

ATMOSPHERIC CHEMISTRY AND PHYSICS

From Air Pollution to Climate Change

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9 Thermodynamics of Aerosols

Several chemical compounds (water, ammonia, nitric acid, organics, etc.) can exist in both the gas and aerosol phases in the atmosphere. Understanding the partitioning of these species between the vapor and particulate phases requires an analysis of the thermodynamic properties of aerosols. Since the most important "solvent" for constituents of atmospheric particles and drops is water, we will pay particular attention to the thermodynamic properties of aqueous solutions.

9.1 THERMODYNAMIC PRINCIPLES

An atmospheric air parcel can be viewed thermodynamically as a homogeneous system that may exchange energy, work, and mass with its surroundings. Let us assume that an air parcel contains k chemical species, has a temperature T , pressure p , and volume V . There are n_i moles of species i in the parcel.

The first section of this chapter is a review of fundamental chemical thermodynamic principles focusing on the chemical potential of species in the gas, aqueous, and solid phases. Further discussion of fundamentals of chemical thermodynamics can be found in Denbigh (1981). Chemical potentials form the basis for the development of a rigorous mathematical framework for the derivation of the equilibrium conditions between different phases. This framework is then applied to the partitioning of inorganic aerosol components (sulfate, nitrate, chloride, ammonium, and water) between the gas and particulate phases. The behavior of organic aerosol components will be discussed in Chapter 13.

9.1.1 Internal Energy and Chemical Potential

In addition to the macroscopic kinetic and potential energy that the air parcel may have, it has internal energy, U , arising from the kinetic and potential energy of the atoms and molecules in the system. Let us assume that the state of the air parcel changes infinitesimally (e.g., it rises slightly) but there is no mass exchange between the air parcel and its surroundings, namely, that the air parcel is a closed system. Then, according to the first law of thermodynamics, the infinitesimal change of internal energy, dU , is given by

$$dU = dQ + dW \quad (9.1)$$

where dQ is the infinitesimal amount of heat that is absorbed by the system and dW is the infinitesimal amount of work that is done to the system. Equation (9.1) can also be viewed as a definition of the internal energy of the system, U .

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The infinitesimal work done to the system by its surroundings is equal to

$$dW = -p dV \quad (9.2)$$

where p is the pressure of the system and dV its infinitesimal volume change. Note that, if the parcel expands, dV is positive and the work done to the system is negative (or alternatively the work done by the system is positive). Because of this expansion, if there is no heat exchange, $dU < 0$ and the internal energy of the system will decrease. On the contrary, if the parcel volume decreases, $dV < 0$, $dW > 0$ and if $dQ = 0$ the internal energy of the system increases.

A thermodynamically reversible process is defined as one in which the system changes infinitesimally slowly from one equilibrium state to the next. According to the second law of thermodynamics, the heat added to a system during a reversible process, dQ_{rev} , is given by

$$dQ_{\text{rev}} = T dS \quad (9.3)$$

where S is the entropy of the system. The entropy is another property of the system (like the temperature, volume, and pressure) measuring the degree of disorder of the elements of the system; the more disorder the greater the entropy. Combining (9.1), (9.2), and (9.3)

$$dU = T dS - p dV \quad (9.4)$$

for a closed system. This equation contains the whole of knowledge obtained from the basic thermodynamic laws for a closed system undergoing a reversible change.

In our discussion so far we have assumed that the system is closed. According to (9.4), if the number of moles of all system species n_1, n_2, \dots, n_k are constant, the change in internal energy U of the system depends only on changes in S and V . However, for variable composition we must have

$$U = U(S, V, n_1, n_2, \dots, n_k)$$

and thus the total differential of U is

$$dU = \left(\frac{\partial U}{\partial S} \right)_{V, n_i} dS + \left(\frac{\partial U}{\partial V} \right)_{S, n_i} dV + \sum_{i=1}^k \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_j} dn_i \quad (9.5)$$

In this expression, the subscript n_i in the first two partial derivatives implies that the amounts of all species are constant during the variation in question. On the other hand, the last partial derivative assumes that all but the i^{th} substance are constant. Note that for a closed system $dn_i = 0$ and from (9.5)

$$dU = \left(\frac{\partial U}{\partial S} \right)_{V, n_i} dS + \left(\frac{\partial U}{\partial V} \right)_{S, n_i} dV \quad (9.6)$$

Comparing (9.4) and (9.6) that are both valid for a closed system, we obtain

$$T = \left(\frac{\partial U}{\partial S} \right)_{V, n_i} \quad \text{and} \quad -p = \left(\frac{\partial U}{\partial V} \right)_{S, n_i} \quad (9.7)$$

Finally, (9.5) can be rewritten as

$$(9.2) \quad dU = T dS - p dV + \sum_{i=1}^k \left(\frac{\partial U}{\partial n_i} \right)_{S,V,n_j} dn_i \quad (9.8)$$

Let us define the chemical potential of species i , μ_i , as

$$\mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{S,V,n_j} \quad (9.9)$$

so that (9.8) can be written as

$$(9.3) \quad dU = T dS - p dV + \sum_{i=1}^k \mu_i dn_i \quad (9.10)$$

The chemical potential, μ_i , has an important function in the system's thermodynamic behavior analogous to pressure or temperature. A temperature difference between two bodies determines the tendency of heat to pass from one body to another while a pressure difference determines the tendency for bodily movement. We will show that a difference in chemical potential can be viewed as the cause for chemical reaction or for mass transfer from one phase to another. The chemical potential, μ_i , greatly facilitates the discussion of open systems, or of closed systems that undergo chemical composition changes.

9.1.2 The Gibbs Free Energy, G

Calculation of changes, dU , of the internal energy of a system U , requires the estimation of changes of its entropy S , volume V , and number of moles n_i . For chemical applications, including atmospheric chemistry, it is inconvenient to work with entropy and volume as independent variables. Temperature and pressure are much more useful. The study of atmospheric processes can therefore be facilitated by introducing other thermodynamic variables in addition to the internal energy U . One of the most useful is the Gibbs free energy, G , defined as

$$G = U + pV - TS \quad (9.11)$$

Differentiating (9.11)

$$dG = dU + p dV + V dp - T dS - S dT \quad (9.12)$$

and combining (9.12) with (9.10) one obtains

$$(9.6) \quad dG = -S dT + V dp + \sum_{i=1}^k \mu_i dn_i \quad (9.13)$$

(9.7)

Note that one can propose using (9.13) as an alternative definition of the chemical potential, that is,

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, p, n_j} \quad (9.14)$$

Both definitions (9.9) and (9.14) are equivalent. Equation (9.13) is the basis for chemical thermodynamics.

For a system at constant temperature ($dT = 0$) and pressure ($dp = 0$)

$$dG = \sum_{i=1}^k \mu_i dn_i \quad (9.15)$$

For a system under constant temperature, pressure, and with constant chemical composition ($dn_i = 0$), $dG = 0$, or the system has a constant Gibbs free energy. Equation (9.13) provides the means of calculating infinitesimal changes in the Gibbs free energy of the system. Let us assume that the system under discussion is enlarged m times in size, its temperature, pressure, and the relative proportions of each component remaining unchanged. Under such conditions the chemical potentials, which do not depend on the overall size of the system, remain unchanged. Let the original value of the Gibbs free energy of the system be G and the number of moles of species i , n_i . After the system is enlarged m times, these quantities are now mG and mn_i . The change in Gibbs free energy of the system is

$$\Delta G = mG - G = (m - 1)G \quad (9.16)$$

and the changes in the number of moles are

$$\Delta n_i = mn_i - n_i = (m - 1)n_i \quad (9.17)$$

and as T , P , and μ_i are constant using (9.15)

$$\Delta G = \sum_{i=1}^k \mu_i \Delta n_i$$

or

$$G = \sum_{i=1}^k \mu_i n_i \quad (9.18)$$

Equation (9.18) applies in general and provides additional significance to the concept of chemical potential. The Gibbs free energy of a system containing k chemical compounds

mical poten-

(9.14)

can be calculated by

$$G = \mu_1 n_1 + \mu_2 n_2 + \cdots + \mu_k n_k$$

that is, by summation of the products of the chemical potentials and the number of moles of each species. Note that for a pure substance

$$\mu_i = \frac{G}{n_i} \quad (9.19)$$

and thus the chemical potential is the value of the Gibbs free energy per mole of the substance. One should note that both (9.13) and (9.18) are applicable in general. It may appear surprising that T and p do not enter explicitly in (9.18). To explore this point a little further, differentiating (9.18),

$$dG = \sum_{i=1}^k n_i d\mu_i + \sum_{i=1}^k \mu_i dn_i \quad (9.20)$$

and combining with (9.13) we obtain

$$-SdT + Vdp = \sum_{i=1}^k n_i d\mu_i \quad (9.21)$$

This relation, known as the *Gibbs–Duhem equation*, shows that when the temperature and pressure of a system change there is a corresponding change of the chemical potentials of the various compounds.

9.1.3 Conditions for Chemical Equilibrium

The second law of thermodynamics states that the entropy of a system in an adiabatic ($dQ = 0$) enclosure increases for an irreversible process and remains constant in a reversible one. This law can be expressed as

$$dS \geq 0 \quad (9.22)$$

Therefore a system will try to increase its entropy and when the entropy reaches its maximum value the system will be at equilibrium. One can show that for a system at constant temperature and pressure the criterion corresponding to (9.22) is

$$dG \leq 0 \quad (9.23)$$

or that a system will tend to decrease its Gibbs free energy. For a proof the reader is referred to Denbigh (1981).

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Consider the reaction $A \rightleftharpoons B$ and let us assume that initially there are n_A moles of A and n_B moles of B. The Gibbs free energy of the system is, using (9.18),

$$G = n_A \mu_A + n_B \mu_B.$$

If the system is closed

$$n_T = n_A + n_B = \text{constant}$$

and this equation can be rewritten as

$$G = n_T(x_A \mu_A + (1 - x_A) \mu_B)$$

where

$$x_A = \frac{n_A}{n_A + n_B} = \frac{n_A}{n_T}$$

the mole fraction of A in the system. Let us assume that the Gibbs free energy of the system is that shown in Figure 9.1. If at a given moment the system is at point K, (9.23) suggests that $dG \leq 0$ and G will tend to decrease, so x_A will increase, B will be converted to A, and the system will move to the right.

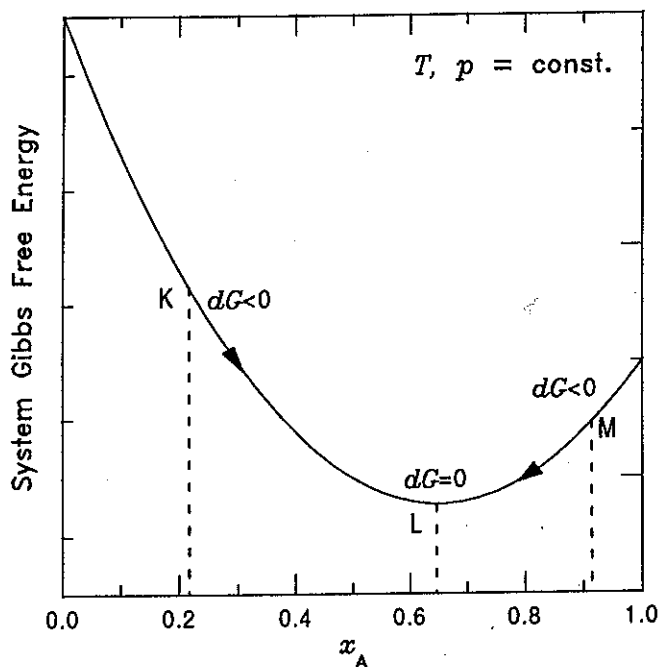
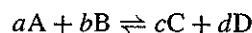


FIGURE 9.1 Sketch of the Gibbs free energy for a closed system where the reaction $A \rightleftharpoons B$ takes place versus the mole fraction of A.

moles of A and

If the system at a given moment is at point M, once more $dG \leq 0$, so the system will move to the left (A will be converted to B). At point L, the Gibbs free energy is at a minimum. The system cannot spontaneously move to the left or right because then the Gibbs free energy would increase, violating (9.23). If the system is forced to move, then it will return to this equilibrium state. Therefore, for a constant T and p , the point L and the corresponding composition is the equilibrium state of the system and $(x_A)_L$ the corresponding mole fraction of A. At this point $dG = 0$.

Let us consider a general chemical reaction,



which can be rewritten mathematically as

$$aA + bB - cC - dD = 0 \quad (9.24)$$

The Gibbs free energy of the system is given by

$$G = n_A \mu_A + n_B \mu_B + n_C \mu_C + n_D \mu_D$$

If dn_A moles of A react, then according to the stoichiometry of the reaction, they will also consume $(b/a)n_A$ moles of B and produce $(c/a)n_A$ moles of C and $(d/a)n_A$ moles of D. The corresponding change of the Gibbs free energy of the system at constant T and p is, according to (9.15),

$$\begin{aligned} dG &= \mu_A dn_A + \mu_B dn_B + \mu_C dn_C + \mu_D dn_D \\ &= \mu_A dn_A + \frac{b}{a} \mu_B dn_A - \frac{c}{a} \mu_C dn_A - \frac{d}{a} \mu_D dn_A \\ &= \left(\mu_A + \frac{b}{a} \mu_B - \frac{c}{a} \mu_C - \frac{d}{a} \mu_D \right) dn_A \end{aligned} \quad (9.25)$$

At equilibrium $dG = 0$ and therefore the condition for equilibrium is

$$\mu_A + \frac{b}{a} \mu_B - \frac{c}{a} \mu_C - \frac{d}{a} \mu_D = 0$$

or

$$a\mu_A + b\mu_B - c\mu_C - d\mu_D = 0 \quad (9.26)$$

Let us try to generalize our conclusions so far. The most general reaction can be written as

$$\sum_{i=1}^k \nu_i A_i = 0 \quad (9.27)$$

on $A \rightleftharpoons B$ takes

where k is the number of species, A_i , participating in the reaction, and v_i the corresponding stoichiometric coefficients (positive for reactants, negative for products). One can easily extend our arguments for the single reaction (9.24) to show that the general condition for equilibrium is

$$\sum_{i=1}^k v_i \mu_i = 0 \quad (9.28)$$

This is the most general condition of equilibrium of a single reaction and is applicable whether the reactants and products are solids, liquids, or gases.

If there are multiple reactions taking place in a system with k species,

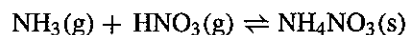
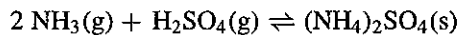
$$\begin{aligned} \sum_{i=1}^k v_{i1} A_i &= 0 \\ \sum_{i=1}^k v_{i2} A_i &= 0 \\ &\vdots \\ \sum_{i=1}^k v_{in} A_i &= 0 \end{aligned} \quad (9.29)$$

the equilibrium condition applies to each one of these reactions and therefore at equilibrium

$$\sum_{i=1}^k v_{ij} \mu_i = 0, \quad j = 1, \dots, n \quad (9.30)$$

where v_{ij} is the stoichiometric coefficient of species i in reaction j (there are n reactions and k species).

For example, let us assume that the following reactions take place:



At equilibrium the chemical potentials of gas-phase NH_3 , and H_2SO_4 and solids $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 satisfy

$$\begin{aligned} 2\mu_{\text{NH}_3} + \mu_{\text{H}_2\text{SO}_4} - \mu_{(\text{NH}_4)_2\text{SO}_4} &= 0 \\ \mu_{\text{NH}_3} + \mu_{\text{HNO}_3} - \mu_{\text{NH}_4\text{NO}_3} &= 0 \end{aligned} \quad (9.31)$$

Determination of the equilibrium composition of this multiphase system therefore requires determination of the chemical potentials of all species as a function of the corresponding concentrations, temperature, and pressure.

9.1.4 Chemical Potentials of Ideal Gases and Ideal Gas Mixtures

In this section we will discuss the chemical potentials of species in the gas, aqueous, and aerosol phases. In thermodynamics it is convenient to set up model systems to which the behavior of ideal systems approximates under limiting conditions. The important models for atmospheric chemistry are the ideal gas and the ideal solution. We will define these ideal systems using the chemical potentials and then discuss other definitions.

The Single Ideal Gas We define the ideal gas as a gas whose chemical potential $\mu(T, p)$ at temperature T and pressure p is given by

$$\mu(T, p) = \mu^\circ(T, 1 \text{ atm}) + RT \ln p \quad (9.32)$$

where μ° is the standard chemical potential defined at a pressure of 1 atm and therefore is a function of temperature only. R is the ideal gas constant. Pressure p actually stands for the ratio $(p/1 \text{ atm})$ and is dimensionless. This definition suggests that the chemical potential of an ideal gas at constant temperature increases logarithmically with its pressure.

Differentiating (9.32) with respect to pressure at constant temperature

$$\left(\frac{\partial \mu}{\partial p}\right)_T = \left(\frac{\partial \mu^\circ}{\partial p}\right)_T + RT \frac{d \ln p}{dp} \quad (9.33)$$

But μ° is not a function of pressure and therefore its derivative with respect to pressure is zero, so for an ideal gas

$$\left(\frac{\partial \mu}{\partial p}\right)_T = \frac{RT}{p} \quad (9.34)$$

Using (9.13), one can calculate the derivative of G with respect to pressure

$$\left(\frac{\partial G}{\partial p}\right)_T = V \quad (9.35)$$

but for a system consisting of n moles of a single gas (see (9.18))

$$G = n\mu \quad (9.36)$$

and therefore from (9.35) and (9.36)

$$\left(\frac{\partial \mu}{\partial p}\right)_T = \frac{V}{n} \quad (9.37)$$

Combining (9.34) and (9.37) we see that our definition of an ideal gas entails

$$pV = nRT \quad (9.38)$$

the traditional ideal gas law.

Deviations from ideal gas behavior are customarily expressed in terms of the compressibility factor C

$$C = \frac{pV}{nRT} \quad (9.39)$$

Both dry air and water vapor have compressibility factors C , in the range $0.998 < C < 1$ for the pressure and temperature ranges of atmospheric interest (Harrison, 1965). Hence both dry air and water vapor can be treated as ideal gases with an error of less than 0.2% for all the conditions of atmospheric interest.

The Ideal Gas Mixture A gaseous mixture is defined as ideal if the chemical potential of its i th component satisfies

$$\mu_i = \mu_i^\circ(T) + RT \ln p + RT \ln y_i \quad (9.40)$$

where $\mu_i^\circ(T)$ is the standard chemical potential of species i , p is the total pressure of the mixture, and y_i is the gas mole fraction of compound i . For $y_i = 1$ (pure component), (9.40) is simplified to (9.32) and therefore μ_i° is precisely the same for both equations. This standard chemical potential is the Gibbs free energy per mole (recall for pure compounds $G = \mu n$) of the gas in the pure state and pressure of 1 atm.

By defining the partial pressure of compound i as

$$p_i = y_i p \quad (9.41)$$

a more compact form of (9.40) is

$$\mu_i = \mu_i^\circ(T) + RT \ln p_i \quad (9.42)$$

One can also prove that (9.42) is equivalent to the more traditional ideal gas mixture definition,

$$p_i V = n_i RT$$

The atmosphere can be treated as an ideal gas mixture with negligible error (Pruppacher and Klett, 1980).¹

9.1.5 Chemical Potential of Solutions

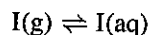
Atmospheric aerosols at high relative humidities are aqueous solutions of species such as ammonium, nitrate, sulfate, chloride, and sodium. Cloud droplets, rain, and so on are also aqueous solutions of a variety of chemical compounds.

Ideal Solutions A solution is defined as ideal if the chemical potential of every component is a linear function of the logarithm of its aqueous mole fraction x_i , according to the relation

$$\mu_i = \mu_i^*(T, p) + RT \ln x_i \quad (9.43)$$

A multicomponent solution is ideal only if (9.43) is satisfied by every component. A solution, in general, approaches ideality as it becomes more and more dilute in all but one component (the solvent). The standard chemical potential μ_i^* is the chemical potential of pure species i ($x_i = 1$) at the same temperature and pressure as the solution under discussion. Note that in general μ_i^* is a function of both T and p but does not depend on the chemical composition of the solution.

Let us discuss the relationship of the above definition with Henry's and Raoult's laws, which are often used to define ideal solutions. Assuming that an ideal solution of i is in equilibrium with an ideal gas mixture, we have the reaction



and at equilibrium

$$\mu_i(g) = \mu_i(aq)$$

according to (9.28). Using (9.42) and (9.43)

$$\mu_i^\circ(T) + RT \ln p_i = \mu_i^*(T, p) + RT \ln x_i$$

or

$$p_i = \exp\left(\frac{\mu_i^* - \mu_i^\circ}{RT}\right) x_i = K_i(T, p) x_i \quad (9.44)$$

The standard chemical potentials μ_i^* and μ_i° are only functions of temperature and pressure and therefore the constant K_i is independent of the solution's composition.

¹For a discussion of nonideal gas mixtures, the reader is referred to Denbigh (1981). The discussion of these mixtures is not necessary here, as the behavior of all gases in the atmosphere can be considered ideal for all practical purposes.

If $x_i = 1$ in (9.44), then $K_i(T, p)$ is equal to the vapor pressure of the pure component i , p_i° , and the equation can be rewritten as

$$p_i = p_i^\circ x_i \quad (9.45)$$

Equation (9.45) states that the vapor pressure of a gas over a solution is equal to the product of the pure component vapor pressure and its mole fraction in the solution. The lower the mole fraction in the solution the more the vapor pressure of the gas over the solution drops. Thus (9.45) is the same as *Raoult's law*.

Most solutions of practical interest satisfy (9.43) only in certain chemical composition ranges and not in others. Let us focus on a binary solution of A and B. If the solution is *ideal* for every composition, then the partial pressures of A and B will vary linearly with the mole fraction of B (Figure 9.2). When $x_A = 0$, the mixture consists of pure B and the equilibrium partial pressure of B over the solution is p_B° and of A zero. The opposite is true at the other end, where $x_A = 1$ and $p_A = p_A^\circ$.

The partial pressures of A and B in a realistic mixture are shown in Figure 9.3. Note that the relationships between p_A , p_B , and x_A are nonlinear with the exceptions of the limits of $x_A \rightarrow 0$ and $x_A \rightarrow 1$. When $x_A \rightarrow 1$, we have a dilute solution of B in A. In this regime

$$p_A \simeq p_A^\circ x_A \quad (9.46a)$$

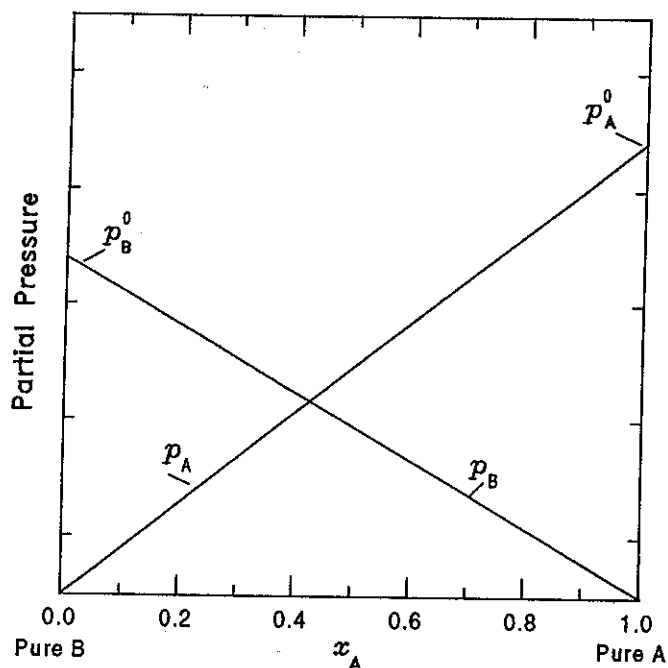


FIGURE 9.2 Equilibrium partial pressures of the components of an ideal binary mixture as a function of the mole fraction of A, x_A .

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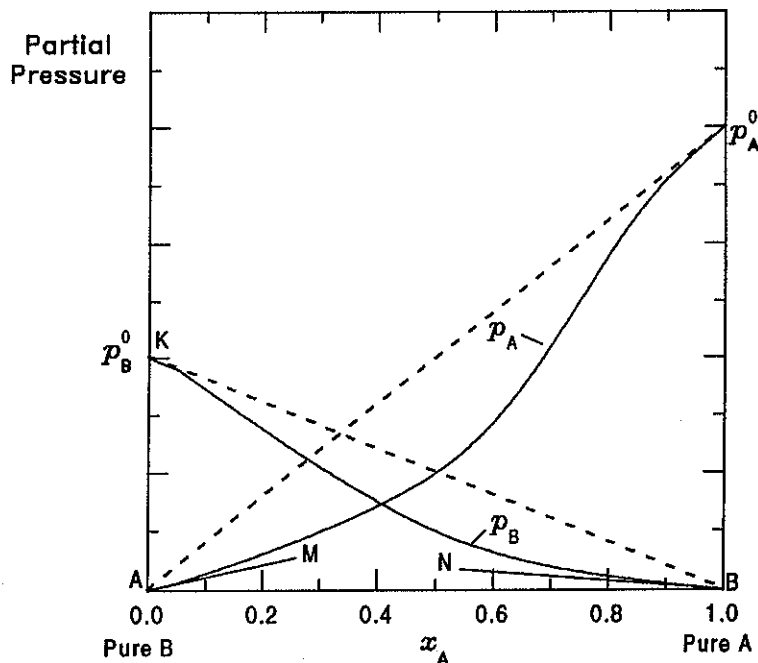


FIGURE 9.3 Equilibrium partial pressures of the components of a nonideal mixture of A and B. Dashed lines correspond to ideal behavior.

and Raoult's law applies to A. In the same regime

$$p_B = H'_B x_B \quad (9.46b)$$

where H'_B is a constant calculated from the slope of the p_B line as $x_A \rightarrow 1$. This relationship corresponds to *Henry's law*, and H'_B is the Henry's law constant² (based on mole fraction) for B in A (equal to the slope of the line BN). At the other end ($x_A \rightarrow 0$) we have

$$\begin{aligned} p_B &\simeq p_B^0 x_B \\ p_A &= H'_A x_A \end{aligned} \quad (9.47)$$

and B obeys Raoult's law while A obeys Henry's law.

Summarizing, if a solution is ideal over the whole composition range (often called *perfect solution*), (9.44) is satisfied for every x_i . In this case K_i is equal to the vapor pressure of pure i , which is also equal in this case to the Henry's law constant of i . Nonideal solutions approach ideality when the concentrations of all components but one approach zero. In that case the solutes satisfy Henry's law ($p_i = H'_i x_i$), where the solvent satisfies Raoult's law ($p_j = p_j^0 x_j$).

²For a dilute aqueous solution (9.46b) is equivalent to

$$[B(aq)] = (0.018 H'_B)^{-1} p_B$$

The Henry's law constant H_B defined in Chapter 6 is then related to H'_B by

$$H_B = (0.018 H'_B)^{-1}$$

mixture as a func-

Non ideal Solutions Atmospheric aerosols are usually concentrated aqueous solutions that deviate significantly from ideality. This deviation from ideality is usually described by introducing the activity coefficient, γ_i , and the chemical potential is given by

$$\mu_i = \mu_i^*(T, p) + RT \ln(\gamma_i x_i) \quad (9.48)$$

The activity coefficient γ_i is in general a function of pressure and temperature together with the mole fractions of *all* substances in solution. For an ideal solution $\gamma_i = 1$. The standard chemical potential μ_i^* is defined as the chemical potential at the hypothetical state for which $\gamma_i \rightarrow 1$ and $x_i \rightarrow 1$ (Denbigh, 1981). The product of the mole fraction x_i of a solution component and its activity coefficient γ_i is defined as the *activity*, α_i , of the component

$$\alpha_i = \gamma_i x_i \quad (9.49)$$

and the chemical potential of a species i is then given by

$$\mu_i = \mu_i^*(T, p) + RT \ln \alpha_i \quad (9.50)$$

As a matter of convenience, the amount of a species in solution is often expressed as a *molality* rather than as a mole fraction. The molality of a solute is its amount in moles per kilogram of solvent. For an aqueous solution containing n_i moles of solute and n_w moles of water (molecular weight $0.018 \text{ kg mol}^{-1}$) the molality, m_i , of the solute is

$$m_i = \frac{n_i}{0.018 n_w} \quad (9.51)$$

Another measure of solution concentration is the molarity, $[I]$, expressed in moles of solute per liter of solvent (denoted by M). For water solutions at ambient conditions, because 1 liter weighs 1 kilogram, the molality and molarity of a solution are practically equal.

Traditionally, the activity of the solvent is almost always defined on the mole fraction scale ((9.48) and (9.50)), but the activity coefficient of the solute is often expressed on the molality scale,

$$\mu_i = \mu_i^\circ + RT \ln(\gamma_i m_i) \quad (9.52)$$

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essed on the

(9.52)

In this case μ_i° is the value of the chemical potential as $m_i \rightarrow 1$ and $\gamma_i \rightarrow 1$.

The activity coefficients γ_i are determined experimentally by a series of methods including vapor pressure, freezing-point depression, osmotic pressure, and solubility measurements (Denbigh, 1981).

Pure Solid Compounds The chemical potential of a pure solid compound i can easily be derived from (9.43) by setting $x_i = 1$, so that

$$\mu_i(\text{solid}) = \mu_i^*(T, p) \quad (9.53)$$

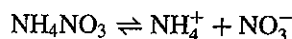
The chemical potential of the solid is therefore equal to its standard potential and is a function only of temperature and pressure.

Solutions of Electrolytes Most of the inorganic aerosol components dissociate upon dissolution, for example, NH_4NO_3 dissociates forming NH_4^+ and NO_3^- . The concentration of each ion in the aqueous solution is traditionally expressed on the molality scale and the chemical potential for each ion in a NH_4NO_3 solution is

$$\mu_{\text{NH}_4^+} = \mu_{\text{NH}_4^+}^\circ + RT \ln(\gamma_{\text{NH}_4^+} m_{\text{NH}_4^+})$$

$$\mu_{\text{NO}_3^-} = \mu_{\text{NO}_3^-}^\circ + RT \ln(\gamma_{\text{NO}_3^-} m_{\text{NO}_3^-})$$

where $m_{\text{NH}_4^+}$ and $m_{\text{NO}_3^-}$ are the ion molalities and $\gamma_{\text{NH}_4^+}$ and $\gamma_{\text{NO}_3^-}$ the corresponding activity coefficients. The dissociation reaction



is at equilibrium and therefore the chemical potential of NH_4NO_3 satisfies

$$\mu_{\text{NH}_4\text{NO}_3} = \mu_{\text{NH}_4^+} + \mu_{\text{NO}_3^-}$$

or

$$\mu_{\text{NH}_4\text{NO}_3} = \mu_{\text{NH}_4^+}^\circ + \mu_{\text{NO}_3^-}^\circ + RT \ln(\gamma_{\text{NH}_4^+} \gamma_{\text{NO}_3^-} m_{\text{NH}_4^+} m_{\text{NO}_3^-}) \quad (9.54)$$

The binary activity coefficient for NH_4NO_3 can be defined as

$$\gamma_{\text{NH}_4\text{NO}_3}^2 = \gamma_{\text{NH}_4^+} \gamma_{\text{NO}_3^-} \quad (9.55)$$

and (9.54) can be rewritten as

$$\mu_{\text{NH}_4\text{NO}_3}^* = \mu_{\text{NH}_4^+}^\circ + \mu_{\text{NO}_3^-}^\circ + RT \ln(\gamma_{\text{NH}_4\text{NO}_3}^2 m_{\text{NH}_4^+} m_{\text{NO}_3^-}) \quad (9.56)$$

If the electrolyte dissociates completely and the initial molality of NH_4NO_3 is $m_{\text{NH}_4\text{NO}_3}$, then

$$m_{\text{NO}_3^-} = m_{\text{NH}_4^+} = m_{\text{NH}_4\text{NO}_3}$$

and

$$\mu_{\text{NH}_4\text{NO}_3}^* = \mu_{\text{NH}_4^+}^\circ + \mu_{\text{NO}_3^-}^\circ + RT \ln(\gamma_{\text{NH}_4\text{NO}_3}^2 m_{\text{NH}_4\text{NO}_3}^2) \quad (9.57)$$

9.1.6 The Equilibrium Constant

The equilibrium expression (9.28) can be used to obtain a useful expression for aerosol equilibrium calculations. Let us consider the general reaction,

$$\sum_{i=1}^k \nu_i M_i = 0$$

Then substituting (9.50) into (9.28)

$$\sum_{i=1}^k \nu_i (\mu_i^\circ + RT \ln \alpha_i) = 0$$

or

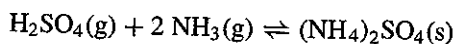
$$\prod_{i=1}^k \alpha_i^{\nu_i} = K_i \quad (9.58)$$

$$K_i = \exp \left(-\frac{1}{RT} \sum_{i=1}^k \nu_i \mu_i^\circ \right) \quad (9.59)$$

If, for example, the species participating in the reaction are all gases, then the activity can be replaced with the partial pressures and

$$\prod_{i=1}^k p_i^{\nu_i} = K_i \quad (9.60)$$

As another example, consider the reaction



for which $\nu_{\text{H}_2\text{SO}_4} = 1$, $\nu_{\text{NH}_3} = 2$, and $\nu_{(\text{NH}_4)_2\text{SO}_4} = -1$. The condition for equilibrium is

$$2 \mu_{\text{NH}_3} + \mu_{\text{H}_2\text{SO}_4} - \mu_{(\text{NH}_4)_2\text{SO}_4} = 0$$

or following (9.59) and noting that $\alpha = 1$ for solids,

$$\exp \left(\frac{\mu_{(\text{NH}_4)_2\text{SO}_4}^* - 2\mu_{\text{NH}_3}^\circ - \mu_{\text{H}_2\text{SO}_4}^\circ}{RT} \right) = K(T) = p_{\text{NH}_3}^2 p_{\text{H}_2\text{SO}_4}$$

NH_4NO_3 is $m\text{NH}_4\text{NO}_3$,



(9.57)

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(9.58)

(9.59)

es, then the activity



(9.60)

r equilibrium is

H_2SO_4

and therefore at equilibrium the product of the square of ammonia partial pressure and of sulfuric acid partial pressure should equal a constant. The value of the constant is a strong function of temperature.

9.2 AEROSOL LIQUID WATER CONTENT

Water is an important component of atmospheric aerosols. Most of the water associated with atmospheric particles is chemically unbound (Pilinis et al., 1989). At very low relative humidities, atmospheric aerosol particles containing inorganic salts are solid. As the ambient relative humidity increases, the particles remain solid until the relative humidity reaches a threshold value characteristic of the aerosol composition (Figure 9.4). At this RH, the solid particle spontaneously absorbs water, producing a saturated aqueous solution. The relative humidity at which this phase transition occurs is known as the deliquescence relative humidity (DRH). Further increase of the ambient RH leads to additional water condensation onto the salt solution to maintain thermodynamic equilibrium (Figure 9.4). On the other hand, as the RH over the wet particle is decreased, evaporation of water occurs. However, the solution generally does not crystallize at the DRH, but remains supersaturated until a much lower RH at which crystallization occurs (Junge, 1952; Richardson and Spann, 1984; Cohen et al. 1987). This hysteresis phenomenon with different deliquescence and crystallization points is illustrated in Figure 9.4 for $(\text{NH}_4)_2\text{SO}_4$. The relative humidities of deliquescence for some inorganic salts, which are common constituents of ambient aerosols, are given in Table 9.1.

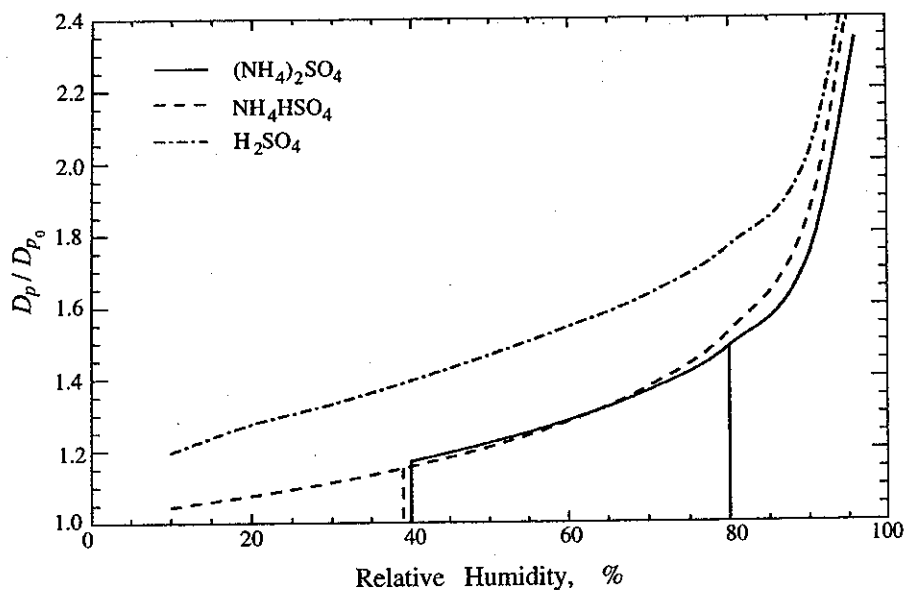


FIGURE 9.4 Diameter change of $(\text{NH}_4)_2\text{SO}_4$, NH_4HSO_4 , and H_2SO_4 particles as a function of relative humidity. D_{p0} is the diameter of the particle at 0% RH.

TABLE 9.1 Deliquescence Relative Humidities of Electrolyte Solutions at 298 K

Salt	DRH (%)
KCl	84.2 ± 0.3
Na ₂ SO ₄	84.2 ± 0.4
NH ₄ Cl	80.0
(NH ₄) ₂ SO ₄	79.9 ± 0.5
NaCl	75.3 ± 0.1
NaNO ₃	74.3 ± 0.4
(NH ₄) ₂ H(SO ₄) ₂	69.0
NH ₄ NO ₃	61.8
NaHSO ₄	52.0
NH ₄ HSO ₄	40.0

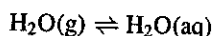
Sources: Tang (1980) and Tang and Munkelwitz (1993).

One should also note that some aerosol species do not exhibit deliquescent behavior. Species like H₂SO₄ are hygroscopic and therefore the water content associated with them changes smoothly as the RH increases or decreases (Figure 9.4).

For each relative humidity a single salt can exist in either of two states: as a solid or as an aqueous solution. For relative humidities lower than the deliquescence relative humidity the Gibbs free energy of the solid salt is lower than the energy of the corresponding solution and the salt remains in the solid state (Figure 9.5). As the relative humidity increases the Gibbs free energy of the corresponding solution state decreases, and at the DRH it becomes equal to the energy of the solid. When the RH increases further the solution represents the lower energy state and the aerosol spontaneously absorbs water to form a saturated salt solution. This deliquescence transition is accompanied by a significant increase in the mass of the particle (Figure 9.4). For even higher RHs the solution state is the preferable one. When the RH decreases reaching the DRH the energies of the two states become once more equal. However, as the RH decreases further, for the particle to attain the lower energy state (solid), all the water in the particle needs to evaporate. This is physically difficult, as salt nuclei need to be formed and salt crystals to grow around them. In the atmosphere, where these salts are suspended in air, this transition does not occur at this point and the particle remains liquid. As the RH keeps decreasing the water in the particle keeps evaporating and the particle is now a supersaturated solution. The solution eventually reaches a critical supersaturation, and nucleation (crystallization) takes place, forming at last a solid particle at RH significantly lower than the DRH (Figure 9.4).

9.2.1 Chemical Potential of Water in Atmospheric Particles

Water vapor exists in the atmosphere in concentrations on the order of grams per m³ of air while its concentration in the aerosol phase is less than 1 mg m⁻³ of air. As a result, transport of water to and from the aerosol phase does not affect the ambient vapor pressure of water in the atmosphere. This is in contrast to the cloud phase where a significant amount of water exists in the form of cloud droplets (see Chapter 15). Thus the ambient RH can be treated as a known constant in aerosol thermodynamic calculations. Considering the equilibrium,



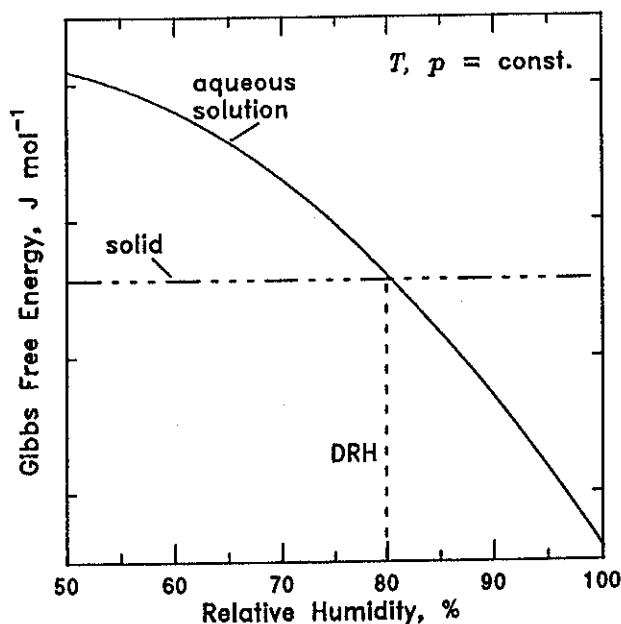


FIGURE 9.5 Gibbs free energy of a solid salt and its aqueous solution as a function of RH. At the DRH these energies become equal.

and using the criterion for thermodynamic equilibrium and the corresponding chemical potentials,

$$\mu_{\text{H}_2\text{O(g)}} = \mu_{\text{H}_2\text{O(aq)}}$$

or

$$\mu_{\text{H}_2\text{O}}^\circ + RT \ln p_w = \mu_{\text{H}_2\text{O}}^\circ + RT \ln \alpha_w \quad (9.61)$$

where p_w is the water vapor pressure (in atm) and α_w is the water activity in solution. For pure water in equilibrium with its vapor, $\alpha_w = 1$ and $p_w = p_w^\circ$ (the saturation vapor pressure of water at this temperature); therefore

$$\mu_{\text{H}_2\text{O}}^\circ - \mu_{\text{H}_2\text{O}}^\circ = RT \ln p_w^\circ \quad (9.62)$$

Using (9.62) in (9.61) yields

$$\alpha_w = \frac{p_w}{p_w^\circ} = \frac{\text{RH}}{100} \quad (9.63)$$

because the ratio p_w/p_w° is by definition equal to the relative humidity expressed in the 0 to 1 scale. Thus the water activity in an atmospheric aerosol solution is equal to the RH (in the 0.0 to 1.0 scale). This result simplifies significantly equilibrium calculations for atmospheric aerosol, because for each RH the water activity for any liquid aerosol solution is fixed.

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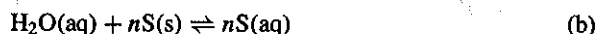
Water equilibrium between the gas and aerosol phases at the point of deliquescence requires that the deliquescence relative humidity of a salt will then satisfy

$$\frac{\text{DRH}}{100} = \alpha_{ws} \quad (9.64)$$

where α_{ws} is the water activity of the saturated solution of the salt at that temperature. The water activity values can be calculated from thermodynamic arguments using aqueous salt solubility data (Cohen et al., 1987; Pilinis and Seinfeld, 1987; Pilinis et al., 1989).

9.2.2 Temperature Dependence of the DRH

The DRH for a single salt varies with temperature. The vapor-liquid equilibrium of a salt S can be expressed by the following reactions:



where n is the solubility of S in water in moles of solute per mole of water (Table 9.2). The heat that is released in reaction (a) is the heat of condensation of water vapor, which is equal to the negative value of its heat of vaporization, $-\Delta H_v$. The heat that is absorbed in reaction (b) is the enthalpy of solution of the salt ΔH_s . This enthalpy can be readily calculated from the heats of formation tabulated in standard thermodynamic tables. Values of ΔH_s are shown in Table 9.3 (Wagman et al., 1966). The overall enthalpy change, ΔH , for the two reactions is

$$\Delta H = n \Delta H_s - \Delta H_v \quad (9.65)$$

The change of the vapor pressure of water over a solution with temperature is given by the Clausius-Clapeyron equation (Denbigh, 1981)

$$\frac{d \ln p_w}{dT} = -\frac{\Delta H}{RT^2} \quad (9.66)$$

which for this case becomes

$$\frac{d \ln p_w}{dT} = \frac{\Delta H_v}{RT^2} - n \frac{\Delta H_s}{RT^2} \quad (9.67)$$

TABLE 9.2 Solubility of Common Aerosol Salts in Water as a Function of Temperature ($n = A + BT + CT^2$, n = mol of solute per mol of water)

Salt	n (at 298 K)	A	B	C
$(\text{NH}_4)_2\text{SO}_4$	0.104	0.1149	-4.489×10^{-4}	1.385×10^{-6}
Na_2SO_4	0.065	0.3754	-1.763×10^{-3}	2.424×10^{-6}
NaNO_3	0.194	0.1868	-1.677×10^{-3}	5.714×10^{-6}
NH_4NO_3	0.475	4.298	-3.623×10^{-2}	7.853×10^{-5}
KCl	0.086	-0.2368	1.453×10^{-3}	-1.238×10^{-6}
NaCl	0.111	0.1805	-5.310×10^{-4}	9.965×10^{-7}

TABLE 9.3 Enthalpy of Solution for Common Aerosol Salts at 298 K

Salt	ΔH_s (kJ mol ⁻¹)
(NH ₄) ₂ SO ₄	6.32
Na ₂ SO ₄	-9.76
NaNO ₃	13.24
NH ₄ NO ₃	16.27
KCl	15.34
NaCl	1.88

Applying the Clausius-Clapeyron equation to pure water we also obtain

$$\frac{d \ln p_w^\circ}{dT} = \frac{\Delta H_v}{RT^2} \quad (9.68)$$

where p_w° is the saturation vapor pressure of the water at temperature T . Combining (9.67) and (9.68)

$$\frac{d \ln(p_w/p_w^\circ)}{dT} = -n \frac{\Delta H_s}{RT^2} \quad (9.69)$$

and substituting (9.63) into (9.69) and applying it to the DRH

$$\frac{d \ln(\text{DRH}/100)}{dT} = -n \frac{\Delta H_s}{RT^2} \quad (9.70)$$

The solubility n can be written as a polynomial in T (see Table 9.2) and the equation can be integrated from $T_0 = 298$ to T to give

$$\ln \frac{\text{DRH}(T)}{\text{DRH}(T_0)} = \frac{\Delta H_s}{R} \left[A \left(\frac{1}{T} - \frac{1}{T_0} \right) - B \ln \frac{T}{T_0} - C(T - T_0) \right] \quad (9.71)$$

or

$$\text{DRH}(T) = \text{DRH}(298) \exp \left\{ \frac{\Delta H_s}{R} \left[A \left(\frac{1}{T} - \frac{1}{298} \right) - B \ln \frac{T}{298} - C(T - 298) \right] \right\} \quad (9.72)$$

The only assumption used in (9.72) is that the heat of solution is almost constant from 298 K to T . Wexler and Seinfeld (1991) proposed a similar expression assuming constant solubility, namely, $B = C = 0$ in (9.72), while expression (9.72) was derived by Tang and Munkelwitz (1993).

The predictions of (9.72) are compared with measurements from a series of investigations in Figure 9.6. These results indicate that the DRH for (NH₄)₂SO₄ is practically constant within the temperature range of atmospheric interest while for others (i.e., NaNO₃) it varies significantly.

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7.853×10^{-5}
-1.238×10^{-6}
9.965×10^{-7}

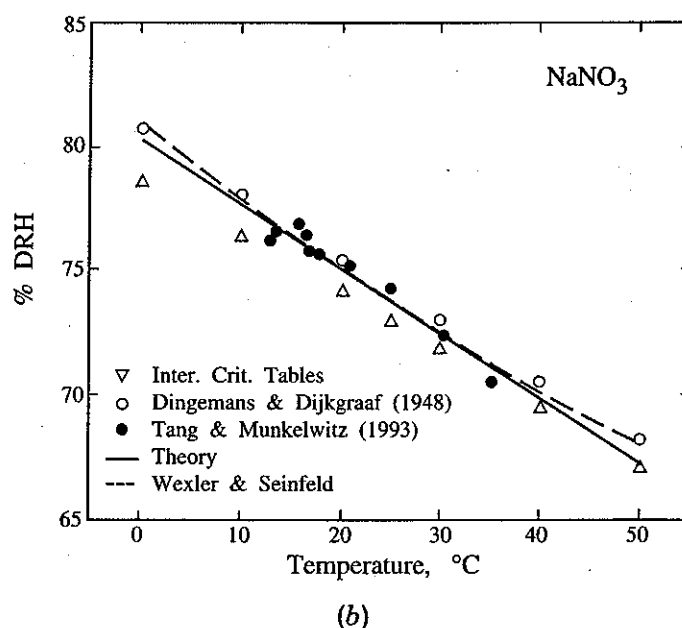
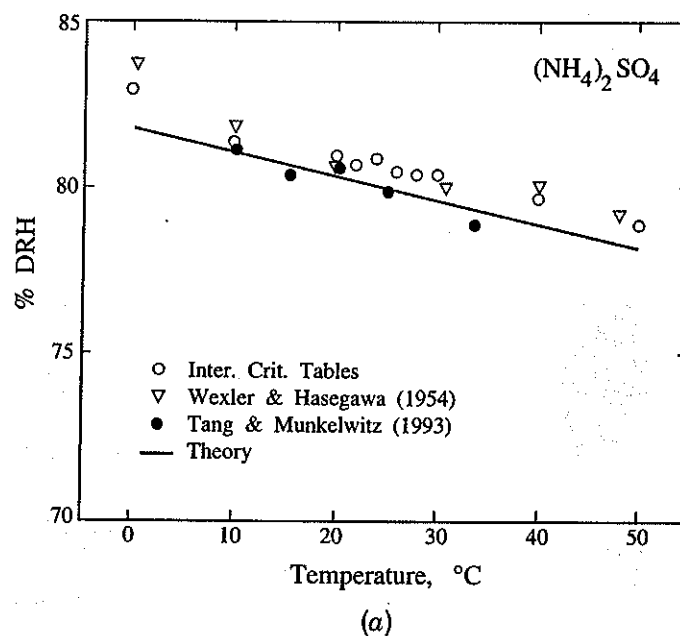
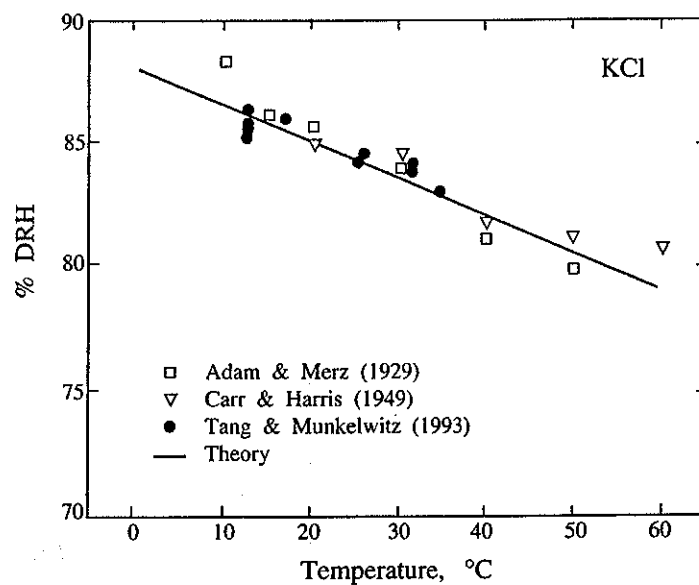
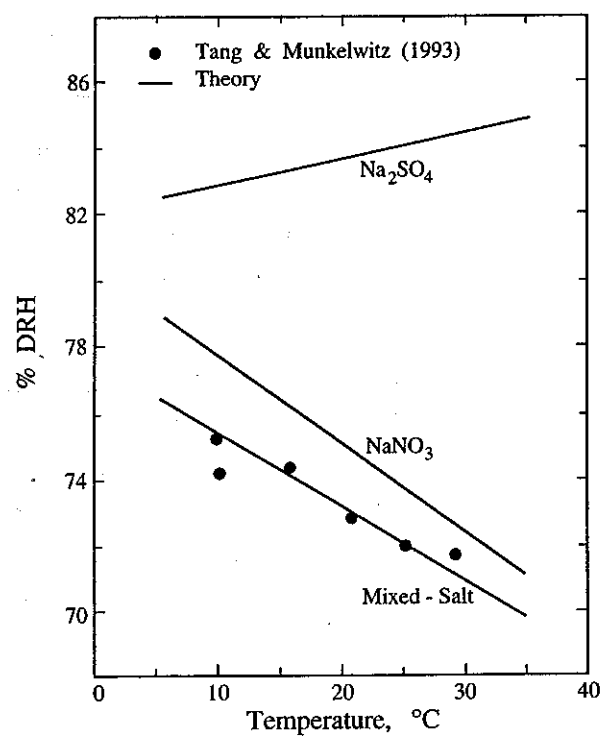


FIGURE 9.6 Deliquescence RH as a function of temperature for (a) $(\text{NH}_4)_2\text{SO}_4$, (b) NaNO_3 , (c) KCl , (d) Na_2SO_4 - NaNO_3 mixed salt, and (e) NaCl - KCl mixed salt. Reprinted from *Atmos. Environ.*, 27A, Tang I. N. and Munkelwitz, H. R., Composition and temperature dependence of the deliquescence properties of hygroscopic aerosols, 467-473, Copyright 1993, with kind permission from Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington OX5 1GB, U.K.



(c)



(d)

FIGURE 9.6 (continued)

SO₄, (b) NaNO₃, (c)
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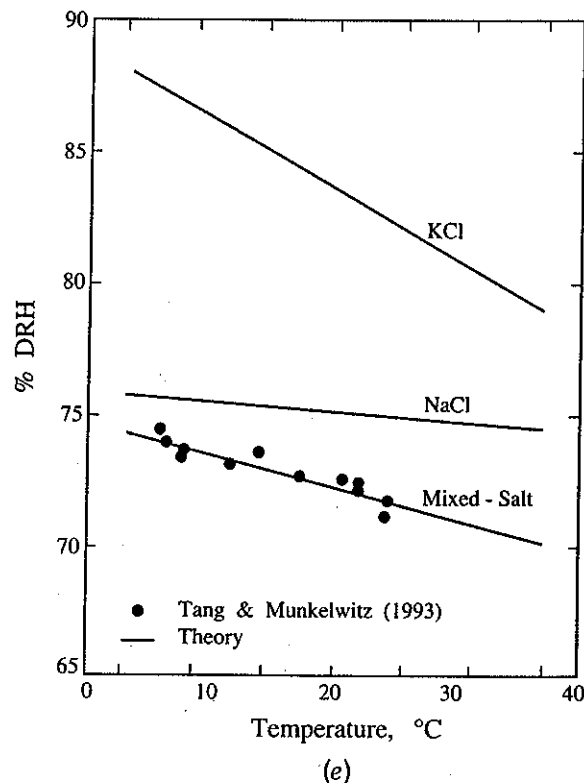


FIGURE 9.6 (continued)

9.2.3 Deliquescence of Multicomponent Aerosols

Multicomponent aerosol particles exhibit similar behavior to single-component salts. As the ambient RH increases the salt mixture is solid, until the ambient RH reaches the deliquescence point of the mixture, at which the aerosol absorbs atmospheric moisture and produces a saturated solution. A typical plot of a multicomponent particle deliquescence, growth, evaporation, and then crystallization is shown in Figure 9.7 for a KCl–NaCl aerosol particle. Note that the DRH for the mixed-salt particle occurs at 72.7% RH, which is lower than the DRH of both NaCl (75.3%) and KCl (84.2%).

Following Wexler and Seinfeld (1991), let us consider two electrolytes in a solution exposed to the atmosphere. The change of the DRH of a single-solute aqueous solution when another electrolyte is added can be calculated using the Gibbs–Duhem equation, (9.21). For constant T and p and for a solution containing two electrolytes (1 and 2) and water (w):

$$n_1 d\mu_1 + n_2 d\mu_2 + n_w d\mu_w = 0 \quad (9.73)$$

where n_1 , n_2 , and n_w are the numbers of moles of electrolytes 1, 2, and water, respectively, while μ_1 , μ_2 , and μ_w are the corresponding chemical potentials. Let us assume that ini-

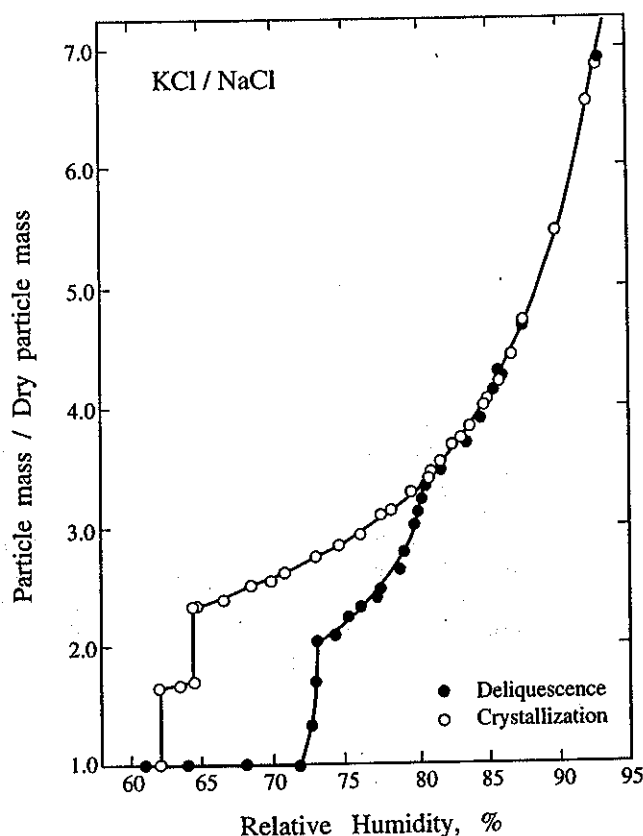


FIGURE 9.7 Hygroscopic growth and evaporation of a mixed-salt particle composed initially of 66% mass KCl and 34% mass NaCl. Reprinted from *Atmos. Environ.*, 27A, Tang I. N. and Munkelwitz, H. R., Composition and temperature dependence of the deliquescence properties of hygroscopic aerosols, 467–473, Copyright 1993, with kind permission from Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington OX5 1GB, UK.

tially electrolyte 1 is in equilibrium with solid salt 1 and the solution does not yet contain electrolyte 2. As electrolyte 2 is added to the solution, the chemical potential of electrolyte 1 does not change, because it remains in equilibrium with its solid phase. Thus $d\mu_1 = 0$ in (9.73). The chemical potentials of electrolyte 2 and water can be expressed using (9.50) to get

$$n_2 d \ln \alpha_2 + n_w d \ln \alpha_w = 0 \quad (9.74)$$

Taking into consideration that $n_2/n_w = M_w m_2/1000$, where m_2 is the molality of electrolyte 2 and M_w is the molecular weight of water,

$$m_2 d \ln \alpha_2 + \frac{1000}{M_w} d \ln \alpha_w = 0 \quad (9.75)$$

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Integration of the last equation from $m'_2 = 0$ to $m'_2 = m_2$ gives

$$\ln \frac{\alpha_w(m_2)}{\alpha_w(0)} = -\frac{M_w}{1000} \int_0^{m_2} \frac{m'_2}{\alpha_2(m'_2)} \frac{d\alpha_2(m'_2)}{dm'_2} dm'_2 \quad (9.76)$$

Wexler and Seinfeld (1991) have argued that $d\alpha_2/dm_2 \geq 0$ and therefore the integral is positive, and then

$$\alpha_w(m_2) \leq \alpha_w(m_2 = 0) \quad (9.77)$$

Hence the activity of water decreases as electrolyte 2 is added to the system, until the solution becomes saturated in that electrolyte too. The aerosol is exposed to the atmosphere and therefore its DRH also decreases.

The above analysis can be extended to aerosols containing more than two salts. Thus one can prove that water activity reaches a minimum at the deliquescence point of the aerosol. Another consequence of this analysis is that the DRH of a mixed salt is always lower than the DRH of the individual salts in the particle. Wexler and Seinfeld (1991) solved (9.76) for the case of the system containing NH_4NO_3 and NH_4Cl . Their calculations at 303 K are depicted in Figure 9.8.

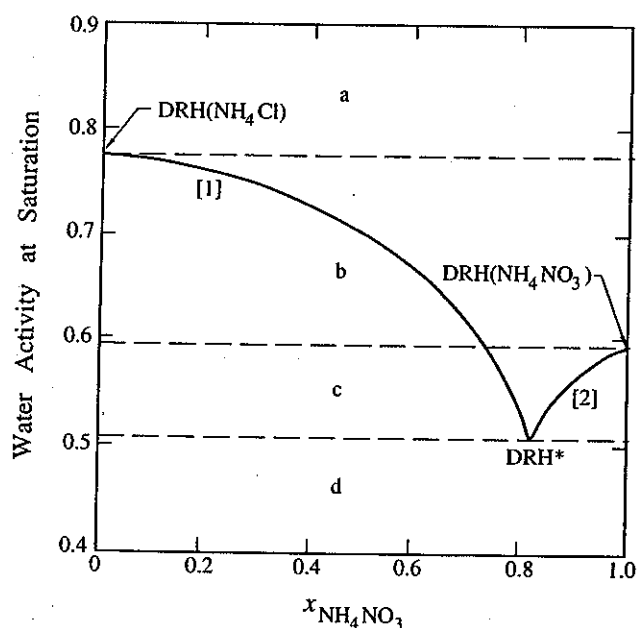


FIGURE 9.8 Water activity at saturation for an aqueous solution of NH_4NO_3 and NH_4Cl at 303 K. Reprinted from *Atmos. Environ.*, 25A, Wexler, A. S. and Seinfeld, J. H., Second-generation inorganic aerosol model, 2731–2748, Copyright 1991, with kind permission from Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington OX5 1GB, UK.

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calculations

When there is only NH_4Cl in the particle ($x_{\text{NH}_4\text{NO}_3} = 0$) the DRH of the particle is 77.4%. If the RH is below 77.4%, the particle is solid; if it is above 77.4% it is an aqueous solution of NH_4^+ and Cl^- . (Note that the calculations in Figure 9.8 are at 303K.)

There are seven different RH composition regimes in the figure:

(a) $\text{RH} > \text{DRH}(\text{NH}_4\text{Cl}) > \text{DRH}(\text{NH}_4\text{NO}_3)$. When the RH exceeds the DRH of both compounds the aerosol is an aqueous solution of NH_4^+ , NO_3^- , and Cl^- .

(b₁) $\text{DRH}(\text{NH}_4\text{Cl}) > \text{RH} > \text{DRH}(\text{NH}_4\text{NO}_3)$ —left of [1]. In this regime the aerosol consists of solid NH_4Cl in equilibrium with an aqueous solution of NH_4^+ , NO_3^- , and Cl^- .

(b₂) $\text{DRH}(\text{NH}_4\text{Cl}) > \text{RH} > \text{DRH}(\text{NH}_4\text{NO}_3)$ —right of [1]. If the aerosol contains enough NH_4NO_3 so that its composition is to the right of line [1], the aerosol is an aqueous solution of NH_4^+ , NO_3^- , and Cl^- . In this regime addition of NH_4NO_3 results in complete dissolution of NH_4Cl even if the RH is higher than its DRH.

(c₁) $\text{DRH}(\text{NH}_4\text{Cl}) > \text{DRH}(\text{NH}_4\text{NO}_3) > \text{RH} > \text{DRH}^*$ —left of [1]. The aerosol consists of solid NH_4Cl in equilibrium with a solution of NH_4^+ , NO_3^- , and Cl^- .

(c₂) Right of [1], left of [2]. In this regime there is no solid phase and the aerosol consists exclusively of an aqueous solution of NH_4^+ , NO_3^- , and Cl^- .

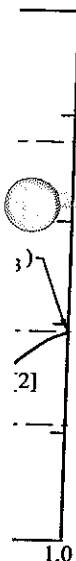
(c₃) Right of [2]. Here the aerosol consists of solid NH_4NO_3 in equilibrium with an aqueous solution of NH_4^+ , NO_3^- , and Cl^- .

(d) $\text{RH} < \text{DRH}^*$. If the relative humidity is below $\text{DRH}^* = 51\%$, the aerosol consists of solid NH_4NO_3 and solid NH_4Cl .

In conclusion, for this mixture of salts, if both are present, the aerosol will contain some liquid water for $\text{RH} > 51\%$. However, if we are below the solid line in Figure 9.8, the aerosol will also contain a solid phase in equilibrium with the solution. Only above the solid line is the particle completely liquid.

It is instructive to follow the changes in a particle of a given composition as RH increases. For example, consider a particle consisting of 40% NH_4NO_3 and 60% NH_4Cl as RH increases from 40 to 90%, assuming that there is no evaporation or condensation of these salts. At the beginning ($\text{RH} = 40\%$) the particle is solid and it remains solid until RH reaches 51.4% ($= \text{DRH}^*$). At this point, the particle deliquesces and consists of two phases—a solid phase consisting of solid NH_4Cl and an aqueous solution with the composition corresponding to the eutonic point ($x_{\text{NH}_4\text{NO}_3} = 0.811$, $x_{\text{NH}_4\text{Cl}} = 0.189$). As the RH increases further, more NH_4Cl dissolves in the solution and the composition of the aqueous solution follows line [1]. For example, at $\text{RH} = 60\%$ the aerosol consists of solid NH_4Cl and a solution of composition $x_{\text{NH}_4\text{NO}_3} = 0.73$, $x_{\text{NH}_4\text{Cl}} = 0.27$. At 70% RH, most of the NH_4Cl has dissolved and the composition of the solution is close to the net particle composition $x_{\text{NH}_4\text{NO}_3} = 0.42$, $x_{\text{NH}_4\text{Cl}} = 0.58$. Finally, when the RH reaches 71%, all the NH_4Cl dissolves and the particle consists of only one phase (the aqueous one) with composition equal to the particle composition. Note that there is only one step change in the mass of the particle corresponding to the mutual DRH^* (e.g., see Figure 9.7). Further increases in the RH cause continuous changes of the aerosol mass and not step changes. On the contrary, step changes are observed during particle evaporation and will be discussed subsequently.

This discussion of phase transitions has been extended to mixtures of more than three salts by Potukuchi and Wexler (1995a,b). The phase diagrams become now three dimen-



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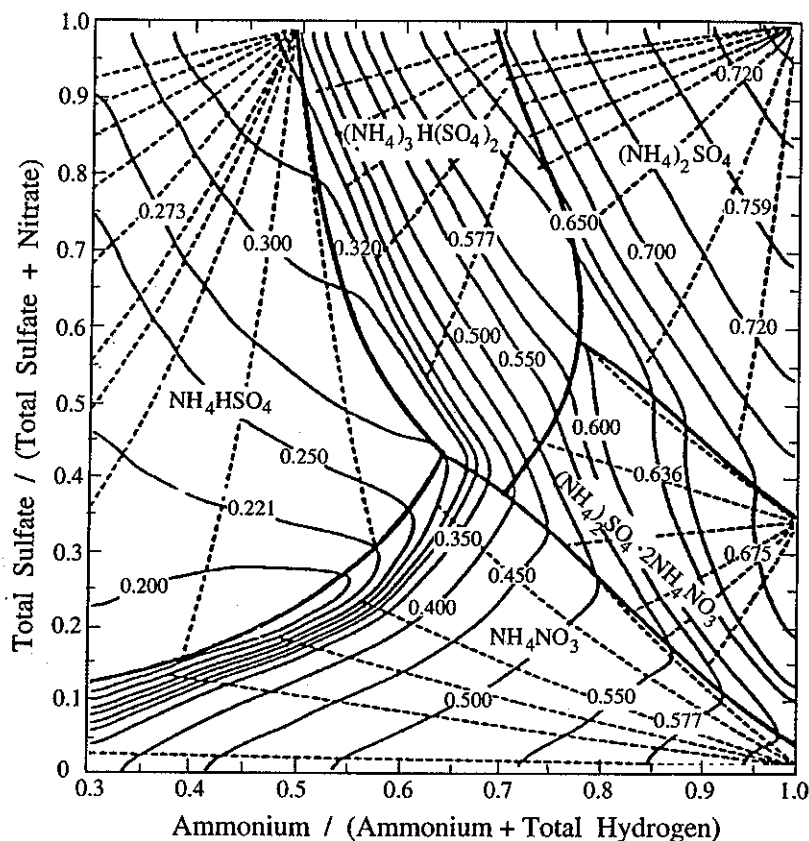


FIGURE 9.9 Deliquescence relative humidity contours (solid lines) for aqueous solutions of $\text{H}^+\text{-NH}_4^+\text{-HSO}_4^-\text{-SO}_4^{2-}\text{-NO}_3^-$ shown together with the lines (dashed) describing aqueous-phase composition with relative humidity. Labels on the contours represent the deliquescence relative humidity values. Total hydrogen is total moles of protons and bisulfate ions. Total sulfate is number of moles of sulfate and bisulfate ions. X = ammonium/(ammonium + total hydrogen). Y = total sulfate (total sulfate + nitrate). Reprinted from *Atmos. Environ.*, **29**, Potukuchi, S. and Wexler, A. S., Identifying solid-aqueous phase transitions in atmospheric aerosols. II Acidic solutions, 3357–3364. Copyright 1995, with kind permission from Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington OX5 1GB, UK.

sional (Figure 9.9). Note that the solid phases that appear are $(\text{NH}_4)_2\text{SO}_4$, NH_4HSO_4 , letovicite $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$, NH_4NO_3 , and the double salt $(\text{NH}_4)_2\text{SO}_4 \cdot 2\text{NH}_4\text{NO}_3$. The labels on the contours show relative humidities at deliquescence. The bold lines in this figure are the phase boundaries separating the various solid phases. On these lines both phases coexist. For example, let us assume that there is enough ammonia present so $X = 1$ in Figure 9.9. If sulfate dominates then $Y = 1$ and the system is in the upper right-hand corner of the diagram with a DRH of 80% corresponding to $(\text{NH}_4)_2\text{SO}_4$. If there is enough nitrate available so that $Y = 0.3$ then the DRH is 68% corresponding to $(\text{NH}_4)_2\text{SO}_4 \cdot 2\text{NH}_4\text{NO}_3$.

The mutual deliquescence points of a series of pairs are given in Table 9.4.

TABLE 9.4 Deliquescence RH (DRH*) at Mutual Solubility Point at 303 K

Compound 1	Compound 2	DRH*	DRH ₁	DRH ₂
NH ₄ NO ₃	NaCl	42.2	59.4	75.2
NH ₄ NO ₃	NaNO ₃	46.3	59.4	72.4
NH ₄ NO ₃	NH ₄ Cl	51.4	59.4	77.2
NaNO ₃	NH ₄ Cl	51.9	72.4	77.2
NH ₄ NO ₃	(NH ₄) ₂ SO ₄	52.3	59.4	79.2
NaNO ₃	NaCl	67.6	72.4	75.2
NaCl	NH ₄ Cl	68.8	75.2	77.2
NH ₄ Cl	(NH ₄) ₂ SO ₄	71.3	77.2	79.2

Source: Wexler and Seinfeld (1991).

9.2.4 Crystallization of Single and Multicomponent Salts

The behavior of inorganic salts when RH is decreased is different from that discussed in the Sections 9.2.2 and 9.2.3 (Figure 9.4). For example, for (NH₄)₂SO₄, as the RH decreases below 80% (the DRH of (NH₄)₂SO₄) the particle evaporates but not completely. The particle remains liquid until a RH of 37%, where crystallization finally occurs. This hysteresis phenomenon is characteristic of most salts. For such salts, knowledge of the RH alone is insufficient for calculation of the aerosol liquid water content in this regime. One needs to know the RH history of the particle.

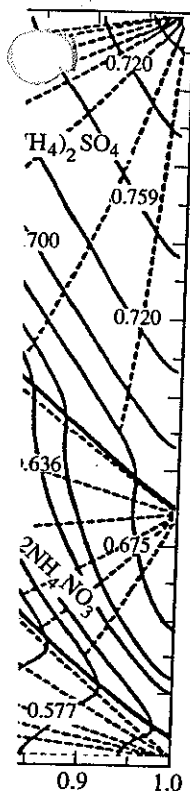
Particles consisting of multiple salts exhibit multiple crystallization points (Figure 9.7). For example, the evaporation of a KCl–NaCl particle is characterized by two step changes at 65% (crystallization of KCl) and one at 62% (crystallization of NaCl).

Spann and Richardson (1985) have shown that for particles of composition between NH₄HSO₄ and (NH₄)₂SO₄ the crystallization RH ranges from 10 to 40%, indicating that for certain compositions the solution cannot be dried in the atmosphere. Particles of this composition would likely be present even at low relative humidities in the atmosphere as supersaturated salts and will not undergo deliquescent behavior. The same is true for NaCl with a crystallization RH of around 42% (Shaw and Rood, 1990).

9.3 EQUILIBRIUM VAPOR PRESSURE OVER A CURVED SURFACE: THE KELVIN EFFECT

In our discussion so far of aerosol thermodynamics, we have assumed that the aqueous aerosol solution has a flat surface. However, the key aspect that distinguishes the thermodynamics of atmospheric particles and drops is their curved interface. In this section we investigate the effect of curvature on the vapor pressure of a species A over the particle surface. Our approach will be to relate this vapor pressure to that over a flat surface. To do so we begin by considering the change of Gibbs free energy accompanying the formation of a single drop of pure A of radius R_p containing n molecules of the substance:

$$\Delta G = G_{\text{droplet}} - G_{\text{pure vapor}}$$



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aqueous solutions of
aqueous-phase com-
cidence relative humidity
fate is number of moles
gen). Y = total sulfate
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