

11 Mass Transfer Aspects of Atmospheric Chemistry

11.1 MASS AND HEAT TRANSFER TO ATMOSPHERIC PARTICLES

Mass and energy transport to or from atmospheric particles accompanies their growth or evaporation. We would like to develop mathematical expressions describing the mass transfer rates between condensed and gas phases. The desired expressions for the vapor concentrations and temperature profiles around a growing or evaporating particle can be obtained by solving the appropriate mass and energy conservation equations.

Let us consider a particle of pure species A in air that also contains vapor molecules of A. Particle growth or evaporation depends on the direction of the net flux of vapor molecules relative to the particle. As we saw in Chapter 7, the mass transfer process will depend on the particle size relative to the mean free path of A in the surrounding environment. We will therefore start our discussion from the simpler case of a relatively large particle (mass transfer in the continuum regime) and then move to the other extreme (mass transfer in the kinetic regime).

11.1.1 The Continuum Regime

$\alpha = 1$

The unsteady-state diffusion of species A to the surface of a stationary particle of radius R_p is described by

$$\frac{\partial c}{\partial t} = -\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \tilde{J}_{A,r}) \quad (11.1)$$

where $c(r, t)$ is the concentration of A, and $\tilde{J}_{A,r}(r, t)$ is the molar flux of A (moles area⁻¹ time⁻¹) at any radial position r . This equation is simply an expression of the mass balance in an infinitesimal spherical cell around the particle. The molar flux of species A through stagnant air is given by Fick's law (Bird et al., 1960),

$$\tilde{J}_{A,r} = x_A(\tilde{J}_{A,r} + \tilde{J}_{\text{air},r}) - D_g \frac{dc}{dr} \quad (11.2)$$

where x_A is the mole fraction of A, $\tilde{J}_{\text{air},r}$ the radial flux of air at position r , and D_g the diffusivity of A in air. Since air is not transferred to or from the particle, $\tilde{J}_{\text{air},r} = 0$ at all r . Assuming dilute conditions, an assumption applicable under almost all atmospheric conditions, $x_A \simeq 0$ and (11.2) can be rewritten as

$$\tilde{J}_{A,r} = -D_g \frac{dc}{dr} \quad (11.3)$$

Combining (11.1) and (11.3), we obtain

$$\frac{\partial c}{\partial t} = D_g \left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} \right) \quad (11.4)$$

which is valid for transfer of A to a particle under dilute conditions. If c_∞ is the concentration of A far from the particle, c_s is its vapor-phase concentration at the particle surface, and the particle is initially in an atmosphere of uniform A with a concentration equal to c_∞ , the corresponding initial and boundary conditions for (11.4) are

$$c(r, 0) = c_\infty, \quad r > R_p \quad (11.5)$$

$$c(\infty, t) = c_\infty \quad (11.6)$$

$$c(R_p, t) = c_s \quad (11.7)$$

The solution of (11.4) subject to (11.5) to (11.7) is (Appendix 11)

$$c(r, t) = c_\infty - \frac{R_p}{r} (c_\infty - c_s) + \frac{2R_p}{r\sqrt{\pi}} (c_\infty - c_s) \int_0^{(r-R_p)/2\sqrt{D_g t}} e^{-\xi^2} d\xi \quad (11.8)$$

The time dependence of the concentration at any radial position r is given by the third term on the right-hand side of (11.8). Note that for large values of t , the upper limit of integration approaches zero and the concentration profile approaches its steady state given by

$$c(r) = c_\infty - \frac{R_p}{r} (c_\infty - c_s) \quad (11.9)$$

We are going to show in Section 11.2.1 that the characteristic time for relaxation to the steady-state value is on the order of 10^{-3} s or smaller for all particles of atmospheric interest. Rearranging (11.9), at steady state,

$$\frac{c(r) - c_\infty}{c_s - c_\infty} = \frac{R_p}{r} \quad (11.10)$$

The total flow of A (moles time⁻¹) toward the particle is denoted by J_c , the subscript c referring to the continuum regime, and is given by

$$J_c = 4\pi R_p^2 (\tilde{J}_A)_{r=R_p} \quad (11.11)$$

or using (11.9) and (11.3),

$$J_c = 4\pi R_p D_g (c_\infty - c_s) \quad (11.12)$$

If $c_\infty > c_s$, the flow of molecules of A is toward the particle and if $c_\infty < c_s$ vice versa. The above result was first obtained by Maxwell (1877) and (11.12) is often called the Maxwellian flux. Note that as c is the molar concentration of A, the units of J_c are moles per time. On the contrary, the units of \tilde{J}_A are moles per surface per time.

A mass balance on the growing or evaporating particle is

$$\frac{\rho_p}{M_A} \frac{d}{dt} \left(\frac{4}{3} \pi R_p^3 \right) = J_c \quad (11.13)$$

where ρ_p is the particle density and M_A the molecular weight of A. Combining (11.12) with (11.13) gives

$$\frac{dR_p}{dt} = \frac{D_g M_A}{\rho_p R_p} (c_\infty - c_s) \quad (11.14)$$

When c_∞ and c_s are constant, (11.14) can be integrated to give

$$R_p^2 = R_{p0}^2 + \frac{2D_g M_A}{\rho_p} (c_\infty - c_s) t \quad (11.15)$$

The use of the time-independent steady-state profile given by (11.9) to calculate the change of the particle size with time in (11.15) may seem inconsistent. Use of the steady-state diffusional flux to calculate the particle growth rate implies that the vapor concentration profile near the particle achieves steady-state before appreciable growth occurs. Since growth does proceed hundreds of times more slowly than diffusion, the profile near the particle in fact remains at its steady-state value at all times. Growth of atmospheric particles for a constant gradient of $M_A(c_\infty - c_s) = 1 \mu\text{g m}^{-3}$ between the bulk and surface concentrations of A is depicted in Figure 11.1.

Temperature Effects During the condensation/evaporation of a particle latent heat is released/absorbed at the particle surface. This heat can be released either toward the particle or toward the exterior gas phase. As mass transfer continues, the particle surface temperature changes until the rate of heat transfer balances the rate of heat generation/consumption. The formation of the external temperature and vapor concentration profiles must be related by a steady-state energy balance to determine the steady-state surface temperature at all times during the particle growth.

The steady-state temperature distribution around a particle is governed by

$$u_r \frac{dT}{dr} = \alpha \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dT}{dr} \right) \quad (11.16)$$

where $\alpha = k/\rho c_p$ is the thermal diffusivity of air and u_r is the mass average velocity at radial position r . The convective velocity u_r is the net result of the fluid motion due to the concentration gradients (Pesthy et al., 1981). Equation (11.16) should be solved subject to

$$T(R_p) = T_s$$

$$T(\infty) = T_\infty$$

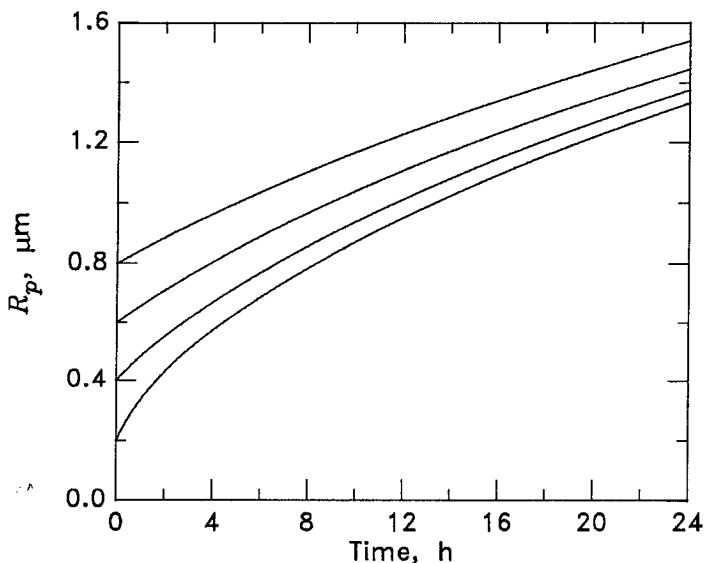


FIGURE 11.1 Growth of aerosol particles of different initial radii as a function of time for a constant concentration gradient of $1 \mu\text{g m}^{-3}$ between the aerosol and gas phases ($D_g = 0.1 \text{ cm}^2 \text{ s}^{-1}$, $\rho_p = 1 \text{ g cm}^{-3}$).

For a dilute system the first term in (11.16) can be neglected and (11.16) is simplified to the pure conduction equation,

$$\frac{d^2T}{dr^2} + \frac{2}{r} \frac{dT}{dr} = 0 \quad (11.17)$$

with solution

$$T = T_\infty + \frac{R_p}{r} (T_s - T_\infty) \quad (11.18)$$

The criterion for neglecting the convective term in (11.16) is

$$\frac{D_g}{\alpha} \left(\frac{M_A}{M_{\text{air}}} \right) \ln \left(\frac{1 - x_{As}}{1 - x_{A\infty}} \right) \ll 1 \quad (11.19)$$

where M_{air} is the molecular weight of air and x_{As} and $x_{A\infty}$ are the mole fractions of A at the particle surface and far away from it. This convective flow is often referred to as Stefan flow and (11.19) provides a quantitative criterion for determining when it can be neglected. In most applications involving mass and heat transfer to atmospheric particles it can be neglected (Davis, 1983).

Up to this point we have been avoiding the complications of the coupled mass and energy balances by treating c_s and T_s as known. The surface temperature is in general unknown and c_s depends on it. To determine T_s we need to write an energy balance on the

particle

$$\tilde{J}_{A,r=R_p} \Delta H_v (4\pi R_p^2) = k \left(\frac{dT}{dr} \right)_{r=R_p} (4\pi R_p^2) + k_p \left(\frac{dT_p}{dr} \right)_{r=R_p} (4\pi R_p^2) \quad (11.20)$$

where k and k_p are the thermal conductivities of air and the particles, respectively, T and T_p are the air and particle temperatures, and ΔH_v is the molar heat released. The left-hand side is the latent heat contribution to the energy balance, while the right-hand side includes the rates of heat conduction outward into the gas and inward from the particle surface. Chang and Davis (1974) solved numerically the coupled mass and energy balances. Their numerical solution shows that the last term in (11.20) can be neglected, indicating that the energy ΔH_v is transferred entirely to the gas phase.

Combining (11.18) and (11.9) with (11.20), we obtain

$$k(T_s - T_\infty) = \Delta H_v D_g (c_\infty - c_s) \quad (11.21)$$

where c_s is in general a function of T_s . For convenience this equation is often written as

$$\frac{T_s - T_\infty}{T_\infty} = \frac{\Delta H_v D_g}{k T_\infty} (c_\infty - c_s) \quad (11.22)$$

If $c_\infty \gg c_s$ then the temperature difference between the particle and the ambient gas is $\Delta H_v D_g c_\infty / k$. For slowly evaporating species and small heat of vaporization this temperature change is sufficiently small so that isothermal conditions are approached and (11.9) can be used. On the other hand, if this is not valid, numerical solutions of (11.4) and (11.17) are necessary.

11.1.2 The Kinetic Regime

For molecules in three-dimensional random motion the number of molecules Z_N striking a unit area per unit time is (Moore, 1962)

$$Z_N = \frac{1}{4} N \bar{c}_A \quad (11.23)$$

where \bar{c}_A is the mean speed of the molecules,

$$\bar{c}_A = \left(\frac{8kT}{\pi m_A} \right)^{1/2} \quad (11.24)$$

Under these conditions the molar flow J_k (moles time⁻¹) to a particle of radius R_p is

$$J_k = \pi R_p^2 \bar{c}_A \alpha (c_\infty - c_s) \quad (11.25)$$

where α is the molecular accommodation coefficient (not to be confused with the thermal diffusivity in (11.16)). The ratio of this kinetic regime flow to the continuum regime flow J_c is

$$\frac{J_k}{J_c} = \frac{\alpha \bar{c}_A}{4D_g} R_p \quad (11.26)$$

The accommodation coefficient will be assumed equal to unity in the next section and the implications of this assumption will be discussed in Section 11.1.4.

11.1.3 The Transition Regime

$$\alpha = 1$$

The steady-state flow of vapor molecules to a sphere, when the particle is sufficiently large compared to the mean free path of the diffusing vapor molecules, is given by Maxwell's equation (11.12). Since this equation is based on the solution of the continuum transport equation, it is no longer valid when the mean free path of the diffusing vapor molecules becomes comparable to the particle diameter. At the other extreme, the expression based on the kinetic theory of gases (11.25) is also not valid in this intermediate regime where $\lambda \approx D_p$. When $Kn \approx 1$, the phenomena are said to lie in the *transition regime*.

The concentration distributions of the diffusing species and background gas in the transition regime are governed rigorously by the Boltzmann equation. Unfortunately, there does not exist a general solution to the Boltzmann equation valid over the full range of Knudsen numbers for arbitrary masses of the diffusing species and the background gas. Consequently, most investigations of transport phenomena avoid solving directly the Boltzmann equation and restrict themselves to an approach based on so-called flux matching. Flux matching assumes that the noncontinuum effects are limited to a region $R_p \leq r \leq \Delta + R_p$ beyond the particle surface and that continuum theory applies for $r \geq \Delta + R_p$. The distance Δ is then of the order of the mean free path λ and within this inner region the simple kinetic theory of gases is assumed to apply.

Fuchs Theory The matching of continuum and free molecule fluxes dates back to Fuchs (1964), who suggested that by matching the two fluxes at $r = \Delta + R_p$, one may obtain a boundary condition on the continuum diffusion equation. This condition is, assuming unity accommodation coefficient,

$$4\pi R_p^2 \left(\frac{1}{4} \bar{c}_A\right) [c(R_p + \Delta) - c_s] = D \left(\frac{dc}{dr}\right)_{r=R_p+\Delta} 4\pi (R_p + \Delta)^2 \quad (11.27)$$

Then solving the steady-state continuum transport equation for a dilute system,

$$\frac{d^2c}{dr^2} + \frac{2}{r} \frac{dc}{dr} = 0 \quad (11.28)$$

using as boundary conditions (11.27) and $c(\infty) = c_\infty$ one obtains the solution

$$c(r) = c_\infty - \frac{R_p}{r} (c_\infty - c_s) \beta_F \quad (11.29)$$

where the correction factor β_F is given by

$$\beta_F = \frac{[1 + (\Delta/R_p)]\bar{c}_A R_p}{\bar{c}_A R_p + 4D[1 + (\Delta/R_p)]} \quad (11.30)$$

Relating the binary diffusivity and the mean free path using $D/\lambda_{AB}\bar{c}_A = \frac{1}{3}$ and letting $Kn = \lambda_{AB}/R_p$, one obtains

$$\frac{J}{J_c} = 0.75 \frac{1 + Kn\Delta/\lambda_{AB}}{0.75 + Kn + (\Delta/\lambda_{AB})Kn^2} \quad (11.31)$$

Note that the definition of the mean free path by $D/\lambda_{AB}\bar{c}_A = \frac{1}{3}$ implies, using (11.26), that, for $\alpha = 1$,

$$\frac{J_k}{J_c} = \frac{3}{4Kn} \quad (11.32)$$

and the Fuchs relation (11.31) also implies, using (11.32),

$$\frac{J}{J_k} = \frac{1 + Kn\Delta/\lambda_{AB}}{1 + Kn\Delta/\lambda_{AB} + 0.75Kn^{-1}} \quad (11.33)$$

The value of Δ used in the expressions above was not specified in the original theory and must be adjusted empirically or estimated by independent theory. Several choices for Δ have been proposed; the simplest, due to Fuchs, is $\Delta = 0$. Other suggestions include $\Delta = \lambda_{AB}$ and $\Delta = 2D/\bar{c}_A$ (Davis, 1983).

Fuchs and Sutugin Approach Fuchs and Sutugin (1971) fitted Sahni's (1966) solution to the Boltzmann equation for $z \ll 1$, where $z = M_A/M_{\text{air}}$ is the molecular weight ratio of the diffusing species and air, to produce the following transition regime interpolation formula

$$\frac{J}{J_c} = \frac{1 + Kn}{1 + 1.71Kn + 1.33Kn^2} \quad (11.34)$$

Equation (11.34) is based on results for $z \ll 1$ and therefore is directly applicable to light molecules in a heavier background gas. The mean free path included in the definition of the Knudsen number in (11.34) is given by

$$\lambda_{AB} = \frac{3D}{\bar{c}_A}$$

For $Kn \rightarrow 0$ both (11.31) and (11.34) reduce to the correct limit $J/J_c = 1$. For the kinetic limit $Kn \rightarrow \infty$ both (11.31) and (11.34) give $J_k/J_c = 3/(4 Kn)$.

Dahneke Approach Dahneke (1983) used the flux matching approach of Fuchs but, assuming that $\Delta = \lambda_{AB}$ and defining $D/(\lambda_{AB}\bar{c}_A) = \frac{1}{2}$, obtained

$$\frac{J}{J_c} = \frac{1 + Kn}{1 + 2 Kn(1 + Kn)} \quad (11.35)$$

where $Kn = \lambda_{AB}/R_p$. The mean free path included in the definition of the Knudsen number in (11.35) is given by

$$\lambda_{AB} = \frac{2D}{\bar{c}_A}$$

Note here that for $Kn \rightarrow 0$, $J/J_c \rightarrow 1$ as expected. On the other hand, for $Kn \rightarrow \infty$, $J/J_c \rightarrow 1/(2 Kn)$. This limit is in agreement with (11.26) because $D/(\lambda_{AB}\bar{c}_A) = \frac{1}{2}$ and therefore the expressions are consistent.

Loyalka Approach Loyalka (1983) constructed improved interpolation formulas for mass transfer in the transition regime by solving the BGK model (Bhatnagar, Gross, and Krook, 1954) of the Boltzmann equation to obtain

$$\frac{J}{J_k} = \frac{\sqrt{\pi} Kn(1 + 1.333Kn)}{1 + 1.333 Kn + (1.333\sqrt{\pi}Kn + \zeta_c)Kn} \quad (11.36)$$

The mean free path used by Loyalka was defined by

$$\lambda_{AB} = \frac{4 D}{\sqrt{\pi} \bar{c}_A} \quad (11.37)$$

and the mass transfer jump coefficient had a value $\zeta_c = 1.0161$. Williams and Loyalka (1991) pointed out that (11.36) does not have the correct shape near the free-molecule limit.

Sitarski and Nowakowski Approach All the above approaches do not describe the dependence of the transition regime mass flux on the molecular mass ratio z of the condensing/evaporating and the surrounding gas. Sitarski and Nowakowski (1979) applied the 13-moment method of Grad (Hirschfelder et al., 1954) to solve the Boltzmann equation to obtain

$$\frac{J}{J_k} = \frac{Kn(1 + aKn)}{b + cKn + dKn^2} \quad (11.38)$$

$$\begin{aligned} a &= \frac{3\beta(1+z)^2}{4(3+5z)}, & b &= \frac{4(9+10z)}{15\pi(1+z)^2}, \\ c &= \frac{\beta(1+2z)}{\pi(3+5z)} + \frac{1}{2\beta}, & d &= \frac{9(1+z)^2}{8(3+5z)} \end{aligned} \quad (11.39)$$

where $\beta = 1$ for unity accommodation coefficient and $z = M_A/M_{air}$ is the molecular weight ratio. This result is obviously incorrect near the free-molecule regime, because in the limit $Kn \rightarrow \infty$, (11.38) yields $J \rightarrow 0.666J_k$. Therefore we expect (11.38) to be in error for relatively high values of Kn .

Table 11.1 summarizes the transition regime expressions that we have presented in this section. Predictions of mass transfer rates of the above four theories are shown as a function of the particle diameter in Figure 11.2. All approaches give comparable results for particle diameters larger than 0.2 μm , even if they employ different definitions of the Knudsen number and different functional dependencies of the mass transfer rate on the Knudsen number. This agreement indicates that as long as one uses a mean free path consistent with the mass transfer theory the final result will differ little from theory to theory. The theory of Sitarski and Nowakowski (1979), although it is the only one that includes an explicit dependence of the mass transfer rate on z , gives erroneous results for particles smaller than 0.2 μm in this case (Figure 11.2). The dependence of the rate itself on z is rather weak and

TABLE 11.1 Transition Regime Formulas for Diffusion of Species A in a Background Gas B to an Aerosol

Author	J/J_c	Mean Free Path Definition
Fuchs (1934)	$\frac{0.75\alpha(1 + Kn \Delta/\lambda_{AB})}{0.75\alpha + Kn + (\Delta/\lambda_{AB})Kn^2}$	$\frac{3D_{AB}}{\bar{c}_A}$
Fuchs and Sutugin (1971)	$\frac{0.75\alpha(1 + Kn)}{Kn^2 + Kn + 0.283 Kn\alpha + 0.75\alpha}$	$\frac{3D_{AB}}{\bar{c}_A}$
Dahneke (1983)	$\frac{1 + Kn}{1 + 2 Kn(1 + Kn)/\alpha}$	$\frac{2D_{AB}}{\bar{c}_A}$
Loyalka (1983) $\alpha = 1$	$\frac{1 + 1.333 Kn}{1 + 1.333 Kn + (1.333\sqrt{\pi}Kn + 1)Kn}$	$\frac{4}{\sqrt{\pi}} \frac{D_{AB}}{\bar{c}_A}$
Sitarski and Nowakowski (1979)	$\frac{b(1 + aKn)}{b + cKn + dKn^2}$	$4b \frac{D_{AB}}{\bar{c}_A}$

(see (11.39) for $a, b, c,$ and d)

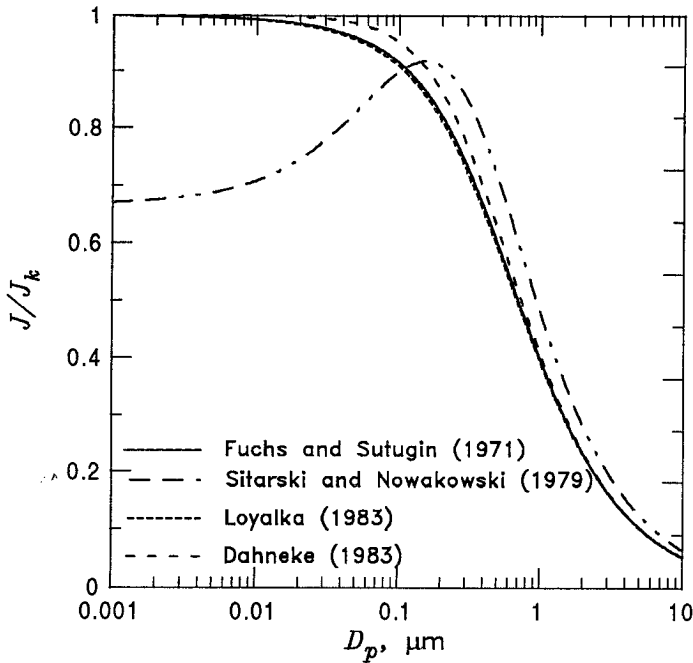


FIGURE 11.2 Mass transfer rate predictions for the transition regime by the approaches of (a) Fuchs and Sutugin, (b) Dahneke, (c) Loyalka and (d) Sitarski and Nowakowski ($z = 15$) as a function of particle diameter. Accommodation coefficient $\alpha = 1$.

for $z = 5$ to 15, the Fuchs, Dahneke, and Loyalka formulas are in agreement with the Sitarski and Nowakowski results. Li and Davis (1995) compared the results of the above theories with measurements of the evaporation rates of dibutyl phthalate (DBP) in air (Figure 11.3). All theories are in agreement with the data with the exception of the theory of Sitarski and Nowakowski (1979), which exhibits deviations for $Kn > 0.2$.

11.1.4 The Accommodation Coefficient

Up to this point we have assumed that once a vapor molecule encounters the surface of a particle its probability of sticking is unity. This assumption can be relaxed by introducing an accommodation coefficient α , where $0 \leq \alpha \leq 1$. The flux of a gas A to a spherical particle in the kinetic regime is then given by (11.25).

The transition regime formulas can then be extended to account for imperfect accommodation by multiplying the left-hand side of (11.27) by α . The Fuchs expression in (11.31) becomes

$$\frac{J}{J_c} = 0.75\alpha \frac{1 + Kn\Delta/\lambda_{AB}}{0.75\alpha + Kn + (\Delta/\lambda_{AB})Kn^2} \quad (11.40)$$

and

$$\frac{J_k}{J_c} = \frac{3\alpha}{4Kn} \quad (11.41)$$

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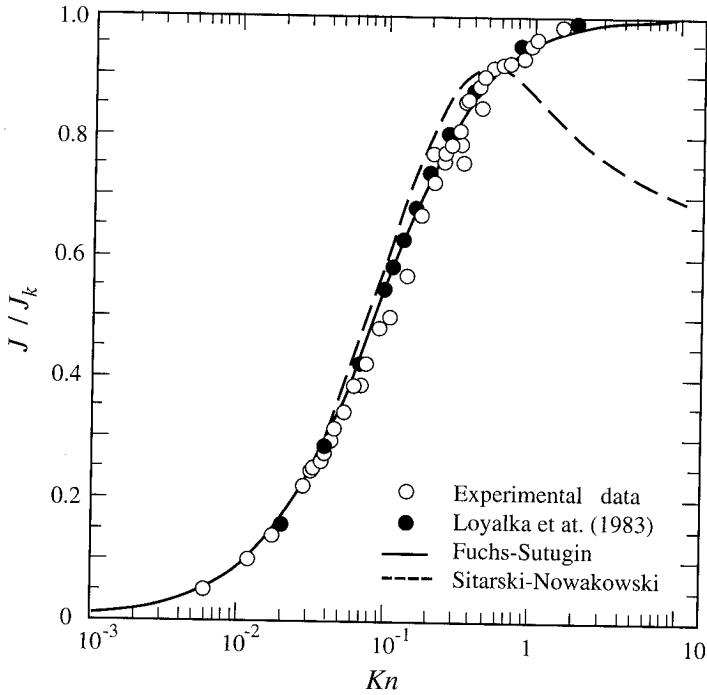


FIGURE 11.3 Comparison of experimental dibutyl phthalate evaporation data with the theories of Loyalka et al. (1989), Sitarski and Nowakowski (1979) (for $z = 15$), and the equation of Fuchs and Sutugin (1970). Reprinted from *Aerosol Science and Technology*, **25**, Li and Davis, 11–21. Copyright 1995, with kind permission from Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington OX5 1GB, UK.

The expression (11.35) by Dahneke (1983) becomes

$$\frac{J}{J_c} = \frac{1 + Kn}{1 + 2 Kn(1 + Kn)/\alpha} \tag{11.42}$$

whereas the Fuchs and Sutugin (1971) approach gives

$$\frac{J}{J_c} = \frac{0.75\alpha(1 + Kn)}{Kn^2 + Kn + 0.283 Kn\alpha + 0.75 \alpha} \tag{11.43}$$

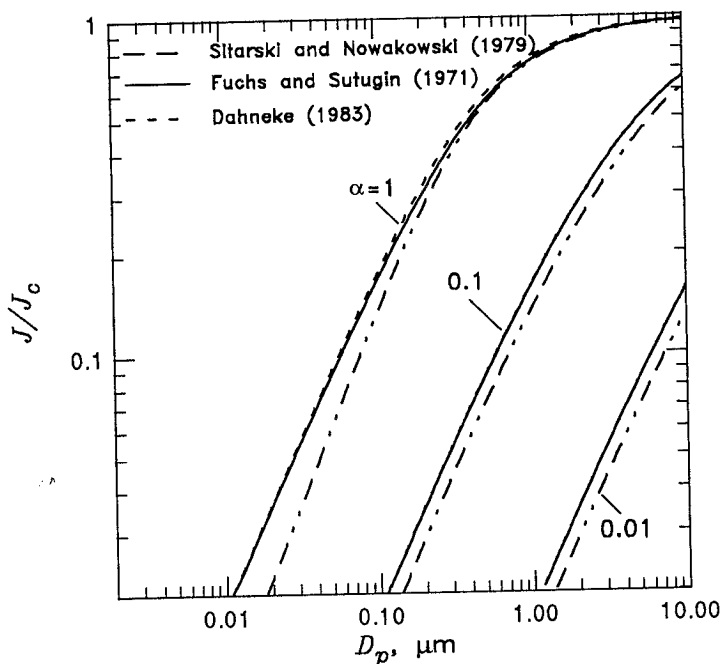


FIGURE 11.4 Mass transfer rates as a function of particle diameter for accommodation coefficient values 1.0, 0.1, and 0.01 for the approaches of SitarSKI and Nowakowski (1979), Fuchs and Sutugin (1970), and Dahneke (1983).

The formula of Loyalka is only applicable for $\alpha = 1$, but the theory of SitarSKI and Nowakowski (1979) can be used for any accommodation coefficient setting

$$\beta = \frac{\alpha}{2 - \alpha} \quad (11.44)$$

Figure 11.4 shows mass transfer rates as a function of particle diameter for the three approaches for accommodation coefficient values of 1, 0.1, and 0.01.

Measurements of accommodation coefficients have recently been made by a series of investigators. These will be presented later in this chapter in Example 11.1.

11.2 MASS TRANSPORT LIMITATIONS IN AQUEOUS-PHASE CHEMISTRY

Dissolution of atmospheric species into cloud droplets followed by aqueous-phase reactions involves the following series of steps:

1. Diffusion of the reactants from the gas phase to the air-water interface.
2. Transfer of the species across the interface.
3. Possible hydrolysis/ionization of the species in the aqueous phase.
4. Aqueous-phase diffusion of the ionic and nonionic species inside the cloud drop.
5. Chemical reaction inside the droplet.