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Surface Science 585 (2005) 59–65
SURFACE SCIENCE
www.elsevier.com/locate/susc

Langmuir approach in the study of interface mass transfer

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Received 22 December 2004; accepted for publication 8 April 2005
Available online 26 April 2005

Abstract

A study of the mass transport of non-reactive species through an infinite planar interface of a gas–liquid phase is presented. On the basis of the Hertz–Knudsen equation and ''cluster'' approaches formulated by Davidovits et al. [Journal of Physical Chemistry 95 (1991) 6337], an analytical formulation of the mass-accommodation coefficient is considered. According to the work reported herein, for the case of an interfacial equilibrium, the mass-accommodation coefficient is inversely proportional to the ''cluster'' factor and directly proportional to the exponential factor of the difference between free energies in the bulk and interface regions. The ''cluster'' factor is determined as a function of the cluster sizes in the bulk and interface. Estimation of the mass-accommodation coefficient for a series of non-reactive compounds gives a good agreement with experimental data.

Keywords: Models of surface kinetics; Molecular kinetics; Semi-empirical models and model calculations; Liquid–gas interfaces

1. Introduction

Heterogeneous reactions taking place at a gas–liquid or gas–solid interface are complicated and involve several processes. In the atmosphere, these reactions can occur on the surfaces of condensed phases such as liquid aerosols and solid particulates examples of which are water droplets and mineral dust. Interfacial phenomena play a key role in multiphase processes in atmospheric chemistry, affecting cloud and aerosol properties and influencing the radiation balance of the Earth. As a consequence of the important influence of aerosols on Earth's atmosphere, for the last decade study of the interfacial processes of liquids has been intensive. It is well known that the chemical composition of aerosols is a function of the interface properties associated with the kinetics of heterogeneous chemical transformation of trace species and their accommodation.

In order to enable the adsorption processes of non-reactive molecules by liquid and solid surfaces to be described parameters such as the uptake

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0039-6028/$ - see front matter
doi:10.1016/j.susc.2005.04.014

coefficient, γ, and mass-accommodation coefficient, α, are used. The uptake coefficient is a dimensionless parameter that is defined as the probability of the removal of a gas-phase molecule through interaction with the condensed phase. The mass-accommodation coefficient describes the "resistance" of a gas-condensed phase interface. The nature of the mass-accommodation coefficient is not clear and there are no formal definitions in the literature. The mass accommodation coefficient has been suitably represented until now by Eq. (1) [2]

$$\alpha = \frac{\text{number of molecules entering the liquid phase}}{\text{number of molecular collisions with the surface}} \tag{1}$$

This is identical to the definition used in the work of Taylor et al. [3], where molecular dynamic simulations were carried out to predict the mass accommodation coefficient of ethanol by water. This work employs the same definition for the mass accommodation coefficient and is the ratio of the number of gas molecules passing through the interface into the liquid phase and the number of the molecules striking the interface.

The maximum flux of gas-phase molecules into the liquid, J, is approximated by Eq. (2)

$$J = \frac{c}{4} n_g \alpha \tag{2}$$

where n_g is the concentration of the trace gas and c is the average thermal velocity (cm/s).

To study the mass-transport of molecules in the case of incoming and outgoing fluxes from the liquid phase, the Hertz–Knudsen approach is used [4]. In this model, the interfacial mass-transport is described by diffusive transport in the liquid phase and the kinetic resistance at the interfacial conditions according to the Hertz–Knudsen equation. The combination of Fick's first law and Hertz–Knudsen equation gives the boundary conditions Eq. (3)

$$|J_l| = D_l \left.\frac{\partial n_l}{\partial x}\right|_{x=0} = \frac{\alpha}{4}\left(1 - \frac{n_l(x=0)}{HRTn_g}\right) n_g c \tag{3}$$

where n_l is the concentration of the trace species in the liquid phase, J_l is the net liquid flux, H is the Henry's law coefficient, D_l is the diffusion coefficient. In Eq. (3), the concentration $n_l(x = 0)$ at the boundary of the liquid phase ($x = 0$) is defined by solving the mass balance equation Eq. (4) for spherical droplets or for a semi-infinite planar surface

$$\frac{\partial n_l}{\partial t} = D_l \frac{1}{x^v} \frac{\partial}{\partial x}\left(x^v \frac{\partial n_l}{\partial x}\right), \tag{4}$$

where $v = 0$ for semi-infinite volume and $v = 2$ for liquid spheres.

Note that the equality of gas-phase and liquid-phase fluxes gives the definition of the uptake coefficient as shown in Eqs. (5) and (6) [4]

$$J_l = J_{gas} = \frac{\gamma}{4} n_g c \tag{5}$$

$$\gamma = \alpha\left(1 - \frac{n_l(x=0)}{HRTn_g}\right) \tag{6}$$

The condition of Eqs. (3)–(6) requires the establishment of a local solubility equilibrium at the interface. Eq. (6) also defines the relation between uptake and mass-accommodation coefficient.

The solution of the mass balance equation for the boundary conditions Eq. (3), was reported by Danckwerts [5]

$$\gamma = \alpha Erfc\left(g\sqrt{t}\right) e^{g^2 t} \tag{7}$$

where $g = \frac{\alpha c}{4HRT\sqrt{D_l}}$. If the uptake process is limited by solubility, Eq. (7) can be approximated to Eq. (8)

$$\gamma_l = \frac{4RTH}{c}\sqrt{\frac{D_l}{\pi t}} \tag{8}$$

In the works of Robinson et al. [6] and Hanson and Ravishankara [7] the mass-accommodation coefficient, diffusion process into the liquid, and reaction in the bulk are connected in the frame of a "resistor" model. Based on the well-developed resistance model, the uptake and accommodation process are connected through Eq. (9),

$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{1}{\Gamma_g} + \frac{1}{\gamma_l} \tag{9}$$

where Γ_g determines the gas-phase diffusion process to the liquid, and γ_l gives the diffusive mass transfer into the bulk liquid. Eq. (9) shows that all terms, which describe independent processes