**ON THE LARCHÉ-CAHN THEORY
FOR STRESS-INDUCED DIFFUSION**

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Summary

The Larché-Cahn theory, developed on the basis of thermodynamics of stressed solids, has been utilized in numerical studies of the Stress Induced Diffusion. The phenomenon of SID has been investigated for various experimental situations (boundary conditions). The results have been compared with the earlier theoretical and experimental evidences. Some new aspects of the phenomenon have also been found and discussed.

1. Introduction.

Hydrogen transport through metallic membranes is an old problem (c.f. [1] and references given therein) but with still unsolved new aspects of its complex behavior. The main feature of this phenomenon, consisting in the coupling of diffusion and elastic fields in the membrane material, has been investigated extensively over the last decades. Theoretical treatment of the effects involved, based on thermodynamics of stressed solids, has been presented in the paper by Li [2] and in a series of works by Larché and Cahn [3,4,5]. Experimental evidence for diffusion-induced stresses, as well as for stress-induced diffusion in $\text{Pd}_{81}\text{Pt}_{19}$ — H system has been given recently by Lewis et al. [6,7,8]. A review paper by Baranowski [9], explaining the main theoretical and experimental difficulties, is also available.

The phenomenon of **SID** (**S**tress **I**nduced **D**iffusion) has been given a proper mathematical description in the form of a partial nonlinear integro-differential equation of second order (with a set of time-dependent boundary conditions), which has not yet been

solved analytically. The full analytical solution may not even be possible in view of the very complex form of the equation.

The present paper discusses the phenomenon of SID for the set of different initial and boundary conditions (IBCs), what seems to be the crucial point in the explanation of the features encountered. We would like to underline that not in all of the references mentioned above, both theoretical and experimental, the IBCs were formulated in the same way (sometimes concerning cases of different geometries). We are interested here in the case of unsymmetrical sorption, considered by Larché [4,5], as well as permeation, investigated by Lewis et al. [6,7,8] and Baranowski [9]. Discussion is based on the numerical solutions of the aforementioned problems. Notation used throughout this work has been made consistent with that of Ref.[9].

2. Formulation of the Problem.

2.1. The Equation.

The analysis of diffusion of some gaseous species (hydrogen) in a metallic membrane (Pd—Pt alloy), based on thermodynamic considerations involving stress fields, yields a one-dimensional partial integro-differential equation of second order [5,9]

$$\begin{aligned} \frac{\partial c}{\partial \tau} = D \left[\left(1 + \frac{\partial \ln f}{\partial \ln c} \right) + \frac{2V^2 Y}{3RT} c \right] \frac{\partial^2 c}{\partial z^2} + \frac{2DV^2 Y}{3RT} \left(\frac{\partial c}{\partial z} \right)^2 + \\ - \left[\frac{8DV^2 Y}{L^3 RT} \int_0^L (c - c_0)(z - L/2) dz \right] \frac{\partial c}{\partial z} \end{aligned} \quad (1)$$

where

$c = c(z, \tau)$ - concentration distribution of interstitial hydrogen in the membrane,

z - distance, τ - time,

D - hydrogen diffusion coefficient,

f - hydrogen activity coefficient,

V - hydrogen partial molar volume,

Y - membrane elastic modulus, $Y = E/(1 - \nu)$

E - Young's modulus, ν - Poisson's ratio,

L - membrane thickness,

c_0 - initial hydrogen equilibrium concentration in the membrane,

and other symbols have their usual meaning. The membrane is shown in Fig.1.

Equation (1) results from the mass balance condition

$$\frac{\partial c}{\partial \tau} = - \frac{\partial J_z}{\partial z} \quad (2)$$

applied to the flux expression

$$J_z = -D \left[1 + \frac{\partial \ln f}{\partial \ln c} + \frac{2V^2 Y}{3RT} c \right] \frac{\partial c}{\partial z} + \frac{8DV^2 Y}{L^3 RT} c \int_0^L (c - c_0)(z - L/2) dz \quad (3)$$

There are two sources of nonideality of the diffusion process involved in Eq.(1), which are connected with the creation of stresses in the membrane material. The first one is of Fickian character and is represented by the term proportional to the local concentration of the gas. This term is always positive and enhances diffusion in the membrane. The second one is a non-local non-Fickian integral term, being made responsible for the phenomenon of SID.

2.2. The Initial and Boundary Conditions (IBCs).

a) The Initial Condition.

We consider here the following initial condition

$$c(z, 0) = c_0, \quad 0 < z < L \quad (4)$$

The experimental realization of this condition, as in [4-9], assumes that prior to the main diffusion experiment the membrane has been equilibrated with the external pressure p_0 of the gas in one (sorption conditions) or both (permeation conditions) of the adjacent reservoirs, thus attaining some uniform concentration c_0 . At time $\tau = 0$ (the beginning

of the experiment) the external pressure in the left reservoir is raised instantly to some higher value $p_L^* > p_0$, thus initiating the diffusion process.

b) *The Boundary Conditions.*

Unsymmetrical Sorption.

This kind of conditions was considered theoretically by Larché and Cahn [4,5] who assumed the membrane to be impermeable at the $z = L$ plane, while material entering from the $z = 0$ plane (see Fig.1). Since the concentration c_L at $z = 0$ results from the chemical potential equality at the interface and in the left reservoir, it has to be time-dependent, "taking up" the instantaneous changes of the pressure in the left reservoir.

$$c(z=0, \tau) = c_L(\tau), \quad c_0 < c_L(\tau) < c_L^*, \quad p_L(\tau > 0) = p_L^* = \text{const.} \quad (5)$$

where c_L^* denotes the new equilibrium concentration of the gas at the plane $z = 0$, corresponding to the new imposed gas pressure p_L^* in the left reservoir. The relationship between c_L and c_L^* is given by (c.f.[9])

$$\begin{aligned} \ln \frac{c_L^* f_L^*}{c_L f_L} = & \frac{2V^2 Y}{3RT} \left[(c_L - c_0) - \frac{1}{L} \int_0^L (c - c_0) dz + \right. \\ & \left. - \frac{12(z - L/2)}{L^3} \int_0^L (c - c_0)(z - L/2) dz \right] \end{aligned} \quad (6)$$

Impermeability of the $z = L$ face implies

$$J_z(z = L, \tau) = 0 \quad (7)$$

Eq.(7) constitutes in fact the time-dependent Neumann boundary condition for the concentration gradient at the right hand side (RHS) of the membrane, which - on the basis of (3) - may be written explicitly

$$\left. \frac{\partial c}{\partial z} \right|_{z=L} = \frac{\frac{8V^2 Y}{L^3 RT} c|_{z=L} \int_0^L (c - c_0)(z - L/2) dz}{1 + \left. \frac{\partial \ln f}{\partial \ln c} \right|_{z=L} + \frac{2V^2 Y}{3RT} c|_{z=L}} \quad (8)$$

Permeation.

This kind of conditions was implemented experimentally by Lewis et al. [6–8] and investigated theoretically and experimentally by Baranowski [9]. The experimental setup was connected with the Baratron technique of gas pressure measurements, which implied the time dependency of the external gas pressure p_R in the RHS reservoir. The boundary conditions for this case differ therefore from those for sorption only at the RHS of the membrane. Instead of (7) we have here

$$c(z = L, \tau) = c_R(\tau, p_R), \quad p_R = p_R(\tau) \quad (9)$$

where p_R is the pressure course measured by the Baratron. Note that to provide permeation from the LHS to the RHS of the membrane we have to keep c_R below c_L : $c_R < c_L$.

3. Nondimensionalization.

For the purposes of numerical treatment further analysis is carried out in the terms of nondimensional variables and equations. Introduction of the following symbols

$$x = z/L \quad \text{dimensionless length} \quad (10)$$

$$t = \frac{D}{L^2} \tau \quad \text{dimensionless time} \quad (11)$$

$$u(x, t) = \frac{c(z, \tau)}{c_0} - 1 \quad \text{dimensionless concentration} \quad (12)$$

$$J = \frac{L}{Dc_0} J_z \quad \text{dimensionless flux} \quad (13)$$

satisfies this requirement. Additionally, to make the problem easier tractable, an assumption of the ideal thermodynamic behavior of the gas in the membrane (i.e. $f = 1$) has been adopted throughout this paper.

3.1. The dimensionless Equation.

Under transformations (10)–(13) the dimensionless form of Eq.(1) reads as follows

$$\frac{\partial u}{\partial t} = \left[1 + B_0 c_0(u + 1)\right] \frac{\partial^2 u}{\partial x^2} + B_0 c_0 \left(\frac{\partial u}{\partial x}\right)^2 - \left[12B_0 c_0 \int_0^1 u(x - 1/2)dx\right] \frac{\partial u}{\partial x} \quad (14)$$

where $B_0 = \frac{2V^2 Y}{3RT}$ may be regarded as the dimensionless material constant and c_0 is the initial uniform concentration of the gas in the membrane.

The dimensionless flux takes the form of

$$J = - \left[1 + B_0 c_0(u + 1)\right] \frac{\partial u}{\partial x} + 12B_0 c_0(u + 1) \int_0^1 u(x - 1/2)dx \quad (15)$$

3.2. The Dimensionless Initial and Boundary Conditions.

a) The Initial Condition.

In view of (12) the initial concentration c_0 of the gas in the membrane acquires the status of a reference "zero" level. Now, the dimensionless concentration u may take positive as well as negative values and the initial condition is given by

$$u(x, 0) = 0, \quad 0 < x < 1 \quad (16)$$

b) The Boundary Conditions.

Unsymmetrical Sorption.

The nondimensional BCs for sorption are as follows

$$u(0, t > 0) = u_L(t), \quad 0 < u_L(t) < u_L^* = \frac{c_L^*}{c_0} - 1 \quad (17)$$

and

$$\frac{\partial u}{\partial x}(x = 1, t) = \frac{12B_0 c_0(u|_{x=1} + 1) \int_0^1 u(x - \frac{1}{2})dx}{1 + B_0 c_0(u|_{x=1} + 1)} \quad (18)$$

Note that the constant u_L^* in (17) may be ascribed the name of "concentration excess", which is the driving force for the phenomenon. Function $u_L(t)$ in (17) is given implicitly by

$$\ln \frac{u_L^* + 1}{u_L + 1} = B_0 c_0 \left[u_L - \int_0^1 u dx - 6 \int_0^1 u(x - 1/2) dx \right] \quad (19)$$

Permeation.

The nondimensional BCs for permeation differ from those for sorption in the form of the RHS condition, which looks as below

$$u(1, t) = u_R(t) = \frac{c_R(\tau)}{c_0} - 1 \quad (20)$$

5. Experiments.

The boundary conditions described above are the most suitable for implementing in a real experiment but not the easiest ones from the mathematical viewpoint. This is in particular true with respect to the time-dependent gas pressure in the RHS reservoir and time-dependent surface concentration, in case of permeation. A much easier mathematical description is obtained when the gas pressure in the RHS reservoir is constant. The possibility of experimental realization of this kind of conditions is connected with the volumetric technique and has been mentioned in Ref.[9].

In order to investigate the influence of this variety of setups on the behavior of the SID phenomenon, numerical calculation for the unsymmetrical sorption and permeation cases, with different boundary conditions imposed, has been performed. These "numerical experiments" have been denoted as follows :

Experiment A

Unsymmetrical sorption (LHS pressure constant, RHS face of the membrane impermeable).

Time-dependent Dirichlet LHS BC : $u_L = u_L(t)$

(time dependency given by (19)),

Time-dependent Neumann RHS BC : $\frac{\partial u}{\partial x}|_{x=1} = g_R(t)$

(time dependency given by (18))

Experiment B

Permeation (surface concentrations constant).

Constant Dirichlet LHS BC : $u_L = u_L^*$,

Constant Dirichlet RHS BC : $u_R = 0$.

Experiment C

Permeation (external pressures in reservoirs constant).

Time-dependent Dirichlet LHS BC : $u_L = u_L(t)$

(time dependency given by (19)),

Time-dependent Dirichlet RHS BC : $u_R = u_R(t)$

(time dependency given by

$$\ln \frac{u_R^* + 1}{u_R + 1} = B_0 c_0 \left[u_R - \int_0^1 u dx - 6 \int_0^1 u(x - 1/2) dx \right] \quad (21)$$

where $u_R^* = 0$ (the gas pressure in the RHS reservoir is kept constant at the original level throughout the experiment).

Experiment D

Permeation (LHS pressure constant, RHS concentration and pressure time-dependent).

Time-dependent Dirichlet LHS BC : $u_L = u_L(t)$

(time dependency given by (19)).

Time-dependent Dirichlet RHS BC : $u_R = u_R(t)$,

implied by the functional form of the RHS reservoir pressure dependence on time, during the experiment. We assumed here a linear relationship between the surface concentration c_R and the gas pressure p_R on the RHS of the membrane

$$c_R = Sp_R, \quad S = \text{const.} \quad (22)$$

what, after taking the equation of state

$$p_R(\tau) - p_{R0} = \frac{RT}{Md} Q_z(\tau) \quad (23)$$

and relationships (10)-(13) into account, gives the nondimensional RHS boundary condition in the form

$$u_R(t) = \frac{RTLS}{MVd} Q(t) \quad (24)$$

In the above relationships $Q_z(t)$ and $Q(t)$ are the dimensional and dimensionless quantity of hydrogen mass accumulated in the RHS reservoir after time τ or t , respectively, and are defined in the following way

$$Q_z(\tau) = \int_0^\tau J_z(1, \tau) d\tau \quad (25)$$

and

$$Q = \frac{1}{c_0 L} Q_z \quad (26)$$

S is the solubility of the gas in the membrane and d means the "depth" of the RHS reservoir measured along x -axis (under the assumption of its constant cross-section area). The assumption of constant S , involved in (22), is a reasonable simplification in view of the shape of the experimental sorption isotherms for the $\text{Pd}_{81}\text{Pt}_{19}$ — H system at 298 K [6] and 323 K [10], within the pressure ranges considered in Refs. [6,7,9].

4. Numerical details.

The numerical scheme used to solve Eq.(14) has been based on the implicit Crank-Nicholson method. The integral involved in (14) has been evaluated using the Simpson method. Transient values of u_L and u_R have been found with the accuracy of 10^{-6} , using linear

interpolation applied to (19) and (21). Dimensionless concentration u has been computed throughout the membrane for all time values up to the steady state conditions. In order to determine the precision of calculations several realizations with different parameters of the numerical scheme have been compared and the parameters settled at the most convenient and accurate values. These have been found to be : $h = 0.02$ (mesh size) and $k = 0.00001$ (numerical time step), what provided the concentration calculation accuracy of 10^{-6} . Then, other related time dependencies have been found, completing the overall picture of the phenomenon for different IBCs.

5. Results and Discussion.

The main aim of our work was to investigate the SID problem numerically, drawing the attention to the importance of the initial and boundary conditions, as well as to compare the results with those obtained or suggested by other authors.

The first thing to underline is that the nondimensional form of the SID operator reflects especially clearly the main feature of the phenomenon, namely the strong dependence of diffusion on both the elastic properties of the membrane (constant B_0 involving its elastic modulus), and the initial equilibrium concentration c_0 of the gas in the membrane. In fact, only the product $B_0 c_0$ is essential and may be treated as a parameter of Eq.(14). It is also easily seen that for $c_0 = 0$ (the membrane evacuated before the experiment) no SID effect may be observed and the diffusion is ideal Fickian.

The results of the numerical experiments have been shown in Figs.2-5 . The range of $B_0 c_0$ product values was 0.0025 to 0.04. The LHS concentration u_L^* has been arbitrarily ascribed the value of 1 (unity) in each experiment. This corresponds to doubling the initial concentration c_0 at the beginning of the experiment at the LHS of the membrane.

Experiment A

Results have been presented in Fig.2.

Part a) shows the concentration profiles in the membrane for $B_0 c_0 = 0.01$. Curves for different values of time have been plotted. At the early times of diffusion the effect

of the concentration decrease below $u = 0$ (corresponding to $c < c_0$), predicted also by Kandasamy [11] for the early times of permeation, is clearly visible. The shape of a profile awaited by Larché [5] for this case is shown in Fig.2a by the dashed line and is not consistent with our calculations.

The corresponding plots of the gas flux $J(0, t)$ through the LHS surface of the membrane, drawn in part b) of Fig.2, show a sharp decreasing tendency. In case of large $B_0 c_0$ parameter values they may even acquire negative transient values, what would suggest the gas being drawn out of the membrane instead of filling it. These phenomena, rather strange from the experimental point of view, might however be possible, if only the $B_0 c_0$ value could be made sufficiently high (obviously by increasing c_0). On the other hand, for high $B_0 c_0$ values the equilibration of the membrane with the external pressure (i.e. the approach of the steady state) may require substantially longer times.

For a clearer picture of the situation the time evolution of the LHS boundary concentration u_L has been plotted in Fig.2c. The shapes of the obtained curves contradict the assumption of the small evolution of u_L at early times, on which the approximate analysis has been based in Ref.[5]. This may explain the incompatibility of the dashed line (Fig.2a), which in fact has been deduced basing on the assumption of the constancy of the LHS surface concentration.

Experiment B

Results have been presented in Fig.3.

Concentration distribution profiles for all values of $B_0 c_0$ parameter and all values of time were found to be positive and concave upward $\left[\frac{d^2 c}{dx^2} \right] > 0$. Steady state distributions for different $B_0 c_0$ values have been shown in Fig.3a. What is surprising these numerical curves do not confirm the expectations expressed in Ref.[9] as to the linear concentration distribution and the removal of stress in the membrane for the steady state. They are rather more consistent with the predictions of Kandasamy [11], showing the more concave character for the greater values of $B_0 c_0$.

Figs.3b and 3c present the time dependency of the RHS flux J and its time integral Q , respectively. The characteristic feature of the SID phenomenon, i.e. the reverse flow at

the early times, is very well seen. However, with the increase of the B_0c_0 value the time interval for the reverse flow increases, leading eventually to the situation in which both $J(t)$ and $Q(t)$ curves lie entirely below the abscissae axis. The physical interpretation of this fact is straightforward – the content of the gas in the membrane is so high that the stress field created by the change of the LHS boundary condition removes the species out of the membrane against the concentration gradient developed. There have been no reports yet of such strange behavior in real experiments but this situation cannot be excluded beforehand.

We have to underline that although the picture of the concentration distributions in the membrane is different here from that of experiment D (see further), it also results in the characteristic effect on the J and Q curves (compare Figs.3b and 3c with the respective Figs.5b and 5c).

Experiment C

Results have been presented in Fig.4.

A plot of the consecutive concentration distributions in the membrane with respect to the intervening time has been drawn in Fig.4a for $B_0c_0 = 0.01$. The characteristic negative "tail" of the distributions at the RHS of the membrane, predicted by Kandasamy [11], originates here from the time dependent RHS boundary condition rather than from the reverse flux, as was the case in the absorption experiment A. The steady state profile conforms to the steady state values of the LHS and RHS boundary conditions. The time evolution of the boundary conditions for this case has been plotted in Fig.4b.

The $J(t)$ and $Q(t)$ plots for different B_0c_0 values have been shown in Figs.4c and 4d, respectively. One can see that the $J(t)$ and $Q(t)$ curves behave now quite differently than in case of experiment B. They exhibit typically non-Fickian shapes and do not show the initial period of reverse flow. For greater values of B_0c_0 product the steady state flow may also be reversed, as in experiment B. A striking fact is that all the $J(t)$ curves, representing the flux courses for different values of B_0c_0 , intersect in precisely the same point. The same is true for the $Q(t)$ curves, yet for some other time coordinate. **These regularities seem to be a characteristic feature of the SID phenomenon, when**

considered for the IBCs represented by this kind of experiment (the boundary conditions realized by the volumetric technique).

Experiment D

Results have been presented in Fig.5.

Concentration profiles in the membrane for $B_0c_0 = 0.01$ and $\beta = 1$ have been presented in part *a*) of the figure. A close resemblance to the unsymmetrical sorption case, shown earlier in Fig.2*a*, is unquestionable. In fact, this kind of experimental conditions has much in common with unsymmetrical sorption, what stems from the use of the Baratron technique (constant volume of the RHS reservoir). The steady state for this experiment is the uniform concentration distribution in the membrane $u(x, t) = \text{const.} = u_L^*$. The curves in Fig.5*a* are generally consistent with the predictions of the concentration profiles given by Baranowski and Lewis [10].

In Figs.5*b* and 5*c* the plots of $J(t)$ and $Q(t)$ have been drawn for $\beta = 1$ and different values of B_0c_0 . The characteristic thing is that the shape of the $Q(t)$ curves is no more linear for longer times and the time lag cannot be determined. This is rather obvious, taking into consideration what has been stated above about the character of the process. For very long times the $Q(t)$ curves tend to a constant value Q_∞ , corresponding to the decrease of the flux $J(t)$ to zero ($J_\infty = 0$), and to equilibration of the membrane with the new level of concentration u_L^* .

One can see that the behavior of the phenomenon at the early times of sorption and permeation (experiment A compared with experiments C or D) possesses the same character, although the reason for that is quite different. In case of sorption the decrease of the RHS boundary condition below the "zero" level is connected with the reverse "stress" flux, while in case of permeation it is implied by the time dependency of the RHS surface concentration itself.

Results presented in Figs.2–5 and commented on above need a few additional remarks.

First of all, the analysis of Baranowski, presented in Ref.[9], concerning the steady state concentration distribution for the Eq.(14), is based on the guess of the linear form

of the solution to the time independent form of (14)

$$\left[1 + B_0 c_0 (u + 1)\right] \frac{\partial^2 u}{\partial x^2} + B_0 c_0 \frac{\partial u^2}{\partial x} - \left[12 B_0 c_0 \int_0^1 u(x - 1/2) dx\right] \frac{\partial u}{\partial x} = 0 \quad (27)$$

but at the same time he ignores the boundary conditions, paying no attention to the well-posedness of the problem. Indeed, the linear concentration profile is a formal solution to the Eq.(27) but this does not imply that it is the only one i.e. that this is the **unique** solution. Another question which has to be raised here is the stability of such a solution, what may not be an easy problem to check. To settle this point we have performed an additional experiment consisting in implementing the linear concentration distribution as the **initial condition** for the equation (14) with constant BCs. Had it really been the stable steady state profile, it would have not been changed in the course of the numerical simulation. This, however, turned out not to be true. The linear solution, as apparently unstable one, evolved slowly - due to truncation errors - towards the stable steady state distributions shown in Fig.3a. Secondly, the understanding of such basic ideas as the time lag and the breakthrough time is not uniform throughout the aforegiven literature. These conceptions are frequently confused with each other, apart from the fact that there is no good definition of the breakthrough time itself. For example, Lewis et al. [6] define this quantity as the time corresponding to the intersection with the time axis of the plot of the RHS pressure $p_R(\tau)$. Baranowski in turn (see [9]) identifies the notion of the breakthrough time with the concept of time lag, using both of these terms interchangeably. The time lag has been precisely defined long ago (c.f.[1]) for the ideal Fickian permeation and we are bound to stress here that the relationship using the time lag τ_L for the evaluation of the diffusion coefficient

$$D = \frac{L^2}{6\tau_L} \quad (28)$$

can only be utilized in the *ideal Fickian case* (c.f.[12]). In other diffusional processes it may obviously yield inaccurate values of D , as is clearly the case for the stress induced diffusion. The time lag itself, in turn, may always have the sense of a parameter characterizing the

process, provided that the shape of the $Q(t)$ curve allows the evaluation of this quantity, according to its definition.

In view of what has been said, some new possibilities may arise from the analysis of the situation presented in experiment C. Apparently, the concept of time lag loses its physical significance for greater values of $B_0 c_0$ product (c.f. Fig.4d). Instead, the time coordinate of the common intersection point might be ascribed some sense, at least being recognized as a useful reference parameter of the SID phenomenon. The following experimental procedure may be applied for the determination of this parameter :

- i) the membrane is subject to the initial and boundary conditions described in experiment C,
- ii) a set of permeation experiments is then performed, each for a different value of the initial equilibrium concentration c_0 , (but the same c_L^*/c_0 ratio, c.f.(17)), in which the time course of the quantity Q of the gas transported through the membrane is being recorded,
- iii) the $Q(t)$ curves for all experiments are plotted in one graph and their intersection point is then found.

This approach seems to be at least promising and should be investigated further.

6. Conclusions.

A few conclusions can be drawn out :

- The value of the initial equilibrium concentration c_0 in the membrane is a crucial parameter for the extent of the SID phenomenon. A very high value of c_0 may reverse the gas flow through the membrane, making it totally "uphill" in the sense of permeation.
- The boundary conditions are the essential part of the mathematical formulation of the problem. They strictly correspond to the setup of the experiment and influence the overall "outlook" of the phenomenon. In particular the value of c_L^* is not meaningless.
- Time lag may not be used for evaluation of the diffusion coefficient (as it appears in Eq.(14)) in case of the SID - this method has been derived for the ideal Fickian

process and will naturally yield inaccurate values for D .

- There is a need for a better recognition between the breakthrough time and the time lag - the breakthrough time, understood as the time of the detection of the first portion of the permeating species at the outgoing side of the membrane, is always connected with certain measuring equipment rather and cannot be used in analytical calculations.
- A new aspect of the phenomenon is being suggested by the results of permeation with volumetric measurements. This should however be investigated further and checked experimentally.

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References

1. J.Crank, "The Mathematics of Diffusion", Sec.Ed., Clarendon Press, Oxford, 1975.
2. J.Chen-Min Li , Metall.Trans.A, 9 (1978) 1353.
3. F.C.Larché and J.W.Cahn, Acta Metall., 21 (1973) 1051.
4. F.C.Larché and J.W.Cahn, Acta Metall., 30 (1982) 1835.
5. F.C.Larché, Solid State Phenomena, 3-4 (1988) 205.
6. F.A.Lewis, J.P.Magennis, S.G.McKee and P.J.M.Ssebuwufu, Nature, 308 (1983) 673.
7. F.A.Lewis, B.Baranowski and K.Kandasamy, J.Less-Common Met., 134 (1987) L27.
8. F.A.Lewis, K.Kandasamy and B.Baranowski, Int.J.Hydrogen Energy, 13 (1988) 439.
9. B.Baranowski, J.Less-Common Met., 154 (1989) 329.
10. B.Baranowski, F.A.Lewis, Ber.Bunsenges.Phys.Chem., 93 (1989) 1225.
11. K.Kandasamy, Scripta Metall., 22 (1988) 479.
12. J.H.Petropoulos and P.P.Roussis, J.Chem.Phys., 47 (1967) 1491, 1496.

Captions to Figures

Fig.1 - The experimental setup for diffusion in a membrane.

Fig.2 - Unsymmetrical sorption (LHS pressure constant, RHS face of the membrane impermeable).

- a) - Concentration profiles for $B_0c_0 = 0.005$. Numbers on curves denote the following time values :

1 – 0.001,	5 – 0.020,
2 – 0.005,	6 – 1.000,
3 – 0.010,	7 – 1.500,
4 – 0.015,	8 – 2.000.

The dashed line shows a profile predicted in ref.[5].

- b) - Time evolution of the LHS flux $J(0,t)$. Numbers on curves are values of B_0c_0 product.
c) - Time evolution of the LHS boundary condition. Numbers on curves are values of B_0c_0 product.

Fig.3 - Permeation (surface concentrations constant).

- a) - Steady state concentration distributions.

Numbers on curves denote the values of B_0c_0 product :

1 - 0.0000 (Fickian case),	2 - 0.0025,
3 - 0.0050,	4 - 0.0100,
5 - 0.0200.	

- b) - Evolution of the RHS flux. Numbers on curves are values of B_0c_0 product.
c) - Evolution of the RHS mass uptake. Numbers on curves are values of B_0c_0 product.

Fig.4 - Permeation (external pressures in reservoirs constant).

- a) - Concentration profiles for $B_0c_0 = 0.01$. Numbers on curves are values of time t .
b) - Evolution of the boundary concentrations for $B_0c_0 = 0.01$.
c) - Evolution of the RHS flux. Numbers on curves are values of B_0c_0 product.

d) - Evolution of the RHS mass uptake. Numbers on curves are values of $B_0 c_0$ product.

Fig.5 - Permeation (LHS pressure constant, RHS concentration and pressure time-dependent).

a) - Concentration profiles for $B_0 c_0 = 0.01$ and $\beta = 1$. Numbers on curves denote the following time values :

1 - 0.001, 4 - 0.075, 7 - 0.900.

2 - 0.010, 5 - 0.100,

3 - 0.050, 6 - 0.500.

b) - Evolution of the RHS flux ($\beta = 1$). Numbers on curves are values of $B_0 c_0$ product.

c) - Evolution of the RHS mass uptake ($\beta = 1$). Numbers on curves are values of $B_0 c_0$ product.

FIG. 1

Fig.2a

Fig.2b

Fig.2c

Fig.3a

Fig.3b

Fig.3c

Fig.4a

Fig.4b

Fig.4c

Fig.4d

Fig.5a

Fig.5b

Fig.5c