Calculation of Supersaturation Profiles in Thermal Diffusion Cloud Chambers

JOSEPH L. KATZ and P. MIRABEL

Dept. of Chemical Engineering and Institute of Colloid and Surface Science, Clarkson College of Technology, Potsdam, N. Y. 13676
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ABSTRACT

The maximum supersaturation in a diffusion cloud chamber as a function of the temperature difference between the two plates has been calculated under various conditions. It is shown that the assumption of linear profiles for the temperature and vapor pressure is a very good one, and that the effect of thermal diffusion is negligible for a water-air mixture.

The thermal diffusion cloud chamber is now being extensively used (e.g., Katz and Kocmony, 1973; Radke and Hobbs, 1969) to measure the supersaturation spectrum of cloud condensation nuclei as well as for the study of homogeneous nucleation (e.g., Katz, 1970; Katz and Ostermeir, 1967; Heist and Reiss, 1973). Several papers analyzing various aspects of its operation and design as a cloud condensation nuclei detector have appeared in this JOURNAL (e.g., Fitzgerald, 1970, 1972; Elliott, 1971). It is the purpose of this note to correct some errors in one of these papers (Fitzgerald, 1972), and to critically examine the limitations of the assumption of linear temperature and pressure (or density) distributions in the diffusion cloud chamber.

The cloud chamber works by evaporating a vapor (e.g., water) from a saturated warm surface, diffusing it through a “carrier gas” (e.g., air) and condensing it on a cooled surface. The partial pressure $P_w$ of the water at the two surfaces is equal to its equilibrium vapor pressure and varies almost linearly with height between the two surfaces. The temperature $T$ also varies almost linearly with height. However, $P_w$, the equilibrium vapor pressure is an exponential function of temperature and therefore the chamber is supersaturated between the two plates. The supersaturation is usually defined as $S = (P/P_e) - 1$. Nucleation occurs at a plane very slightly above the plane of peak supersaturation in the chamber.

It is not necessary to assume that the temperature and partial pressure gradients are linear. For chambers whose diameter is much larger than their height, one can show that plane parallel diffusion is an excellent approximation (Elliott, 1971). The heat and mass flux equations for a two-component system in which only one component (i.e., water) is diffusing can then be shown to be given by (Hirschfelder et al., 1954, Grew and Ibbs, 1952, Katz, 1970):

$$F = -\frac{n_i D_{12}}{(1-X)} \int \frac{dX}{dZ} + \alpha X (1-X) \frac{d}{dZ} \ln T$$

(1)

$$Q = -\lambda \frac{dT}{dZ} + F \int C_p dT + \alpha F (1-X) R T$$

(2)

where $F$ is the mass flux of water and $X$ is its mole fraction, $Q$ the heat flux, $n_i$ the total molar density ($n_i = P_i / RT$), $R$ the gas constant, $P_i$ the total pressure, $D_{12}$ the binary diffusion coefficient of water in air, $\lambda$ the thermal conductivity of the water-air mixture, $C_p$ the specific heat of water vapor, $T$ the temperature, and $\alpha$ the thermal diffusion factor. Since the vapor phase is essentially a mixture of ideal gases, $X = \rho_w / \rho_i = n_w / n_i = P_w / P_i$, where $\rho_w$, $n_w$, and $P_w$ are the mass density, molar density and partial pressure of the water and $\rho_i$, $n_i$, and $P_i$ are the total mass density, molar density and pressure. In Eq. (1), the first term represents the mass flux in a fixed coordinate system due to the gradient in concentration and the second term is the mass flux due to the temperature gradient, known as the Soret effect. In Eq. (2), the first term is the heat flux due to the temperature gradient, the second term the heat flux carried by the flux of molecules, and

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1 Present affiliation: Université Louis Pasteur, Institut de Chimie 67008-Strasbourg-France.
the third term the “reciprocal process” to the Soret effect, known as the Dufour effect.

Eqs. (1) and (2) can be solved numerically without having to make any approximations (Katz, 1970).\(^2\) However, users of diffusion cloud chambers often obtain the supersaturation vs temperature profiles by assuming that the temperature gradient is linear and that either the water vapor density gradient (Fitzgerald, 1970) or its partial pressure gradient is linear, thus avoiding the problem of solving Eqs. (1) and (2).

In his recent paper, Fitzgerald (1972) discusses the errors that result from the neglect of the effects of the phenomenon of thermal diffusion and of the temperature dependence of the diffusion coefficients in deriving the steady-state distributions of temperature and water vapor.” Unfortunately, Fitzgerald’s heat and mass flux equations [his Eqs. (1) and (2); referred to in this paper as F1 and F2] are incomplete and not self-consistent. Using our notation, his equations are

\[
\frac{d}{dZ} \left[ D_{12} \frac{d\rho_w}{dZ} + \alpha \rho_w D_{12} \frac{d}{dZ} \ln T \right] = 0, \tag{F1}
\]

\[
\frac{d}{dZ} \left[ \frac{d\rho_w}{dZ} \right] = 0. \tag{F2}
\]

His heat flux equation (F2) does not include the convective heat flux, i.e., the heat carried by the diffusing water molecules, the \(F/C_PdT\) term in our Eq. (2). It also does not include the Dufour effect, which must be included for consistency if the Soret effect is included in the mass flux equation. In addition, to obtain (F1) from the correct mass diffusion equation, Fitzgerald explicitly assumed that the total density is constant. However, since the total pressure is constant\(^3\) but the temperature varies, the total density cannot be constant. As a result, in his Eq. (3) [referred to here as (F3)],

\[
\frac{d}{dZ} \left[ D_{12} \frac{d\rho_w}{dZ} + (\alpha - 1) \frac{\rho_w D_{12} \ln T}{T} \right] = 0, \tag{F3}
\]

which he obtains by substituting the partial pressure for the density, he has a term \((\alpha - 1)\) as the coefficient of \(d\ln T/dZ\) when he should actually have \(\alpha\). Since he uses \(\alpha = 0.5\) for water + air, then the coefficient \(\alpha - 1\) in (F3) equals \(-0.5\) instead of \(+0.5\). Thus the effects due to thermal diffusion in his solution have the wrong

\(^2\)These equations are solved by dividing the height between the plates into \(N\) equal increments (usually 50) and computing the solution at each of the mesh points using a scheme of successive iterative linearizations. A copy of the computer program which solves Eqs. (1) and (2) appears in the Appendix.

\(^3\)Since the speed of sound is about eight orders of magnitude larger than the diffusional velocity of water through air, the gradient pressure due to the diffusional process is about eight orders of magnitude smaller than is the gradient in concentration.

Fig. 1. Plot of the percent relative difference between the maximum supersaturation calculated assuming linear temperature and vapor pressure gradients:

- A, linear temperature and vapor density gradients
- B, exact solution of Eqs. (1) and (2) with \(\alpha = 0\) and \(C_P = 8.0\)
- C, exact solution of Eqs. (1) and (2) with \(\alpha = 0.15\) and \(C_P = 8.0\)
- D, exact solution of Eqs. (1) and (2) with \(\alpha = 0\) and \(C_P = 0\)
- E, exact solution of Eqs. (1) and (2) with \(\alpha = 0.15\) and \(C_P = 0\)

as a function of the temperature difference between the two plates, using 20°C as the temperature of the top plate.

sign. However, in fact, \(\alpha\) is much smaller than 0.5 and is probably equal to 0.01 for water + air.

Fitzgerald cites a paper on water + hydrogen thermal diffusion by Whalley (1951) as the source of his value of \(\alpha = 0.5\) at a mole fraction of water vapor of 0.03. On examining this paper we found that, at a water vapor mole fraction of 0.03, \(\alpha = 0.2\). However, even 0.2 is too high a value for \(\alpha\) in water + air diffusion cloud chambers since \(\alpha\) for water + air is not the same as that for water + hydrogen. Mason and Monchick (1965), in a paper on the transport properties of moist air, predicted that \(\alpha = 0.2\) for water + hydrogen, in perfect agreement with Whalley’s (1951) value. Using the same equations which made this correct prediction, they predicted that \(\alpha\) should equal 0.01 for water + air.

We shall now examine the various terms in Eqs. (1) and (2) and quantitatively discuss their significance. In Fig. 1, we plot the relative difference (in percent) of the maximum supersaturation in the cloud chamber obtained under the various conditions described below and the maximum supersaturation obtained by assuming linear temperature and partial pressure profiles for a cloud chamber with a top (warm) surface at 20°C as a function of the temperature difference \(\Delta T\) between the two surfaces. Curve A is obtained by assuming that the temperature and the partial density profiles are linear. Curves B and C are obtained by setting \(\alpha = 0\) and 0.15, respectively, and numerically solving Eqs. (1) and (2), including all effects, such as the temperature and composition dependence of the binary diffusion coefficient and of the mixture (air + water) thermal
conductivity, the heat carried by the diffusing water molecules (the $F \int C_p dT$ term), and both the Soret and Dufour effects, for a chamber at a total pressure equal to 1 atm.\footnote{For these calculations, the following data have been used: binary diffusion coefficient of the air-water mixture $D_{12}=1.87(10^{-6}) \ T^{0.077}$ [mol cm$^{-2}$ s$^{-1}$], specific heat of the water vapor $C_p=8.0 \ \text{cal mol}^{-1} \text{K}^{-1}$, thermal conductivity of air $\lambda_1=-2.7762(10^{-6}) +2.5675(10^{-2})T-1.3126(10-10) T^2$ [cal cm$^{-1}$ s$^{-1}$ K$^{-1}$], thermal conductivity of water $\lambda_2=-1.6487(10^{-6})+1.9895(10^{-2})T$ [cal cm$^{-2}$ s$^{-1}$ K$^{-1}$]. The thermal conductivity of the gas mixture was calculated by using the Wassiljewa equation $\lambda(T)=\frac{\lambda_1(T)X_1+\lambda_2(T)X_2}{X_1+A_{12}X_2+X_2+A_{21}X_1}$ with $A_{12}=1.1624$ and $A_{21}=0.9699.$} Curves D and E are identical to B and C, respectively, except that we used $C_p=0$, i.e., we did not include the heat carried by the diffusing water molecules.

As can be seen, thermal diffusion has a negligible effect. Even when we use an $\alpha=0.15$, which is 10–15 times larger than its “best” value, it only changes the answer by less than 1%. If we had actually used $\alpha=0.01$, it would have been impossible to plot since the curves would lie close to B and D, respectively.

However, the $F \int C_p dT$ term does have a significant effect, changing the answers from 2 to 5%. It is interesting to note that the “best” solution, i.e., curve B, which is the solution to the complete heat and mass flux equations including all effects, differs from that obtained by assuming linear temperature and partial pressure gradients by only 1%. Curve A, the linear temperature and partial density solution, differs by 11 to 13%.

We conclude that for water+air thermal diffusion cloud chambers there is no reason to use anything except the linear temperature and linear partial pressure solution at reasonable supersaturations. At low total pressures (e.g., total pressures about 2–5 times the vapor pressure at the top plate instead of 43 times as was used here), it would be necessary to solve Eqs. (1) and (2) numerically. For example, at a $\Delta T$ of 20°C, a top plate temperature of 20°C, and a total pressure of 1/20 atm, the linear solution would be in error by 7.7%.

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FUNCTION CONDI1(T,CD1)
    REAL*8 T,CD1
    C T: TEMPERATURE
    C CD1: THERMAL CONDUCTIVITY OF WATER
    C
    CD1 = 0.607*10**(-6) + 0.302*10**(-6)*T + 0.151*10**(-6)*T**2
    RETURN
END

FUNCTION CONDI2(T,CD2)
    REAL*8 T,CD2
    C T: TEMPERATURE
    C CD2: THERMAL CONDUCTIVITY OF THE FOLLOWING ELEMENTS
    C
    CD2 = 0.6*AIR + 0.4*H20 + 0.2*N20 + 0.1*O2 + 0.1*N2 + 0.05*CO2
    RETURN
END

FUNCTION EXPSRES(T,PEF)
    REAL*8 T,PEF
    C T: TEMPERATURE
    C PEF: THERMAL PRESSURE OF WATER
    C
    PEF = 1.00*10**(-6) + 2.00*10**(-6)*T + 3.00*10**(-6)*T**2
    RETURN
END

FUNCTION FMC1(T)
    REAL*8 T
    C T: TEMPERATURE
    C FMC: MOLECULAR WEIGHT OF THE FOLLOWING ELEMENTS
    C
    FMC = 0.1*AIR + 0.5*H20 + 0.3*N20 + 0.1*O2 + 0.1*N2 + 0.05*CO2
    RETURN
END

FUNCTION FMC2(T)
    REAL*8 T
    C T: TEMPERATURE
    C FMC: MOLECULAR WEIGHT OF THE FOLLOWING ELEMENTS
    C
    FMC = 0.1*AIR + 0.5*H20 + 0.3*N20 + 0.1*O2 + 0.1*N2 + 0.05*CO2
    RETURN
END
REFERENCES


