

USE OF A LENNARD-JONES CALCULATION FOR MOLECULAR DIFFUSIVITY OF POLLUTANT GASES IN THE PBL AND ITS BEARING ON SCAVENGING MODELS

(Research Note)

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Abstract. Use of a Lennard-Jones calculation for estimation of molecular diffusivity of gases like SO₂ for use in scavenging models is recommended. A profile of molecular diffusivity of SO₂ in air through the PBL is obtained. Results indicate a change of about 17.5% between the diffusivity values at the surface and at the top of the PBL. The possible changes that could result in scavenging model calculations due to this change are also discussed.

1. Introduction

During recent years much effort has been directed towards gas scavenging models largely because of the 'Acid Rain' problem. In this connection, both analytic and numerical models have been developed to model the transport of a pollutant gas like sulphur dioxide into a raindrop.

Transport of a pollutant gas within the gas phase to the droplet proceeds by turbulent and molecular diffusion. Far away from the droplet surface, eddy motions are responsible for mass transfer of the pollutant species, while at the gas-liquid interface, mass transfer is governed by *molecular diffusion*.

The molecular diffusion coefficient invariably comes into the calculation, be it in film theory, penetration theory or boundary-layer theory – and its accurate determination, thus has a direct bearing on estimates of scavenging. However, a literature search reveals that this parameter has been chosen rather arbitrarily. (For an extensive review on scavenging models, see Teasley (1984).) In general the following facts emerge:

(i) Molecular diffusivity values as adopted by various authors are different even at the same temperature. (Table I).

(ii) The values adopted are all at one atmospheric pressure and at a particular temperature, though in reality the process of gas scavenging occurs at all levels in the PBL, where both the pressure and temperature change with height.

(iii) In scavenging models which consider chemical reactions within the rain drop, temperature plays a significant role. It is sometimes observed that while chemical kinetics data are used for a particular temperature, molecular diffusivity data are used at a different temperature, even in the same model.

The foregoing discussion clearly elucidates the necessity for using a scheme which enables one to compute the molecular diffusivity of gases as a function of temperature and pressure.

2. The Lennard-Jones (L-J) method

Reid and Sherwood (1958) emphasise that of all the available methods for estimation of diffusion coefficients of binary gas mixtures, the best method is that obtained from a Lennard-Jones calculation. The only restriction is that the calculations must be for pressures less than 15 atmospheres. In the PBL, this condition is always fulfilled.

Based on the recommendations of Reid and Sherwood (1958), a Lennard-Jones (L-J) 6-12 potential model was used to calculate the molecular diffusivity of SO₂ in air. The L-J 6-12 potential is given by

$$\Phi(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (1)$$

where

$\Phi(r)$ = potential energy

r = distance between centres of colliding molecules.

ε, σ = L-J potential parameters.

Starting with this relation, an expression for the molecular diffusivity, D_{AB} in binary low-pressure gas mixtures is given by:

$$D_{AB} = \frac{0.001858 T^{3/2}}{P \sigma_{AB}^2 \Omega_D} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2} \text{ cm}^2 \text{ s}^{-1} \quad (2)$$

where T = temperature, K

M_A, M_B = Molecular weights of constituents A & B

P = absolute pressure, atmosphere

Ω_D = Collision integral, $f(kT/\varepsilon_{AB})$, obtainable from standard tables.

$\varepsilon_{AB}, \sigma_{AB}$ = L-J force constants

k = Boltzmann's constant.

The constants ε_{AB} and σ_{AB} are obtained from the corresponding values for pure substances by the binary rules:

$$\varepsilon_{AB} = \left(\frac{\varepsilon_A}{k} \frac{\varepsilon_B}{k} \right)^{1/2}$$

$$\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B). \quad (3)$$

3. A Sample Calculation for an SO₂-Air Binary System

Temperature and pressure data were obtained from the India Meteorological Department. By a spline fitting procedure, a profile of temperature and pressure was obtained from the surface to the top of the PBL (2000 m in the present calculation). Equation (2) was then used directly. The collision integral was calculated for each value of temperature (which varied with height). The other constants were obtained from standard tables.

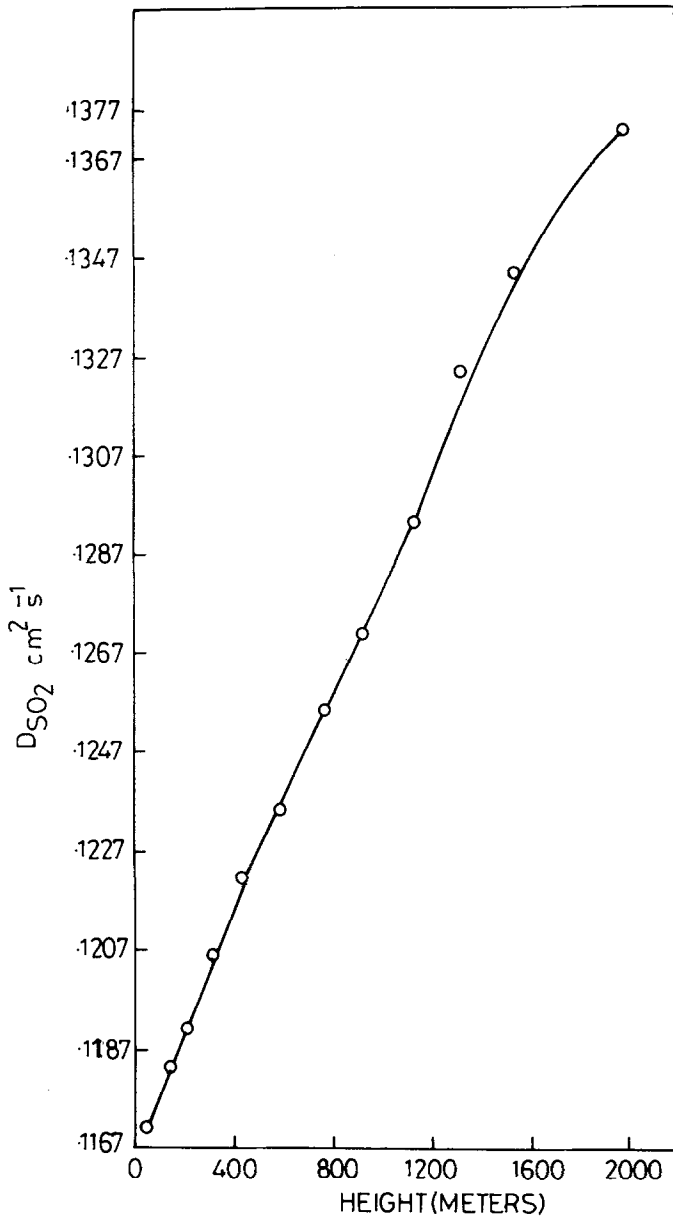


Fig. 1. Variation of molecular diffusivity of SO_2 in air with vertical distance.

In this way the molecular diffusivity for SO_2 in air at several levels in the PBL could be obtained, as shown in Figure 1. It is seen that there is about 17.5% change in the molecular diffusivity of SO_2 in air through the PBL.

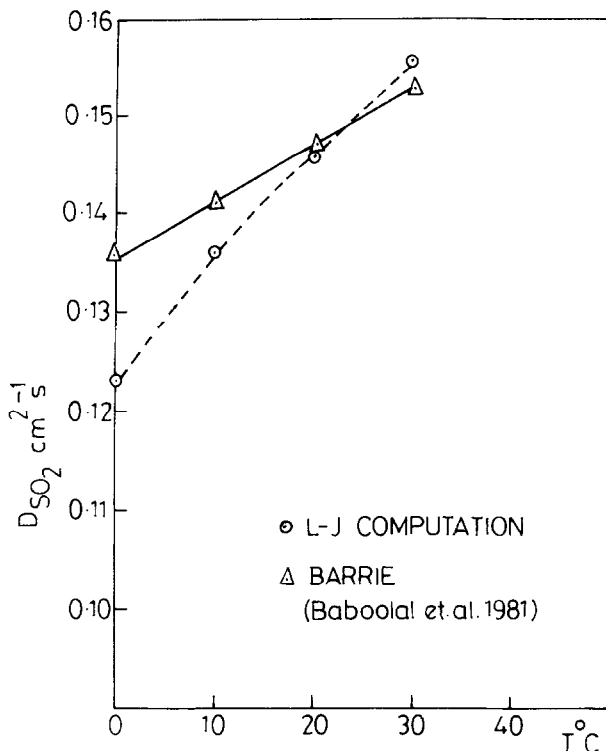


Fig. 2. Comparison of L-J calculations for molecular diffusivity of SO₂ in air with those adopted by Barrie (1978) at various temperatures under one atmospheric pressure.

In atmospheric scavenging model calculations, if a constant diffusivity value were applied at all levels, an inherent error automatically creeps into the calculations. This is illustrated as follows.

The quantity of diffusing SO₂, $M_i(g)$ which has entered a droplet of radius r , in time t , is given by:

$$M_i(g) = 4\pi D r C_o \left(t + \frac{2r\sqrt{t}}{\sqrt{\pi D}} \right). \quad (\text{Bielke and Gravenhorst, 1978})$$

Taking $r = 10 \mu\text{m}$, $C_o = 100 \mu\text{g m}^{-3}$, $t = 10^{-5} \text{S}$, we have calculated $M_i(g)$ using two values of diffusivity from figure 1. We obtained a value of $300.52 \times 10^{-14} \mu\text{g}$ at the surface (taking D as $1167 \text{cm}^2 \text{s}^{-1}$ at the surface) and $338.62 \times 10^{-14} \mu\text{g}$, at the top of the PBL (taking D as $1371 \text{cm}^2 \text{s}^{-1}$). If D were the same at both heights, then there would be an error of about 12.6% in calculating $M_i(g)$. Even a trace amount of diffusing pollutants entering a droplet significantly affects the chemistry within. A precise calculation of this quantity thus involves an accurate specification of molecular diffusivity.

It may be noted that present L-J computations for the molecular diffusivity profile of SO₂ in air are based on mean monthly data (for the month of January 1968 at 0000

TABLE I

Comparative Statement of Molecular diffusivity of SO₂ adopted in different Scavenging models: (All at one atmospheric pressure)

Temp.	Investigators	D_{SO_2} cm ² s ⁻¹
0 °C	*Barrie	0.136
10 °C	Barrie	0.141
	Bielke and Gravenhorst	0.10
20 °C	*Barrie	0.147
	Baboolal	0.126
25 °C	Overton	0.136
30 °C	*Barrie	0.153

* These values have been suggested by Barrie (as quoted in the work of L. B. Baboolal *et al.* (1981)).

GMT), differences in temperature between the surface and the top of PBL being about 6 °C. On particular days, however, the corresponding difference of temperature could be as high as 12 to 15 °C which would magnify the difference of 17.5% in the value of the coefficient of diffusivity, which in turn would increase the error in the estimation of mass transfer of pollutant in a rain drop.

The preceding discussion clearly demonstrates the need for an accurate prescription of molecular diffusivity of pollutant gases in scavenging models. For the sake of completeness the present calculations must be compared with other results. At this stage it must be pointed out that of the various scavenging models reviewed, only Barrie has suggested the use of diffusivity values of SO₂ at four different temperatures. It may also be noted that Barrie himself has used a single D_{SO_2} value at 10 °C (Barrie, 1978). However, he suggested four D_{SO_2} values for four different temperatures, which have been quoted by Baboolal *et al.*, 1981. All other investigators have used diffusivity values only at a particular temperature. So it is possible to compare the results of the present L-J computations only with those suggested by Barrie. This is shown in Figure 2. It is clear that at 20 °C the present calculations are nearly in exact agreement. At other temperatures the deviations are within 7%.

4. Conclusions

The L-J calculation can be adopted to obtain values of molecular diffusivities of pollutant gases for atmospheric scavenging model calculations instead of adopting arbitrarily specified values.

In multilevel models, this coefficient can now be calculated* by the scheme described at each level desired as a function of temperature and pressure.

* From Equation (2) $D \sim T^{3/2}/p$. Also, as the hydrostatic assumption is fairly accurate for the atmosphere, it can be shown in a straightforward manner that D varies linearly with height provided that the lapse rate, $-dT/dz$, is constant. In Figure 1, we find an almost linear relation because the lapse rate in the PBL is nearly constant during January in Delhi.

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