Lecture 9: Thermodynamics of Aerosols

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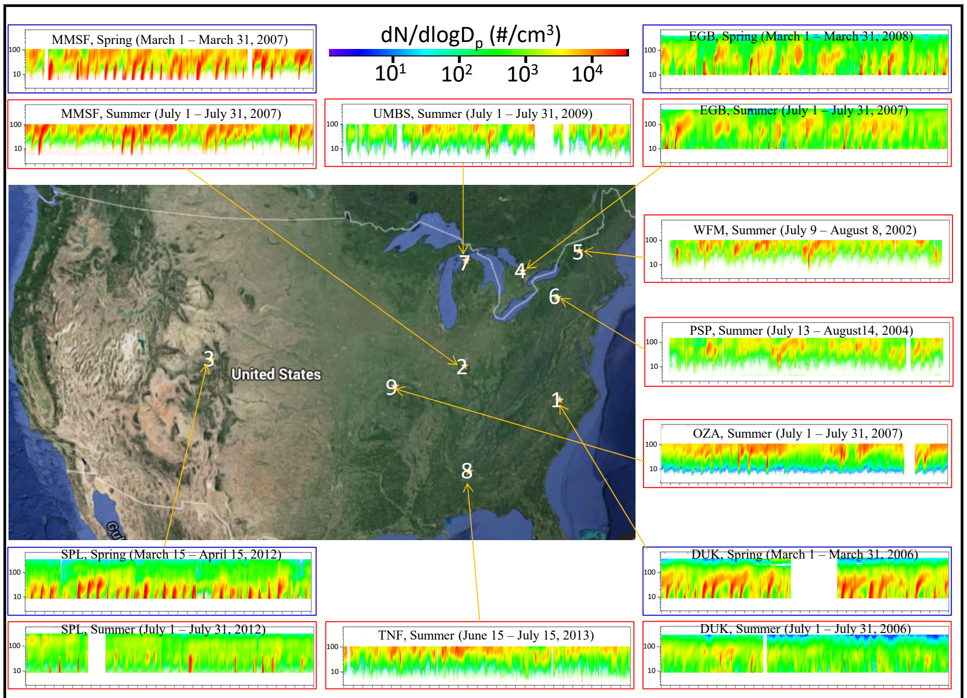

Figure 1

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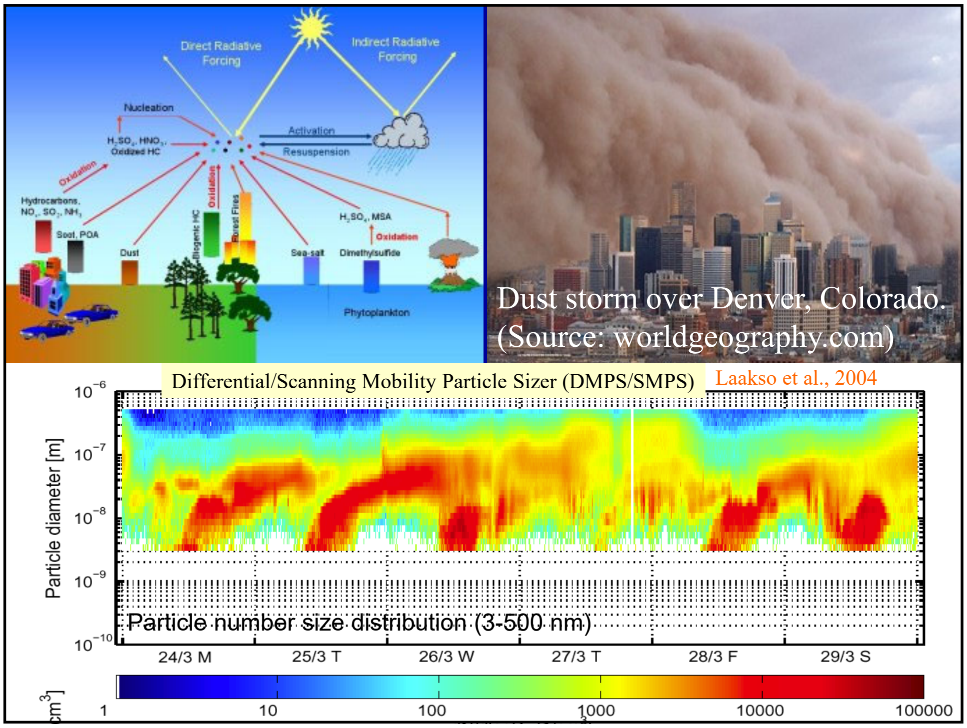

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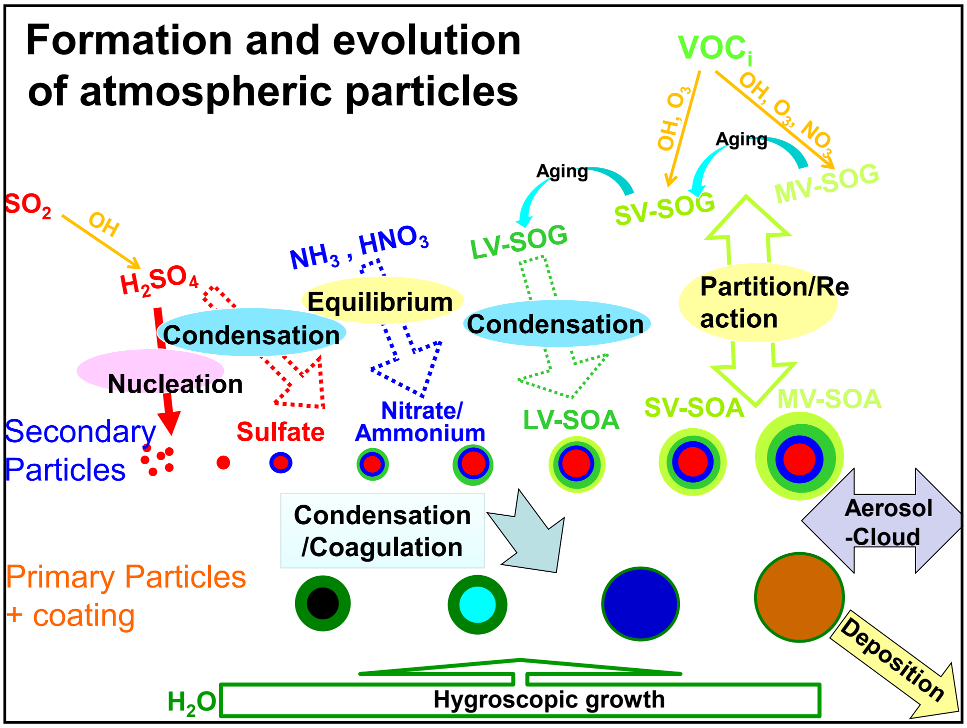
Formation and evolution of atmospheric particles



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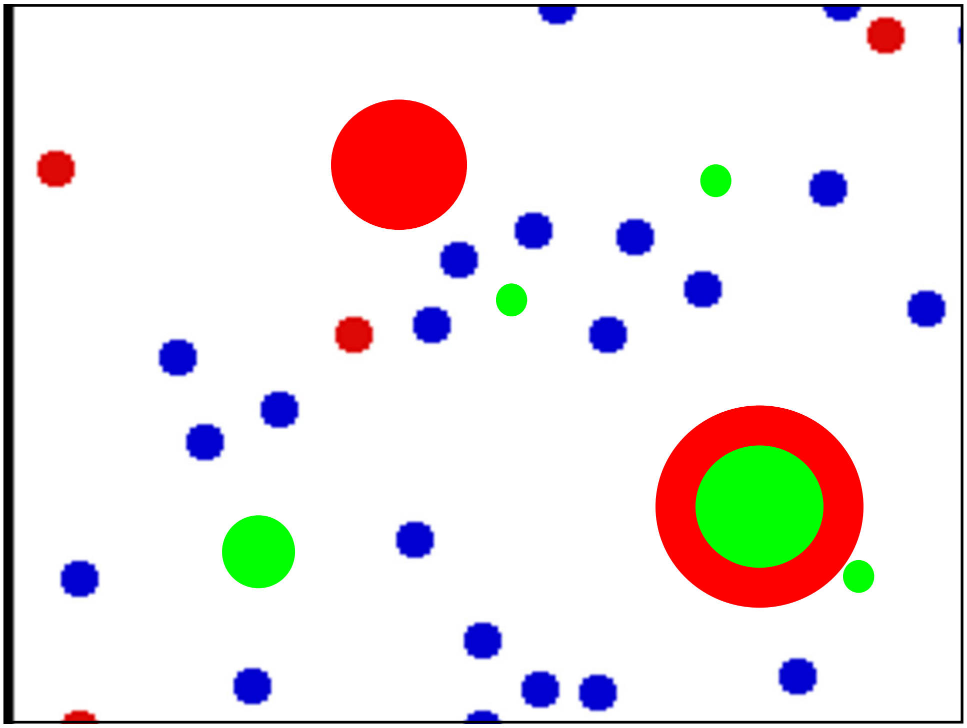

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Thermodynamics of Aerosols

Gibbs free energy:

$$G = H - TS = U + PV - TS$$

H is the enthalpy, *S* is the entropy, and *T* is the absolute temperature, *U* is the internal energy, *P* is the pressure, and *V* is the volume.

Gibbs free energy of a system containing *k* chemical compounds can be calculated by summation of the products of the chemical potentials and the number of moles of each species

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

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Chemical potential:

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

n_j the number of moles of system species

The chemical potential has an important function in the system's thermodynamic behavior analogous to pressure or temperature …

A difference in chemical potential can be viewed as the cause for chemical reaction or for mass transfer from one phase to another.

Conditions for Chemical Equilibrium

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}$$

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

ν_i is the corresponding stoichiometric coef (positive for reactants, negative for products)

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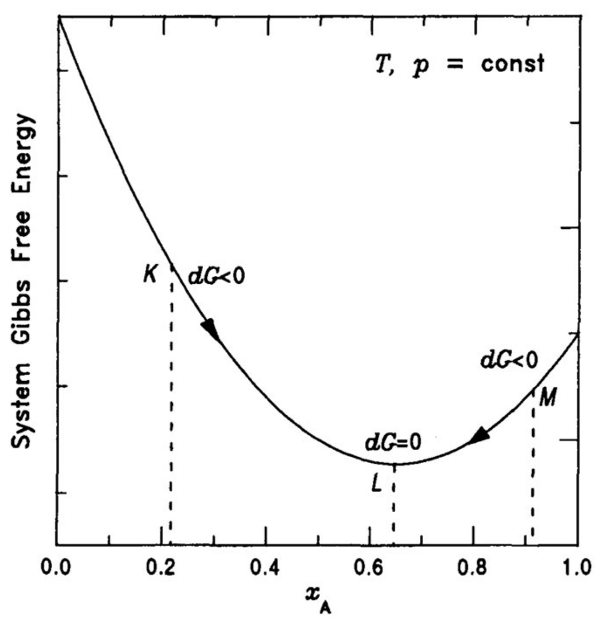

FIGURE 10.1 Sketch of the Gibbs free energy for a closed system where the reaction A ⇌ B takes places versus the mole fraction of A.

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Chemical Potentials of Ideal Gases and Ideal Gas Mixtures

The Single Ideal Gas

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

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.

The Ideal Gas Mixture

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

the partial pressure of compound i $\quad p_i = y_i p$

y_i is the gas mole fraction of compound i.

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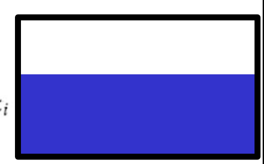
Chemical Potential of Solutions

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

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

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.



$\mathrm{I(g)} \rightleftharpoons \mathrm{I(aq)}$ $\qquad \mu_i^\circ(T) + RT \ln p_i = \mu_i^*(T, p) + RT \ln x_i$

$\mu_i(\mathrm{g}) = \mu_i(\mathrm{aq})$ $\qquad p_i = \exp\left(\dfrac{\mu_i^* - \mu_i^\circ}{RT}\right) x_i = K_i(T, p) x_i$

$$\boxed{p_i = p_i^\circ x_i}$$

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$$p_i = p_i^\circ x_i$$

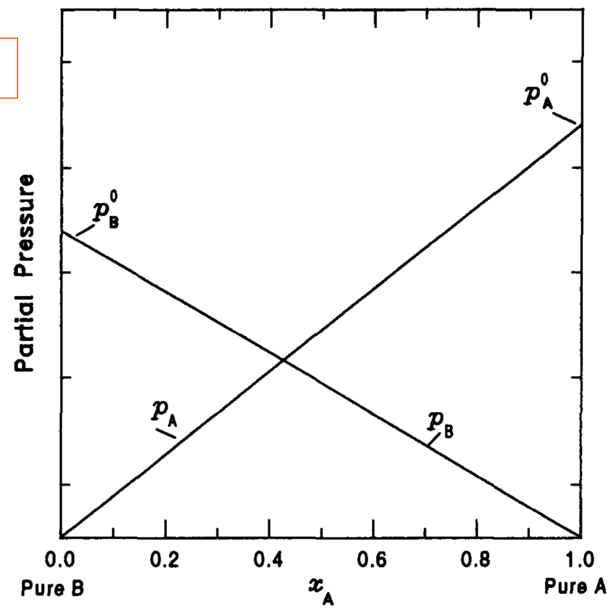

FIGURE 10.2 Equilibrium partial pressures of the components of an ideal binary mixture as a function of the mole fraction of A, x_A.

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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

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

Activity $\quad \alpha_i = \gamma_i x_i$

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

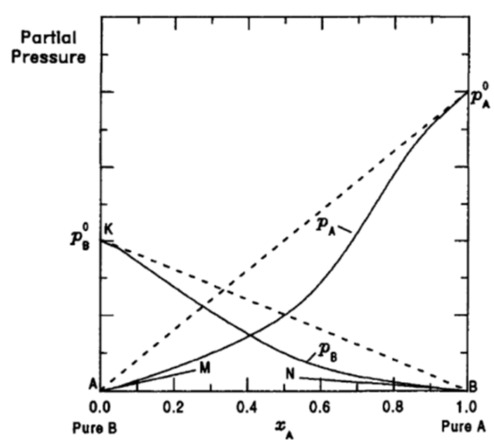

FIGURE 10.3 Equilibrium partial pressures of the components of a nonideal mixture of A and B. Dashed lines correspond to ideal behavior.

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Chemical Potential of Water in Atmospheric Particles

$$H_2O(g) \rightleftharpoons H_2O(aq)$$

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

$$\mu_{H_2O(g)} = \mu_{H_2O(aq)}$$

or

$$\mu^{\circ}_{H_2O} + RT \ln p_w = \mu^{*}_{H_2O} + RT \ln \alpha_w \qquad (10.61)$$

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 $p_w = p^{\circ}_w$ (the saturation vapor pressure of water at this temperature); therefore

$$\mu^{*}_{H_2O} - \mu^{\circ}_{H_2O} = RT \ln p^{\circ}_w \qquad (10.62)$$

Using (10.62) in (10.61) yields

$$\boxed{\alpha_w = \frac{p_w}{p^{\circ}_w} = \frac{\mathrm{RH}}{100} \qquad (10.63)}$$

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T (K)	T (^{o}C)	**Saturation vapor pressure** p_w^{o} (hpa)
230	-43.15	0.136
240	-33.15	0.377
250	-23.15	0.954
260	-13.15	2.227
270	-3.15	4.847
280	6.85	9.916
290	16.85	19.193
300	26.85	35.352
310	36.85	62.287

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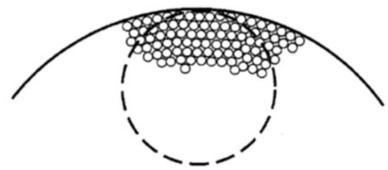
EQUILIBRIUM VAPOR PRESSURE OVER A CURVED SURFACE

Gibbs free energy change for the formation of a single droplet of pure A of radius Rp containing n molecules



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

$$\Delta G = n(g_l - g_v) + 4\pi R_p^2 \sigma$$

$$n = \frac{4\pi R_p^3}{3 v_l} \qquad \Delta G = \frac{4\pi R_p^3}{3 v_l}(g_l - g_v) + 4\pi R_p^2 \sigma$$

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$$g_l - g_v = -kT \ln \frac{p_A}{p_A^\circ} \qquad \Delta G = -\frac{4}{3}\pi R_p^3 \frac{kT}{v_l} \ln S + 4\pi R_p^2 \sigma$$

$$R_p^* = \frac{2\sigma v_l}{kT \ln S}$$

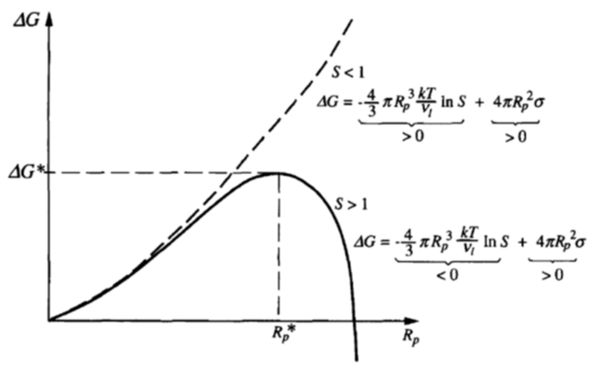

FIGURE 10.10 Gibbs free energy change for formation of a droplet of radius R_p from a vapor with saturation ratio S.

Kelvin Equation

$$p_A = p_A^\circ \exp\left(\frac{2\sigma v_l}{kT R_p}\right) \qquad p_A = p_A^\circ \exp\left(\frac{2\sigma M}{RT \rho_l R_p}\right)$$

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THERMODYNAMICS OF ATMOSPHERIC AEROSOL SYSTEMS

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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

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

Activity $\alpha_i = \gamma_i x_i$

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

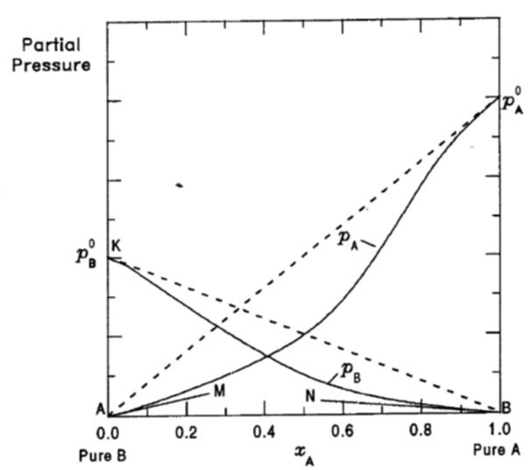

FIGURE 9.3 Equilibrium partial pressures of the components of a nonideal mixture of A and B. Dashed lines correspond to ideal behavior.

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The H_2SO_4–H_2O System

The importance of sulfuric acid in aerosol formation in the atmosphere has been well recognized. Sulfuric acid is very hygroscopic, absorbing significant amounts of water even at extremely low relative humidities.

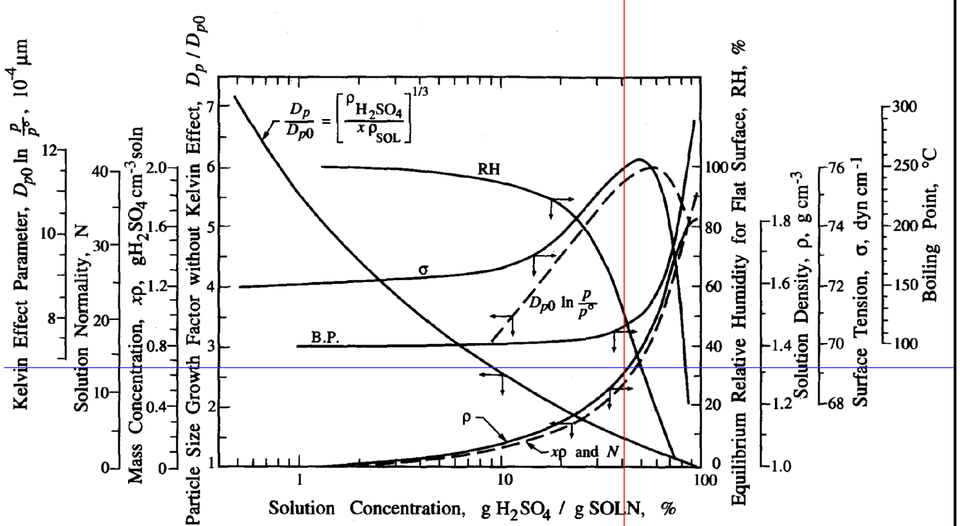

FIGURE 10.13 Properties of sulfuric acid–water droplets.

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Calculation of the Properties of a H_2SO_4 Droplet. Consider a 1 µm H_2SO_4-H_2O droplet in equilibrium at 50% RH. Using Figure 10.13, calculate the following:

1. The H_2SO_4 concentration in the solution
2. The density of the solution
3. The boiling point of the solution
4. The droplet surface tension
5. The solution normality
6. The mass concentration of H_2SO_4 in the solution
7. The size of the droplet if all the water were removed
8. The Kelvin effect parameter
9. The size of this droplet at 90% RH.

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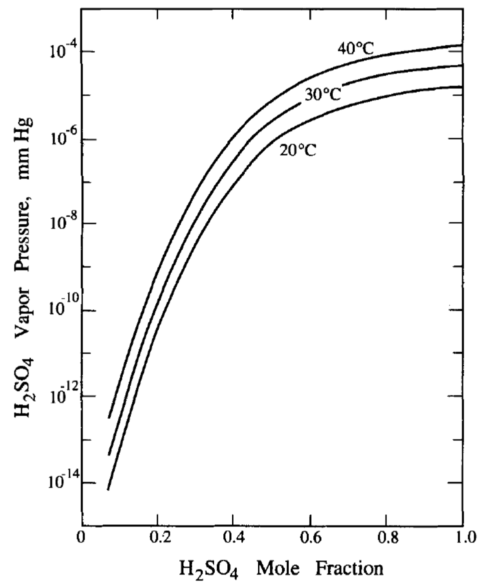

FIGURE 10.15 Equilibrium vapor pressure of H_2SO_4 in a mixture with water over a flat surface as a function of composition and temperature.

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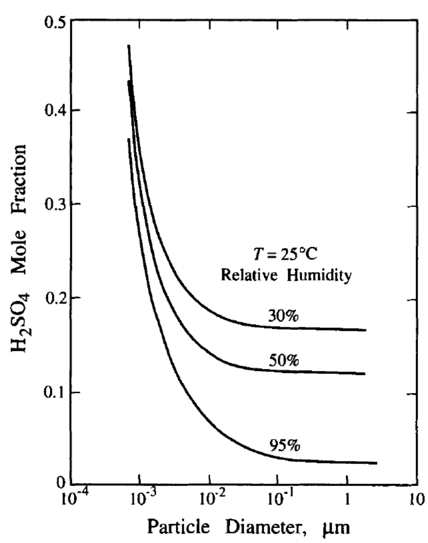

FIGURE 10.16 Equilibrium concentration of H_2SO_4 in a spherical droplet of H_2SO_4 and H_2O as a function of relative humidity and droplet diameter.

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The Ammonia–Nitric Acid–Sulfuric Acid–Water System

1. Sulfuric acid possesses an extremely low vapor pressure.
2. $(NH_4)_2SO_4$ solid or aqueous is the preferred form of sulfate.

Based on these observations, we can define two regimes of interest, ammonia-rich and ammonia-poor. If [TA], [TS], and [TN] are the total (gas + aqueous + solid) molar concentrations of ammonia, sulfate, and nitrate, respectively, then the two cases are

1. Ammonia-poor, $[TA] < 2[TS]$.
2. Ammonia-rich, $[TA] > 2[TS]$.

Case 1: Ammonia-Poor. In this case there is insufficient NH_3 to neutralize the available sulfate. Thus the aerosol phase will be acidic. The vapor pressure of NH_3 will be low, and the sulfate will tend to drive the nitrate to the gas phase. Since the NH_3 partial pressure will be low, the NH_3–HNO_3 partial pressure product will also be low so ammonium nitrate levels will be low or zero. Sulfate may exist as bisulfate.

Case 2: Ammonia-Rich. In this case there is excess ammonia, so that the aerosol phase will be neutralized to a large extent. The ammonia that does not react with sulfate will be available to react with nitrate to produce NH_4NO_3.

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