COMMUNICATIONS TO THE EDITOR

On a Transformation of the Equation Describing Steady Diffusion through a Stagnant Gas

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The classic Stefan problem, of steady one-dimensional diffusion through a stagnant gas, has long been employed as a pedagogical tool and has been the basis for experimental studies in binary gas diffusion. A solution to the problem of steady diffusion through a stagnant gas in a three-dimensional geometry has not been presented in the literature. A transformation is used here to reduce the descriptive equation for this situation to the Laplace relation.

THEORY

The equation (*1*) describing the concentration distribution of component b in a nonreacting binary mixture of gases a and b may be written as follows

$$\frac{\partial C_b}{\partial t} + \nabla \cdot [C_b \, \bar{v}^*] = \nabla \cdot CD\nabla X_b \tag{1}$$

Under the assumptions of constant molal density and diffusion coefficient, Equation (1) may be rewritten in terms of the mole fraction X_b as

$$\frac{\partial X_b}{\partial t} + \bar{v}^* \cdot \nabla \, X_b = D\nabla^2 X_b \tag{2}$$

Now consider a problem of the following nature: Gas b enters a region of arbitrary shape through a surface impermeable to a. (A common example of this condition is evaporation at a liquid surface.) The region has one or more small openings to the environment which consists of a binary mixture of a and b. The entire system is maintained at constant temperature and pressure and the gases are assumed to behave ideally. Thermodynamic coupling effects which would induce temperature gradients are considered to be negligibly small. In addition the molal flux of a across each opening is assumed to be zero. The net flux of a within the system will also be zero everywhere, as required by continuity.

Under these conditions it is readily shown (*1*) that the molal flux of b at any point is given by

$$N_b = C \, \bar{v}^* = C \, (X_b \, \bar{v}^* - D\nabla X_b) \tag{3}$$

Thus

$$\bar{v}^* = \frac{-D}{(1 - X_b)} \nabla X_b \tag{4}$$

Substitution into Equation (2) yields the following expression for the mole fraction of b at steady state in a system satisfying the stated conditions:

$$\nabla X_b \cdot \nabla X_b + (1 - X_b) \, \nabla^2 X_b = 0 \tag{5}$$

Equation (5) is a nonlinear second-order equation, but it can be transformed to a form easier to solve. To accomplish this it is first rewritten in terms of the mole fraction of a where $X_a = (1 - X_b)$. When expanded in Cartesian coordinates the resulting expression is

$$\left[\frac{\partial X_a}{\partial x}\right]^2 + \left[\frac{\partial X_a}{\partial y}\right]^2 + \left[\frac{\partial X_a}{\partial z}\right]^2 = X_a \left[\frac{\partial^2 X_a}{\partial x^2} + \frac{\partial^2 X_a}{\partial y^2} + \frac{\partial^2 X_a}{\partial z^2}\right] \tag{6}$$

This equation can be transformed by defining a new dependent variable, $\alpha(x, y, z)$, where

$$X_a = \exp(-\alpha) \tag{7}$$

In terms of this new variable Equation (6) becomes

$$\nabla^2\alpha = 0 \tag{8}$$

Thus the transformation of Equation (7) has reduced the problem to that of finding solutions to the Laplace equation. Equation (7) also allows transformation of the boundary conditions. It should be noted that the condition $X_a = 0$ ($X_b = 1$) cannot be handled, since this implies an infinite value of α. This is to be expected, since the basic equations lose their meaning in this case. The condition $X_b = 1$ applies, for example, to the case where gas b is supplied by a boiling liquid, a process which is not diffusion controlled.

EXAMPLE

As an example of the application of the transformation given here consider the classic Stefan problem. An evaporating liquid b is contained at the bottom of a constant area column of height h located in an environment of gases a and b. In this case Equation (6) reduces to

$$\left[\frac{dX_a}{dz}\right]^2 - X_a\frac{d^2X_a}{dz^2} = 0 \tag{9}$$

In terms of α this becomes

$$\frac{d^2\alpha}{dz^2} = 0 \tag{10}$$

and the solution is

$$\alpha = \alpha_o + \frac{\alpha_h - \alpha_o}{h}\, z \tag{11}$$

where $\alpha_o = -\ln x_{a_o}$ and $\alpha_h = -\ln x_{a_h}$. Equation (11) is readily reduced to the expression which Stefan (2) first obtained by means of a direct application of Fick's law:

$$\frac{1 - X_b}{1 - X_{b_o}} = \left[\frac{1 - X_{b_h}}{1 - X_{b_o}}\right]^{z/h} \tag{12}$$

NOTATION

α = parameter defined by Equation (7)
C = molar concentration, g.-moles/cc.
D = diffusion coefficient, sq.cm./sec.
h = length of diffusion path, cm.
$\bar{N}$ = molal flux, g.-moles/sq.cm. sec.
$\bar{v}^*$ = molal average velocity, cm./sec.
t = time, sec.
X = mole fraction
(x, y, z) = Cartesian coordinates

Subscripts

a = parameter for gas a
b = parameter for gas b
h = boundary condition at $z = h$
o = boundary condition at $z = o$

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Comments on Simplified Method for the Predictions of Multicomponent Adsorption Equilibria from Single Gas Isotherms

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The method presented by Kidney and Myers (*1*) is a refined way to predict the multicomponent adsorption, if the mutual interactions for the adsorbed molecules are ideal. In the chemisorption, however, the interaction is not always ideal, and sometimes the mutual enhancements of adsorptions have to be expected, as evidenced in the systems of hydrogen-nitrogen on iron (*2*) and hydrogen-carbon monoxide on zinc oxide + copper chromate (*3*). It has also been reported (*4*) that the simultaneous chemisorption of mixed gases is unpredictable from the single gas adsorption of their components.

The ideal adsorbed solution theory was confirmed by Kidney and Meyers for physisorption data. We would like to point out that the use of this theory is limited to the physical adsorption, since it can not predict the mutual enhancement of the adsorption of gases.

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