



## Effect of transport ratio on source term in determination of surface emission coefficient

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**ABSTRACT :** A surface reaction may be regarded as occurring in following five consecutive steps which are, diffusion of the reactants molecules to the surface, adsorption of gases on the surface, reaction on the surface, desorption of the products and finally diffusion of the desorbed products into the main body of the gas. In general, at the surface of the liquid or solid, the foreign molecules of the substance of the gas solid or liquid experiences resultant inward attraction. If the molecule is in the interior, it experiences equal force of attraction by the surrounding molecules and the resultant force is zero. Thus, the molecule of the adsorbate on the surface of adsorbent experiences resultant inward pull by the molecule of the adsorbent. This way the process of adsorption held on to the surfaces and these forces are Vanderwaal's forces and then it is termed as physical adsorption. However, there may be some bond formation between the adsorption molecules and adsorbent molecules which is then known as chemical adsorption. This work analyzes the effect of transport ratio on source term by drawing some graphs using MATLAB and this describes the variation of source term with respect to the dimensionless time for sorption and desorption process.

**Keywords :** Diffusion coefficient, surface emission coefficient, Vanderwaal's forces, chemical bond, hydrogen bond, covalent bond

### INTRODUCTION

Adsorption is the process of attraction and accumulation of any substance on the surface of another. In fact adsorption (either physical or chemical) is a surface phenomena at which the concentration of the adsorbate is more at the surface than in the bulk of adsorbent. The forces between adsorbate and adsorbent molecules are either weak Vanderwaal's forces or strong chemical bond forces. The rate of adsorption decreases with the passage of time till the time of equilibrium is attained. On the other hand absorption is a bulk phenomenon where the concentration is same throughout, that at the surface as well as in the bulk of the solvent. The forces may be hydrogen bond or covalent bond with the constant rate of absorption. Sometimes absorption may be followed by adsorption and such a process in which both adsorption and absorption take place, normally the term sorption should be used, while the reverse of it, is called desorption. When diffusion is taking place within the medium then movement of diffusing substance is controlled by the diffusion coefficient whereas at the surface of the medium it is controlled by the surface emission coefficient. Also adsorption depends upon the surface area of the adsorbent and it increases as the surface area of adsorbent increases.

Adsorption of gases in multi-molecular layers was shown by Brunauer *et. al.* [2], which describe that the adsorption isotherm of gases at high temperatures not far removed from their condensation points, show two regions for most adsorbents: at low pressure the isotherms are concave, at higher pressures convex toward the pressure

axis. The higher pressure convex portion has been variously interpreted. Sometimes it is assumed that it has been attributed to condensation in the capillaries of the adsorbent on the assumptions that in capillaries of molecular dimensions condensation can occur at pressures far below the vapor pressure of the liquid, while in some other situations such isotherms are believed to indicate the formation of multi-molecular adsorbed layers. Mathematical equations for the surface emission coefficient corresponding to the variable diffusion coefficient obtained by Liu [6], where surface emission coefficient in isothermal diffusion equation was derived along with the assumption that the variable diffusion coefficient can be taken to be exponential function of the concentration of diffusing substances.

The mathematical relationship between surface emission coefficient and diffusion coefficient was established by Liu and Simpson [8] in capillary porous solids and also presented a theoretical explanation for the phenomena of sorption and desorption. On the other hand, a study on the separation of diffusion and surface emission coefficient in wood was also proposed by, Cai and Avvamidis [3], where a non-linear technique was used to obtain optimum pair of surface emission coefficient and diffusion coefficient from a single sorption curve which was also tested with the experimental data. Diffusion coefficient and surface emission coefficient can also be evaluated by optimization technique which was presented by Chen Youg *et. al.* [4]. The optimization technique was used to calculate the following two coefficients where first is the diffusion coefficient as an indication of internal resistance to moisture removal and

another is surface emission coefficient, as an indication of external resistant to moisture removal, where both coefficients express the rate at which wood dries. Yeo *et. al.* [11] also determined the internal moisture transport and surface emission coefficients for eastern white pine. They evaluate wood specimens during drying at specific temperature and RH conditions and built an appropriate numeric analysis model for predicting moisture profile changes in wood. They also shows that the internal moisture transport coefficients were dependent on the temperature and average moisture content and the surface emission coefficients on the wood vapor pressure in air adjacent to the surface. The internal moisture transport coefficient decreased with decreasing temperature and internal moisture content and surface emission coefficients increased with increasing temperature and decreasing surface moisture content.

A closed form solution of the non-steady state diffusion equation with constant transport coefficient has already been obtained Liu and Simpson [9]. An inverse moisture diffusion algorithm for the determination of diffusion coefficient was presented by Liu *et. al.* [10]. Furthermore this inverse determination of the diffusion coefficient in one dimensional non-steady state diffusion equation which is based on desorption test data was also explained and inverse problem is then defined in the resulting system of finite difference equations. Diffusion coefficient of porous solids obtained from isothermal sorption tests again presented by Liu [7], according to which a derivation of mathematical equation to separate the diffusion coefficient and the surface emission coefficient in Newman's solution of unsteady state diffusion equation from an experimental sorption curve was, defined Liu [7]. Crank's uses Newman's solution with the assumption that  $S$  the, surface emission coefficient was infinity to obtain the constant  $D$ , the diffusion coefficient for each curve and then derived  $D$  as a function of the concentration of chloroform. However in many practical sorption or desorption tests, the value for  $S$  is finite. Much of this work was also done by Kim and Kim [5] and Boznani *et. al.* [1].

## MATHEMATICAL MODEL

The governing equations which govern the model are as follows. If  $l$  is the half of thickness of sheet of a considered porous medium and  $C$  is the concentration of the diffusing substance then a one-dimensional form of diffusion equation with the diffusing substance moving in one direction is,

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial X} \left( D \frac{\partial C}{\partial X} \right) + Q \quad (0 < X < l, t > 0) \quad \dots(1)$$

where  $D$  is diffusion coefficient which assumed to be an exponential function of  $C$ ,  $t$  is time,  $X$  is space coordinate measured from the center of the sheet, and  $Q$  denotes the source term.

Consider the initial condition is

$$C = C_0 \quad (0 < X < l, t = 0) \quad \dots(2)$$

and the boundary conditions are

$$\frac{\partial C}{\partial X} = 0 \quad (X = 0, t \geq 0) \quad \dots(3)$$

$$D \frac{\partial C}{\partial X} = S (\bar{C} - C), \quad (X \approx l, t > 0) \quad \dots(4)$$

where  $C_0$  is a constant concentration in the medium,  $S$  is surface emission coefficient and  $\bar{C}$  is equilibrium concentration. Also the equation (4) prescribes the boundary condition just within the surface of the sheet but not at the surface.

Now consider the following two cases in different dimensionless formulations with assuming that diffusion coefficient as a function of concentration in the form  $D = D_0 e^{kc}$ , where  $D_0$  and  $k$  are constants,

### Case : I Sorption ( $\bar{C} > C$ )

Let the following non-dimensional parameters are introduced to reduce the system of equations (1)-(4) in dimensionless form :

$$c = (C - C_0) / (\bar{C} - C_0), \quad \bar{D} = D / D_0, \quad \tau = D_0 t / l^2,$$

$$x = X / l \text{ and } f(c) = \frac{l^2}{D_0 (\bar{C} - C)} Q.$$

Now equations (1) to (4) in dimensionless form using the above dimensionless parameters along with  $L$ , transport ratio defined as  $L = l S / D_0$ , and  $\epsilon \rightarrow 0$  :

$$\frac{\partial c}{\partial \tau} = \frac{\partial}{\partial x} \left( \bar{D} \frac{\partial c}{\partial x} \right) + f(c) \quad (0 < x < 1, \tau > 0) \quad \dots(5)$$

$$c = 0 \quad (0 < x < 1, \tau = 0) \quad \dots(6a)$$

$$\frac{\partial c}{\partial x} = 0 \quad (x = 0, \tau \geq 0) \quad \dots(6b)$$

$$\frac{\bar{D}}{L} \frac{\partial c}{\partial x} + c = 1, \quad (x = 1 - \epsilon, \tau > 0) \quad \dots(6c)$$

### Case: II Desorption ( $\bar{C} < C$ )

The mathematical formulation for the desorption will be differ only in the initial and boundary conditions to sorption with  $c = (C - \bar{C}) / (C_0 - \bar{C})$ ,

Therefore,

$$\frac{\partial c}{\partial \tau} = \frac{\partial}{\partial x} \left( \bar{D} \frac{\partial c}{\partial x} \right) + f(c) \quad (0 < x < 1, \tau > 0) \quad \dots(7)$$

$$c = 1 \quad (0 < x < 1, \tau = 0) \quad \dots(8a)$$

$$\frac{\partial c}{\partial x} = 0 \quad (x = 0, \tau \geq 0) \quad \dots(8b)$$

$$\frac{\bar{D}}{L} \frac{\partial c}{\partial x} + c = 0, \quad (x = 1 - \varepsilon, \tau > 0) \quad \dots(8c) \quad \text{or} \quad M(\tau) \left[ \frac{d(\tau+1/L \ln E)}{d\tau} \right] - [M(\tau) - c(\tau, 1 - \varepsilon)]$$

It should be noted here that equation (1) to (4) will be applicable in the case of desorption when  $C_e < C$ , that is equilibrium concentration will be less than the concentration of the diffusing substance.

Considering the mathematical procedures for desorption process in detail, we proceed as follows. Suppose the total concentration in the medium,  $M$  be defined as

$$M(\tau) = \int_0^{1-\varepsilon} c(\tau, x) dx, \quad \text{where} \quad \varepsilon \rightarrow 0 \quad \dots(9)$$

so that the fraction of total concentration within the medium is

$$E = \frac{M(\tau)}{M(\infty)}, \quad \dots(10)$$

where  $M(\infty) = 1$

From equations (7) and (8b) to (10), we obtain

$$\begin{aligned} \frac{\partial E}{\partial \tau} &= \frac{\partial}{\partial \tau} \int_0^{1-\varepsilon} c(\tau, x) dx \\ &= \int_0^{1-\varepsilon} \left[ \frac{\partial}{\partial x} \left( \frac{\bar{D}}{L} \frac{\partial c}{\partial x} \right) + f(c) \right] dx \\ &= \frac{\bar{D}}{L} \frac{\partial c(\tau, 1 - \varepsilon)}{\partial x} + \int_0^{1-\varepsilon} f(c) dx \end{aligned}$$

(as  $\frac{\partial c}{\partial x}$  at  $x = 0$  is zero and  $\frac{\bar{D}}{L} \frac{\partial c}{\partial x} = -Lc$  at  $x = 1 - \varepsilon$ )

$$\frac{\partial E}{\partial \tau} = -Lc(\tau, 1 - \varepsilon) + \int_0^{1-\varepsilon} f(c) dx \quad \dots(11)$$

Now, from equations (10) and (11), we may write

$$\begin{aligned} E + \frac{1}{L} \frac{\partial E}{\partial \tau} &= E \left[ \frac{d(\tau+1/L \ln E)}{d\tau} \right] \\ &= E + \frac{1}{L} \left[ -Lc(\tau, 1 - \varepsilon) + \int_0^{1-\varepsilon} f(c) dx \right] \\ &= [M(\tau) - c(\tau, 1 - \varepsilon)] + \frac{1}{L} \int_0^{1-\varepsilon} f(c) dx \quad \dots(12) \end{aligned}$$

Equation (12) may also be written as

$$\begin{aligned} E \left[ \frac{d(\tau+1/L \ln E)}{d\tau} \right] - M [M(\tau) - c(\tau, 1 - \varepsilon)] \\ - \frac{1}{L} \int_0^{1-\varepsilon} f(c) dx = 0 \quad \dots(13) \end{aligned}$$

$$- \frac{1}{L} \int_0^{1-\varepsilon} f(c) dx = 0$$

and make the use of equations (9) and (10) to obtain

$$\int_0^{1-\varepsilon} \left\{ c(\tau, x) \frac{d(\tau+1/L \ln E)}{d\tau} - [c(\tau, x) - c(\tau, 1 - \varepsilon)] dx - \frac{1}{L} \int_0^{1-\varepsilon} f(c) dx \right\} = 0 \quad \dots(14)$$

Taking derivative with respect to  $(\tau : 1/L \ln E)$

$$\begin{aligned} \int_0^{1-\varepsilon} \left\{ \frac{\partial c(\tau, x)}{\partial \tau} \frac{d(\tau+1/L \ln E)}{d\tau} + c(\tau, x) \frac{\partial}{\partial (\tau+1/L \ln E)} \right. \\ \left. \times \frac{d(\tau+1/L \ln E)}{d\tau} - \frac{\partial [c(\tau, x) - c(\tau, 1 - \varepsilon)]}{\partial (\tau+1/L \ln E)} \right\} dx \\ - \int_0^{1-\varepsilon} \frac{\partial f(c)}{\partial (\tau+1/L \ln E)} dx = 0 \quad \dots(15) \end{aligned}$$

$$\begin{aligned} \int_0^{1-\varepsilon} \left\{ \frac{\partial c(\tau, x)}{\partial \tau} - \frac{\partial [c(\tau, x) - c(\tau, 1 - \varepsilon)]}{\partial (\tau+1/L \ln E)} \right\} dx \\ - \frac{1}{L} \int_0^{1-\varepsilon} \frac{\partial f(c)}{\partial (\tau+1/L \ln E)} dx = 0 \quad \dots(16) \end{aligned}$$

$$\begin{aligned} \int_0^{1-\varepsilon} \left\{ \frac{\partial}{\partial x} \left( \frac{\bar{D}}{L} \frac{\partial c(\tau, x)}{\partial x} \right) - \frac{\partial [c(\tau, x) - c(\tau, 1 - \varepsilon)]}{\partial (\tau+1/L \ln E)} \right\} dx \\ - \frac{1}{L} \int_0^{1-\varepsilon} \frac{\partial f(c)}{\partial (\tau+1/L \ln E)} dx = 0 \quad \dots(17) \end{aligned}$$

$$\begin{aligned} \int_0^{1-\varepsilon} \left\{ \frac{\partial}{\partial x} \left( \frac{\bar{D}}{L} \frac{\partial [c(\tau, x) - c(\tau, 1 - \varepsilon)]}{\partial x} \right) - \frac{\partial [c(\tau, x) - c(\tau, 1 - \varepsilon)]}{\partial (\tau+1/L \ln E)} \right\} dx \\ - \frac{1}{L} \int_0^{1-\varepsilon} \frac{\partial f(c)}{\partial (\tau+1/L \ln E)} dx = 0 \quad \dots(18) \end{aligned}$$

$$\begin{aligned} \int_0^{1-\varepsilon} \left\{ \frac{\partial}{\partial x} \left( \frac{\bar{D}}{L} \frac{\partial [c(\tau, x) - c(\tau, 1 - \varepsilon)]}{\partial x} \right) - \frac{\partial [c(\tau, x) - c(\tau, 1 - \varepsilon)]}{\partial (\tau+1/L \ln E)} \right\} dx \\ - \frac{1}{L} \frac{\partial f(c)}{\partial (\tau+1/L \ln E)} dx = 0 \quad \dots(19) \end{aligned}$$

Let  $[c(\tau, x) - c(\tau, 1 - \varepsilon)] = c'(\tau', x)$

$$\text{and} \quad \tau' = \tau + \frac{1}{L} \ln E \quad \dots(20)$$

$$\int_0^{1-\varepsilon} \left\{ \frac{\partial}{\partial x} \left( \frac{\bar{D}}{L} \frac{\partial c'}{\partial x} \right) - \frac{\partial c'(\tau', x)}{\partial \tau'} - \frac{1}{L} \frac{\partial f(c')}{\partial \tau'} \right\} dx = 0 \quad \dots(21)$$

This is true when

$$\frac{\partial}{\partial x} \left( \frac{\bar{D}}{L} \frac{\partial c'}{\partial x} \right) - \frac{\partial c'}{\partial \tau'} - \frac{1}{L} \frac{\partial f(c')}{\partial \tau'} = 0$$

or 
$$\frac{\partial c'}{\partial \tau'} = \frac{\partial}{\partial x} \left( \frac{\bar{D}}{L} \frac{\partial c'}{\partial x} \right) - \frac{1}{L} \frac{\partial f(c')}{\partial \tau'} \quad \dots(22)$$

When we consider  $f(c') = e^{-L\tau'}$  then equation (22) will turn into the original form as :

$$\frac{\partial c'}{\partial \tau'} = \frac{\partial}{\partial x} \left( \frac{\bar{D}}{L} \frac{\partial c'}{\partial x} \right) + f(c') \quad (0 < x < 1, \tau' > 0) \quad \dots(23)$$

Equation (23) is as same as equation (7) in the case-II of desorption, now with the help of equation (19) and (20), the initial and boundary conditions for equation (23) becomes [1],

$$c' = 0, \quad (0 < x < 1, \tau' > 0) \quad \dots(24)$$

$$\frac{\partial c'}{\partial x} = 0, \quad (x = 0, \tau' \geq 0) \quad \dots(25)$$

$$\frac{\bar{D}}{L} \frac{\partial c'}{\partial x} + c' = \frac{D}{L} \frac{\partial c'}{\partial x} + c(\tau, 1 - \varepsilon) - c(\tau, 1 - \varepsilon) = 0$$

i.e., 
$$\frac{\bar{D}}{L} \frac{\partial c'}{\partial x} = 0 \quad (x = 1 - \varepsilon', \tau' > 0) \quad \dots(26)$$

since  $\frac{\bar{D}}{L} \frac{\partial c'}{\partial x} \neq 0$ , we must have  $L \rightarrow \infty$  to satisfy equation (26), however this result does not give the needed boundary conditions.

Comparing equation (23)-(25) with the equation (5)-(6b), we observe a one to one correspondence between (symmetry) these set of equations. The needed boundary must be obtained from equation from (6c). If we set  $L \rightarrow \infty$  in equation (6c), we have  $c = 1$  at  $x = 1 - \varepsilon$  and  $\tau > 0$ . Thus we obtain the boundary condition replacing equation (26) as :

$$c' = 1 \quad (x = 1 - \varepsilon', \tau' > 0) \quad \dots(27)$$

The justification of equation (27) as the needed boundary condition exists in the fact that the boundary condition is just within the surface but not at the surface. Therefore if we consider equation (6c) to be true at  $x = 1 - \varepsilon$  with,  $\varepsilon \rightarrow 0$ , we may consider equation (27) to be true at  $x = 1 - \varepsilon'$  with  $\varepsilon' < \varepsilon$ , and all the boundary conditions are also satisfied.

Treating  $k$  in  $\bar{D}$  being a constant quantity and also consider and , then we obtain from equation (20)

$$\tau'(\infty, E') = \tau(L, E) + \frac{1}{L} \ln E \quad \dots(28)$$

where  $\tau'$  and  $E'$  are associated with the sorption while  $\tau$ ,  $E$  and  $L$  with desorption.

Let  $L'$  be associated with the sorption then in the same manner, the corresponding equation for sorption becomes

$$\tau(\infty, E) = \tau'(L', E') + \frac{1}{L'} \ln E' \quad \dots(29)$$

The surface emission coefficients,  $S$  for desorption and  $S'$  for sorption, which are contained in  $C$  and  $C'$ , respectively can now be expressed from equation (28) and (29) as follows.

$$\text{For desorption, } S = \frac{D_0}{l} \left[ \frac{\ln E}{\tau'(\infty, E') - \tau(L, E)} \right] \quad \dots(30)$$

$$\text{For sorption, } S' = \frac{D_0}{l} \left[ \frac{\ln E'}{\tau(\infty, E) - \tau'(L', E')} \right] \quad \dots(31)$$

We note that in above equation,

$$E + E' = 1 \quad \dots(32)$$

$$\tau(L, E) = \frac{D_0 t}{l^2} \quad \dots(33)$$

$$\tau'(L', E') = \frac{D_0 t'}{l^2} \quad \dots(34)$$

In equation (32) and (33)  $t$  and  $t'$  are to be evaluated from experimental desorption and sorption time curves corresponding to satisfied values of  $E$  and  $E'$ , respectively. The  $\tau'(\infty, E')$  in equation (30) and  $\tau(\infty, E)$  in equation (31) are to be evaluated using numerical techniques.

## RESULTS AND DISCUSSION

In connection with the mechanism of the surface reactions an important concept is the molecularity, which is the number of molecules that come together during the course of reaction. The molecularity of a surface reaction is deduced from the kinetics on the basis of the experimental results and of theoretical considerations. Our results show the variation of source term with respect to dimensionless time for sorption and desorption process through the Fig.1. While drawing graphs, different values of transport ratio in a desorption process is taken and as we are increase the values of transport ratio then  $f(c')$  increases with a slight change, graphs also indicates that as the value of the dimensionless  $\tau'$  time increases the value of the source term  $f(c')$  increases, that is there is a linear relationship between  $\tau'$  and  $f(c')$  through the Fig. 3. The corresponding results for the sorption process can also be determined by the same process, which are shown through Fig. 2 and Fig. 4.

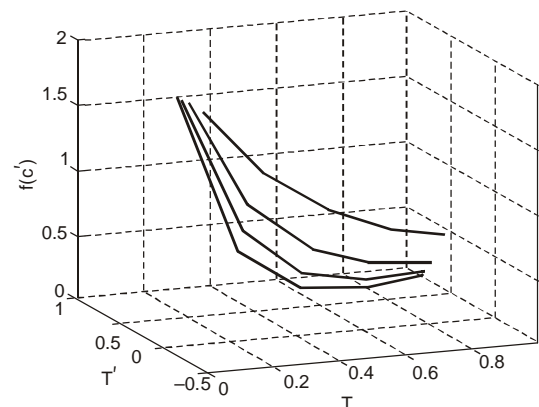


Fig.1. Variation in  $f(c')$  for different increasing values of  $L$ .

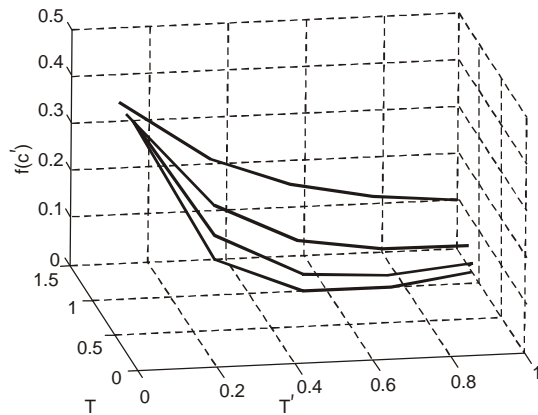


Fig.2. Variation in  $f(c)$  for different increasing values of  $L$ .

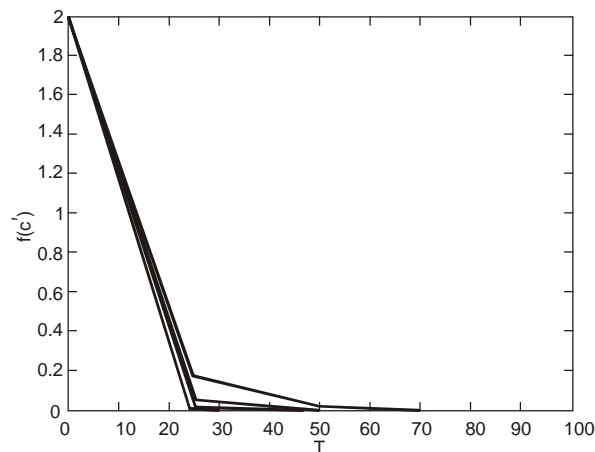


Fig.3. Variation in  $f(c)$  with respect to  $T$  for different values of  $L$ .

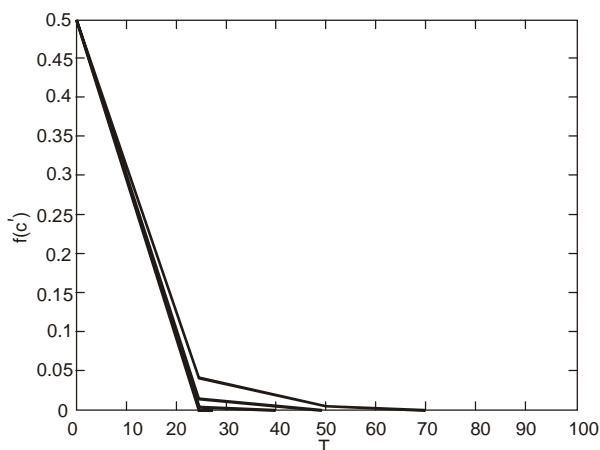


Fig.4. Variation in  $f(c)$  with respect to  $T$  for different values of  $L$ .

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