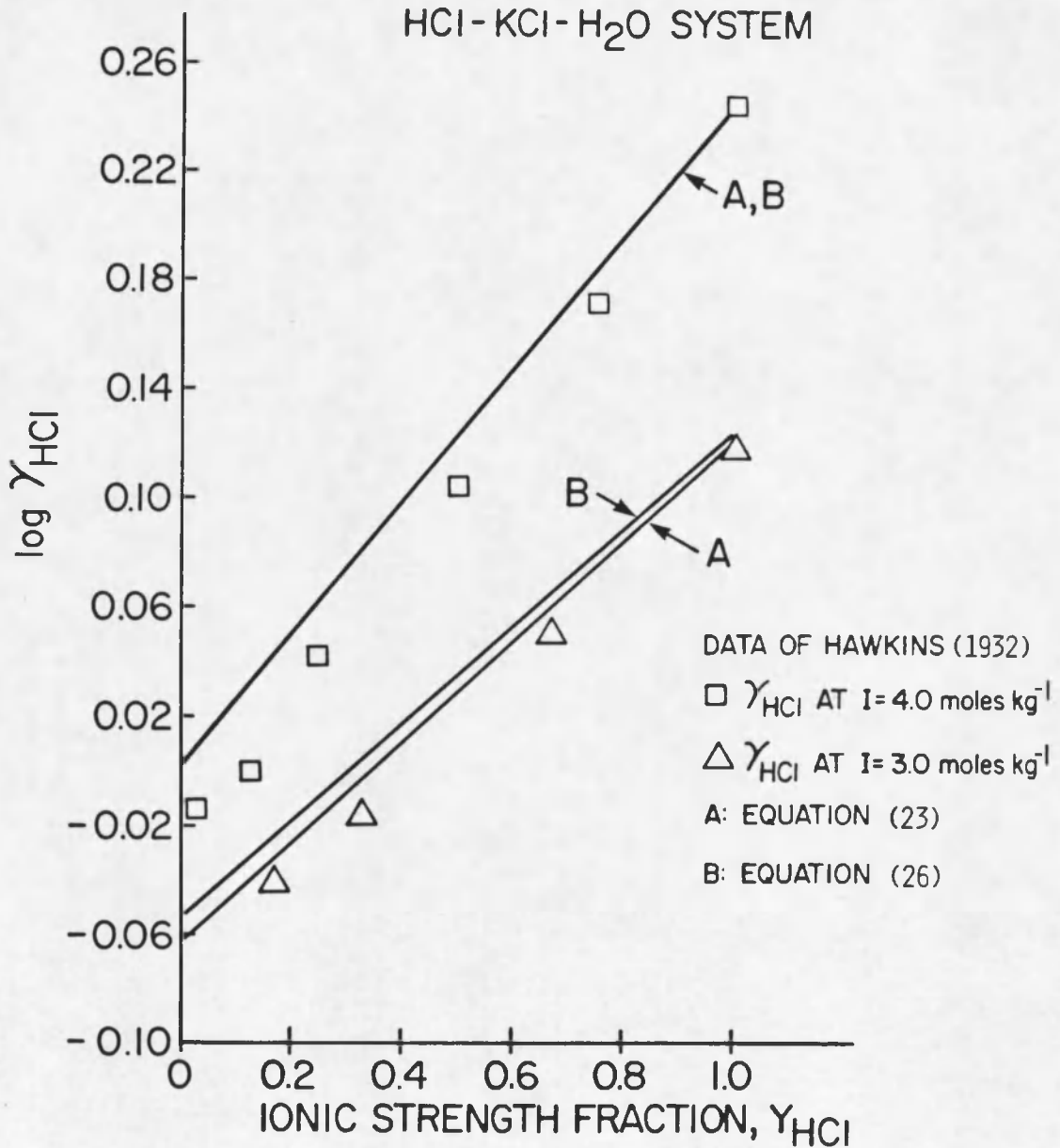
Figure 1. Activity coefficients for HCl vs. ionic strength fraction
of HCl in the HCl-KCl-H_2O system. Data of Hawkins (1932),
predictions of Equations (23) and (26).

HBr – BaBr₂ – H₂O SYSTEM
Data of Khoo et al·(1979)

○ γ_HBr at I = 1.0 moles – kg⁻¹
△ γ_HBr at I = 1.5 moles – kg⁻¹
□ γ_HBr at I = 2.0 moles – kg⁻¹
——— EQUATION [23]
– – – – EQUATION [26]
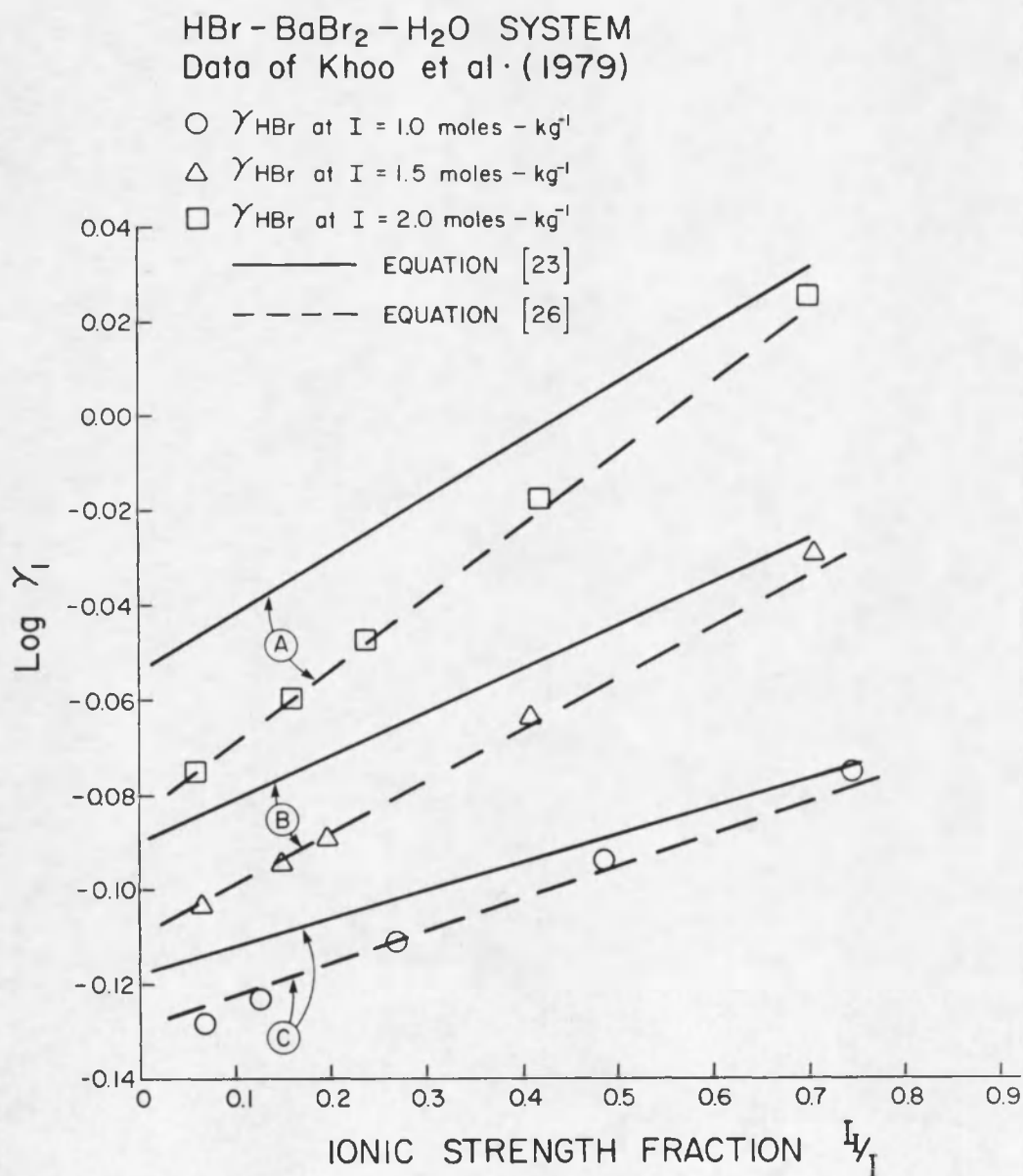
Figure 2.   Activity coefficients for HBr vs. ionic strength fraction
            of HBr in the HBr-BaBr₂-H₂O system. Data of Khoo, Lim and
            Chan (1979), predictions of Equations (23) and (26) for ionic
            strengths of (A.) 2.0; (B.) 1.5; (C.) 1.0 moles kg⁻¹.
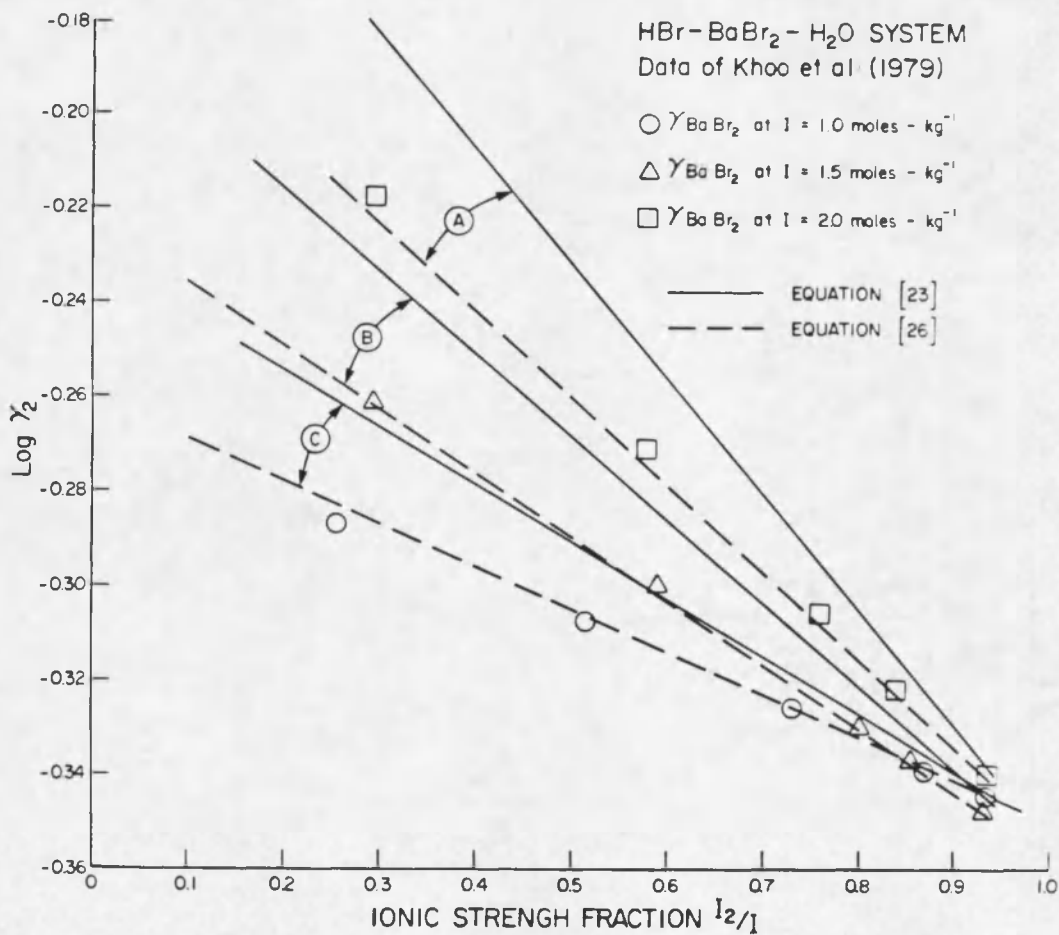
Figure 3. Activity coefficients for $BaBr_2$ vs. ionic strength fraction of $BaBr_2$ in the $HBr-BaBr_2-H_2O$ system. Data of Khoo, Lim and Chan (1979), predictions of Equations (23) and (26) for ionic strengths of (A.) 2.0; (B.) 1.5; (C.) 1.0 moles Kg $^{-1}$

Water activities are calculated from Eq. (23) with the help of
the Gibbs-Duhem equation (25) and from Eq. (32). In previous aerosol
growth calculations (Peterson and Seinfeld, 1980; Beyak and Peterson,
1980; Tang, 1976), multicomponent water activities have been estimated
using the ZSR model (Eq. 36), which is much simpler to use than either
of the two methods mentioned here. The LS(II) model has been used for
the accurate prediction of the osmotic coefficients of multicomponent
electrolyte solutions at ionic strengths as high as 9.0 moles-Kg^{-1},
and this model is also considered. The results of Eqs. (36) and (37)
are included in water activity comparisons, even though these models
do not predict solute activity coefficients, as previously discussed.

The applicability of these models for predicting water activi-
ties is illustrated in Figs. 4, 5, 6, and 7, where the predicted vs.
measured water activities for various ternary electrolytic systems are
presented. Obviously, a single measured value of water activity in a
ternary system does not uniquely define the solution composition, but
the purpose of these figures is simply to show the relative accuracy
of the models discussed here. Table 1 describes the specific systems
presented in Figs. 4 through 7, including the range of ionic strength
ratios, water mole-fraction, maximum ionic strength and minimum water
activity for these systems. All measurements are for a temperature of
25°C. It should be noted that the LS(I) model is proposed for solutions
with a common ion only, which accounts for the somewhat larger devia-
tions seen with the data of the KCl-Na$_2$SO$_4$ system. Results of Figs. 4
through 7 are summarized in Fig. 8 to provide an overall comparison of
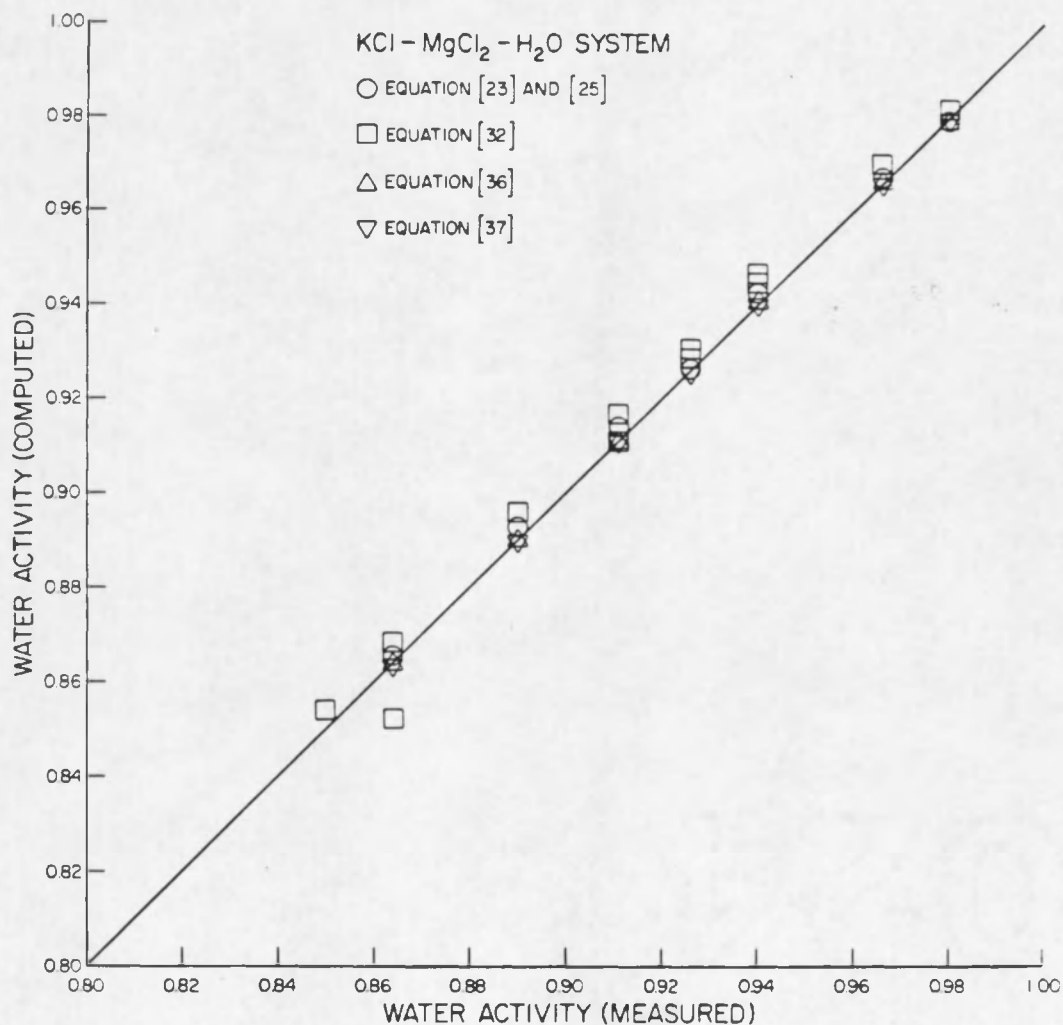
Figure 4. Comparison of experimentally determined water activity vs.
           computed water activity using predictions of Equation (23)
           with (25), Equation (32), Equation (36), Equation (37) and
           data of Padova and Saad (1977) for the system KCl-MgCl$_2$- H$_2$O.
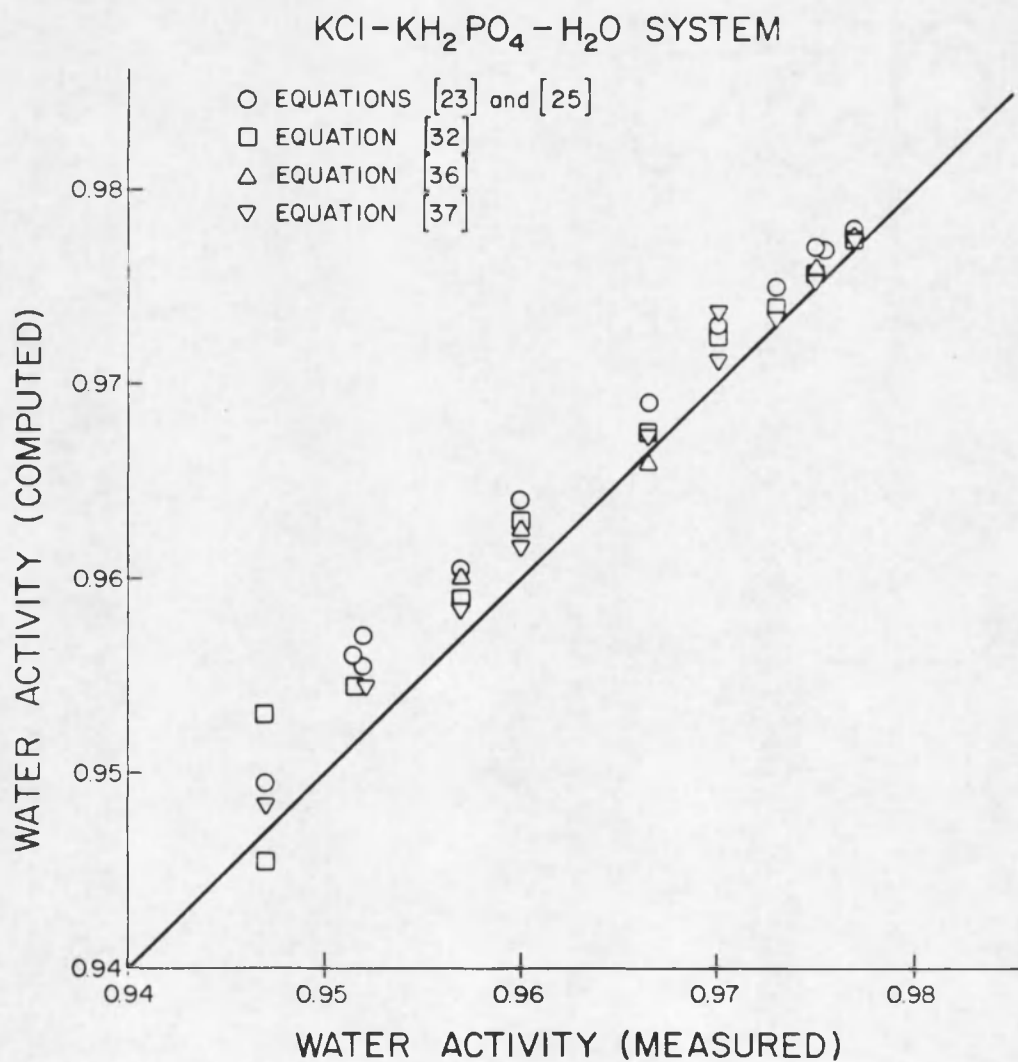
Figure 5. Comparison of experimentally determined water activity vs. computed water activity using predictions of Equation (23) with (25), Equation (32), Equation (36), Equation (37) and data of Childs, Downes and Platford (1974) for the system $KCl-KH_2PO_4-H_2O$.
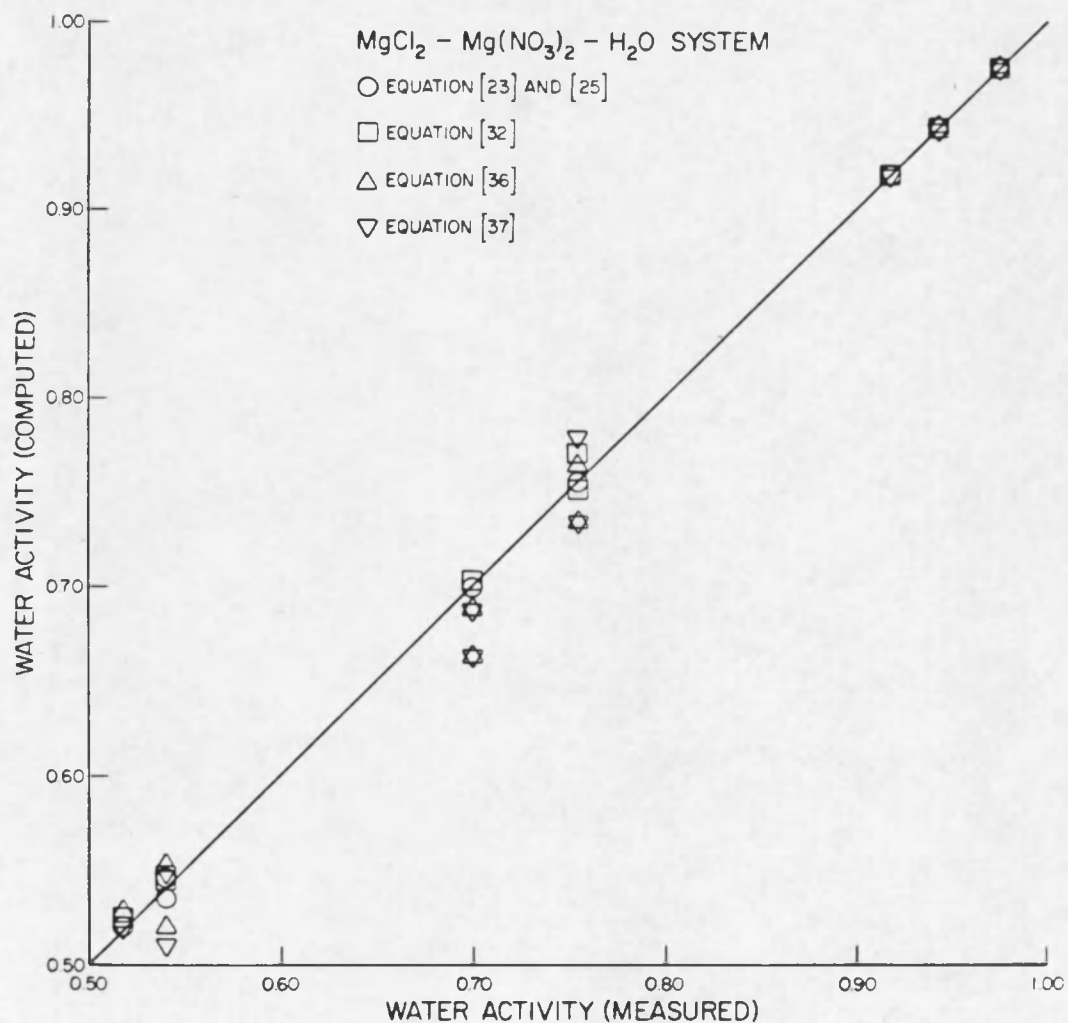
Figure 6. Comparison of experimentally determined water activity vs. computed water activity using predictions of Equation (23) with (25), Equation (32), Equation (36), Equation (37) and data of Platford (1971) for the system $MgCl_2-Mg(NO_3)_2-H_2O$.
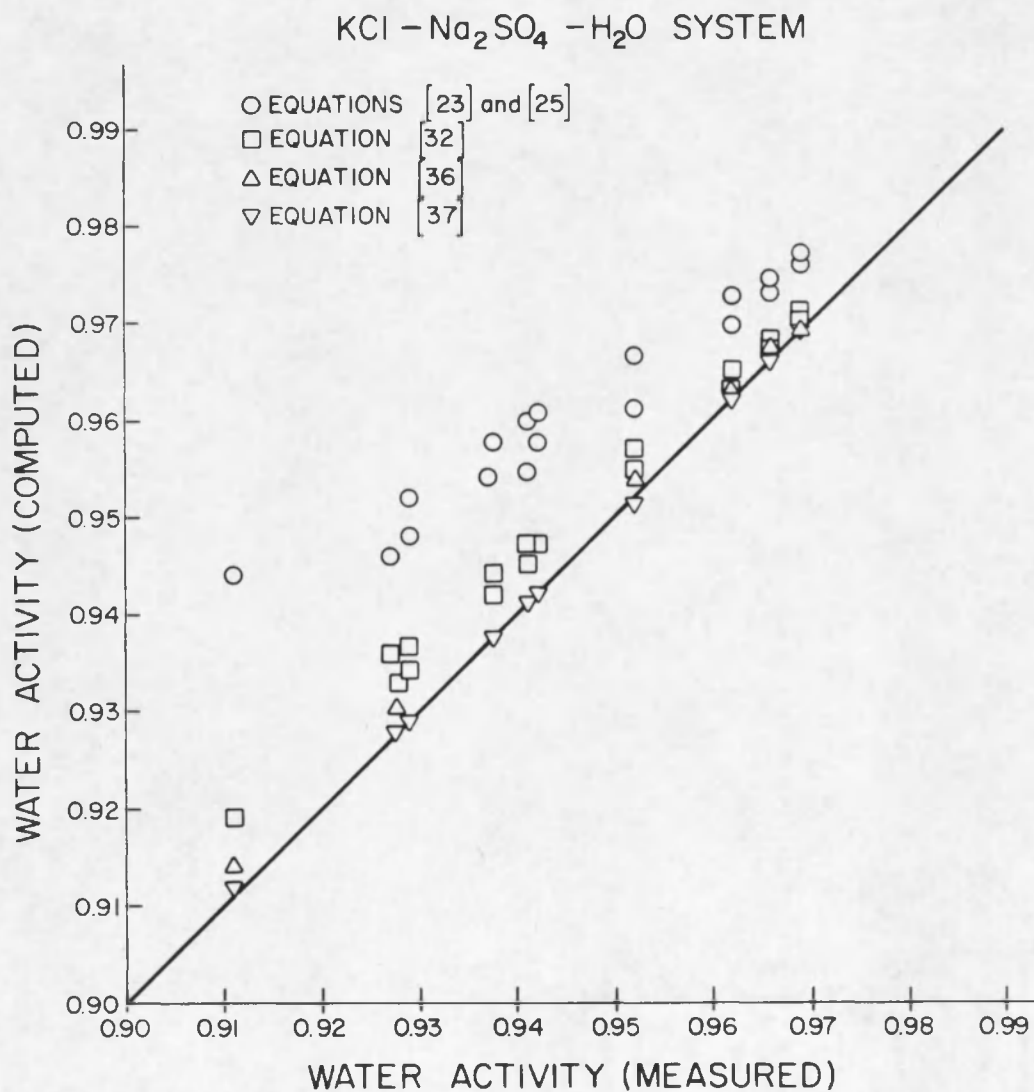
Figure 7. Comparison of experimentally determined water activity vs. computed water activity using predictions of Equation (23) with (25), Equation (32), Equation (36), Equation (37) and data of Robinson, Platford and Childs (1972) for the system $KCl-Na_2SO_4-H_2O$.

Table 1

Experimental Parameters for Electrolytes Presented in Figure 8

Electrolyte		Range of Ionic Strength Ratio (min/max)		Range of Water Mole Fraction (min/max)	Maximum Ionic Strength (mole/kg)	Minimum Water Activity	Maximum % Error in Water Activity Estimates				Reference
1	2	Y_1	Y_2	x_w	I	a_w	Bromley	LS(I)	ZSR	LS(II)	
KCl	$MgCl_2$	0.25/0.84	0.16/0.75	0.88/0.98	5.64	0.86	−1.39	0.41	0.98	0.077	(a)
KCl	KH_2PO_4	0.23/0.74	0.26/0.78	0.94/0.99	2.1	0.95	0.62	0.52	0.35	0.35	(b)
$MgCl_2$	$Mg(NO_3)_2$	0.14/0.87	0.13/0.86	0.79/0.97	14.1	0.52	3.76	1.02	5.13	8.09	(c)
KCl	Na_2SO_4	0.37/0.63	0.37/0.64	0.91/0.97	4.39	0.92	0.95	3.57	0.32	2.02	(d)

(a) Padova and Saad 1977
(b) Childs, Downes and Platford 1974
(c) Platford 1971
(d) Robinson, Platford and Childs 1972
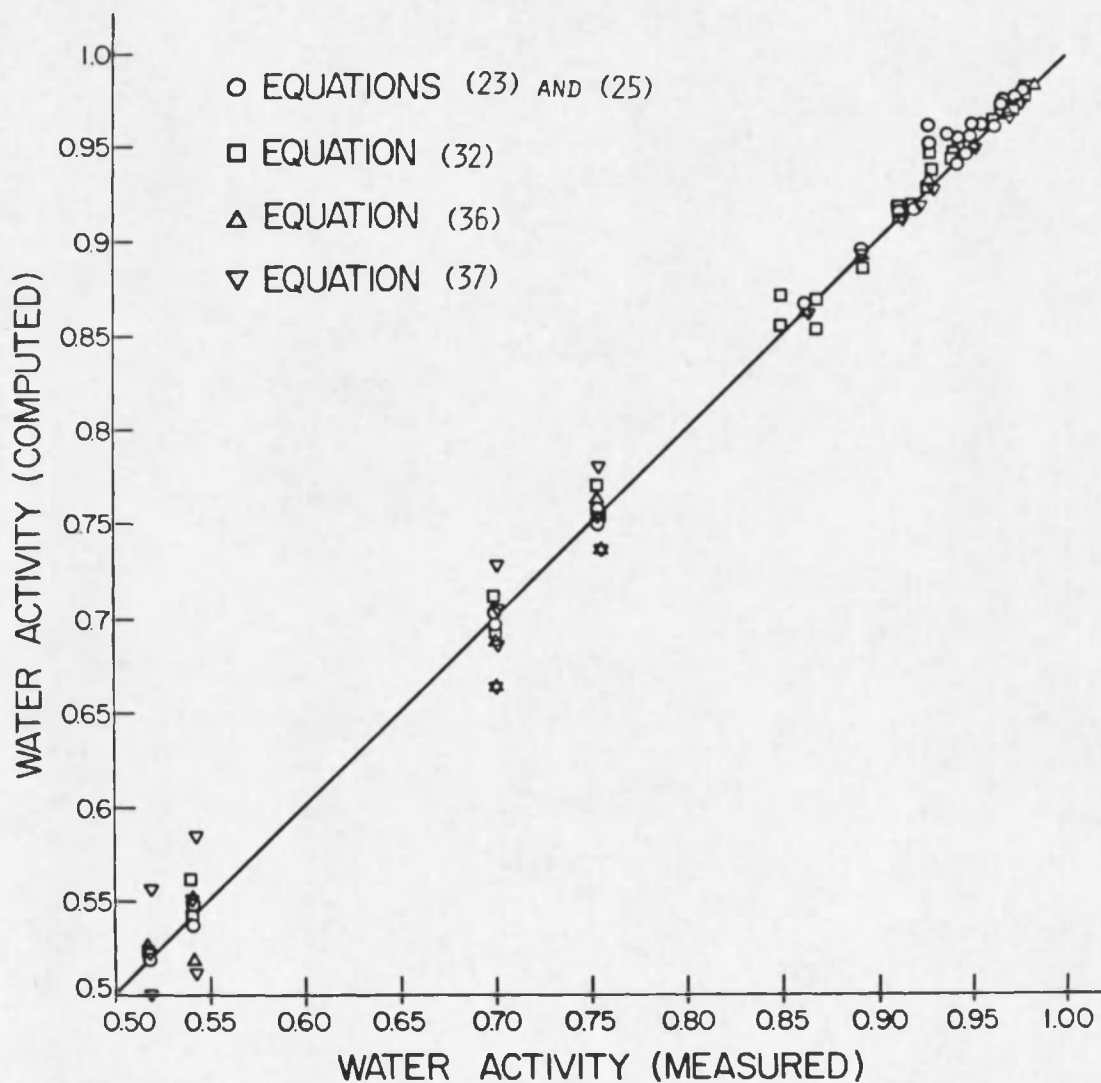
Figure 8. Comparison of experimentally determined water activity vs. computed water activity using predictions of Equation (23) with (25), Equation (32), Equation (36), Equation (37), for ternary electrolytic systems defined in Table 1.

the relative applicability of different models. While the systems presented in Fig. 8 and Table 1 are not purported to represent ambient electrolytic aerosols, they are nonetheless typical electrolytic systems, and provide a reasonable test of model effectiveness. Moreover most of the ionic species considered are found to be present in atmospheric aerosols (Hitchcock, Spiller and Wilson, 1980; Forrest, Garber and Newman, 1979).

Of greater interest from an atmospheric aerosol standpoint are the comparisons made for the $H_2SO_4-(NH_4)_2SO_4-H_2O$ and $(NH_4)_2SO_4-NH_4NO_3-H_2O$ systems. The data from these systems quite possibly represent conditions found in atmospheric aerosols.

Isopiestic measurements of Frolov and Nasonova (1974) are used for the comparisons made for the $H_2SO_4-(NH_4)_2SO_4-H_2O$ system and the results are shown in Table 2. It should be noted that the measurements of Frolov and Nasonova for the binary system $H_2SO_4-H_2O$ are significantly different from those reported in Robinson and Stokes (1965), and used in this present work. As a result, the error in prediction decreases as we move from a binary $H_2SO_4-H_2O$ system (i.e., $Y_1=1.0$) to lower ionic strength ratios of H_2SO_4. Emons and Hahn (1970) have made vapor pressure measurements of saturated ternary solutions of $(NH_4)_2SO_4$ and NH_4NO_3 at different temperatures. It is not possible to use the ZSR, LS(I) or LS(II) models to estimate water activities for comparison with these measurements. The measurements were made for ionic strengths ranging from 17 to 25, and all these models require binary data for $(NH_4)_2SO_4-H_2O$ and $NH_4NO_3-H_2O$ systems for these ionic strengths. At $25°C$, the aqueous solution of $(NH_4)_2SO_4$ saturates at an approximate

Table 2

Comparison of Predicted vs. Measured Water Activity for
the $H_2SO_4-(NH_4)_2SO_4-H_2O$ System

I moles/Kg	Y_1	Water Activity (Measured)	Water Activity (LS(I))	Water Activity (Bromley)	Water Activity (ZSR)	Water Activity (LS(II))	Average Percent Absolute Error			
							LS(I)	Bromley	ZSR	LS(II)
2.2341	1.0000	0.9543	0.9724*	0.9724*	0.9724*	0.9724*				
3.0471	0.7150	0.9543	0.9715	0.9584	0.9627	0.9624				
3.5127	0.5974	0.9543	0.9665	0.9519	0.9570	0.9568	1.42	0.90	0.84	0.84
4.026	0.5000	0.9543	0.9610	0.9445	0.9515	0.9509				
2.868	1.0000	0.9418	0.9636*	0.9636*	0.9636*	0.9636*				
3.6729	0.7816	0.9418	0.9620	0.9496	0.9535	0.9534				
4.2693	0.6503	0.9418	0.9565	0.9410	0.9500	0.9461	1.51	1.14	1.03	0.99
4.7196	0.5819	0.9418	0.9520	0.9344	0.9415	0.9406				
5.28	0.5000	0.9418	0.9460	0.9261	0.9350	0.9340				
4.896	1.000	0.8870	0.9318*	0.9318*	0.9318*	0.9318*				
5.6394	0.8720	0.8870	0.9310	0.9206	0.9225	0.9217				
6.3348	0.7815	0.8870	0.9240	0.9099	0.9130	0.9118	3.90	2.50	2.36	2.34
7.5135	0.6504	0.8870	0.9110	0.8911	0.8980	0.8966				
8.2245	0.5819	0.8870	0.9030	0.8795	0.8890	0.8861				
8.9700	0.5000	0.8870	0.8940	0.8671	0.8805	0.8771				
5.2800	0.5000	0.9418	0.9460	0.9261	0.9350	0.9340				
5.6394	0.3475	0.9418	0.9430	0.9206	0.9330	0.9319				
5.7060	0.2677	0.9418	0.9430	0.9196	0.9335	0.9326	0.18	1.75	0.67	0.75
5.7222	0.1766	0.9418	0.9430	0.9193	0.9350	0.9343				
5.268	0.0000	0.9418	0.9426*	0.9426*	0.9426*	0.9426*				

Table 2 (Continued)

7.404	0.5000	0.9190	0.9180	0.8929	0.9050	0.9026				
7.9749	0.4014	0.9190	0.9130	0.8836	0.9000	0.8975				
7.6533	0.2715	0.9190	0.9190	0.8889	0.9090	0.9071	0.32	2.82	1.23	1.41
7.848	0.1689	0.9190	0.9220	0.8857	0.9100	0.9085				
7.092	0.0000	0.9190	0.9236*	0.9236*	0.9236*	0.9236*				
8.688	0.5000	0.9123	0.8950	0.8718	0.8849	0.8818				
9.3729	0.4231	0.9123	0.8920	0.8604	0.8780	0.8744				
9.8538	0.3512	0.9123	0.8880	0.8522	0.8747	0.8707	1.75	4.78	2.78	3.08
9.6507	0.2675	0.9123	0.8930	0.8557	0.8820	0.8789				
9.4065	0.1821	0.9123	0.8980	0.8598	0.8895	0.8873				
8.0910	0.0000	0.9123	0.9124*	0.9124*	0.9124*	0.9124*				

---

*Binary data as reported in Robinson and Stokes (1965).

molality of 5.8 (I=17.40) and hence no activity data are available for higher ionic strengths.

The values of constant B in Eq. (32), reported by Bromley (1973), are recommended for ionic strengths up to 6. In Figs. 9 and 10 we have made a comparison for experimental values of water activities for the systems $(NH_4)_2SO_4-H_2O$ (Robinson and Stokes, 1965) and $NH_4NO_3-H_2O$ (Wu and Hamer, 1969) with those predicted by B values in Table 1 of Bromley (1973) and Eqs. (31) and (32). It is evident that these predictions are grossly inaccurate and call for a better representation of binary data. On the basis of suggestions made by the author (Bromley, 1973), the following alternatives for better data representation were attempted:

(a.) Estimation of new values of B by fitting the entire range of available binary data to Eq. (32) by least squares. Curve B in Figs. 9 and 10 depicts these fits.

(b.) Inclusion of a second order term in ionic strength in the expression for solute activity coefficient which now reads:

$$\log \gamma_\pm = -\frac{A_\gamma |z^+z^-| I^{\frac{1}{2}}}{1 + \rho I^{\frac{1}{2}}} + \frac{(0.06+0.6B)|z^+z^-| I}{(1 + aI)^2} + BI + CI^2 \quad (38)$$

The expression for osmotic coefficient is modified to:

$$1 - \phi = 2.303 \, A_\gamma |z^+z^-| \, \frac{I^{\frac{1}{2}}}{3} \, \sigma(\rho I^{\frac{1}{2}})$$

$$-2.303(0.06 + 0.6B)|z^+z^-| \, \frac{I}{2} \, \psi(aI)$$

$$-2.303B \, \frac{I}{2} - 4.606C \, \frac{I^2}{3} \quad (39)$$
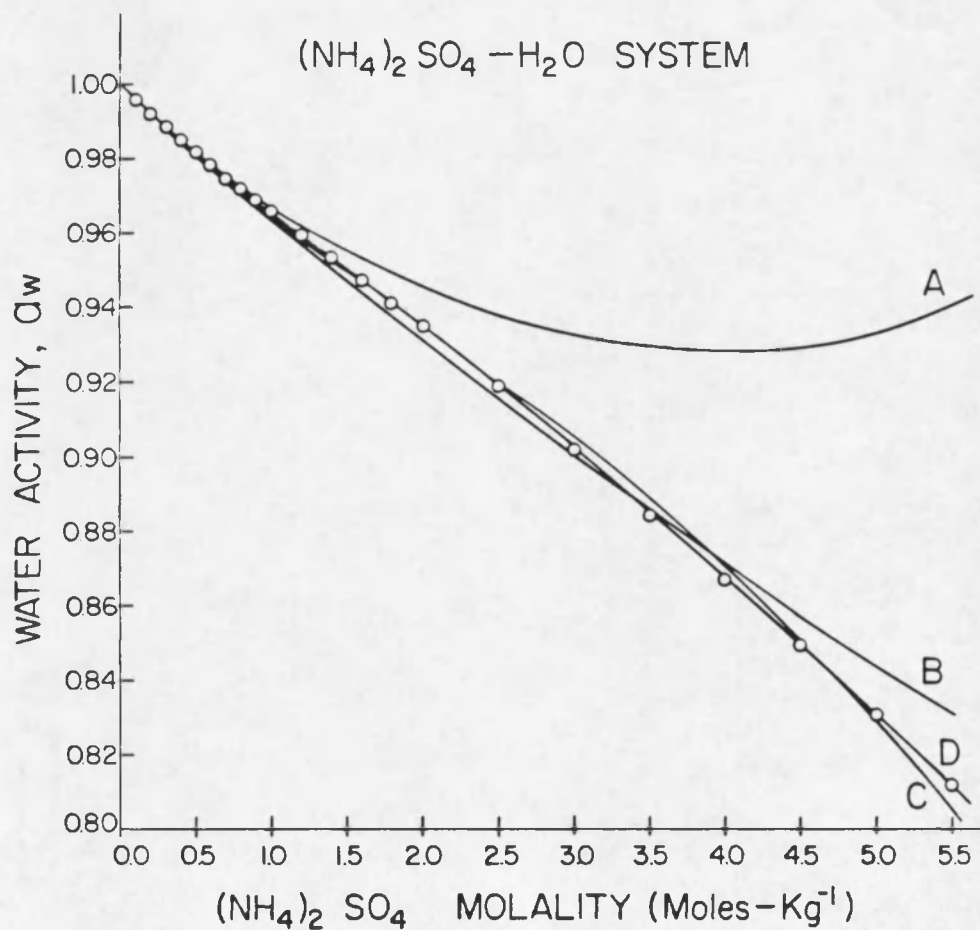
Figure 9. Water activity vs. $(NH_4)_2SO_4$ molality for binary $(NH_4)_2SO_4-H_2O$ system. Data reported in Robinson and Stokes (1965) and model predictions from (A.) Equation (32) and parameter B reported in Bromley (1973); (B.) Equation (32) and parameter B by least squares; (C.) Equation (39) and parameters B and C by least squares; (D.) Equation (41) and parameters B, C and D by least squares.
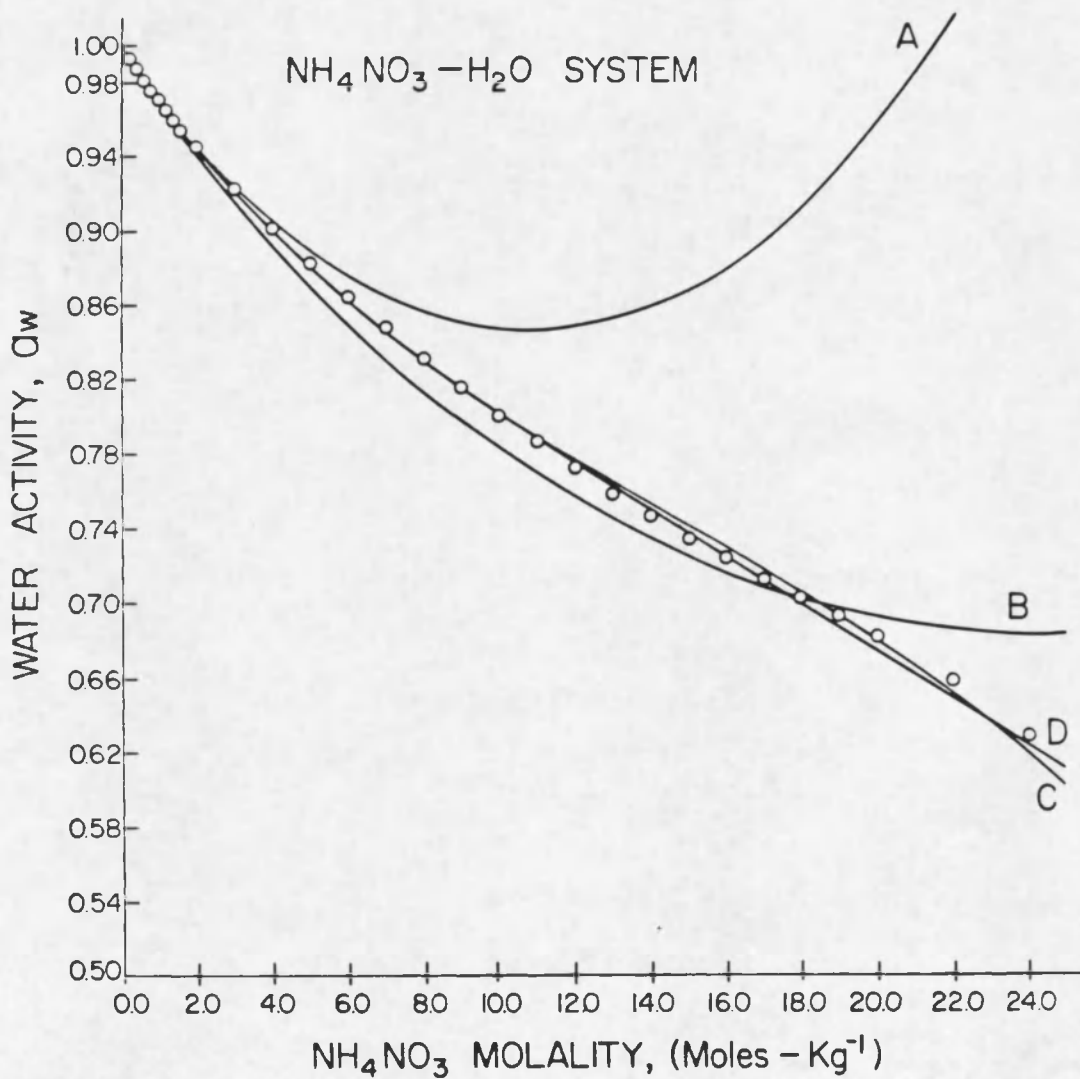
Figure 10. Water activity vs. NH_4NO_3 molality for binary $NH_4NO_3-H_2O$ system. Data reported in Wu and Hamer (1969) and model predictions from (A.), (B.), (C.) and (D.) described in Figure 9.

Constants B and C are estimated by the fit of binary data to
Eq. (39) by least squares. Results of such fits are shown
in Figs. 9 and 10 (Curve C).

(c.) Inclusion of both second and third order term in ionic strength
in the expression for solute activity coefficient. Equation (38)
now reads:

$$\log \gamma_\pm = - \frac{A_\gamma |z^+ z^-| I^{\frac{1}{2}}}{1 + \rho I^{\frac{1}{2}}} + \frac{(0.06 + 0.6B)|z^+ z^-| I}{(1 + aI)^2}$$

$$+ BI + CI^2 + DI^3 \tag{40}$$

and consequently (39) is changed to

$$1 - \phi = 2.303 A_\gamma |z^+ z^-| \frac{I^{\frac{1}{2}}}{3} \sigma(\rho I^{\frac{1}{2}})$$

$$-2.303(0.06 + 0.6B)|z^+ z^-| \frac{I}{2} \psi(aI)$$

$$-2.303 \, B \frac{I}{2} - \frac{4.606 CI^2}{3} - \frac{6.909 DI^3}{4} \tag{41}$$

As apparent in Figs. 9 and 10 (Curve D), this yields the best fit to
binary data for both systems.

Table 3 and Fig. 11 summarize the comparisons of ternary water
activity data of Emons and Hahn (1970) with:

1. The results of Eq. (32) and binary B values reported by Bromley
    (1973),

2. The results of Eq. (32) and binary B values estimated in this
    work as described in (a),

3. The results of Eq. (39) and binary B and C values estimated in
    this work as described in (b) and

Table 3

Comparison of Predicted vs. Measured Water Activity for the $(NH_4)_2SO_4-NH_4NO_3-H_2O$ System

I (Mol/Kg)	Y_1	a_w experimental (Emons and Hahn, 1970)	$a_w^{(1)}$	$a_w^{(2)}$	$a_w^{(3)}$	$a_w^{(4)}$
17.46	1.00	0.801	0.939 (17.23)	0.853 (6.49)	0.801 (0.00)	0.812 (1.37)
18.06	0.874	0.767	0.936 (22.03)	0.833 (8.60)	0.769 (0.26)	0.786 (2.48)
19.64	0.629	0.727	0.939 (29.16)	0.833 (14.58)	0.694 (-4.54)	0.733 (0.83)
20.76	0.543	0.700	0.950 (35.71)	0.795 (13.57)	0.653 (-6.71)	0.714 (2.00)
23.25	0.386	0.655	0.992 (51.45)	0.754 (15.11)	0.559 (-14.66)	0.691 (5.50)
23.84	0.360	0.662	1.005*	0.750 (13.29)	0.538 (-18.73)	0.691 (4.38)
24.54	0.303	0.657	1.022*	0.742 (12.94)	0.507 (-22.83)	0.690 (5.02)
25.02	0.242	0.651	1.037*	0.734 (12.75)	0.482 (-25.96)	0.689 (5.84)
25.91	0.207	0.625	1.065*	0.730 (16.80)	0.449 (-28.16)	0.702 (12.32)
25.30	0.00	0.615	1.052*	0.704 (14.47)	0.427 (-30.52)	0.659 (7.15)

Numbers in parentheses denote the % error in a_w.

1. Water activities computed from binary B's reported in Table 1 of Bromley (1973) and Equation (32).
2. Water activities computed from binary B's computed by the fit of binary data to Equation (32) by least squares over the entire range of binary activity data available.
3. Water activities computed from binary B's and C's computed by the fit of binary data to Equation (39) by least squares over the entire range of binary activity data available.
4. Water activities computed from binary B's, C's and D's computed by the fit of binary data to Equation (41) by least squares over the entire range of binary activity data available.

*Physically impossible values.
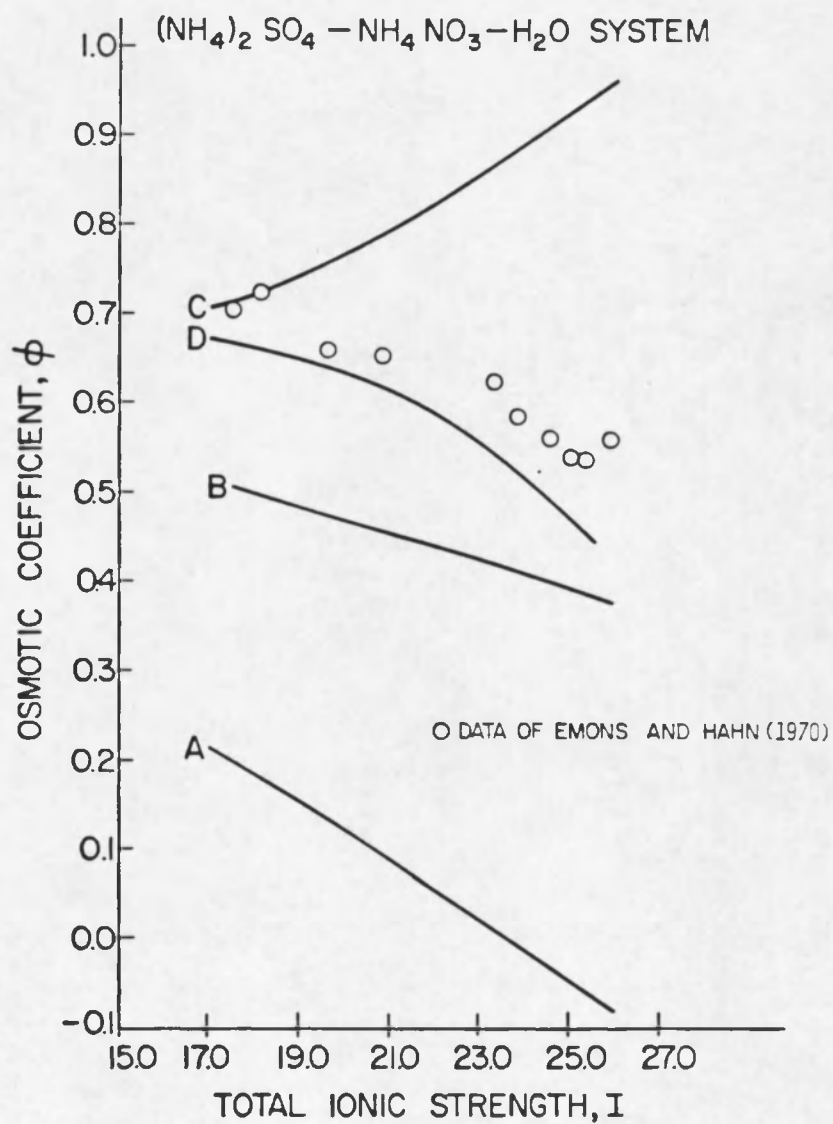
Figure 11. Osmotic coefficient vs. total ionic strength for ternary
$(NH_4)_2SO_4-NH_4NO_3-H_2O$ system. Data of Emons and Hahn (1970)
and model predictions from (A.), (B.), (C.) and (D.)
described in Figure 9 for fit of binary data.

4. The results of Eq. (41) and binary B, C and D values estimated
in this work as described in (c).

Complex constants C and D are obtained by using binary constants
and equations similar to Eq. (31).

Equation (41) gives the best estimates with maximum error less
than 13%. Finally we have used Eqs. (40) and (41) to generate activity
data for another system of importance in atmospheric aerosol studies,
namely the aqueous H_2SO_4-HNO_3 system. Osmotic coefficient data for
these two binary systems (H_2SO_4-H_2O and HNO_3-H_2O) were fit to Eq. (41)
to yield the values of the constants B, C, and D for each system. For
nitric acid, the maximum error in water activity estimation up to an
ionic strength of 28.0 was less than 1%. Equation (41) well represents
binary activity data for aqueous H_2SO_4 up to ionic strengths as high as
84.0 (maximum error in water activity estimation is 5%).

Figure 12 presents the activity coefficients for H_2SO_4 and HNO_3
for the H_2SO_4-HNO_3-H_2O system as a function of mole fraction. Figure 13
presents the water activity as a function of solute mole fraction for the
same system.

Summary and Conclusions

In this work we have compared the applicability of four differ-
ent models for estimation of activity coefficients and water activities
of multicomponent aqueous electrolytes. Particular emphasis has been
placed on each model's ability to estimate these parameters for a wide
range of ionic strengths, since equilibrium conditions of atmospheric
aerosols in low humidity environments require such application.
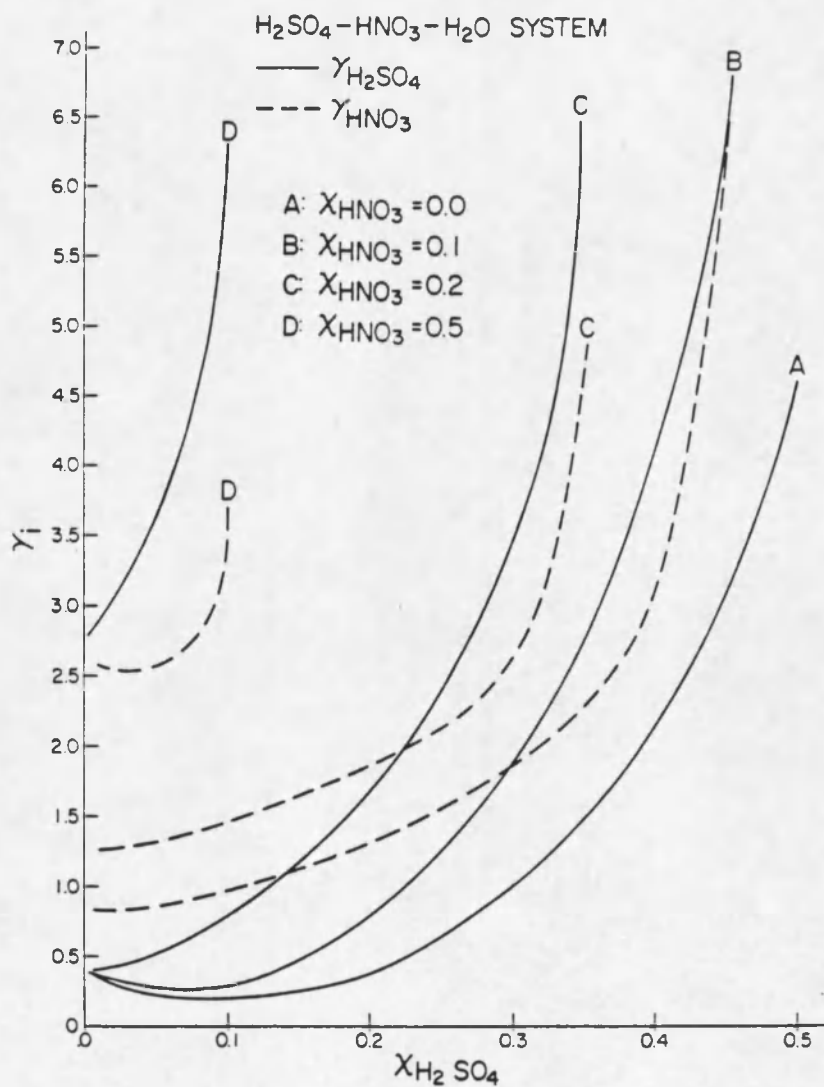
Figure 12. Activity coefficients for H_2SO_4 and HNO_3 in $H_2SO_4-HNO_3-H_2O$ system vs. mole fraction H_2SO_4 (mole fraction HNO_3 as a parameter), as estimated by Equation (40) and parameters B , C and D by least squares fit of binary data.
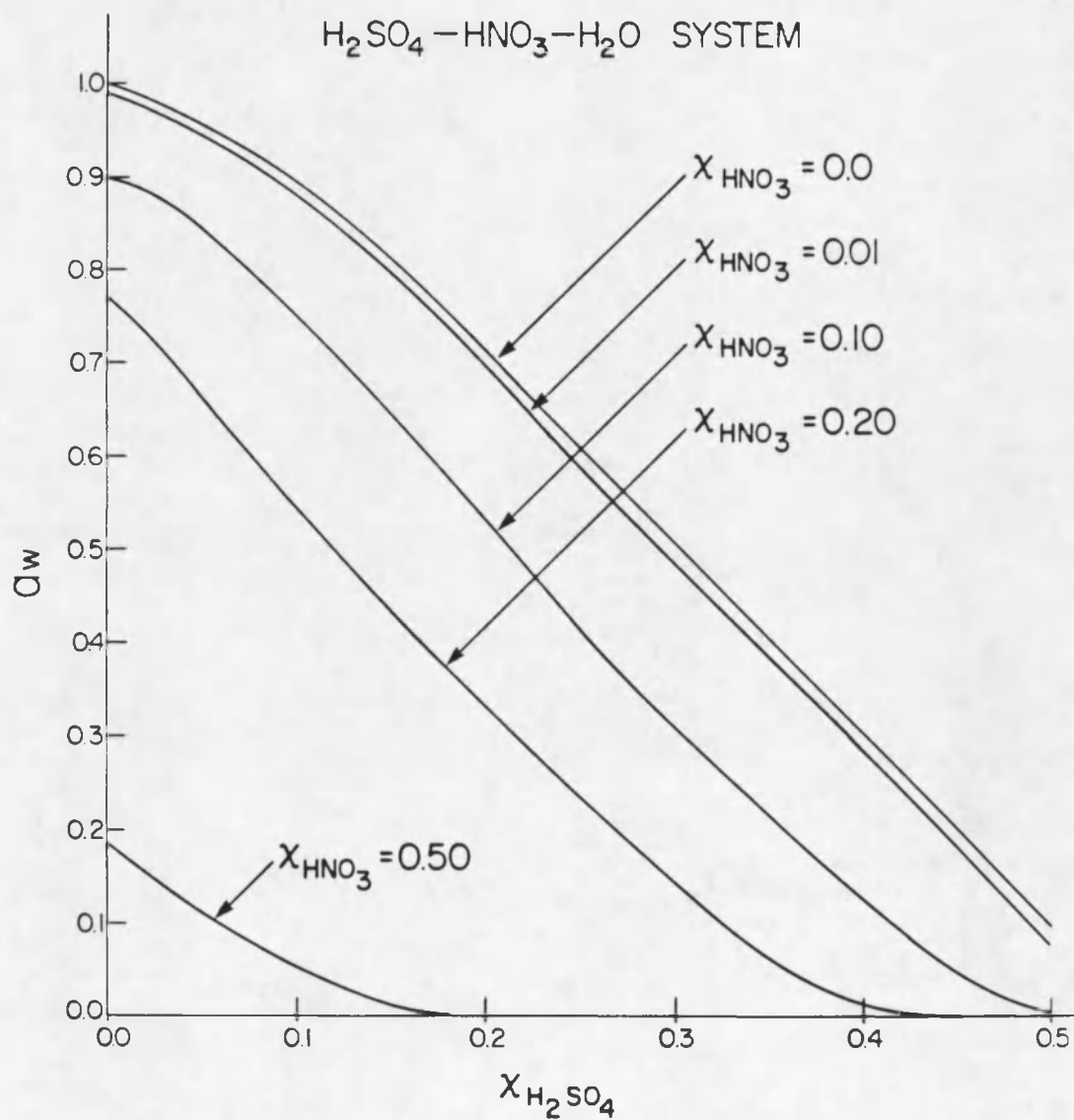
Figure 13. Water activity in $H_2SO_4-HNO_3-H_2O$ system vs. mole fraction H_2SO_4 (mole fraction HNO_3 as a parameter), as estimated by Equation (41) and parameters B , C and D by least squares fit of binary data.

Successful comparisons have been made between model predictions and experimental data for a number of ternary systems, including two systems important in atmospheric aerosol modeling.

With proper use, there are no major differences in accuracy among the models considered. However, there are major differences in applicability, ease of use and the information provided among the models.

The ZSR and LS(II) models are relatively easy to use, but provide estimates for water activity only. These models require water activity data for all binary systems present up to the total ionic strength of the multicomponent solution. This can cause problems not only due to the paucity of such data, but because electrolytes in a multicomponent system are often at total ionic strength that would exceed the saturation point in the binary system, and as such no binary data would exist. This is true particularly for aerosols containing $(NH_4)_2SO_4$ in low humidity environments.

The LS(I) model is strictly proposed for common-ion electrolytes only. It also suffers from the requirement of binary data at the total ionic strength of the multicomponent system. The model provides estimates of both solute activities and water activity, but the latter is obtained only by numerical differentiation and integration of the Gibbs-Duhem equation. This would become extremely cumbersome with more than three components, and is not amenable for water activity estimation at specified composition.

The Bromley model provides estimates of both solute activities and water activity without the necessity to numerically integrate the Gibbs-Duhem equation. Rather than rely on the actual binary activity data, this model utilizes parameters estimated from these data. Binary data are not required up to the total ionic strength of the multicomponent system, but more accurate predictions are available by estimating the binary parameters for ionic strengths over the most likely range of interest.

It appears that by appropriate improvement of the form of the Bromley model (e.g., Eqs. (38) through (41)) and careful estimation of the binary parameters of the model, successful prediction of water activity and solute activities can be made. It has yet to be determined how successful such a model will be for four- and five-component electrolytic aerosols, containing, for example, $(NH_4)_2SO_4-NH_4NO_3-HNO_3-H_2SO_4-H_2O$. Data of this type are difficult to find.

CHAPTER 5

APPLICATIONS FOR ATMOSPHERIC
AEROSOL GROWTH STUDIES

As discussed earlier, various gases in urban atmospheres undergo

chemical transformations resulting in the formation of multicomponent

electrolytic aerosols. The impact of such secondary aerosols, formed

by gas to particle conversion processes, on human health and visibility

is directly related to the particle size and chemical composition.

Mathematical modeling of aerosol behavior must therefore accurately

predict chemical composition and size of multicomponent atmospheric

aerosols. In this chapter the prediction of size and chemical composi-

tion of an aerosol droplet exposed to pollutant gases, identified in

the atmosphere, is presented.

Modeling of Gas-to-particle Conversion Process

Consider the fate of a submicron size water droplet exposed

to atmospheric concentrations of SO_2, NO, NO_2, NH_3, H_2SO_4 and water

vapor. These gases diffuse into the aerosol phase due to concentration

gradients and are transformed into more stable nitrate and sulfate salts

by chemical reactions. This leads to a lowering of water activity of

the droplet and, to maintain the interfacial equilibrium, water condenses

into the droplet causing it to grow. This continuous process can be

divided into three steps:

1. Transport from the gas phase to the particle surface.

2. Interfacial Equilibria and

3. Chemical reactions within the droplet.

Figure 14 illustrates these processes.

Transport from the Bulk (Gas)
Phase to the Particle Surface

The following relations describe the diffusion of various gases and vapors from the gas phase to the particle surface (Peterson and Seinfeld, 1980):

$$\frac{d[SO_2]}{dt} = \frac{4\pi r D_{SO_2}}{RT(1 + \ell Kn)} \left(P_{\infty SO_2} - P_{surf\ SO_2} \right)$$

$$\frac{d[NO]}{dt} = \frac{4\pi r D_{NO}}{RT(1 + \ell Kn)} \left(P_{\infty NO} - P_{surf\ NO} \right)$$

$$\frac{d[NO_2]}{dt} = \frac{4\pi r D_{NO_2}}{RT(1 + \ell Kn)} \left(P_{\infty NO_2} - P_{surf\ NO_2} \right)$$

$$\frac{d[NH_3]}{dt} = \frac{4\pi r D_{NH_3}}{RT(1 + \ell Kn)} \left(P_{\infty NH_3} - P_{surf\ NH_3} \right)$$

$$\frac{d[H_2O]}{dt} = \frac{4\pi r D_{H_2O}}{RT(1 + \ell Kn)} \left(P_{\infty H_2O} - P_{surf\ H_2O} \right)$$

$$\frac{d[H_2SO_4]}{dt} = \frac{4\pi r D_{H_2SO_4}}{RT(1 + \ell Kn)} \left(P_{\infty H_2SO_4} - P_{surf\ H_2SO_4} \right)$$

$$\text{where} \quad \ell = \frac{4/3 + 0.71\ Kn^{-1}}{1 + Kn^{-1}}$$
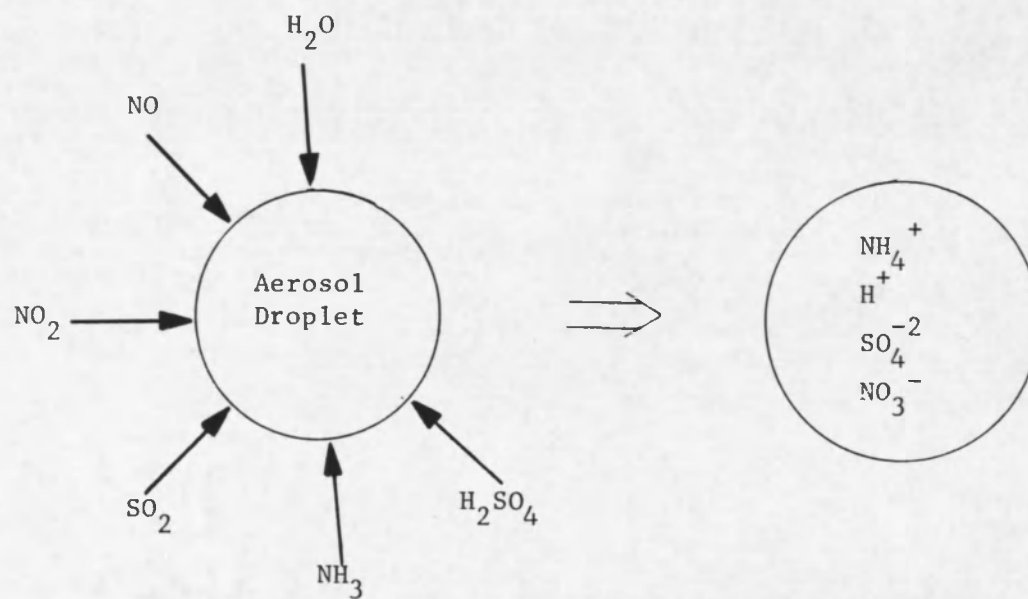
Figure 14.   Gas-to-Particle Conversion Process

where Kn = λ/r is the Knudsen number; λ is the mean free path and r is the particle radius.

Interfacial Equilibrium

The combined Kelvin and solute effect (Eq. 21) describes the interfacial equilibrium for water. The interfacial equilibria for pollutant gases is represented by the Henry's law. Effect of curvature (Kelvin effect, Eq. 18) on the surface pressures to be used in Henry's law should be accounted for.

Chemical Reactions within the Droplet

A series of equilibrium and kinetic steps oxidize oxides of sulfur and nitrogen into sulfate and nitrate ions respectively and these species are subsequently neutralized by ammonia. Details of aqueous chemistry shall be considered in later case studies. Transport within the droplet is ignored because the particles have very small radii (1 μm or less) and diffusion in the liquid phase is rapid as compared to other rate controlling processes (typical value of diffusivity is of the order of 10^{-5} cm^2/sec and this gives a diffusion time of $r^2 \times 10^{-3}$ sec where r is the particle radius in μm). Thus the liquid phase can be safely assumed to be well-mixed.

Equilibrium Nitrate Chemistry

Though nitrate salts are identified as some of the major components dominating atmospheric aerosols, relatively few workers have investigated the nitrate formation processes (Orel and Seinfeld, 1977; Peterson and Seinfeld, 1979).

The purpose of this first study is to check the applicability of Bromley's model for water activity and solute activity coefficients prediction on the equilibrium chemistry of a water droplet exposed to NO, NO_2, NH_3 and water vapor. Table 4 summarizes the equilibrium chemical reactions included. Bromley's model, with three parameters, is used to predict solute activity coefficients and water activities needed to solve chemical equilibrium equations in Table 4 for species concentrations. As we wish to study the applicability of Bromley's model to solve the atmospheric equilibrium chemistry problems exclusively, growth, diffusion and chemical kinetic processes are not included. Thus surface concentrations of all gases are assumed to be equal to bulk (gas) phase concentrations, i.e.,

$$\frac{d[NO_2]}{dt} \approxeq 0$$

$$\frac{d[NH_3]}{dt} \approxeq 0$$

$$\frac{d[NO]}{dt} \approxeq 0$$

Furthermore gas-phase concentrations used are those measured in the polluted urban atmospheres (Tuazon, Winer, Graham and Pitts, 1980; Doyle et al., 1979). As we are restricting ourselves to equilibrium chemistry, sulfate conversion or condensation kinetics and time-dependent growth of particle due to intake of water are not considered. Parameters used for simulations are listed in Table 5. It should be noted that the

Table 4

Equilibrium Chemistry for Nitrate Aerosols

Reaction	Equilibrium Constant	Value at 25°C	Reference
$H_2O(g) \rightleftharpoons H_2O(\ell)$	$1/P_{Sat_w} = a_w/P_{H_2O}$	$31.99\ atm^{-1}$	Perry 1974
$H_2O(\ell) \rightleftharpoons H^+ + OH^-$	$K_w = \dfrac{[H^+][OH^-]\ \gamma_{H^+}\ \gamma_{OH^-}}{a_w}$	$1.008 \times 10^{-14}\ moles^2\ \ell^{-2}$	Robinson and Stokes 1965
$NH_3(g) \rightleftharpoons NH_3(\ell)$	$K_{HA} = [NH_3(\ell)]/P_{NH_3}$	$57\ moles\ \ell^{-1}\ atm^{-1}$	Morgan and Maass 1931
$NH_3(\ell) \rightleftharpoons NH_4^+ + OH^-$	$K_{1A} = \dfrac{[NH_4^+][OH^-]\ \gamma_{NH_4^+}\ \gamma_{OH^-}}{[NH_3(\ell)]}$	$1.774 \times 10^{-5}\ moles\ \ell^{-1}$	Robinson and Stokes 1965
$H_2O(\ell) + NO(g) + NO_2(g) \rightleftharpoons 2HNO_2$	$K_{1N} = \dfrac{[HNO_2]^2}{P_{NO}\ P_{NO_2}\ a_w}$	$122\ moles^2\ \ell^{-2}\ atm^{-2}$	Orel and Seinfeld 1977
$2NO_2(g) + H_2O(\ell) \rightleftharpoons HNO_2 + H^+ + NO_3^-$	$K_{2N} = \dfrac{[HNO_2][H^+][NO_3^-]\ \gamma_{H^+}\ \gamma_{NO_3^-}}{P_{NO_2}^2\ a_w}$	$4.3 \times 10^5\ moles^3\ \ell^{-3}\ atm^{-2}$	Pick 1920
$HNO_2 \rightleftharpoons H^+ + NO_2^-$	$K_{3N} = \dfrac{[H^+][NO_2^-]\ \gamma_{H^+}\ \gamma_{NO_2^-}}{[HNO_2]}$	$5.1 \times 10^{-4}\ moles\ \ell^{-1}$	Kolthoff and Elving 1959

Table 5

Parameters for Equilibrium Nitrate Chemistry

Run	P_{NH_3}	P_{NO_2}
I	1.E-7	5.E-8
II	4.E-8	5.E-8
III	1.E-8	5.E-8
IV	1.E-9	5.E-8
V	1.E-9	5.E-7

water activity is included in equilibrium chemistry (Table 4) because

it must be significantly different from 1 in arid environments. Results

of simulations are shown in Figs. 15, 16, and 17.

Ionic strength is plotted as a function of partial pressure of

NO in Fig. 15. Only chemical compound present in appreciable quantity

is ammonium nitrate with small amounts of unneutralized nitric acid

that causes an acidic pH. The formation of ammonium nitrate in liquid

phase can be delineated as a two step process involving the conversion

of oxides of nitrogen to nitrate and subsequent neutralization of this

nitrate by the atmospheric ammonia. As evident from Table 4, nitrate

concentration is directly proportional to P_{NO_2} ($NO_3^- \propto P_{NO_2}^{3/2} P_{NO}^{-1/2}/[H^+]$)

and thus increased P_{NO_2} would result in higher concentration of ammonium

nitrate. Similarly higher concentration of ammonia, by increasing the pH,

would stimulate nitrate formation. Nitrate concentration in general

would decrease with increasing P_{NO} due to the inverse proportionality

between $[NO_3^-]$ and P_{NO}. Higher concentrations of ammonia would make

solution less acidic, while increased P_{NO_2} causes pH to drop sharply.

Of particular interest is the fact that ionic strengths as high as 24,

very close to the saturation point of ammonium nitrate, and water

activities as low as 0.40 are predicted. This substantiates the evidence

for the existence of highly concentrated aerosol droplets (with or with-

out the separation of solid phase) in low humidity regions.

Simultaneous Sulfate and Nitrate
Formation and Droplet Growth

In this final section, characteristic parameters of an aerosol

particle experiencing chemical reactions and growth due to exposure to
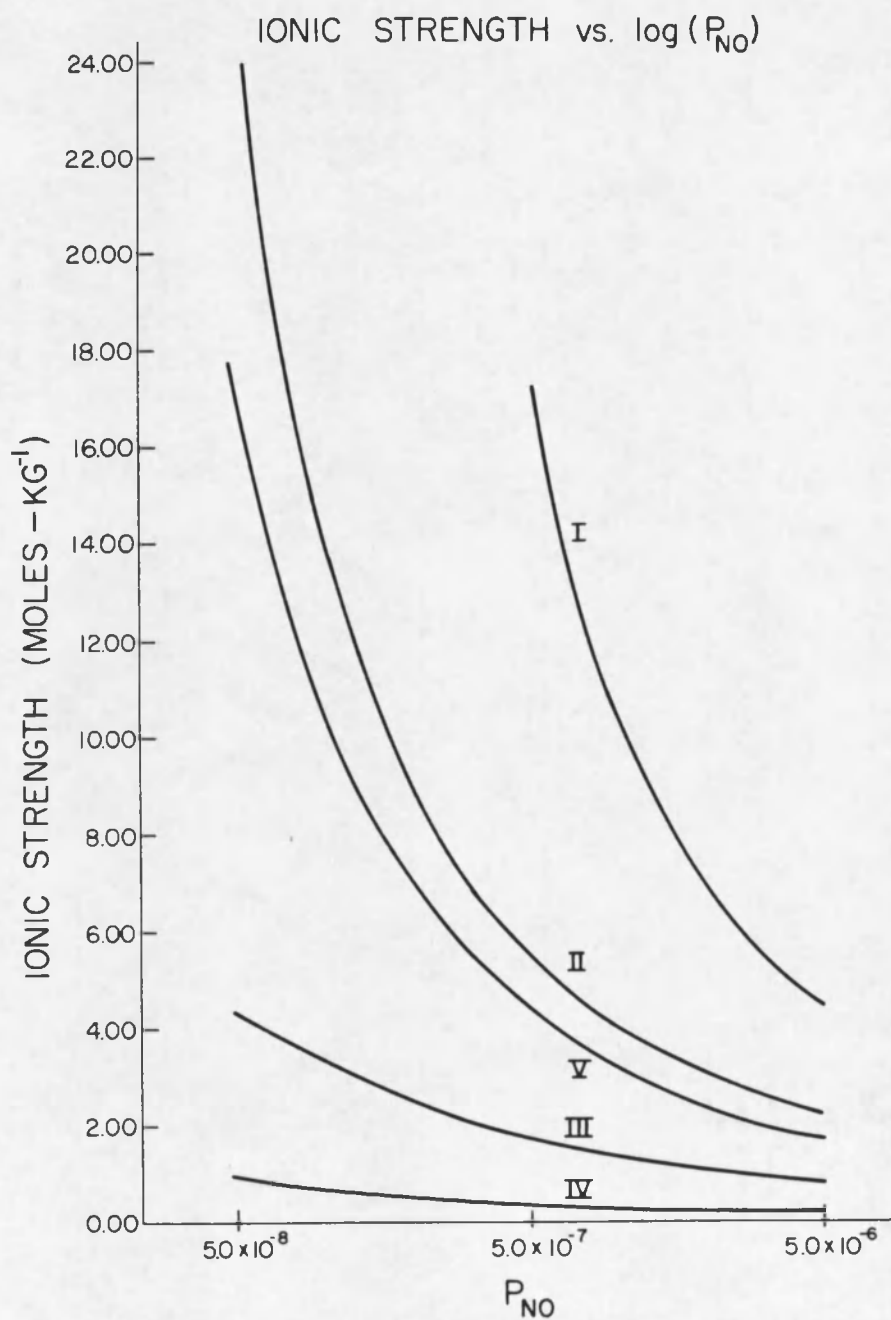
Figure 15.   Ionic strength vs. partial pressure of NO for nitrate
aerosols for five different runs.   Parameters are listed
in Table 5.
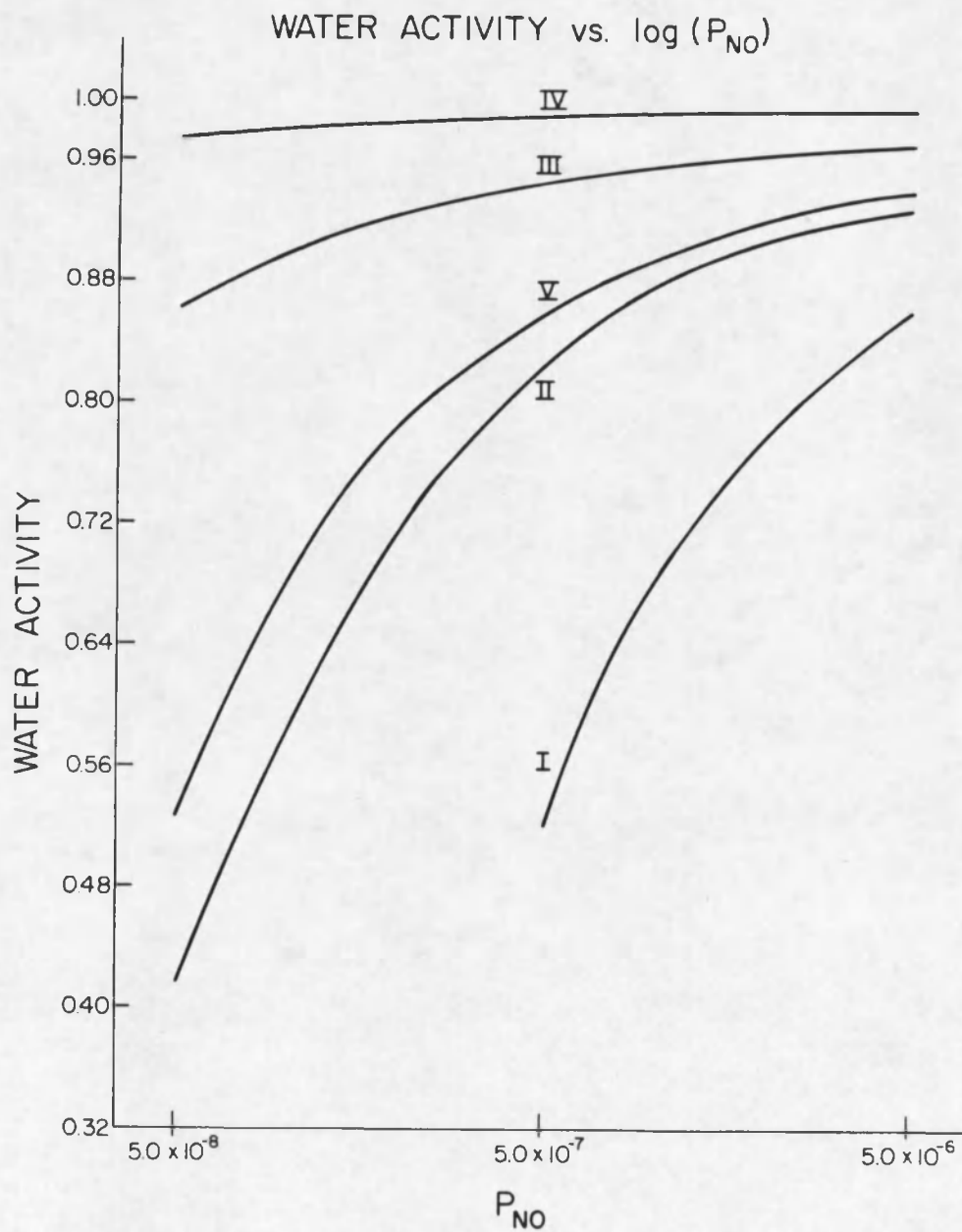
Figure 16. Water activity vs. partial pressure of NO for nitrate
aerosols for five different runs. Parameters are listed
in Table 5.
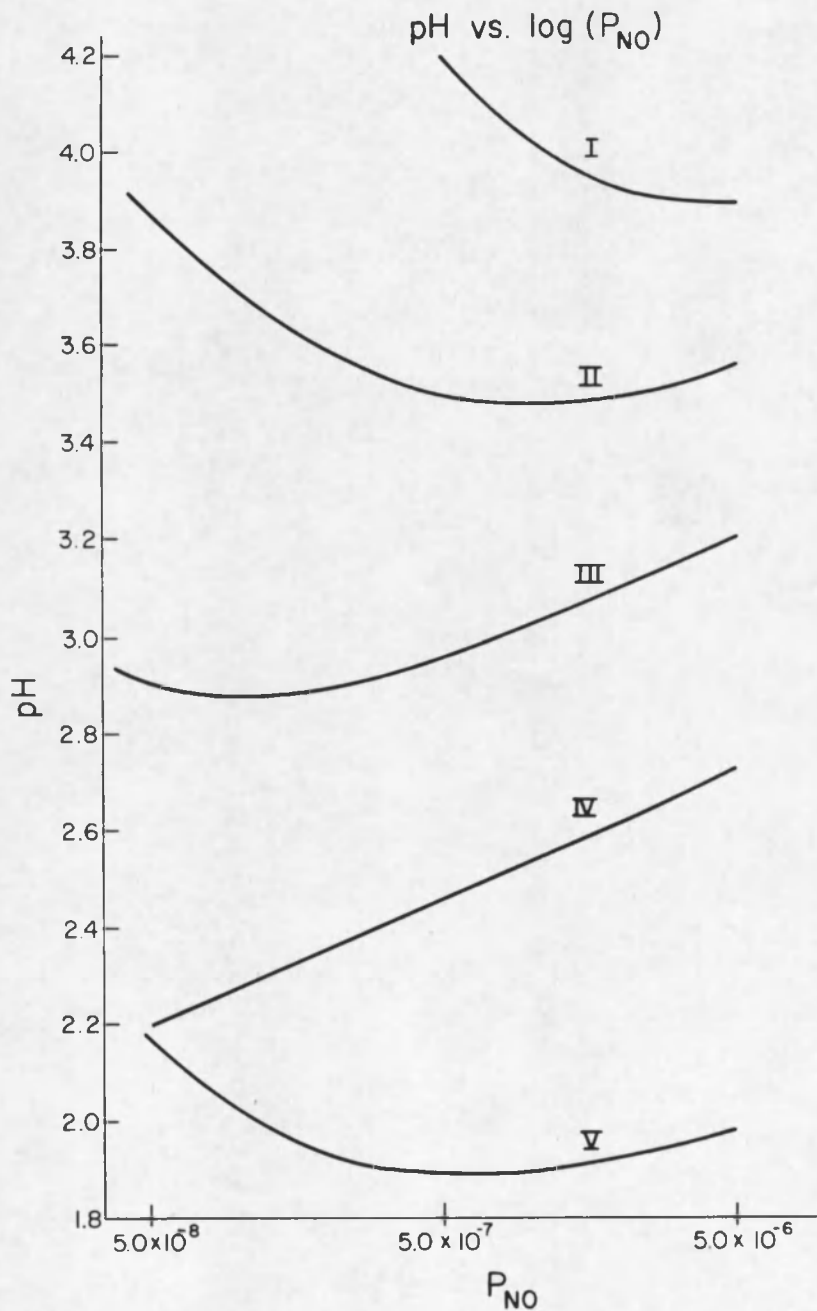
Figure 17.   pH vs. partial pressure of NO for nitrate aerosols for five
different runs.   Parameters are listed in Table 5.

SO_2, NO, NO_2, NH_3, H_2SO_4 and water vapor are predicted as a function of time. In addition to liquid phase nitrate formation, described in first study, we have included:

1. Aqueous chemistry of SO_2,

2. Gas phase oxidation of SO_2 to sulfuric acid and kinetics of diffusion of this sulfuric acid into the aerosol droplet,

3. Condensation of water vapor and resultant time dependent growth of the particle.

It is assumed that

1. The surface pressures of all pollutant gases except H_2SO_4 are in equilibrium with respective gas phase pressures.

2. Due to the extremely low vapor pressure of H_2SO_4, the surface pressure of H_2SO_4 is negligible, i.e., there is no resistance to transport of H_2SO_4 across the interface.

Hence

$$\frac{d[SO_2]}{dt} \cong 0$$

$$\frac{d[NO]}{dt} \cong 0$$

$$\frac{d[NO_2]}{dt} \cong 0$$

$$\frac{d[NH_3]}{dt} \cong 0$$

$$\frac{d[H_2O]}{dt} \cong 0$$

and

$$P_{surfH_2SO_4} \cong 0$$

Thus we have

$$\frac{d[H_2SO_4]}{dt} = \frac{4\pi r D_{H_2SO_4} P_{\infty H_2SO_4}}{RT(1 + \ell Kn)}$$

Details of aqueous equilibrium chemistry are given in Table 6. Peterson and Seinfeld (1979) have proved that the total sulfuric acid content of an aerosol droplet is unaffected if liquid phase oxidation of SO_2 to H_2SO_4 (both catalysed and uncatalysed) is included in addition to the condensation of H_2SO_4 from gas phase. Peterson and Seinfeld (1979) have used relatively simple ZSR model and Davies approximation respectively, to compute the water activity and the solute activity coefficients. We have duplicated their (Peterson and Seinfeld, 1979) runs for aerosol growth studies for marine aerosol in the Los Angeles area except that we have used more involved three parameter Bromley's model to compute water activity and solute activity coefficients. By comparing the results of these two studies, both qualitatively and quantitatively, we can discern the impact of different methods of thermo-dynamic data prediction on the results of aerosol growth studies. We have studied the formation of sulfate and nitrate in a marine aerosol, i.e., an aerosol particle initially comprising an aqueous solution of the major sea-salts, NaCl and $MgCl_2$ in equilibrium. This aerosol droplet, upon exposure to pollutant gases, undergoes chemical composition and size changes. Gas phase concentration levels used for three different runs are listed in Table 7. These are typical ambient levels for Los Angeles area and were used by Peterson and Seinfeld (1979) in their simulations.

Table 6

Equilibrium Chemistry for Nitrate and Sulfate Aerosols

Reaction	Equilibrium Constant	Value at 25°C	Reference
$H_2O(g) \rightleftharpoons H_2O(\ell)$	$1/P_{Sat_w} = a_w/P_{H_2O}$	31.99 atm^{-1}	Perry 1974
$H_2O(\ell) \rightleftharpoons H^+ + OH^-$	$K_w = \dfrac{[H^+][OH^-]\ \gamma_{H^+}\ \gamma_{OH^-}}{a_w}$	1.008×10^{-14} moles^2 ℓ^{-2}	Robinson and Stokes 1965
$SO_2(g) \rightleftharpoons SO_2(\ell)$	$K_{HS} = [SO_2(\ell)]/P_{SO_2}$	1.24 moles ℓ^{-1} atm^{-1}	Johnstone and Leppla 1934
$SO_2(\ell) \rightleftharpoons H^+ + HSO_3^-$	$K_{1S} = \dfrac{[H^+][HSO_3^-]\ \gamma_{H^+}\ \gamma_{HSO_3^-}}{[SO_2(\ell)]}$	0.0127 moles ℓ^{-1}	Yui 1940
$HSO_3^- \rightleftharpoons H^+ + SO_3^{-2}$	$K_{2S} = \dfrac{[H^+][SO_3^{-2}]\ \gamma_{H^+}\ \gamma_{SO_3^{-2}}}{[HSO_3^-]\ \gamma_{HSO_3^-}}$	6.24×10^{-8} moles ℓ^{-1}	Yui 1940
$NH_3(g) \rightleftharpoons NH_3(\ell)$	$K_{HA} = [NH_3(\ell)]/P_{NH_3}$	57 moles ℓ^{-1} atm^{-1}	Morgan and Maass 1931

Table 6 (Continued 1)

$NH_3(\ell) \rightleftharpoons NH_4^+ + OH^-$
$K_{1A} = \dfrac{[NH_4^+][OH^-] \, \gamma_{NH_4^+} \gamma_{OH^-}}{[NH_3(\ell)]}$
1.774×10^{-5} moles ℓ^{-1}
Robinson and Stokes 1965

$H_2O(\ell) + NO(g) + NO_2(g)$
$\rightleftharpoons 2HNO_2$
$K_{1N} = \dfrac{[HNO_2]^2}{P_{NO} \, P_{NO_2} \, a_w}$
122 moles^2 ℓ^{-2} atm^{-2}
Orel and Seinfeld 1977

$2NO_2(g) + H_2O(\ell)$
$\rightleftharpoons HNO_2 + H^+ + NO_3^-$
$K_{2N} = \dfrac{[HNO_2][H^+][NO_3^-] \, \gamma_{H^+} \gamma_{NO_3^-}}{P_{NO_2}^2 \, a_w}$
4.3×10^5 moles^3 ℓ^{-3} atm^{-2}
Pick 1920

$HNO_2 \rightleftharpoons H^+ + NO_2^-$
$K_{3N} = \dfrac{[H^+][NO_2^-] \, \gamma_{H^+} \gamma_{NO_2^-}}{[HNO_2]}$
5.1×10^{-4} moles ℓ^{-1}
Kolthoff and Elving 1959

$MgCl_2 \rightleftharpoons Mg^{+2} + 2Cl^-$
$K_{1M} = \dfrac{[Mg^{+2}][Cl^-]^2 \, \gamma_{Mg^+} \gamma_{Cl^-}^2}{[MgCl_2(\ell)]}$
∞
Peterson and Seinfeld 1979

$NaCl \rightleftharpoons Na^+ + Cl^-$
$k_{1NA} = \dfrac{[Na^+][Cl^-] \, \gamma_{Na^+} \gamma_{Cl^-}}{[NaCl(\ell)]}$
∞
Peterson and Seinfeld 1979

Table 6 (Continued 2)

$HCl(g) \rightleftharpoons HCl(\ell)$ $\qquad$ $K_{HH} = [HCl(\ell)]/P_{HCl}$ $\qquad$ 19 moles ℓ^{-1} atm^{-1} $\qquad$ International Critical Tables 1928

$HCl(\ell) \rightleftharpoons H^+ + Cl^-$ $\qquad$ $K_{1H} = \dfrac{[H^+][Cl^-]\,\gamma_{H^+}\,\gamma_{Cl^-}}{[HCl(\ell)]}$ $\qquad$ 1.3×10^6 moles ℓ^{-1} $\qquad$ Robinson 1936

Table 7

Gas Phase Concentrations for Three Different Runs
for Nitrate and Sulfate Aerosols

Run	Initial Radius r_i (μm)	P_{H_2O} (ppm)	P_{SO_2} (ppm)	P_{NH_3} (ppm)	$P_{H_2SO_4}$ (ppm)	P_{NO} (ppm)	P_{NO_2} (ppm)	Remarks
A	0.1	28,140	0.01	0.01	5.E-6	0.1	0.05	Base Case
B	0.1	28,450	0.01	0.01	5.E-6	0.1	0.05	Relative Humidity Increased
C	0.1	28,140	0.01	0.01	5.E-6	0.1	0.01	P_{NO_2} Decreased

Figures 18 through 22 describe the variations of particle size, pH, sulfate concentration, nitrate concentration and ammonium concentration, respectively, as a function of time.

Figure 18 illustrates the particle radius with respect to time. The rate of particle growth increases with increasing humidity. This is due to the fact that to maintain the interfacial equilibrium at higher humidity, larger quantities of water must condense as sulfuric acid is transported across the interface. A decreased value of P_{NO_2} results in slower growth rates because the concentration of NO_3^- is reduced ($NO_3^- \alpha (P_{NO_2})^{3/2}$). This implies a higher value of water activity and thus smaller driving force for particle growth by condensation of the water vapor.

From Figure 19 it can be easily inferred that the increasing relative humidity tends to increase the pH by dilution. A lower value of P_{NO_2} causes a sharp decrease in nitrate level and thus increases the water activity. As a result, the particle grows slowly and contains a higher concentration of sulfate, making the particle more acidic.

Figure 20 describes the sulfate concentration as a function of time. An increased relative humidity leads to higher dilution or smaller concentration of sulfate. At a constant relative humidity, a decrease in P_{NO_2} would result in lower nitrate concentration and higher water activity as earlier discussed. Thus the particle grows slowly and contains higher levels of sulfate.

Figure 21 shows the nitrate level as a function of exposure time. Increasing relative humidity decreases nitrate concentration by dilution.
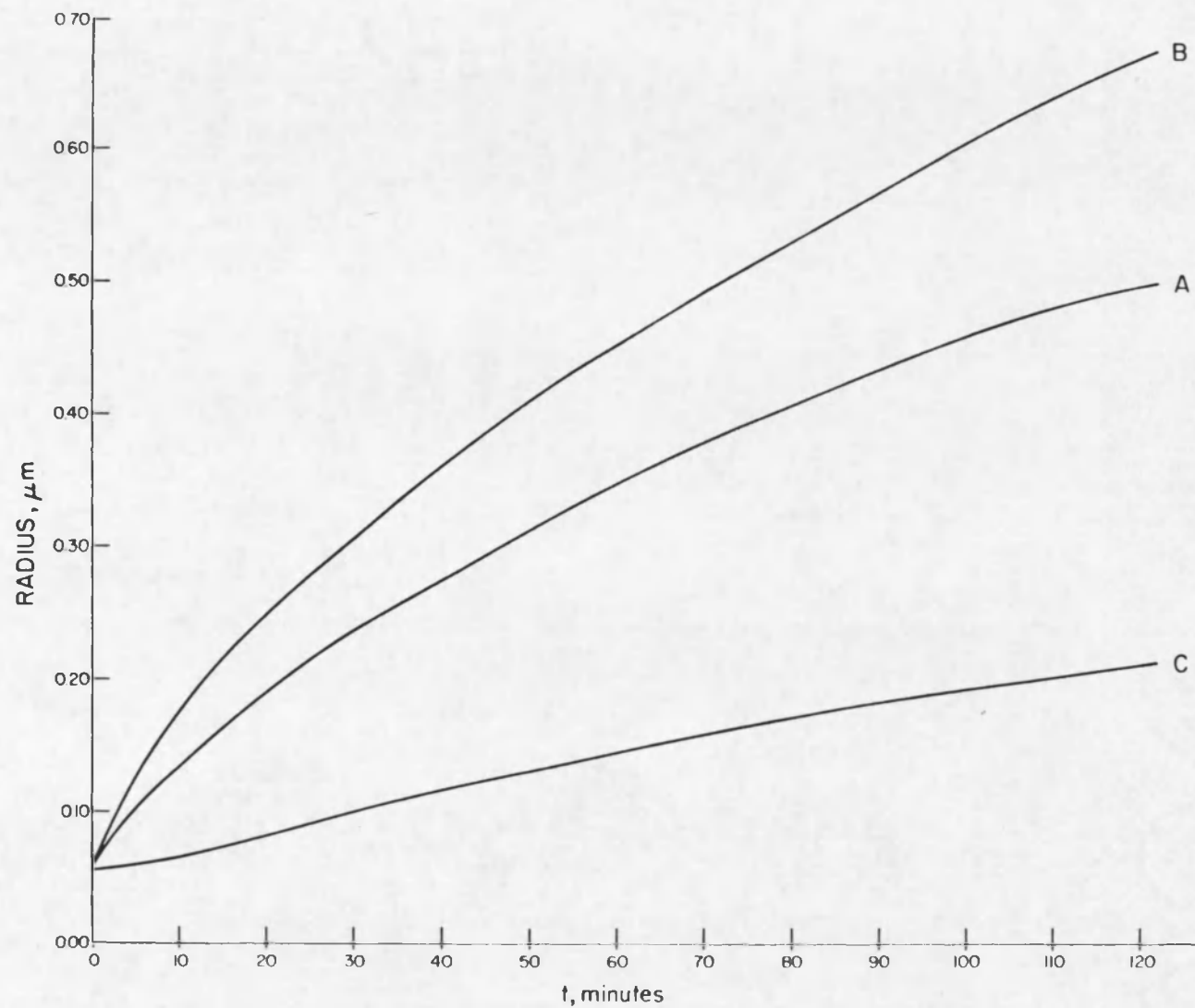
Figure 18. Radius vs. exposure time for a growing, reacting aerosol. Parameters are listed in Table 7.

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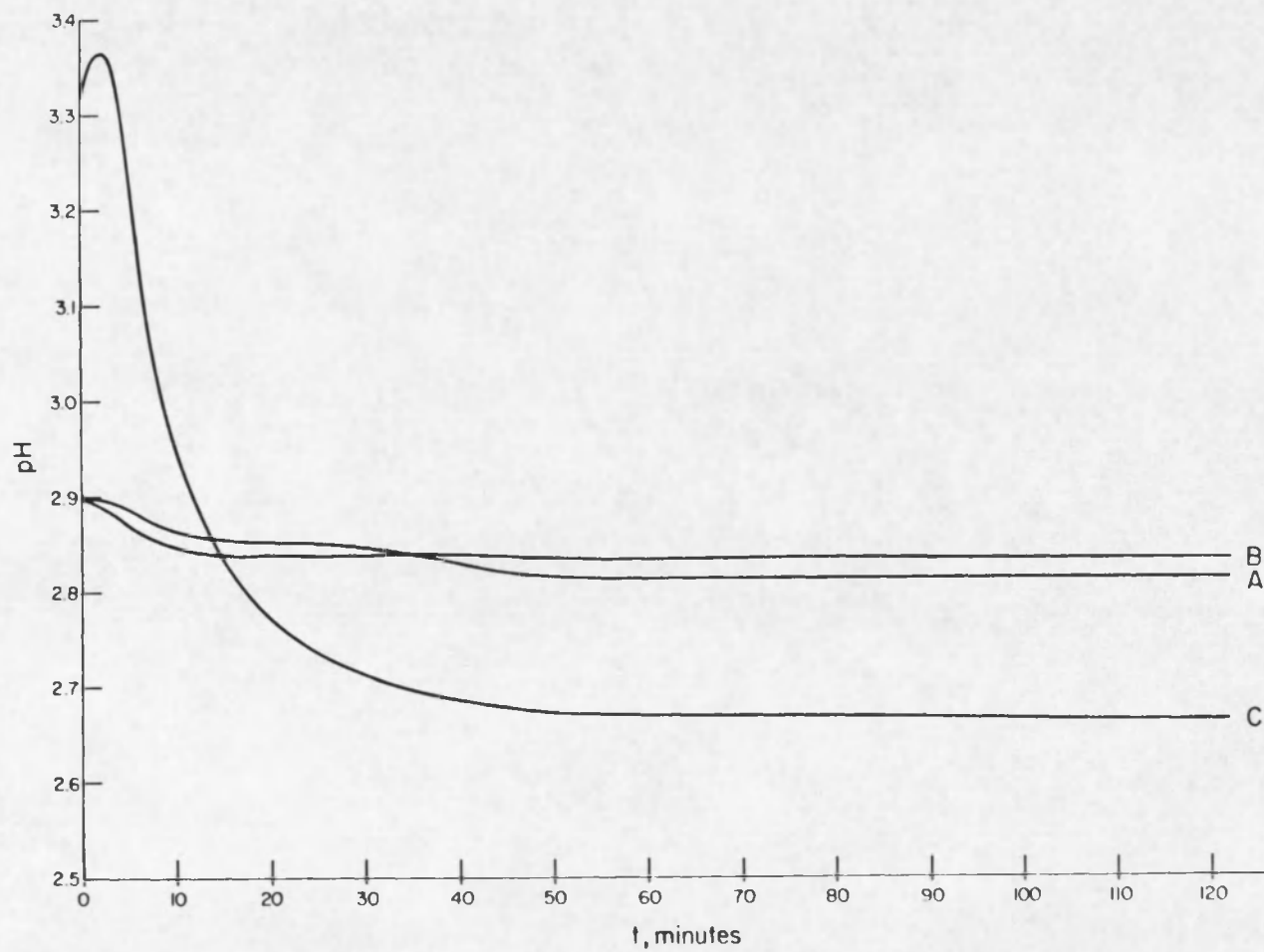
Figure 19. pH vs. exposure time for a growing, reacting aerosol. Parameters are listed in Table 7.
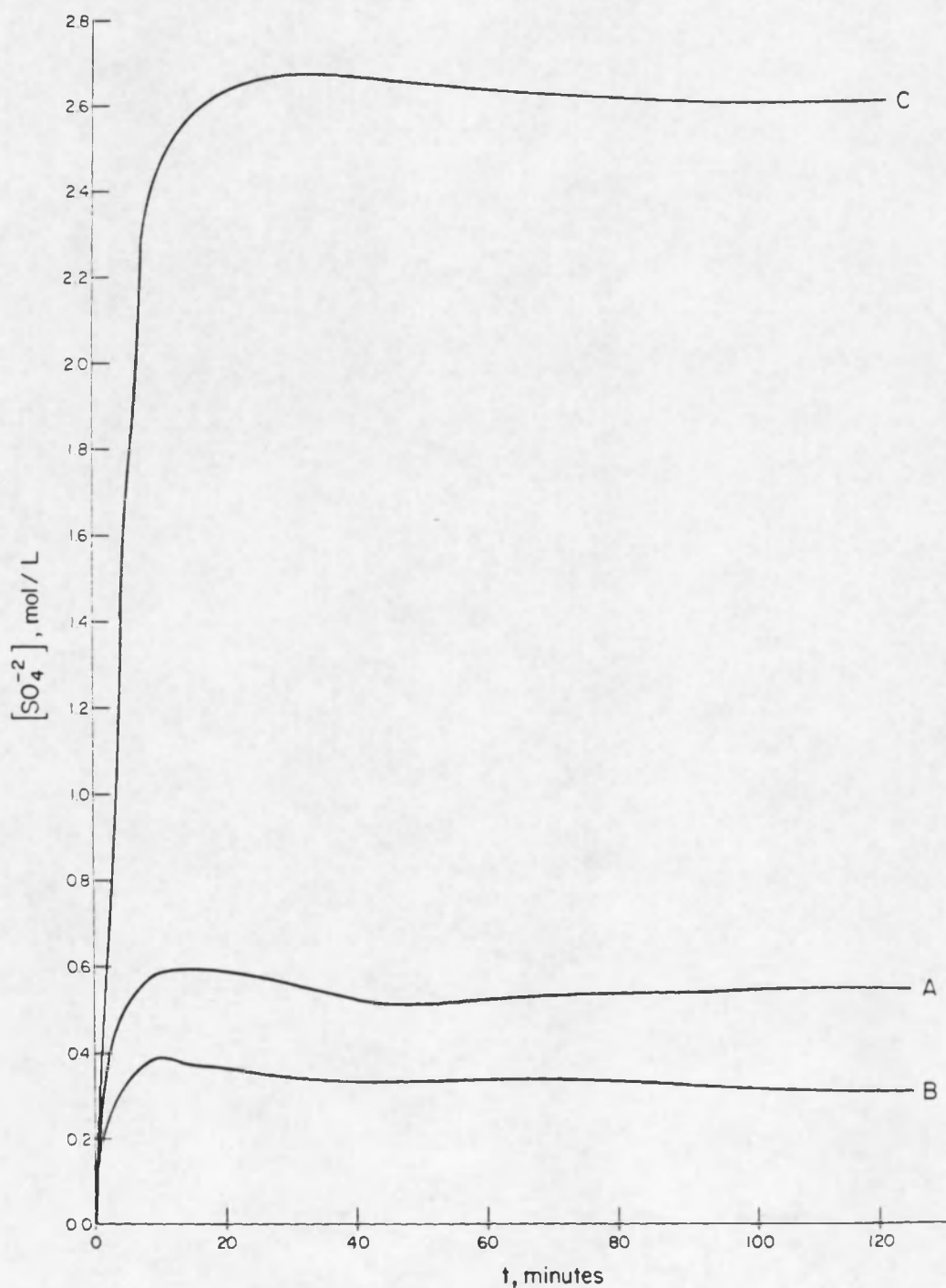
Figure 20. Sulfate concentration vs. exposure time for a growing, reacting aerosol. Parameters are listed in Table 7.
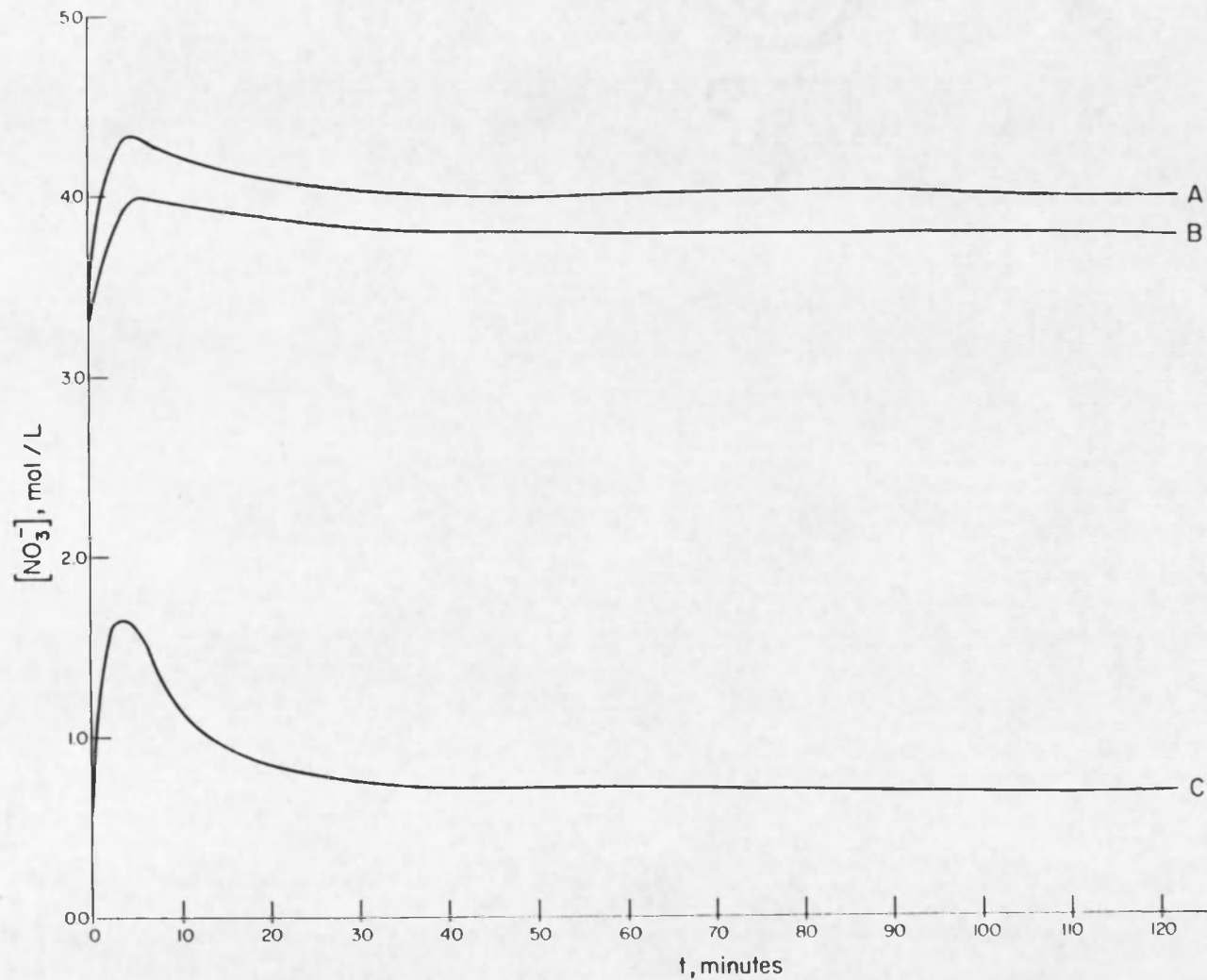
Figure 21. Nitrate concentration vs. exposure time for a growing, reacting aerosol. Parameters are listed in Table 7.
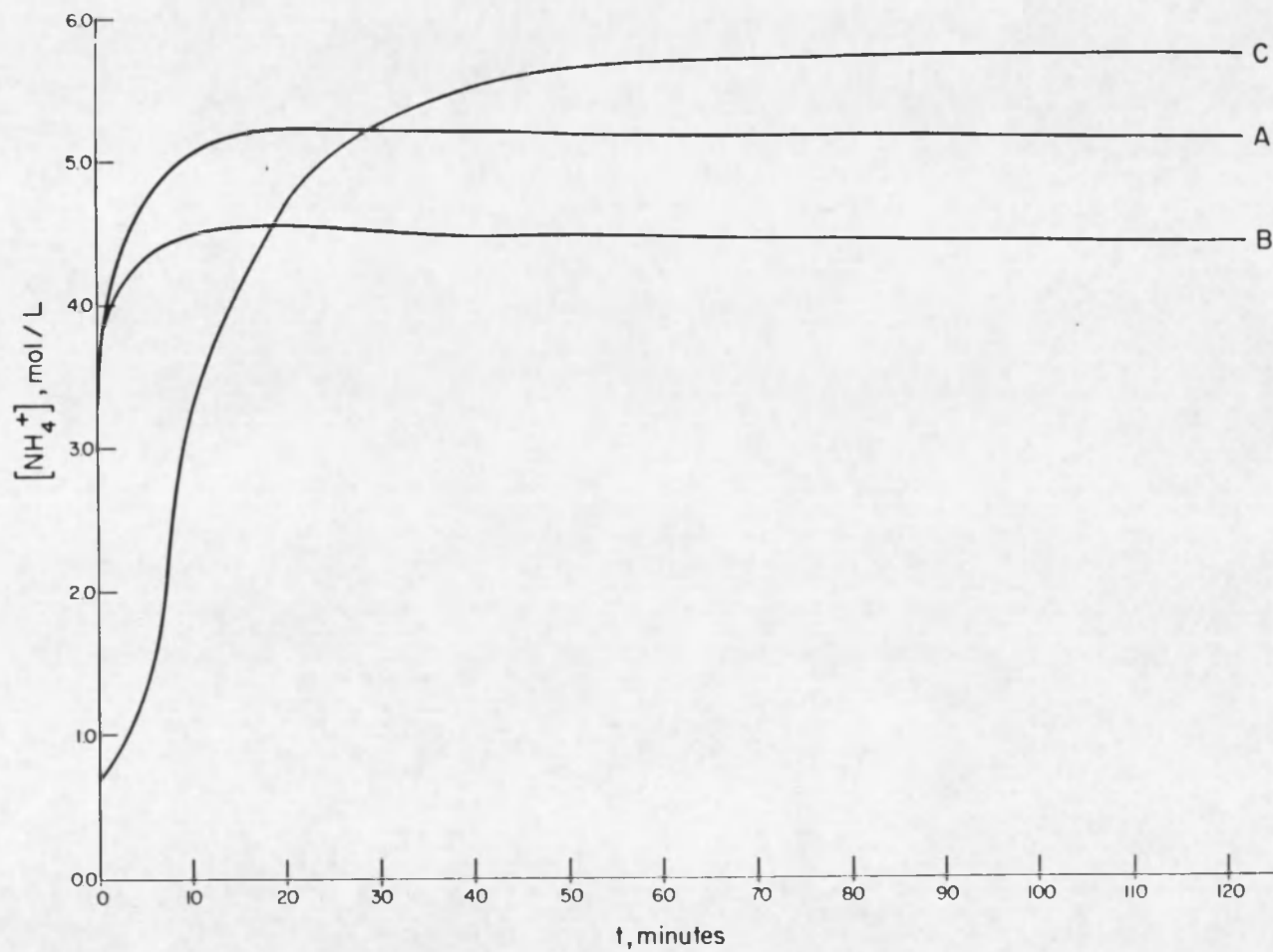
Figure 22. Ammonium concentration vs. exposure time for a growing, reacting aerosol. Parameters are listed in Table 7.

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As previously noted, nitrate concentration drops sharply due to decrease in P_{NO_2} ($NO_3^- \propto P_{NO_2}^{3/2}$).

Ammonium concentration is plotted as a function of time in Fig. 22. Increasing relative humidity increases the pH by dilution, and as the concentration of ammonium is directly proportional to the acidity of the solution, decreases the ammonium concentration. Similarly a lowered P_{NO_2} value, as earlier explained, decreases the pH (i.e., increases the concentration of hydrogen ion) and thus increases the ammonium ion concentration.

Table 8 provides a comparison of results of this study with those of Peterson and Seinfeld (1979). There is a very good qualitative agreement in terms of both the functional dependence on time of parameters predicted and the impact of variations in relative humidity and P_{NO_2} on this functional dependence. Quantitatively, results are significantly different. Present study predicts smaller particle radii with higher concentration of sulfate, nitrate and ammonium ions. The values of pH predicted in these two studies are close. This indicates that the disagreement in numbers is entirely due to the method used for solute activity coefficients and water activity predictions. The quantitative disagreement between the results of Peterson and Seinfeld (1979) and present study over the effect of increasing humidity on nitrate concentration may also be attributed to different methods used for thermodynamic data predictions. It should be noted that for only one percent change in relative humidity (Runs A and B are for relative humidities of 90 and 91 percent respectively), there is a significant change in the concentrations

Table 8

Comparisons with Previous Study

Run	Particle Radius µm		pH		Sulfate Conc. MOL/L		Nitrate Conc. MOL/L		Ammonium Conc. MOL/L	
	I	II	I	II	I	II	I	II	I	II
A	0.74	0.50	2.84	2.82	0.26	0.55	0.94	4.00	1.46	5.13
B	1.31	0.67	2.90	2.83	0.12	0.30	1.28	3.77	1.08	4.41
C	0.41	0.21	2.77	2.66	0.83	2.59	0.073	0.70	1.69	5.74

I: Results from Peterson and Seinfeld (1979) for an exposure time of 120 min.

II: Results from present study for an exposure time of 120 min.

predicted and particles at lower humidity tend to be more concentrated.

Keeping in mind the fact that relative humidities in arid regions can be

much lower (annual average for Tucson is approximately 38%), one is led

to believe that aerosols in such environments are highly concentrated in

secondary pollutants. Low humidities coupled with deliquescent and

efflorescent properties of $(NH_4)_2SO_4$, NH_4HSO_4 and NH_4NO_3 may generate

aerosols comprising saturated solution of these compounds with possible

separation of solid phase in thermodynamic equilibrium with saturated

solution.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

We have addressed ourselves to the problem of accurate
description of interfacial and chemical equilibria for multicomponent
electrolytic aerosols in this study. The effect of low humidities on
the chemical properties of these atmospheric aerosols was elucidated.
It was found that atmospheric aerosols in arid regions could be domi-
nated by multicomponent aqueous solutions of $(NH_4)_2SO_4$, NH_4NO_3, H_2SO_4
and HNO_3 at relatively high concentrations of solutes. We showed that
the assumption of ideality of these concentrated solutions would lead
to erroneous results, and for an accurate description of aerosol growth
process, these non-idealities must be accounted for in terms of solute
activity coefficients and solvent activity.

It was found that multicomponent thermodynamic data were not
available for electrolytic systems believed to exist in the atmosphere.
In view of this paucity of thermodynamic data, four different models
used for water activity and solute activity coefficients predictions
were examined. All these models utilize binary activity data which are
more readily available. To check the applicability and accuracy of these
models, the predictions of these four models were compared to species
activity coefficients or water activity data of various electrolyte
solutions. Comparisons were also made for two systems of importance in
atmospheric aerosol studies, namely the $H_2SO_4-(NH_4)_2SO_4-H_2O$ and the

$(NH_4)_2SO_4-NH_4NO_3-H_2O$ systems. The applicability of these models for concentrated solution was tested by making these comparisons for high ionic strength solutions. There were no major differences in accuracy of the predictions from four models examined. There were, however, major differences in applicability. It was found that Bromley's model, with appropriate modification and careful estimation of the binary parameters, could accurately predict water activity and solute activity coefficients for a wide range of concentrations.

The ability of Bromley's model to deal with atmospheric chemistry problems was examined in the first case study. Characteristic parameters of a nitrate aerosol were predicted by using equilibrium nitrate chemistry, i.e., equilibrium chemistry of a water droplet exposed to atmospheric NO, NO_2 and NH_3. Bromley's model with three parameters was used for predicting thermodynamic data required. No diffusion, growth or kinetic mechanisms were included. Fairly high concentrations predicted strongly supported the evidence for the existence of aqueous atmospheric aerosols in arid regions at high ionic strengths.

Temporal variations in size and chemical composition of a water droplet exposed to SO_2, NO, NO_2, NH_3, H_2SO_4 and water vapor were predicted in the second case study. Homogeneous sulfate formation mechanisms, diffusion of this sulfuric acid into aerosol phase and equilibrium chemistry of aqueous SO_2 were included. Again, to check the impact of Bromley's model for species activity coefficients and water activity predictions on the overall aerosol growth process, the runs

of a previous study were duplicated. Relatively simple ZSR model and Davies approximation, for water activity and solute activity coefficients predictions respectively, were used by Peterson and Seinfeld (1979) to study the growth of a marine aerosol. There was a qualitative agreement between the results of this present study and earlier study due to Peterson and Seinfeld (1979). However, the present study tends to predict smaller aerosol particles at higher concentrations of solutes. It was shown that a decrease in relative humidity results in an increase in the ionic strength of the aerosol droplet and that an aerosol droplet in low humidity regions may comprise saturated solutions of secondary pollutants with possible separation of solid phase.

In light of deliquescent and efflorescent properties of salts dominating atmospheric aerosols, future work in this field should consider the existence and properties of aerosol particles in equilibrium with solid phase. Analytical tools should be developed to predict the physical and chemical properties, e.g., size, composition and mass of each phase, for certain given gas phase concentrations and humidity.

APPENDIX A

NUMERICAL SOLUTION OF GIBBS-DUHEM EQUATION

Water activities were computed from Lietzke and Stoughton model (Eq. 23) for solute activity coefficients with the help of Gibbs-Duhem equation (Eq. 25). An example of such procedure for the ternary system $MgCl_2$ - $Mg(NO_3)_2$ - H_2O is given in the program. Equation (25) is solved by the trapezoidal rule. Each numerical integration is performed for constant X_2 (e.g., X_2 = 0.005, 0.01, etc.). Step size or width of the interval is kept small $((M1)_{i+1} - (M1)_i = 0.2)$. For each interval, X_1, X_2, and X_3 are approximated by average values of these parameters for that interval.

M2 can be computed for each M1 from the relationship.

$$X_2 = \frac{3M2}{3M1 + 3M2 + 55.51}$$

Lietzke and Staughton model is used to compute multicomponent activity coefficients (gama 1 and gama 2) from those molalities and binary activity coefficients data contained in two subroutines. Point "a" (lower limit of integration) is chosen to be a point of relatively low concentration (M1 = 0.2 and M2 defined by X_2) so that ZSR model can be used to compute the water activity. Once the results of the simulations are available, they (exponential of R.H.S. of Equation (25)) can be multiplied by $(f_3)_b$ to obtain $(f_3)_a$. A graphical presentation of these results (a_w as a function of X_1 with X_2 as a parameter) makes it possible to read activities at any desired concentration.

```
      PROGRAM VERF10(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
C     THIS PROGRAM CALCULATES THE ACTIVITY COEFFICIENTS AND
C     WATER ACTIVITY IN THE SYSTEM MAGNESIUM NITRATE-
C     MAGNESIUM CHLORIDE-WATER
C     ...........................................'........
C     THIS PROGRAM IS LISTED IN A FILE CALLED MAT65.F4
C     (PPN 5700,22453)
C     ...................................................
      REAL M1,M2,IONICST,M10,M20,MEANX1,MEANX3,LUP,LLOW
      REAL NEWX1,NEWX2,NEWX3,NEWW1,NEWW2,NEWW3,NEWM1,NEWM2
C     EACH INTEGRATION STEP IS PERFORMED AT CONSTANT X2
      X2=0.
10    X2=X2+0.01
      IF(X2.GT.0.20)  GO  TO  50
      WRITE(6,6)
6     FORMAT(1H1,20X,41H STARTING NEW ITERATION FOR A CONSTANT X2,//////)
      GAMA1=GAMA2=GAMA10=GAMA20=1.
      DELOG1=DELOG2=MEANX1=MEAN73=OLDX1=OLDLGF1=OLDLGF2=OMEGA=M10=0.
C     M1=MOLALITY OF MAGNESIUM NITRATE
C     M2=MOLALITY OF MAGNESIUM CHLORIDE
C     SUBSCRIPT 0 INDICATES BINARY PROPERTIES AT THE TOTAL
C     IONIC STRENGTH OF THE SOLUTION
      M1=0.
      M10=0.
      AREA=0.
      I=1
20    M2=(3*M1*X2+55.51*X2)/(3.*(1.-X2))
      IONICST=3.*M1+3.*M2
      IF(IONICST.GT.15.)  GO  TO  10
      M20=IONICST/3.
      IF(M1.EQ.0.)  GO  TO  110
      M10=IONICST/3.
      CALL DATAMAN(M10,ACTVTY1,ACTVTY2,LLOW,LUP)
      GAMA10=((LUP-M10)*ACTVTY1+(M10-LLOW)*ACTVTY2)/(LUP-LLOW)
110   CALL DATAMAC(M20,ACTVTY3,ACTVTY4,XLOW,XUP)
      GAMA20=((XUP-M20)*ACTVTY3+(M20-XLOW)*ACTVTY4)/(XUP-XLOW)
      IF(M1.EQ.0.)  GO  TO  120
C     FOLLOWING ARE GAMA1 AND GAMA2 FROM LIETZKE AND STOUGHTON
C     MODEL(1972)
      GAMA1=EXP(ALOG(GAMA10)+M2/(2.*M20)*(ALOG(GAMA20/GAMA10)))
      GAMA2=EXP(ALOG(GAMA20)+M1/(2.*M10)*(ALOG(GAMA10/GAMA20)))
C     F1 AND F2 ARE ACTIVITY COEFFICIENTS ON RATIONAL SCALE
      F1=GAMA1*(1.+0.018*(3.*M1+3.*M2))
      F2=GAMA2*(1.+0.018*(3.*M1+3.*M2))
      GO  TO  130
120   GAMA2=GAMA20
      F1=1.
      F10=1.
      F2=GAMA2*(1.+0.018*3.*M2)
C     W1,W2,W3 ARE WT. PERCENTS.
130   W1=14800.*M1/(148.*M1+95.*M2+1000.)
      W2=9500.*M2/(148.*M1+95.*M2+1000.)
      W3=100.-W1-W2
      X1=3.*M1/(3.*M2+3.*M1+55.51)
      X3=1.-X1-X2
      IF(M1.EQ.0.)  GO  TO  25
      DELOGF1=ALOG(F1)-OLDLGF1
      DELOGF2=ALOG(F2)-OLDLGF2
      DELX1=X1-OLDX1
      MEANX1=(X1+OLDX1)/2.
      MEANX3=(X3+OLDX3)/2.
```

```
C       FOLLOWING IS THE SOLUTION OF GIBBS-DUHEM EQUATION
        OMEGA=-(DELOGF1/DELX1*MEANX1/MEANX3+DELOGF2/DELX1*X2/MEANX3)
        IF(I.LT.3)   GO   TO   25
        AVOMEGA=(OMEGA+OLDMEGA)/2.
        AREA=AREA+AVOMEGA*(MEANX1-OLDMNX1)
        RTGAMA3=EXP(AREA)
        RTACTV3=MEANX3*RTGAMA3
25      WRITE(6,15)X2,X1,X3,M1,M2,W1,W2,W3,IONICST,GAMA1O,GAMA2O,GAMA1,
        /GAMA2,OMEGA
15      FORMAT(1H0,2X,3(F5.3,3X),2(F6.3,3X),3(F5.2,3X),F6.3,3X,4(F6.3,3X),
        /F7.4)
        IF(I.LT.3)   GO   TO   35
        NEWX1=MEANX1
        NEWX3=MEANX3
        NEWX2=1.-NEWX1-NEWX3
        NEWM1=NEWX1/NEWX3*55.51/3.
        NEWM2=NEWX2/NEWX3*55.51/3.
        NEWW1=14800.*NEWM1/(148.*NEWM1+95.*NEWM2+1000.)
        NEWW2=9500.0*NEWM2/(148.*NEWM1+95.*NEWM2+1000.)
        NEWW3=100.-NEWW1-NEWW2
        WRITE(6,45) NEWX2,NEWX1,NEWX3,NEWM1,NEWM2,NEWW1,NEWW2,NEWW3,
        /AREA,RTGAMA3,RTACTV3
45      FORMAT(3X,3(F5.3,3X),2(F6.3,3X),3(F5.2,3X),F6.3,2X,2(F7.4,4X))
35      OLDX1=X1
        OLDX3=X3
        OLDLGF1=ALOG(F1)
        OLDLGF2=ALOG(F2)
        IF(I.LT.2)   GO   TO   40
        OLDMEGA=OMEGA
        OLDMNX1=MEANX1
40      M1=M1+0.2
        I=I+1
60      GO   TO   20
50      STOP
        END
        SUBROUTINE DATAMAN(M10,ACTVTY1,ACTVTY2,LLOW,LUP)
C       THIS SUBROUTINE LINEARLY INTERPOLATES THE BINARY
C       DATA OF MAGNESIUM NITRATE
C       ACTIVITY COEFFICIENT DATA OF MAGNESIUM  NITRATE
        REAL LLOW,LUP,M10
        DIMENSION ACTVTY(21),Z1(21)
        DATA ACTVTY/.522,.48,.467,.465,.469,.478,.488,.501,.518,.536,.58,
        /.631,.691,.758,.835,1.088,1.449,1.936,2.59,3.50,4.74/
        DATA Z1/.1,.2,.3,.4,.5,.6,.7,.8,.9,1,1.2,1.4,1.6,1.8,2.0,2.5,3.0,
        /3.5,4.0,4.5,5.0/
        I=1
70      IF(M10.LE.Z1(I))   GO   TO   30
        I=I+1
        GO   TO   70
30      LLOW=Z1(I-1)
        LUP=Z1(I)
        ACTVTY1=ACTVTY(I-1)
        ACTVTY2=ACTVTY(I)
        RETURN
        END
        SUBROUTINE   DATAMAC(M20,ACTVTY3,ACTVTY4,XLOW,XUP)
C       THIS SUBROUTINE LINEARLY INTERPOLATES THE BINARY DATA
C       OF MAGNESIUM CHLORIDE.
C       ACTIVITY COEFFICIENT DATA FOR MAGNESIUM CHLORIDE
        REAL M20
        DIMENSION  ACTVTX(21),Z2(21)
```

```
      DATA ACTVTX/.528,.488,.476,.474,.48,.49,.505,.521,.543,.569,.63,
     /.708,.802,.914,1.051,1.538,2.32,3.55,5.53,8.72,13.92/
      DATA Z2/0.1,.2,.3,.4,.5,.6,.7,.8,.9,1,1.2,1.4,1.6,1.8,2.,2.5,3.0,
     /3.5,4.0,4.5,5.0/
      I=1
70    IF(M20.LE.Z2(I)) GO TO 30
      I=I+1
      GO TO 70
30    XLOW=Z2(I-1)
      XUP=Z2(I)
      ACTVTY3=ACTVTX(I-1)
      ACTVTY4=ACTVTX(I)
      RETURN
      END
```

APPENDIX B

BROMLEY'S MODEL PARAMETERS ESTIMATION BY LEAST SQUARE FIT

XTRACTR-10 package was used to fit binary osmotic coefficient
data to Bromley's model with one, two, or three parameters (Equations
(32), (39), and (41) respectively). Details of this package could be
found in the User's Manual for XTRACTOR (Parameters Estimation Through
Nonlinear Regression) available in the Chemical Engineering Department
of the University of Arizona. This program is designed to run on the
DEC System - 10 of the University of Arizona. HANDLR, an interactive
program, sets up the batch run input data file. User model has to be
defined in a user subroutine called USUBR. An example of this subroutine
for the fit of binary osmotic coefficient data of aqueous sulfuric acid
to the Bromley's model with three parameters is presented on the next
page.

```
      SUBROUTINE USUBR(NPROB,NDATA,NUPAR,ND,F)
C     FIT OF BINARY DATA OF H2SO4 WITH THREE PARAMETERS
C     BY LEAST SQUARES METHOD(EXTRACTOR)
      DIMENSION F(200),X(200),Y(200)
      COMMON/USER/B,C,D,DUM(37)
      COMMON/USER/Y,X,ARRAY(200,8)
      COMMON/USER/LP
      DATA NSTRT/1/
      DO 20 I=1,NDATA
      T1=1.+SQRT(X(I))
      T2=1.+1.5*X(I)
      T3=1.+0.75*X(I)
      T4=X(I)*X(I)
      TERM1=2.3537/X(I)*(T1-1./T1-2.*ALOG(T1))
      TERM2=T2/(T3*T3)-ALOG(T3)/(0.75*X(I))
      TERM3=2.303*X(I)/2.
      TERM4=4.606*T4/3.
      TERM5=6.909*T4*X(I)/4.
      F(I)=TERM1-0.3685*TERM2-B*(3.6848*TERM2+TERM3)-C*TERM4-D*TERM5
   20 CONTINUE
      RETURN
      END
```

APPENDIX C

AN OUTLINE OF THE PROGRAM FOR GROWTH CALCULATIONS

The program GROWTH predicts the size and chemical composition of a marine aerosol exposed to atmospheric concentrations of SO_2, NO, NO_2, NH_3, H_2SO_4, and water vapor as a function of the exposure time. Equilibrium chemistry of nitrate formation and aqueous SO_2, gas phase oxidation of SO_2 to H_2SO_4 and subsequent diffusion kinetic of this H_2SO_4 into the aerosol droplet are included. The condensation of water causes the particle to grow.

GROWTH: This is the main program and it reads all the information required, i.e., bulk (gas) phase concentrations, initial conditions for differential equations, number and size of time steps and the initial composition and size of the particle. It prints out results; particle size and composition as a function of time.

EQLBRM: This subroutine calculates the concentrations of various ionic species from initial guesses of the hydrogen ion concentration, the solute activity coefficients and the water activity. It checks to see whether the electroneutrality equation is satisfied and if not, it calls the subroutine BROMLEY to compute activity coefficients. From a new guess of hydrogen ion concentration obtained by the bisection method and these new activity coefficients, it again predicts the ionic concentrations of the different species. This procedure is repeated until the electroneutrality equation is satisfied.

DIFFUN: This subroutine provides the differential equations to be solved by RKGS routine. It utilizes subroutine EQLBRM to obtain ionic concentrations and subroutine SIZE to obtain a new particle size. Two differential equations are solved; one describing the diffusion of sulfuric acid into the particle and another describing the diffusion of the hydrochloric acid from the particle.

BROMLEY: This subroutine is called by EQLBRM. It computes the solute activity coefficients and osmotic coefficients for the given concentrations of various ionic species. It uses Bromley's model with three parameters for calculating these multicomponent properties.

RKGS: This is a standard integration package. It uses a fourth order Runge-Kutta algorithm with variable step size to solve the differential equations. Subroutine DIFFUN provides these differential equations. RKGS can solve up to twenty differential equations.

OUTP: This is a dummy subroutine and is not used anywhere. But it must be supplied for RKGS subroutine.

SIZE: This subroutine computes a new particle size from total amounts of each ionic species that lowers the water activity and the osmotic coefficient provided by BROMLEY.

Initial Region Limits for pH and Estimates

for Activity Coefficients and Water Activity

It is important to provide these estimates with a certain degree of accuracy to enable the equilibrium calculations to converge. The accuracy at which these estimates should be provided increases with increasing expected ionic strength of the solution. Program GARCIA predicts the activity coefficients of HNO_3 and NH_4NO_3 and water activity for the ternary $HNO_3-NH_4NO_3-H_2O$ system as a function of the ionic strength of NH_4NO_3. Concentration of hydrogen ions is taken to be 1.0 E-3 though the results are not significantly affected if pH is between 2 and 5. An example of the utilization of results of GARCIA to provide initial guesses for equilibrium calculations is presented here.

From Table 4:

$$[NO_3^-] = \frac{K_{2N} \, P_{NO_2}^2 \, a_w}{(K_{1N} \, P_{NO} \, P_{NO_2} \, a_w)^{\frac{1}{2}} \, [H^+] \, \gamma_{H^+} \, \gamma_{NO_3^-}}$$

and

$$[NH_4^+] = \frac{K_{1A} \, K_{HA} \, P_{NH_3} \, [H^+] \, \gamma_{H^+}}{K_w \, a_w \, \gamma_{NH_4^+}}$$

For electroneutrality equation to be satisfied,

$$[NH_4^+] \cong [NO_3^-]$$

also

$$\frac{\gamma_{H^+}}{\gamma_{NH_4^+}} = \left(\frac{\gamma_{HNO_3}}{\gamma_{NH_4NO_3}}\right)^2 = avgama2$$

and

$$\gamma_{H^+}\,\gamma_{NO_3^-} = (\gamma_{HNO_3})^2 = avgama3$$

Let $P_{NO_2} = 5.E-8$

$P_{NH_3} = 4.E-8$

$P_{NO} = 5.E-7$

Let $I = 6.0$, then from the results of GARCIA:

gamal = $0.5720 = \gamma_{HNO_3}$

gama2 = $0.2904 = \gamma_{NH_4NO_3}$

$a_w = 0.8089$

$[NH_4^+] = 1.9248 \times 10^4\ [H^+]$

$[NO_3^-] = \dfrac{1.6916 \times 10^{-3}}{[H^+]}$

for $[NH_4^+] \cong [NO_3^-]$

$$[H^+] = 2.9645 \times 10^{-4}$$

which in turn predicts

$$[NH_4^+] = 5.7$$

$$[NO_3^-] = 5.7$$

I should be decreased thus:

Let $I = 5.4$

By following the identical procedure, we get:

$$[NH_4^+] = [NO_3^-] = 5.41$$

$$[H^+] = 3.209 \times 10^{-4}$$

and   gama1 = 0.5676

gama2 = 0.3043

a_w = 0.8279

Ionic strength is thus between 5.4 and 6.0 and the values of hydrogen ions predicted can be used as upper and lower bounds.

```
       PROGRAM GROWTH(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
C      ...............................................................
C      THIS PROGRAM IS ON A FILE CALLED FIJI.F4 (PPN 5700,22453)
C      ...............................................................
       REAL M1,M2,M3,M4,M5,M6,M7,M8,M9,M12,M14,M16
       REAL M50,M60,M70,MT5,MT6,MT7
       DIMENSION DTMN(2),DTMX(2),STEP(2),TINC(2),TFINL(2)
       DIMENSION PRMT(5),DERY(3)
       DIMENSION Y(2),YY(2),AUX(8,2)
       DIMENSION CH(2),GAM1(2),GAM2(2),WATA(2),CION(1)
       EXTERNAL DIFFUN
       EXTERNAL OUTP
       COMMON/XMOL/M1,M2,M3,M4,M5,M6,M7,M8,M12,M14,M16
       COMMON/XMOLO/M50,M60,M70,MT5,MT6,MT7
       COMMON/XMISCL/FLAM,RGAS,TEMP,PSAT,SIGMA
       COMMON/XVOL/VH2O,VSO2,VNH3,VNO1,VNO2,VHCL,VHNO3,VH2SO4
       COMMON/XDIFF/DH2SO4,DHCL
       COMMON/XYES/NY,YY
       COMMON/XVARE/VT,VOL,R,TH2O,CURVE
       COMMON/XBULK/PBNO1,PBNO2,PBNH3,PBSO2,PBH2SO4,PBH2O
       COMMON/XSURF/PSNO1,PSNO2,PSNH3,PSSO2,PSH2SO4,PSH2O,PSHCL
       COMMON/XPRES/PNO1,PNO2,PNH3,PSO2,PH2O
       COMMON/XEQLB/CH,AW,CION,GAM1,GAM2,WATA
       COMMON/XIONIC/I,GAMA1,GAMA2,NUGAM14,NUGAM34,NUAW
       ONE=1.0D+00
       TWO=2.0D+00
       THREE=3.0D+00
       FOUR=4.0D+00
       PI=FOUR*ATAN(ONE)
C      MEAN FREE PATH(UM)
       FLAM=0.055D+00
C      GAS CONSTANT(LITER-ATMOSPHERE/GMOLE.DEG K)
       RGAS=0.0821
C      TEMPERATURE(DEG K)
       TEMP=298.0D+00
C      WATER SATURATION PRESSURE(ATM)
       PSAT=23.76D+00/760.
C      SURFACE TENSION OF PARTICLE(ERG/CM**2)
       SIGMA=72.0D+00
C      ERROR CRITERION(TEPS)
       TEPS=0.05
C      NO. OF DIFFERENT TIME INTERVALS(NTIME)
       NTIME=2
C      NO. OF  DIFFERENTIAL EQUATIONS TO BE SOLVED(NY)
       NY=2
C      READ MINIMUM AND MAXIMUM ALLOWABLE STEP SIZE,
C      INITIAL STEP SIZE,TIME BETWEEN OUTPUTS AND FINAL TIME.
       DTMN(1)=0.001
       DTMX(1)=1.0
       STEP(1)=0.05
       TINC(1)=1.0
       TFINL(1)=10
       DTMN(2)=0.001
       DTMX(2)=1.0
       STEP(2)=0.05
       TINC(2)=10.
       TFINL(2)=120.
C      SUBSCRIPT CODE IS EXPLAINED HERE
C      ALL CATIONS ARE DESIGNATED BY ODD NOS.
C      ALL ANIONS ARE DESIGNATED BY EVEN NOS.
C      1=HYDROGEN
```

```
C        3=AMMONIUM
C        5=MAGNESIUM
C        7=SODIUM
C        2=SULFATE
C        4=NITRATE
C        6=CHLORIDE
C        8=HYDROXIDE
C        12=SULFITE
C        14=HYDROGEN SULFITE
C        16=NITRITE
C        INITIAL "STOICHIOMETRIC" CONCENTRATION(MOLES/LITER)
         M50=0.0460
         M60=0.7227
         M70=0.6307
C        INITIAL DROPLET RADIUS(UM)
         R=0.1D+00
C        PARTIAL LIQUID MOLAR VOLUMES FOR DIFFUSING SPECIES
C        IN LITERS/MOLE
C        VH2O=PARTIAL MOLAR VOLUME OF H2O
C        VSO2=PARTIAL MOLAR VOLUME OF SO2
C        VNH3=PARTIAL MOLAR VOLUME OF NH3
C        VNO1=PARTIAL MOLAR VOLUME OF NO
C        VNO2=PARTIAL MOLAR VOLUME OF NO2
C        VHCL=PARTIAL MOLAR VOLUME OF HCL
C        VHNO3=PARTIAL MOLAR VOLUME OF HNO3
C        VH2SO4=PARTIAL MOLAR VOLUME OF H2SO4
C        MOLAR VOLUME OF A GAS IN LIQUID PHASE IS APPROXIMATED
C        BY THE MOLAR VOLUME OF ITS ACID (VSO2=VH2SO4 ETC.)
         VH2O=0.018
         VSO2=0.05368
         VNH3=0.039
         VNO1=0.04189
         VNO2=0.04189
         VHCL=0.045
         VHNO3=0.04189
         VH2SO4=0.05368
C        DIFFFUSIVITY OF H2SO4(CM**2/SEC)
         DH2SO4=0.54
C        DIFFUSIVITY OF HCL(HYDROCHLORIC ACID)
         DHCL=0.185
C        BULK  POLLUTANT CONCENTRATIONS(PB)IN ATMOSPHERE
         PBNO1=1.0D-07
         PBNO2=5.0D-08
         PBNH3=1.0D-08
         PBSO2=1.0D-08
         PBH2SO4=5.0D-12
         PBH2O=2.814D-02
C        INITIAL CONDITION FOR Y(UUMOLES OF SULFATE AND CHLORIDE)
         Y(1)=0.00
         Y(2)=3.0274D-06
         YY(1)=Y(1)
         YY(2)=Y(2)
C        CALCULATE......
C        CALCULATE INITIAL PARTICLE VOLUME(UM**3)
         VT=FOUR*PI*R*R*R/THREE
         VOL=VT
C        CALCULATE INITIAL WATER IN PARTICLE(UUMOLES)
         TH2O=55.51*VT*1.0E-03
C        CALCULATE INITIAL MASS(MOLES) OF MAGNESIUM,SODIUM AND
C        CHLORIDE.
         MT5=M50*VT*1.0D-15
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       MT6=M60*VT*1.0D-15
       MT7=M70*VT*1.0D-15
       WRITE(6,131)VT
   131 FORMAT(1H0,11H VT(UM**3)=,D15.5)
C      CALCULATE CURVATURE TERM TO BE USED IN KELVIN EQUATION
C      THE UNITS(AFTER CONVERSION FATORS)ARE UM*(MOLES/LITER)
       CURVE=THO*SIGMA*10.41D-03/(RGAS*TEMP*1.055D+00)
C      PS IS SURFACE PRESSURE(ATM)
C      P IS PRESSURE OVER A FLAT SURFACE(FOR HENRY'S LAW)IN ATM.
       PSNO1=PBNO1
       PSNO2=PBNO2
       PSNH3=PBNH3
       PSSO2=PBSO2
       PSH2SO4=PBH2SO4
       PSH2O=PBH2O
       PNO1=PSNO1*EXP(-CURVE*VNO1/R)
       PNO2=PSNO2*EXP(-CURVE*VNO2/R)
       PNH3=PSNH3*EXP(-CURVE*VNH3/R)
       PSO2=PSSO2*EXP(-CURVE*VSO2/R)
       PH2O=PSH2O*EXP(-CURVE*VH2O/R)
C      PROVIDE INITIAL CONDITIONS FOR DIFFERENTIAL EQUATION
       TLAST=0.0D+00
       TNEXT=0.0D+00
       DT=STEP(1)
C      PROVIDE PARAMETERS FOR RKGS ROUTINE
C      SEE RKGS FOR DESCRIPTION OF PARAMETERS
       PRMT(1)=0.0D+00
       PRMT(2)=TINC(1)
       PRMT(3)=STEP(1)
       PRMT(4)=TEPS
       DERY(1)=ONE/NY
       DERY(2)=ONE/NY
       DERY(3)=ONE/NY
       T=0.0D+00
       NT=1
C      SET INITIAL REGION LIMITS FOR PH
C      AND GUESSES FOR ACTIVITY COEFFICIENTS AND WATER ACTIVITY
C      THE PROCEDURE FOR GETTING THESE INITIAL GUESSES IS
C      EXPLAINED IN THE APPENDIX OF M.S. THESIS OF PRADEEP
C      SAXENA.
       CH(1)=1.2845D-03
       CH(2)=1.2845D-03
       AW=PH2O/PSAT
       GAM1(1)=0.5592
       GAM2(1)=0.3723
       WATA(1)=0.8907
       GAM1(2)=0.5592
       GAM2(2)=0.3723
       WATA(2)=0.8907
       WRITE(6,27)Y(2),MT5,MT6,MT7
   27 FORMAT(1H0,6H Y(2)=,D12.5,5X,5H MT5=,D12.5,5X,5H MT6=,
      /D12.5,5X,5H MT7=,D12.5)
       WRITE(6,200)VT
   200 FORMAT(1H0,4H VT=,D12.5)
       CALL EQLBRM(Y)
     7 CONTINUE
       IF(T.LT.TNEXT) GO TO 12
       TNEXT=TNEXT+TINC(NT)
       WRITE(6,114)T,VT,R
   114 FORMAT(1H0,8H T(MIN)=,D12.5,5X,11H VT(UM**3)=,D12.5,
      / 5X,7H R(UM)=,D12.5)
```

```
      WRITE(6,107)PNO1,PNO2,PNH3,PSO2,PH2O
  107 FORMAT(1HO,6H PNO1=,D12.5,3X,6H PNO2=,D12.5,3X,
     / 6H PNH3=,D12.5,3X,6H PSO2=,D12.5,3X,6H PH2O=,D12.5)
      WRITE(6,108)PSNO1,PSNO2,PSNH3
  108 FORMAT(1HO,7H PSNO1=,D12.5,5X,7H PSNO2=,D12.5,5X,
     /7H PSNH3=,D12.5)
      WRITE(6,109)PSSO2,PSH2O
  109 FORMAT(1HO,7H PSSO2=,D12.5,5X,7H PSH2O=,D12.5)
      WRITE(6,157)M1,M3,M5,M7
  157 FORMAT(1HO,4H M1=,D12.5,5X,4H M3=,D12.5,5X,4H M5=,D12.5,5X,
     /4H M7=,D12.5)
      WRITE(6,158)M2,M4,M6,M8
  158 FORMAT(1HO,4H M2=,D12.5,5X,4H M4=,D12.5,5X,4H M6=,D12.5,5X,
     /4H M8=,D12.5)
      WRITE(6,159)M12,M14,M16
  159 FORMAT(1HO,5H M12=,D12.5,5X,5H M14=,D12.5,5X,5H M16=,D12.5)
   13 CONTINUE
   12 CONTINUE
C     PERFORM NEXT TIME STEP
C         2). ALLOW H2SO4 AND HCL DIFFUSION KINETICS
C         2).ALLOW PARTICLE TO GROW/SHRINK BY
C         CONDENSATION/EVAPORATION.
C     CHECK TO SEE IF FINAL TIME HAS BEEN REACHED
      IF(TLAST.GE.TFINL(NTIME) ) CALL EXIT
      IF(TLAST.LT.TFINL(NT) ) GO TO 16
      NT=NT+1
C     RESET THE STEP SIZE
      PRMT(2)=PRMT(2)-TINC(NT-1)
      DT=STEP(NT)
      PRMT(2)=PRMT(2)+TINC(NT)
      PRMT(3)=DT
   16 CONTINUE
      CALL RKGS(PRMT,Y,DERY,NY,IND,DIFFUN,OUTP,AUX)
      T=PRMT(2)
      TLAST=T
      IF(IND.GE.11) GO TO 11
      DERY(1)=ONE/NY
      DERY(2)=ONE/NY
      DERY(3)=ONE/NY
      PRMT(1)=PRMT(2)
      PRMT(2)=PRMT(2)+TINC(NT)
      CALL SIZE
      GO TO 7
   11 CONTINUE
      WRITE(6,123)IND,T,Y
  123 FORMAT(1X,7H ERROR=,I5,/,1X,3(8D15.5,/) )
      CALL EXIT
      END
      SUBROUTINE EQLBRM(Y)
C     THIS SUBROUTINE......
C         1).CALCULATES THE CONCENTRATIONS OF VARIOUS IONIC
C     SPECIES FROM AN INITIAL GUESS OF H+ CONCENTRATION,
C     ACTIVITY COEFFICIENTS OF NH4NO3 AND HNO3 AND AW.
C         2).CHECKS TO SEE WHETHER THE ELECTRONEUTRALITY
C     EQUATON IS SATISFIED.
      REAL KW,K1A,KHA,K1S,KHS,K2S,K1N,K2N,K3N,KHH,K1H
      REAL NUGAMA1,NUGAMA2,NUGAMA3,NUAW
      REAL NUPH,I
      REAL NUGAM14,NUGAM34
      REAL M1,M2,M3,M4,M5,M6,M7,M8,M9,M12,M14,M16
      REAL MT5,MT7
```

```
      DIMENSION CION(1),CH(2),GAM1(2),GAM2(2),WATA(2)
      DIMENSION DCH(2)
      DIMENSION Y(2)
      COMMON/XMOL/M1,M2,M3,M4,M5,M6,M7,M8,M12,M14,M16
      COMMON/XMOLO/M50,M60,M70,MT5,MT6,MT7
      COMMON/XMISCL/FLAM,RGAS,TEMP,PSAT,SIGMA
      COMMON/XVOL/VH2O,VSO2,VNH3,VNO1,VNO2,VHCL,VHNO3,VH2SO4
      COMMON/XDIFF/DH2SO4,DHCL
      COMMON/XYES/NY,YY
      COMMON/XVARE/VT,VOL,R,TH2O,CURVE
      COMMON/XBULK/PBNO1,PBNO2,PBNH3,PBSO2,PBH2SO4,PBH2O
      COMMON/XSURF/PSNO1,PSNO2,PSNH3,PSSO2,PSH2SO4,PSH2O,PSHCL
      COMMON/XPRES/PNO1,PNO2,PNH3,PSO2,PH2O
      COMMON/XEQLB/CH,AW,CION,GAM1,GAM2,WATA
      COMMON/XIONIC/I,GAMA1,GAMA2,NUGAM14,NUGAM34,NUAW
C     EPSLON IS THE MAXIMUM TOLERABLE ERROR IN THE
C     ELECTRONEUTRALITY EQUATION.
      EPSLON=0.01
C     FOLLOWING ARE THE EQUILIBRIUM CONSTANTS( FOR REF.
C     SEE PETERSON AND SEINFELD,AICHEJ 1979,P.831 ).
      KW=1.008D-14
      K1A=1.774D-05
      KHA=57.0
      K1S=0.0127
      KHS=1.24
      K2S=6.24D-08
      K1N=122.
      K2N=4.3D+05
      K3N=5.1D-04
      KHH=19.0
      K1H=1.3D+06
      TEMP=298
      INDEX=1
C     PARAMETER J IS A COUNTER FOR ITERATIONS ON ACTIVITY
C     COEFFS. FOR EVERY GUESS OF CION(1).NORMALLY IT SUFFICES
C     TO DO ONE ITERATION( J.LT.2 IN IF STATEMENT).SOMETIMES
C     RESULTS MAY CONVERGE FASTER IF THE NO. OF ITERATIONS
C     IS INCREASED ( TO AS MUCH AS 20).SUCH COMPUTATIONS ARE
C     NOT PERFORMED FOR INITIAL "BOUNDARIES SETTING" AND J
C     IS ALWAYS KEPT EQUAL TO 20
      J=20
C     PARAMETER K INDICATES WHEN TWO SUCCESSIVE COMPUTATIONS
C     SHOW EQUAL VALUES OF CH(1) AND CH(2).THIS WOULD IMPLY THAT
C     ACTUAL SOLUTION HAS BEEN "JUMPED" OVER.
      K=0
      ONE=1.0D+00
      TWO=2.0D+00
      FOUR=4.0D+00
    7 CONTINUE
C     XMULT IS A VARIABLE MULTIPLIER TO INITIALLY CHANGE
C     UPPER AND LOWER BOUNDS
      XMULT=1.001
      CION(1)=CH(INDEX)
      GAMA1=GAM1(INDEX)
      GAMA2=GAM2(INDEX)
      AW=WATA(INDEX)
      GO TO 1
    8 CONTINUE
      J=0
   10 J=J+1
      CION(1)=CHNEXT
```

```
C       GAMA1 IS THE ACTIVITY COEFFICIENT OF HNO3(ALSO CALLED
C       GAMA14)
C       GAMA2 IS THE ACTIVITY COEFFICIENT OF NH4NO3 ( ALSO CALLED
C       GAMA34 )
        GAMA1=NUGAM14
        GAMA2=NUGAM34
      1 CONTINUE
C       CALCULATE IONIC CONCENTRATIONS,GIVEN AN INITIAL
C       GUESS FOR THE H+ CONCENTRATION (CION(1) )
C       AVERAGE GAMAS ARE THE RATIOS OF MEAN IONIC ACTIVITY
C       COEFFICIENTS (SEE M.S. THESIS,PRADEEP SAXENA )
        AVGAMA2=(GAMA1/GAMA2)**2.
        AVGAMA3=GAMA1*GAMA1
        C1=K1A*KHA*PSNH3*AVGAMA2/(AW*KW)
        C2=KW*AW
        C3=K1S*KHS*PSSO2
        C4=K1S*KHS*K2S*PSSO2
        C5=K3N*SQRT(K1N*PSNO1*PSNO2*AW)
        C6=K2N*(PSNO2*PSNO2*AW)/(SQRT(K1N*PSNO1*PSNO2*AW)*AVGAMA3)
        M1=CION(1)
        M3=C1*CION(1)
        M5=MT5/(VT*1.0D-15)
        M7=MT7/(VT*1.0D-15)
        M2=Y(1)*1.0D+03/VT
        M4=C6/CION(1)
        M6=Y(2)*1.0D+03/(VT*(ONE+CION(1)/K1H) )
        M8=C2/CION(1)
        M12=C4/(CION(1) )**2.
        M14=C3/CION(1)
        M16=C5/CION(1)
C       ELECTRONEUTRALITY EQN. IS SOLVED HERE.........
C       1). SPLUS=SUMMATION OF CONCENTRATIONS OF CATIONS.
C       2). SMINUS=SUMMATION OF CONCENTRATIONS OF ANIONS.
C       THEN ABS(SPLUS-SMINUS)/(SMALLER OF THE TWO)
C       SHOULD BE LESS THAN EPSLON.
        SPLUS=M1+M3+M7+2.*M5
        SMINUS=M4+M6+M8+M14+M16+2.*(M2+M12)
        DELT=SPLUS-SMINUS
        CHPLUS=SMINUS-SPLUS+CION(1)
        DELCH=CHPLUS-CION(1)
        ABSDELT=ABS(DELT)
        IF(SPLUS.GT.SMINUS ) EROR=ABSDELT/SMINUS
        IF(SPLUS.LE.SMINUS ) EROR=ABSDELT/SPLUS
        CALL BROMLEY
        IF(EROR.LE.EPSLON) GO TO 9
        IF(I.GT.100 ) GO TO 66
        IF(J.LT.2) GO TO 10
        IF(INDEX.GT.2)  GO  TO   2
        DCH(INDEX)=DELCH
        SIGN=DCH(INDEX)*((-ONE)**(INDEX+1) )
        NPOWER=(-ONE)**INDEX
        IF(SIGN.GT.0.0D+00 ) GO TO   3
        CH(INDEX)=CH(INDEX)*(XMULT**NPOWER)
        XMULT=XMULT*1.01
        GAM1(INDEX)=NUGAM14
        GAM2(INDEX)=NUGAM34
        GO  TO   7
      3 CONTINUE
        INDEX=INDEX+1
        IF(INDEX.GT.2 ) GO TO 6
        GO TO 7
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    2 CONTINUE
C       DEPENDING UPON SIGN OF DELCH, REPLACE LEFT OR RIGHT
C       HAND VALUES OF SEARCH INTERVAL
        IF (DELCH.GT.0.0D+00 ) GO TO 5
        CH(2)=CION(1)
        DCH(2)=DELCH
        GAM1(2)=NUGAM14
        GAM2(2)=NUGAM34
        GO TO 6
    5 CONTINUE
        CH(1)=CION(1)
        DCH(1)=DELCH
        GAM1(1)=NUGAM14
        GAM2(1)=NUGAM34
    6 CONTINUE
C       GET NEXT GUESS FOR C(H+) BY BISECTION METHOD
        A1=ALOG10(CH(1) )
        A2=ALOG10(CH(2) )
        B1=A1+(A2-A1)/TWO
        CHNEXT=10.0**B1
        INDEX=INDEX+1
        IF(CH(1).EQ.CH(2) ) K=K+1
        IF(K.GT.2 ) GO TO 77
        IF(INDEX.GT.1000) GO TO 20
        GO TO 8
    9 CONTINUE
        TERM1=1.0D+03/(VT*KHH*(1.0D+00+K1H/CION(1) ) )
        PSHCL=TERM1*Y(2)*EXP(CURVE*VHCL/R)
        PH=-ALOG10(CION(1) )
        GO TO 85
   66 WRITE(6,67)I
   67 FORMAT(1H0,3H I=,F6.3)
        GO TO 85
   77 WRITE(6,78)CH(1),CH(2),K
   78 FORMAT(1H0,36H CH(1) AND CH(2) VALUES BECOME EQUAL,
       /5X,7H CH(1)=,D12.5,5X,7H CH(2)=,D12.5,5X,3H K=,I2)
        GO TO 85
   20 WRITE(6,55)
   55 FORMAT(1H0,20X,29H CALCULATIONS DO NOT CONVERGE,//////)
   85 CONTINUE
        RETURN
        END
        SUBROUTINE DIFFUN(T,Y,YDOT)
C       THIS SUBROUTINE CALCULATES THE DERIVATIVES OF THE
C       FUNCTIONS TO BE INTEGRATED.THE TIME STEP IS ALWAYS MIN.
        DIMENSION YY(2),Y(2),YDOT(2)
        DIMENSION CH(2),CION(1)
        DIMENSION GAM1(2),GAM2(2),WATA(2)
        COMMON/XMOL/M1,M2,M3,M4,M5,M6,M7,M8,M12,M14,M16
        COMMON/XMOLO/M50,M60,M70,MT5,MT6,MT7
        COMMON/XMISCL/FLAM,RGAS,TEMP,PSAT,SIGMA
        COMMON/XVOL/VH2O,VSO2,VNH3,VNO1,VNO2,VHCL,VHNO3,VH2SO4
        COMMON/XDIFF/DH2SO4,DHCL
        COMMON/XYES/NY,YY
        COMMON/XVARE/VT,VOL,R,TH2O,CURVE
        COMMON/XBULK/PBNO1,PBNO2,PBNH3,PBSO2,PBH2SO4,PBH2O
        COMMON/XSURF/PSNO1,PSNO2,PSNH3,PSSO2,PSH2SO4,PSH2O,PSHCL
        COMMON/XPRES/PNO1,PNO2,PNH3,PSO2,PH2O
        COMMON/XEQLB/CH,AW,CION,GAM1,GAM2,WATA
        COMMON/XIONIC/I,GAMA1,GAMA2,NUGAM14,NUGAM34,NUAW
        DO 2 J=1,NY
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```
         YY(J)=Y(J)
       2 CONTINUE
         ONE=1.0D+00
         TWO=2.0D+00
         THREE=3.0D+00
         FOUR=4.0D+00
         PI=4.0*ATAN(ONE)
         R=(THREE*VT/(FOUR*PI) )**(ONE/THREE)
C        UNITS OF P ARE ATMOSPHERES
         PNO1=PSNO1*EXP(-CURVE*VNO1/R)
         PNO2=PSNO2*EXP(-CURVE*VNO2/R)
         PNH3=PSNH3*EXP(-CURVE*VNH3/R)
         PSO2=PSSO2*EXP(-CURVE*VSO2/R)
         PH2O=PSH2O*EXP(-CURVE*VH2O/R)
         AW=PH2O/PSAT
         CH(1)=CION(1)
         CH(2)=CION(1)
         GAM1(1)=GAMA1
         GAM2(1)=GAMA2
         WATA(1)=AW
         GAM1(2)=GAMA1
         GAM2(2)=GAMA2
         WATA(2)=AW
         CALL EQLBRM(Y)
         CALL SIZE
         GNUD=FLAM/R
         EL=(0.71D+00+FOUR*GNUD/THREE)/(ONE+GNUD)
         ELKN=EL*GNUD
         CONST=FOUR*PI*R/(RGAS*TEMP*(ONE+ELKN) )
C        RETURN DERIVATIVES IN UNITS OF (UUMOLES/MINUTE)
         YDOT(1)=6.0D+00*CONST*DH2SO4*PBH2SO4*1.0D+06
         YDOT(2)=-6.0D+00*CONST*DHCL*PSHCL*1.0D+06
         RETURN
         END
         SUBROUTINE BROMLEY
C        THIS SUBROUTINE CALCULATES:
C            1).ACTIVITY COEFFICIENTS OF HNO3 AND NH4NO3
C            2),OSMOTIC COEFFICIENT
C        FROM EQNS 6 THRU 11 AND EQNS 19 AND 20 OF SAXENA AND
C        PETERSON(1980)
C        FOR ACTIVITY COEFFICIENTS COMPUTATION PURPOSE
C        THE MULTICOMPONENT SOLUTION IS ASSUMED TO CONSIST OF
C        H2SO4,HNO3,(NH4)2SO4 AND NH4NO3.
C        ....................................................
C        FOR OSMOTIC COEFF. COMPUTATION MGCL2(MAGNESIUM CHLORIDE)
C        AND NACL(SODIUM CHLORIDE) ARE ALSO INCLUDED.
C        ....................................................
         REAL M1,M2,M3,M4,M5,M6,M7
         REAL I,NUAW,NUGAM14,NUGAM34
         COMMON/XMOL/M1,M2,M3,M4,M5,M6,M7,M8,M12,M14,M16
         COMMON/XMOLO/M50,M60,M70,MT5,MT6,MT7
         COMMON/XMISCL/FLAM,RGAS,TEMP,PSAT,SIGMA
         COMMON/XVOL/VH2O,VSO2,VNH3,VNO1,VNO2,VHCL,VHNO3,VH2SO4
         COMMON/XDIFF/DH2SO4,DHCL
         COMMON/XYES/NY,YY
         COMMON/XVARE/VT,VOL,R,TH2O,CURVE
         COMMON/XBULK/PBNO1,PBNO2,PBNH3,PBSO2,PBH2SO4,PBH2O
         COMMON/XSURF/PSNO1,PSNO2,PSNH3,PSSO2,PSH2SO4,PSH2O,PSHCL
         COMMON/XPRES/PNO1,PNO2,PNH3,PSO2,PH2O
         COMMON/XEQLB/CH,AW,CION,GAM1,GAM2,WATA
         COMMON/XIONIC/I,GAMA1,GAMA2,NUGAM14,NUGAM34,NUAW
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```
      COMMON/XBROM/OSMO,SUM1
C     HERE ARE CONSTANTS IN BROMLEY'S MODEL......
      B12=0.03772
      C12=-0.0001679
      D12=-0.000000284
      B32=-0.03398
      C32=0.002868
      D32=-0.00007936
      B14=0.08337
      C14=-0.002743
      D14=0.00003034
      B34=-0.03564
      C34=0.001124
      D34=-0.00001484
      B56=0.1129
      C56=0.00
      D56=0.00
      B76=0.0574
      C76=0.00
      D76=0.00
C     COMPLEX B ,C AND D ARE COMPUTED FROM EQUATION(15)
C     OF BROMLEY(1973) WITH MOLALITIES INSTEAD OF NU
C     THESE COMPLEX COEFFICIENTS ARE DESIGNATED AS BMEAN,CMEAN
C     AND DMEAN
      SUM1=M1+M2+M3+M4+M5+M6+M7
      SUM2=M1+4.*M2+M3+M4+4.*M5+M6+M7
      SUM3=B34*M3*M4+B14*M1*M4+B76*M7*M6+9./4.*
     /(B32*M3*M2+B12*M1*M2+B56*M5*M6)
      SUM4=C34*M3*M4+C14*M1*M4+C76*M7*M6+9./4.*
     /(C32*M3*M2+C12*M1*M2+C56*M5*M6)
      SUM5=D34*M3*M4+D14*M1*M4+D76*M7*M6+9./4.*
     /(D32*M3*M2+D12*M1*M2+D56*M5*M6)
      BMEAN=4.*SUM3/(SUM1*SUM2)
      CMEAN=4*SUM4/(SUM1*SUM2)
      DMEAN=4.*SUM5/(SUM1*SUM2)
C     IONIC STRENGTH(I) COMPUTATION
      I=0.5*SUM2
      ZOT1=0.511*SQRT(I)/(1.+SQRT(I) )
      ZOT2=2.*I/(1.+0.75*I)**2.
      ZOT3=I/(1.+1.5*I)**2.
      ZOT4=I*I
      ZOT5=ZOT4*I
C     GAMA120,GAMA140,GAMA320 AND GAMA340 ARE BINARY ACTIVITY
C     COEFFICIENTS(EQN. 19 OF SAXENA AND PETERSON 1980)
      GAMA120=10.**(-2.*ZOT1+(0.06+0.6*B12)*ZOT2+B12*I+C12*ZOT4
     /+D12*ZOT5)
      GAMA140=10.**(-ZOT1+(0.06+0.6*B14)*ZOT3+B14*I+C14*ZOT4+
     /D14*ZOT5)
      GAMA320=10.**(-2.*ZOT1+(0.06+0.6*B32)*ZOT2+B32*I+C32*ZOT4+
     /D32*ZOT5)
      GAMA340=10.**(-ZOT1+(0.06+0.6*B34)*ZOT3+B34*I+C34*ZOT4+
     /D34*ZOT5)
      S1=9./4.*M2/I*ALOG10(GAMA120)+M4/I*ALOG10(GAMA140)
      S2=ZOT1*(0.45*M2/I+M4/I)
      F1=S1+S2
      S3=9./4.*M2/I*ALOG10(GAMA320)+M4/I*ALOG10(GAMA340).
      S4=ZOT1*(0.45*M2/I+M4/I)
      F3=S3+S4
      S5=M1/I*ALOG10(GAMA140)+M3/I*ALOG10(GAMA340)
      S6=ZOT1*(M1/I+M3/I)
      F4=S5+S6
```

```
      GAMA14=10.**(-ZOT1*0.5*(F1+F4) )
      GAMA34=10.**(-ZOT1*0.5*(F3+F4) )
C     GAMA14 AND GAMA34 ARE ACTIVITY COEFFICIENTS OF
C     HNO3 AND NH4NO3 RESPECTIVELY
C     HERE IS THE COMPUTATIONN OF OSMOTIC COEFFICIENT(OSMO)
      ZOT6=1.+SQRT(I)
      T1=ZOT6-1./ZOT6-2.*ALOG(ZOT6)
      TERM1=2.303*0.511*1.6/I*T1
      ZOT7=1.0+1.875*I
      ZOT8=1.0+0.9375*I
      T2=ZOT7/(ZOT8*ZOT8)-ALOG(ZOT8)/(ZOT8-1.0)
      TERM2=2.303*(0.06+0.6*BMEAN)*1.6/0.9375*T2
      TERM3=2.303*BMEAN*I/2.
      TERM4=4.606*CMEAN*ZOT4/3.
      TERM5=6.909*DMEAN*ZOT5/4.
      COMP=TERM1-TERM2-TERM3-TERM4-TERM5
      OSMO=1.-COMP
C     THIS OSMOTIC COEFF. IS USED IN SUBROUTINE SIZE
      NUGAM14=GAMA14
      NUGAM34=GAMA34
      RETURN
      END
C
C
C     .........................................................................
C
C        SUBROUTINE RKGS
C
C        PURPOSE
C TO SOLVE A SYSTEM OF FIRST ORDER ORDINARY DIFFERENTIAL
C EQUATIONS WITH GIVEN INITIAL VALUES.
C
C        USAGE
C CALL RKGS (PRMT,Y,DERY,NDIM,IHLF,FCT,OUTP,AUX)
C PARAMETERS FCT AND OUTP REQUIRE AN EXTERNAL STATEMENT.
C
C        DESCRIPTION OF PARAMETERS
C PRMT   - AN INPUT AND OUTPUT VECTOR WITH DIMENSION GREATER
COR EQUAL TO 5, WHICH SPECIFIES THE PARAMETERS OF
CTHE INTERVAL AND OF ACCURACY AND WHICH SERVES FOR
CCOMMUNICATION BETWEEN OUTPUT SUBROUTINE (FURNISHED
CBY THE USER) AND SUBROUTINE RKGS. EXCEPT PRMT(5)
CTHE COMPONENTS ARE NOT DESTROYED BY SUBROUTINE
CRKGS AND THEY ARE
C PRMT(1)- LOWER BOUND OF THE INTERVAL (INPUT),
C PRMT(2)- UPPER BOUND OF THE INTERVAL (INPUT),
C PRMT(3)- INITIAL INCREMENT OF THE INDEPENDENT VARIABLE
C(INPUT),
C PRMT(4)- UPPER ERROR BOUND (INPUT). IF ABSOLUTE ERROR IS
CGREATER THAN PRMT(4), INCREMENT GETS HALVED.
CIF INCREMENT IS LESS THAN PRMT(3) AND ABSOLUTE
CERROR LESS THAN PRMT(4)/50, INCREMENT GETS DOUBLED.
CTHE USER MAY CHANGE PRMT(4) BY MEANS OF HIS
COUTPUT SUBROUTINE.
C PRMT(5)- NO INPUT PARAMETER. SUBROUTINE RKGS INITIALIZES
CPRMT(5)=0. IF THE USER WANTS TO TERMINATE
CSUBROUTINE RKGS AT ANY OUTPUT POINT, HE HAS TO
CCHANGE PRMT(5) TO NON-ZERO BY MEANS OF SUBROUTINE
COUTP. FURTHER COMPONENTS OF VECTOR PRMT ARE
CFEASIBLE IF ITS DIMENSION IS DEFINED GREATER
CTHAN 5. HOWEVER SUBROUTINE RKGS DOES NOT REQUIRE
CAND CHANGE THEM. NEVERTHELESS THEY MAY BE USEFUL
```

```
CFOR HANDING RESULT VALUES TO THE MAIN PROGRAM
C(CALLING RKGS) WHICH ARE OBTAINED BY SPECIAL
CMANIPULATIONS WITH OUTPUT DATA IN SUBROUTINE OUTP.
C Y      - INPUT VECTOR OF INITIAL VALUES.  (DESTROYED)
CLATERON Y IS THE RESULTING VECTOR OF DEPENDENT
CVARIABLES COMPUTED AT INTERMEDIATE POINTS X.
C DERY   - INPUT VECTOR OF ERROR WEIGHTS.  (DESTROYED)
CTHE SUM OF ITS COMPONENTS MUST BE EQUAL TO 1.
CLATERON DERY IS THE VECTOR OF DERIVATIVES, WHICH
CBELONG TO FUNCTION VALUES Y AT A POINT X.
C NDIM   - AN INPUT VALUE, WHICH SPECIFIES THE NUMBER OF
CEQUATIONS IN THE SYSTEM.
C IHLF   - AN OUTPUT VALUE, WHICH SPECIFIES THE NUMBER OF
CBISECTIONS OF THE INITIAL INCREMENT. IF IHLF GETS
CGREATER THAN 10, SUBROUTINE RKGS RETURNS WITH
CERROR MESSAGE IHLF=11 INTO MAIN PROGRAM. ERROR
CMESSAGE IHLF=12 OR IHLF=13 APPEARS IN CASE
CPRMT(3)=0 OR IN CASE SIGN(PRMT(3)).NE.SIGN(PRMT(2)-
CPRMT(1)) RESPECTIVELY.
C FCT    - THE NAME OF AN EXTERNAL SUBROUTINE USED. THIS
CSUBROUTINE COMPUTES THE RIGHT HAND SIDES DERY OF
CTHE SYSTEM TO GIVEN VALUES X AND Y. ITS PARAMETER
CLIST MUST BE X,Y,DERY. SUBROUTINE FCT SHOULD
CNOT DESTROY X AND Y.
C OUTP   - THE NAME OF AN EXTERNAL OUTPUT SUBROUTINE USED.
CITS PARAMETER LIST MUST BE X,Y,DERY,IHLF,NDIM,PRMT.
CNONE OF THESE PARAMETERS (EXCEPT, IF NECESSARY,
CPRMT(4),PRMT(5),...) SHOULD BE CHANGED BY
CSUBROUTINE OUTP. IF PRMT(5) IS CHANGED TO NON-ZERO,
CSUBROUTINE RKGS IS TERMINATED.
C AUX    - AN AUXILIARY STORAGE ARRAY WITH 8 ROWS AND NDIM
CCOLUMNS.
C
C        REMARKS
C THE PROCEDURE TERMINATES AND RETURNS TO CALLING PROGRAM, IF
C (1) MORE THAN 10 BISECTIONS OF THE INITIAL INCREMENT ARE
C     NECESSARY TO GET SATISFACTORY ACCURACY (ERROR MESSAGE
C     IHLF=11),
C (2) INITIAL INCREMENT IS EQUAL TO 0 OR HAS WRONG SIGN
C     (ERROR MESSAGES IHLF=12 OR IHLF=13),
C (3) THE WHOLE INTEGRATION INTERVAL IS WORKED THROUGH,
C (4) SUBROUTINE OUTP HAS CHANGED PRMT(5) TO NON-ZERO.
C
C        SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED
C THE EXTERNAL SUBROUTINES FCT(X,Y,DERY) AND
C OUTP(X,Y,DERY,IHLF,NDIM,PRMT) MUST BE FURNISHED BY THE USER.
C
C        METHOD
C EVALUATION IS DONE BY MEANS OF FOURTH ORDER RUNGE-KUTTA
C FORMULAE IN THE MODIFICATION DUE TO GILL. ACCURACY IS
C TESTED COMPARING THE RESULTS OF THE PROCEDURE WITH SINGLE
C AND DOUBLE INCREMENT.
C SUBROUTINE RKGS AUTOMATICALLY ADJUSTS THE INCREMENT DURING
C THE WHOLE COMPUTATION BY HALVING OR DOUBLING. IF MORE THAN
C 10 BISECTIONS OF THE INCREMENT ARE NECESSARY TO GET
C SATISFACTORY ACCURACY, THE SUBROUTINE RETURNS WITH
C ERROR MESSAGE IHLF=11 INTO MAIN PROGRAM.
C TO GET FULL FLEXIBILITY IN OUTPUT, AN OUTPUT SUBROUTINE
C MUST BE FURNISHED BY THE USER.
C FOR REFERENCE, SEE
C RALSTON/WILF, MATHEMATICAL METHODS FOR DIGITAL COMPUTERS,
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C WILEY, NEW YORK/LONDON, 1960, PP.110-120.
C
C     ............................................................
C
      SUBROUTINE RKGS(PRMT,Y,DERY,NDIM,IHLF,FCT,OUTP,AUX)
C
C
      DIMENSION Y(1),DERY(1),AUX(8,1),A(4),B(4),C(4),PRMT(1)
      DO 1 I=1,NDIM
    1 AUX(8,I)=.06666667*DERY(I)
      X=PRMT(1)
      XEND=PRMT(2)
      H=PRMT(3)
      PRMT(5)=0.
      CALL FCT(X,Y,DERY)
C
C     ERROR TEST
      IF(H*(XEND-X))38,37,2
C
C     PREPARATIONS FOR RUNGE-KUTTA METHOD
    2 A(1)=.5
      A(2)=.2928932
      A(3)=1.707107
      A(4)=.1666667
      B(1)=2.
      B(2)=1.
      B(3)=1.
      B(4)=2.
      C(1)=.5
      C(2)=.2928932
      C(3)=1.707107
      C(4)=.5
C
C     PREPARATIONS OF FIRST RUNGE-KUTTA STEP
      DO 3 I=1,NDIM
      AUX(1,I)=Y(I)
      AUX(2,I)=DERY(I)
      AUX(3,I)=0.
    3 AUX(6,I)=0.
      IREC=0
      H=H+H
      IHLF=-1
      ISTEP=0
      IEND=0
C
C
C     START OF A RUNGE-KUTTA STEP
    4 IF((X+H-XEND)*H)7,6,5
    5 H=XEND-X
    6 IEND=1
C
C     RECORDING OF INITIAL VALUES OF THIS STEP
    7 CALL OUTP(X,Y,DERY,IREC,NDIM,PRMT)
      IF(PRMT(5))40,8,40
    8 ITEST=0
    9 ISTEP=ISTEP+1
C
C
C     START OF INNERMOST RUNGE-KUTTA LOOP
      J=1
   10 AJ=A(J)
```

```
      BJ=B(J)
      CJ=C(J)
      DO 11 I=1,NDIM
      R1=H*DERY(I)
      R2=AJ*(R1-BJ*AUX(6,I))
      Y(I)=Y(I)+R2
      R2=R2+R2+R2
   11 AUX(6,I)=AUX(6,I)+R2-CJ*R1
      IF(J-4)12,15,15
   12 J=J+1
      IF(J-3)13,14,13
   13 X=X+.5*H
   14 CALL FCT(X,Y,DERY)
      GOTO 10
C     END OF INNERMOST RUNGE-KUTTA LOOP
C
C
C     TEST OF ACCURACY
   15 IF(ITEST)16,16,20
C
C     IN CASE ITEST=0 THERE IS NO POSSIBILITY FOR TESTING OF ACCURACY
   16 DO 17 I=1,NDIM
   17 AUX(4,I)=Y(I)
      ITEST=1
      ISTEP=ISTEP+ISTEP-2
   18 IHLF=IHLF+1
      X=X-H
      H=.5*H
      DO 19 I=1,NDIM
      Y(I)=AUX(1,I)
      DERY(I)=AUX(2,I)
   19 AUX(6,I)=AUX(3,I)
      GOTO 9
C
C     IN CASE ITEST=1 TESTING OF ACCURACY IS POSSIBLE
   20 IMOD=ISTEP/2
      IF(ISTEP-IMOD-IMOD)21,23,21
   21 CALL FCT(X,Y,DERY)
      DO 22 I=1,NDIM
      AUX(5,I)=Y(I)
   22 AUX(7,I)=DERY(I)
      GOTO 9
C
C     COMPUTATION OF TEST VALUE DELT
   23 DELT=0.
      DO 24 I=1,NDIM
   24 DELT=DELT+AUX(8,I)*ABS(AUX(4,I)-Y(I))
      IF(DELT-PRMT(4))28,28,25
C
C     ERROR IS TOO GREAT
   25 IF(IHLF-10)26,36,36
   26 DO 27 I=1,NDIM
   27 AUX(4,I)=AUX(5,I)
      ISTEP=ISTEP+ISTEP-4
      X=X-H
      IEND=0
      GOTO 18
C
C     RESULT VALUES ARE GOOD
   28 CALL FCT(X,Y,DERY)
      DO 29 I=1,NDIM
```

```
      AUX(1,I)=Y(I)
      AUX(2,I)=DERY(I)
      AUX(3,I)=AUX(6,I)
      Y(I)=AUX(5,I)
   29 DERY(I)=AUX(7,I)
      CALL OUTP(X-H,Y,DERY,IHLF,NDIM,PRMT)
      IF(PRMT(5))40,30,40
   30 DO 31 I=1,NDIM
      Y(I)=AUX(1,I)
   31 DERY(I)=AUX(2,I)
      IREC=IHLF
      IF(IEND)32,32,39
C
C     INCREMENT GETS DOUBLED
   32 IHLF=IHLF-1
      ISTEP=ISTEP/2
      H=H+H
      IF(IHLF)4,33,33
   33 IMOD=ISTEP/2
      IF(ISTEP-IMOD-IMOD)4,34,4
   34 IF(DELT-.02*PRMT(4))35,35,4
   35 IHLF=IHLF-1
      ISTEP=ISTEP/2
      H=H+H
      GOTO 4
C
C
C     RETURNS TO CALLING PROGRAM
   36 IHLF=11
      CALL FCT(X,Y,DERY)
      GOTO 39
   37 IHLF=12
      GOTO 39
   38 IHLF=13
   39 CALL OUTP(X,Y,DERY,IHLF,NDIM,PRMT)
   40 PETURN
      END
      SUBROUTINE OUTP(X,Y,DERY,IHLF,NDIM,PRMT)
C     THIS DUMMY SUBROUTINE IS NOT USED,
C     BUT MUST BE SUPPLIED FOR RKGS.
      DIMENSION Y(2),DERY(3),PRMT(5)
      RETURN
      END
      SUBROUTINE SIZE
      REAL M1,M2,M3,M4,M5,M6,M7,M8,M12,M14,M16
      REAL M50,M60,M70,MT5,MT6,MT7,I
      DIMENSION CH(2),CION(1),GAM1(2),GAM2(2),WATA(2)
      COMMON/XMOL/M1,M2,M3,M4,M5,M6,M7,M8,M12,M14,M16
      COMMON/XMOLO/M50,M60,M70,MT5,MT6,MT7
      COMMON/XMISCL/FLAM,RGAS,TEMP,PSAT,SIGMA
      COMMON/XVOL/VH2O,VSO2,VNH3,VNO1,VNO2,VHCL,VHNO3,VH2SO4
      COMMON/XDIFF/DH2SO4,DHCL
      COMMON/XYES/NY,YY
      COMMON/XVARE/VT,VOL,R,TH2O,CURVE
      COMMON/XBULK/PBNO1,PBNO2,PBNH3,PBSO2,PBH2SO4,PBH2O
      COMMON/XSURF/PSNO1,PSNO2,PSNH3,PSSO2,PSH2SO4,PSH2O,PSHCL
      COMMON/XPRES/PNO1,PNO2,PNH3,PSO2,PH2O
      COMMON/XEQLB/CH,AW,CION,GAM1,GAM2,WATA
      COMMON/XIONIC/I,GAMA1,GAMA2,NUGAM14,NUGAM34,NUAW
      COMMON/XBRCM/OSMO,SUM1
      ONE=1.CD+00
```

```
          THREE=3.0D+00
          FOUR=4.0D+00
          PI=FOUR*ATAN(ONE)
C         THIS SUBROUTINE CALCULATES..........
C              1).TOTAL MOLES OF EACH IONIC SPECIES FROM NEW
C              CONCENTRATIONS AND OLD VOLUME.
C         .    2).FROM EQUATION (5) OF BROMLEY(WITH THREE
C              PARAMETERS) R.H.S IS EVALUATED BY USING NEW IONIC
C              STRENGTHS.THIS GIVES A NEW OSMOTIC COEFFICIENT.
C              3).FROM OLD WATER ACTIVITY,NEW OSMOTIC COEFFICIENT
C              AND TOTAL MOLES OF ALL SPECIES NEW VOLUME IS
C              COMPUTED.THIS VOLUME GIVES A NEW RADIUS
          TMOLES=SUM1*VT
          VNEW=-TMOLES*0.018*OSMO/ALOG(AW)
          RNEW=(THREE*VNEW/(FOUR*PI) )**(ONE/THREE)
          R=RNEW
          VT=VNEW
          VOL=VT
          RETURN
          END
```

```
      PROGRAM GARCIA(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
C     THIS PROGRAM CALCULATES ACTIVITY COEFFICIENTS OF
C     HNO3 AND NH4NO3 AND AW IN THE TERNARY SYSTEM(AQUEOUS)
C     CONCENTRATION OF HYDROGEN ION IS KEPT CONSTANT.
C     AS THE CONCENTRATION OF HNO3 IS VERY SMALL THE SOLUTION
C     IS PREDOMINANTLY THAT OF NH4NO3.THIS PROGRAM  PREDICTS
C     THE ACTIVITY DATA AS A FUNCTION OF THE IONIC STRENGTH OF
C     NH4NO3 (FROM I=0.2 TO I=30 )
C     THE RESULTS OF THIS PROGRAM ARE USEFUL IN MAKING A GUESS
C     FOR H+ CONCENTRATION AND GAMA1,GAMA2 AND AW FOR EQLBRM
C     CALCULATIONS
      REAL M1,M2,M3,M4,NUAW,NUGAMA1,NUGAMA2,NUGAMA3,NITRATE,I
C     1 STANDS FOR HYDROGEN ION
C     3 STANDS FOR AMMONIUM ION
C     4 STANDS FOR NITRATE ION
      DO 100 J=2,300,2
      I=J/10.
      SIGMA=2*I
      M1=1.0D-03
      M3=I
      M4=I
      Y41=Y43=M4/I
      X12=X14=M1/I
      X32=X34=M3/I
      B14=0.08337
      B34=-0.03564
      C14=-0.002743
      C34=0.001124
      D14=0.00003034
      D34=-0.00001484
      bmean=(b14+b34)/2.
      CMEAN=(C14+C34)/2.
      dmean=(d14+d34)/2.
      ZOT1=0.511*SQRT(I)/(1.+SQRT(I))
      ZOT2=I/((1.+1.5*I)*(1.+1.5*I))
      ZOT3=I*I
      ZOT4=I*ZOT3
      ZOT5=1.+SQRT(I)
      ZOT6=1.+3.*I
      ZOT7=1.+1.5*I
      TERM1=1.1768/I*(ZOT5-1./ZOT5-2.*ALOG(ZOT5))
      TERM2=ZOT6/(ZOT7*ZOT7)-ALOG(ZOT7)/(1.5*I)
      TERM3=2.303*I/2.
      TERM4=4.606*ZOT3/3.
      TERM5=6.909*ZOT4/4.
      TERM6=1.-TERM1+0.0921*TERM2
      OSMO=TERM6+BMEAN*(0.9212*TERM2+TERM3)+CMEAN*TERM4+DMEAN*TERM5
      NUAW=EXP((-SIGMA)*0.018*OSMO)
      GAMA140=10.**(-ZOT1+(0.06+0.6*B14)*ZOT2+B14*I+C14*ZOT3+D14*ZOT4)
      GAMA340=10.**(-ZOT1+(0.06+0.6*B34)*ZOT2+B34*I+C34*ZOT3+D34*ZOT4)
      s1=x14*alog10(gama140)+x34*alog10(gama340)
      f1=y41*alog10(gama140)+zot1*y41
      f3=y43*alog10(gama340)+zot1*y43
      f4=s1+zot1*(x14+x34)
      GAMA14=10.**(-ZOT1+(F1+F4)/2.0)
      GAMA34=10.**(-ZOT1+(F3+F4)/2.0)
      NUGAMA1=GAMA14
      NUGAMA2=GAMA34
      WRITE(6,120)I,GAMA140,GAMA340,GAMA14,GAMA34,NUAW
120   FORMAT(1H0,6(F10.6,5X))
100   CONTINUE
```

STOP
END

A, Aγ Constant in Debye-Huckel limiting law (0.5085 mole$^{\frac{1}{2}}$ -Kg$^{-\frac{1}{2}}$ for water)

a   Activity

a$_w$ Water activity

c   Molarity

D   Diffusivity

f   Activity coefficient on mole fraction scale

g   Osmotic coefficient on mole fraction scale

I   Ionic strength

Kn   Knudsen number, Kn = λ/r

ℓ Noncontinuum correction factor

m   Molality

N   Mole fraction

P   Total pressure

P$_A$, P$_{satA}$ Vapor pressure of solvent

P$_i$. p$_i$ Partial pressure of i

P$_{ci}$ Partial pressure of i over a curved surface

P$_{fi}$ Partial pressure of i over a flat surface

P$_\infty$ Ambient pressure

R   Universal gas constant

r   Droplet radius

r$_i$ Initial droplet radius

T   Absolute temperature

t   time

$\overline{V}$ Partial molar volume (liquid phase)

W	Molecular weight
X, x	Mole fraction
Y	Ionic strength fraction
y	Activity coefficient on molar scale
Z, z	Ionic charge
γ	Activity coefficient on molal scale
γ_i^o	Activity coefficient of component i in binary solution at the total ionic strength of the solution
ΔH	Enthalpy change of mixing
ΔV	Volume change of mixing
λ	Mean free path
μ	Chemical potential
μ_i^o	Chemical potential of component i in standard state
ν_i	Number of ions formed by complete dissociation of one molecule of i
σ	Surface tension
ψ	Osmotic coefficient on molal scale

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