DIFFUSION WITH TRAPPING AND FAST DIFFUSION PATHS

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1. INTRODUCTION

This paper presents some new analytical results and formulations for two diffusion problems relevant to aircraft structural materials. The first arises in connection with hydrogen embrittlement of high-strength steels and the second involves the transient re-distribution of lithium during a novel heat-treatment for aluminium-lithium alloys.

Hydrogen typically enters steel in service either as a by-product of cadmium plating (which is done for corrosion protection), or during the application of paint strippers, or during stress-corrosion cracking in aqueous environments [1-3]. The problem of characterizing the detrimental effect of hydrogen can be conceptually divided into two stages : (i) quantify the transport aspect, by solving the relevant diffusion equation subject to appropriate initial and boundary conditions; (ii) quantify the damage kinetics, assuming a given local hydrogen content. It is known that hydrogen diffusion in steels is non-Fickian, and this has been attributed to the trapping of hydrogen at various sites such as lattice dislocations, grain boundaries or the interfaces with precipitates within the grains. A phenomenological theory of diffusion with trapping, due to McNabb and Foster [4], requires three parameters to characterize trapping. These parameters can be estimated experimentally from permeation tests. The McNabb-Foster equations are non-linear and therefore generally intractable analytically, but an exact analytical expression has been derived in [4] for the time-lag in a permeation test, when the boundary condition at the input face is one of fixed concentration, which is appropriate for gas-phase charging. An extension of this result is presented in §2 for the more complicated boundary condition describing electrolytic charging under potentiostatic control. This form of charging simulates more closely than gas-phase charging the hydrogen-entry conditions during plating or stress corrosion.

The non-linearity in the McNabb-Foster equations is associated with trap saturation. A simplified formulation is presented in §3 which retains the essential feature of a characteristic time for trap saturation, but which can be reduced to a standard (Fickian) diffusion problem by a Danckwerts - type transformation.

The second problem derives from a two-stage ageing treatment, which has been found experimentally to greatly enhance the fracture toughness of aluminium-lithium alloys [5]. This new class of aluminium alloys is of considerable interest in the aerospace context because of their lower density, and consequently their enhanced specific stiffness and strength. It has been suggested by Lynch [5] that the observed improvement in toughness is due to a transient re-distribution of the solute (lithium) along the grain boundaries and within the adjacent precipitate-free zones. A model is formulated in §4 for testing this claim, and for estimating the hold time during the second ageing treatment which should result in maximum toughness.

2. PERMEATION TIME-LAG FOR ELECTROLYTIC CHARGING

2.1 McNabb-Foster equations for trapping

Let $c(x,t)$ denote the concentration of hydrogen held in solution, and $c_1(x,t) = N\phi(x,t)$ the concentration of hydrogen held in traps, where N denotes the trap density (number of traps per unit volume, each trap being imagined to hold at the most one hydrogen atom) and ϕ the fractional coverage ($0 \leq \phi \leq 1$). It is assumed that diffusion of the hydrogen dissolved in the crystal lattice obeys Fick's first law,

$$\mathbf{J} = -D \operatorname{grad} c, \tag{1a}$$

but that there is an exchange of hydrogen between lattice sites and traps, so that the matter conservation law leads to

$$\operatorname{div} \mathbf{J} + \partial c/\partial t = -\partial c_1/\partial t = -N\,\partial\phi/\partial t\,. \tag{1b}$$

McNabb and Foster [4] characterize the exchange between lattice sites and traps in terms of two rate constants kN, p, for capture and for release respectively, which leads to the following equation for the rate of change of trap coverage ϕ

$$\partial\phi/\partial t = kc(1-\phi) - p\phi. \tag{1c}$$

Eqs. (1a,b,c) constitute the governing equations for diffusion with trapping. They involve three trapping parameters N, k, p, as material constants, in addition to the lattice diffusivity D. These equations look deceptively simple. Analytical difficulties arise from the non-linear term $-kc\phi$ in Eq.(1c), which occurs because the rate of capture by traps must be proportional to the fraction $(1-\phi)$ of available empty traps. If the trap coverage is always low ($\phi << 1$), this term can be neglected, and the resulting linear equations can be solved by standard integral-transform techniques [4,6]. Typically the traps do saturate however, and the resulting non-linearity cannot be ignored. An analytically tractable for the effects of trap saturation is presented in §3.

2.2 Boundary condition for hydrogen entry

A permeation test generally involves one-dimensional diffusion through a membrane (or slab) of uniform thickness L. The input face is usually taken as the origin $x = 0$, and the output face as $x = L$. McNabb and Foster [4] deal exclusively with boundary conditions of the form

$$c(x=0,\ t\geq 0) = c_o \qquad (= constant), \tag{2}$$

$$c(x=L,\ t\geq 0) = 0, \tag{3a}$$

which, in conjunction with the initial condition

$$c = c_1 = 0, \qquad 0<x<L,\ t\leq 0, \tag{3b}$$

characterizes gas-phase charging, as in the experimental work of Johnson *et al.*[7].

For electrolytic charging, Eq. (2) should be replaced by

$$-D\,\partial c/\partial x = k_a\,\theta - k_d\,c, \qquad x=0+,\ t\geq 0, \tag{4a}$$

where k_a, k_d represent rate constants for hydrogen absorption and desorption respectively, and θ denotes the surface coverage of adsorbed hydrogen, which can be assumed to be constant under potentiostatic charging [8,9]. Eq.(4a) can be re-written as

$$- D\, \partial c/\partial x = \kappa \{c_e - c(0+, t)\}, \qquad x = 0+, t \geq 0, \tag{4b}$$

$$\kappa \equiv k_d, \quad c_e \equiv k_a \theta / k_d, \tag{4c}$$

where c_e can be interpreted as the equilibrium hydrogen concentration which would prevail for two-sided charging (instead of one-sided charging) at the given electrode potential.

Eqs. (3a, 3b, 4b) constitute a complete set of boundary and initial conditions. The boundary condition (4b) can be re-stated in terms of normalized variables, as follows

$$\xi = x/L, \quad \tau = t/(L^2/D), \quad C(\xi,\tau) = c(x,t)/c_e, \tag{5a}$$

$$- \partial C/\partial \xi = \zeta\{1-C\}, \qquad \xi = 0+, \tau \geq 0, \tag{5b}$$

$$\zeta = \kappa L/d, \tag{5c}$$

where ζ is an important non-dimensional parameter analogous to the Biot number for heat-transfer problems. The boundary condition (5b) approaches one of constant flux for $\zeta << 1$, and of constant concentration for $\zeta >> 1$.

2.3 The time-lag

Let $J(t)$ denote the permeation flux at time t from the output face at $x = L$, and $Q(t)$ the total efflux up to time t :

$$J(t) = D\, \partial c/\partial x, \qquad x = L, t > 0, \tag{6a}$$

$$Q(t) = \int_0^t J(t)\, dt. \tag{6b}$$

With the initial condition (3b), $J(t)$ increases from zero at $t = 0$ to approach eventually a steady-state value which will be denoted by J_∞. At the same time, $Q(t)$ becomes asymptotically a linearly increasing function of t. The time-lag t_L is defined from this asymptotic behaviour as follows,

$$Q(t \to \infty) = J_\infty (t - t_L), \tag{7a}$$

$$\Rightarrow \quad t_L = \lim_{t \to \infty} \{t - Q(t)/J_\infty\}, \tag{7b}$$

$$= \lim_{t \to \infty} \int_0^t \{J_\infty - J(t)\}/J_\infty\, dt. \tag{7c}$$

McNabb [10] noted that an exact expression could be derived for t_L in the presence of trapping, even though the governing equations are non-linear and quite intractable analytically. This arises because the time-lag can be shown to depend only on the eventual steady-state configuration. We follow here the simpler approach introduced by Frisch [11]. This approach has been used by Paul [12], working in the context of polymer science, to derive t_L for diffusion with trapping, assuming a local equilibrium between the solute in the matrix and in the traps, and the boundary condition of fixed concentration at the input face, Eq.(2). Paul's result, which is recorded by Crank [13], is the same as that given several years earlier (but in a different context) by McNabb and Foster [4], because the assumption of local equilibrium proves to be appropriate for the eventual steady-state.

The starting point is the equation expressing conservation of matter applied to the region within the interval (x,L):

$$\partial/\partial t \int_x^L \{ c + c_1 \} \, dx = J(x,t) - J(t), \tag{8a}$$

$$J(x,t) = -D \;\; \partial c(x,t)/\partial x . \tag{8b}$$

Integrating over time and re-arranging using the notation in Eq. (6b), we obtain

$$Q(t) = \int_0^t J(x,t)\, dt - \int_x^L \Delta c(x,t)\, dx, \tag{9a}$$

$$\Delta c(x,t) \equiv \{c(x,t) + c_1(x,t)\} - \{c(x,0) + c_1(x,0)\} . \tag{9b}$$

2.3.1 Constant flux

Consider first a constant flux boundary condition

$$-D\, \partial c/\partial x = J_\infty , \qquad\qquad x = 0+, t>0, \tag{10a}$$

where the notation J_∞ for the constant flux at the input face highlights the fact that at the eventual steady-state, the flux across $x=0$ must be the same as the flux across $x=L$ (or at any other value of x in that interval). Setting $x=0+$ in Eq.(9a), we have

$$Q(t) = J_\infty t - \int_0^L \Delta c(x,t)\, dx\,, \tag{10b}$$

and hence from Eq.(7b)

$$t_L = [\int_0^L \Delta c(x,t \to \infty)\, dx\,]/ J_\infty\,. \tag{10c}$$

2.3.2 Constant concentration

Next consider the constant concentration boundary condition in Eq.(2), retaining Eq.(3a) for the exit face. Frisch's [11] procedure, which applies to this case, is to integrate Eq.(9a) over x, noting first that

$$\int_0^L J(x,t)\, dx = - \int_0^L D(\partial c/\partial x)\, dx\,,$$

$$= \int_0^{c_0} D\, dc\,, \tag{11a}$$

$$= D\, c_0\,, \tag{11b}$$

where Eq.(11b) applies if the diffusivity does not depend on concentration, which we shall assume to be the case, whereas Eq.(11a) holds more generally. The steady-state flux is now given by

$$J_\infty = D\, c_0/L\,. \tag{11c}$$

Using this result and Eq.(11b) when integrating Eq.(9a) with respect to x over $(0,L)$, we obtain

$$L\, Q(t) = L\, J_\infty t - \int_0^L dx \int_x^L \Delta c(z,t)\, dz\,, \tag{12a}$$

and hence on interchanging the order of integration and using Eq.(7b),

$$t_L = [\int_0^L \Delta\, c(x,t\to\infty)\, x\, dx\,] / (\, L J_\infty\,)\,, \tag{12b}$$

2.3.3 Electrolytic charging

We can now derive t_L for the boundary condition (4b) by combining the ideas used above for constant flux and constant concentration. The procedure is clearer if Eq.(4b) is re-stated in the following form, with a constant on the right-hand side,

$$-D/\kappa\ \partial c(0+,t)/\partial x + c(0+,t) \ = \ c_e\,. \tag{13a}$$

Then, $1/\kappa$ times Eq.(9a) evaluated at $x=0+$, added to $1/D$ times the integral of Eq.(9a) over $(0,L)$, leads to

$$Q(t)\,\{1/\kappa + L/D\} \ = \ c_e t - \int_0^L \{1/\kappa + x/D\}\,\Delta c(x,t)\,dx\,. \tag{13b}$$

Before using Eq.(7b) to derive an expression for t_L, we note that the steady-state flux is now given by

$$J_\infty \ = \ D\,c(0+,\infty)/L\,, \tag{14a}$$

i.e. with $c(0+,\ \infty)$ replacing c_0 in Eq.(11c). From the boundary condition (4b),

$$J_\infty \ = \ \kappa\,\{c_e - c(0+,\ \infty)\}, \tag{14b}$$

so that

$$c(0+,\ \infty) \ = \ \{\zeta/(1+\zeta)\}\,c_e\,, \tag{14c}$$

$$J_\infty = \kappa\,c_e/(1+\zeta)\,, \tag{14d}$$

$$\zeta \ = \ \kappa L/D\,.$$

Using these relations and re-arranging Eq.(13b) to derive t_L according to the definition in Eq.(7b), we obtain

$$t_L = \ [\int_0^L (1 + \kappa\,x/D)\,\Delta c(x,\,t\to\infty)\,dx\,]/\,(\kappa c_e) \tag{15}$$

The main result of this section, Eq.(15), is not tied to the exchange relation in Eq.(1c), which is specific to the McNabb-Foster theory. To obtain a more explicit expression for t_L, however, we shall now adopt this particular relation, which leads to the following steady-state relations,

$$c_1(x,\infty) \ = \ Nkc(x,\infty)\ /\ \{kc(x,\infty) + p\}\ , \tag{16a}$$

$$c(x,\infty) \ = \ c(0+,\infty)\,\{1 - x/L\}. \tag{16b}$$

Using these and the initial condition (3b) in the definition (9b) for Δc, we can evaluate the integral in Eq.(15) to obtain

$$t_L/(L^2/6D) = \{3+\zeta+3(2+\zeta)\gamma+6\gamma/\beta[\zeta-\{1+\zeta/\beta\,(1+\beta)\log(1+\beta)\}]\}/(1+\zeta)\,, \quad (17a)$$

$$\gamma = N/c(0+,\infty) = ND/(J_\infty L)\,, \quad (17b)$$

$$\beta = kc(0+,\infty)/p = kJ_\infty L/(Dp)\,. \quad (17c)$$

This gives the permeation time-lag for electrolytic charging in terms of the non-dimensional parameter ζ defined by Eq.(5c), and the trapping parameters N, k, p, as well as the diffusivity D and membrane thickness L. It is recalled that for diffusion without trapping [13], the time-lag under constant concentration at the input face $x = 0$ is given by

$$t_L = L^2/6D\,, \quad (18a)$$

and under constant flux by

$$t_L = L^2/2D\,. \quad (18b)$$

Eq.(17a) reduces to these expressions for no trapping ($N = c = 0$), in the appropriate limits.

It is emphasized that Eq.(15) also holds when c_1 in Eq.(9b) represents the hydrogen concentration in several trap populations having distinct values for the trapping parameters N_i, k_i, p_i, $i=1,...,n$, or even for a continuous spectrum for these parameters. The appropriate steady-state distributions, and hence the relevant extension of Eq.(17a), can be readily determined.

3. TRAP SATURATION

It has already been mentioned that analytical difficulties in solving the McNabb-Foster equations arise from the non-linear term $-kc\phi$ in Eq.(1c). If we temporarily regard the concentration c as a given constant, Eq.(1c) can be integrated to obtain

$$\phi(t) = \phi_\infty\{1-e^{-(kc+p)t}\}\,, \quad (19a)$$

$$\phi_\infty = kc/(kc+p)\,, \quad (19b)$$

indicating an exponential approach to an equilibrium coverage ϕ_∞, over a time scale $(kc+p)^{-1}$. If $kc << p$, so that $\phi_\infty << 1$, one could reasonably ignore the non-linear term in Eq.(1c), and proceed analytically using standard integral-transform techniques [14].

Eqs.(1a-c) would then be equivalent to those for diffusion with a first-order, reversible chemical reaction.[13,§14.4].

In the hydrogen embrittlement context, however, one typically finds $kc/p \geq 10^2$, so that $(1 - \phi_\infty) << 1$. This means that $\partial\phi/\partial t \rightarrow 0$ because the traps saturate, rather than because the capture rate is balanced by a release rate, as would be the case when $kc/p << 1$.

We can attempt to simulate this behaviour by replacing Eq.(1c) by

$$\partial\phi/\partial t = k\, e^{-\chi t}\, c(x,t)\,, \tag{20a}$$

where χ^{-1} represents a prescribable time-scale. The effective rate constant for capture would then decay to zero, simulating the effect of trap saturation, provided that we use $\chi \approx kc$, where c is a "representative" value of the concentration $c(x,t)$, so that χ^{-1} is an equally representative characteristic time for trap saturation. For the boundary condition (4b), an obvious choice would be

$$\chi = kc_e\,. \tag{20b}$$

On using Eq.(20a) instead of Eq.(1c), and assuming a constant diffusivity D, the governing equations reduce to

$$D\, \nabla^2 c = \partial c/\partial t + k\, e^{-\chi t}\, c\ , \tag{20c}$$

which is similar to the equation for diffusion with an irreversible first-order reaction [13, §14.3], but with the rate constant decaying exponentially.

More generally, using the same notation as above, consider the equation

$$D\, \partial^2 c/\partial x^2 = \partial c/\partial t + \lambda(t)\, c\ , \tag{21a}$$

subject to the following initial and boundary conditions

$$c(0 < x < L\,, t \leq 0) = 0\,, \tag{21b}$$

$$c(x = L\,, t > 0) = 0\,, \tag{21c}$$

and either

$$c(x = 0\,, t > 0) = c_o\,, \tag{21d}$$

or

$$D\, \partial c/\partial x = \kappa\, \{c_e - c\}\,, \qquad x = 0, t > 0. \tag{21e}$$

The solution can be expressed in the form

$$c(x,t) = e^{-\Lambda(t)}\, u(x,t) + \int_0^t \lambda(\tau)\, e^{\Lambda(s)}\, u(x,s)\, ds\,, \tag{22a}$$

where

$$\Lambda(t) = \int_0^t \lambda(\tau)\, d\tau\,, \tag{22b}$$

and u satisfies the conventional diffusion equation

$$D\, \partial^2 u/\partial x^2 = \partial u/\partial t\,, \tag{22c}$$

subject to the same initial and boundary conditions as c, *viz.* Eqs. (21b, c) and either Eq.(21d) or Eq.(21e).

This represents a generalization of Danckwert's transformation [13,§14.3]. It can be established by noting that if $c(x,t)$ is a solution of Eq.(21a) subject to Eqs.(21b,c) and either Eq.(21d) or Eq.(21e), then

$$w(x\,,\,t) = e^{\Lambda(t)}\, c(x,t) \tag{23a}$$

satisfies the conventional diffusion equation (22c), with conditions (21b,c) and either

$$w(x = 0, t > 0) = c_0\, e^{\Lambda(t)}\,, \tag{23b}$$

or

$$(D/\kappa)\, \partial w/\partial x + w = c_e\, e^{\Lambda(t)}\,, \qquad x = 0, t > 0\,. \tag{23c}$$

This solution $w(x,t)$ can be constructed from the solution $u(x,t)$ for constant right-hand sides in Eq.(23b) or Eq.(23c) by Duhamel's principle. Using the relation (23a) then gives $c(x\,,\,t)$ in the form (22a).

If Λ is a monotonic function of time, it can be used as a time-like parameter. Expressing concentrations as functions of x and Λ, the solution (22a) assumes the simpler form

$$c(x,\Lambda) = e^{-\Lambda}\, u(x,\Lambda) + \int_0^{\Lambda} e^{\omega}\, u(x,\omega)\, d\omega \tag{24}$$

Explicit results for $u(x,t)$ are available in standard books [13, 14], but detailed calculations for $c(x\,,\,t)$ using parameter values of interest in the hydrogen embrittlement context have yet to be performed.

4. REDISTRIBUTION OF SOLUTE DURING TWO-STAGE AGEING

Lynch [5] has suggested that the toughness improvement due to second ageing in aluminium-lithium alloys is due to a transient reduction in the solute (lithium) content on the grain boundary. For the purposes of mathematical modelling, one can assume that this boundary is planar on a length-scale comparable with the spacing between the solute-rich precipitates (δ-phase) lying on the boundary. That spacing is approximately $1\mu m$, whereas the grain dimension along the boundary is typically $100\mu m$. The precipitates can be considered to be lenticular, with a diameter of approximately $0.1\mu m$ in the grain boundary plane, and their height normal to that plane could be neglected for the purposes of stating boundary conditions, in the spirit of slender-body theory. Anticipating a simplified formulation as a two-dimensional problem, we may choose coordinates such that $y = 0$ is the boundary plane and the precipitates form a periodic array along the x-axis, with spacing $2b \approx 1\mu m$. On both sides of the boundary there is a solute-depleted layer known as the precipitate-free zone. During the first ageing treatment, when the alloy is held at a temperature $T_1 = 170°C$ for several hours, the thickness h of this zone increases (approximately) linearly with the square-root of ageing time. (This growth can be formulated as a Stefan problem similar to those discussed by other contributors at this conference). At the end of the first ageing, the thickness $h \approx 0.1\mu m$ and h can be assumed to remain unchanged during the second ageing, which lasts only for several minutes, albeit at a higher temperature $T_2 = 200°C$.

The material within a few atomic layers of the mathematical dividing plane $y = 0$ can be expected to differ structurally from the bulk matrix, and may be considered as a special "boundary phase" allowing much faster diffusion, as well as higher equilibrium solute content, than the adjacent bulk.

The mathematical problems are:

(i) to determine the quasi-equilibrium distribution of solute at the end of the first ageing, especially the solute concentration at the mid-point ($x=b$, $y=0$) between two boundary precipitates;

(ii) to determine the transient re-distribution due to an increase in temperature from T_1 to T_2, especially at $x=b$, $y=0$, starting from the quasi-equilibrium distribution determined in (i).

The aim is to see whether a transient reduction in the solute content on the boundary is predicted by a mathematical model, and if so whether an optimum duration for the second ageing can be identified. Since it is the concentration at the mid-point between two precipitates which is of greatest interest, it is not necessary to model the precipitates themselves in accurate detail: they may be treated as point sources (or sinks) distributed periodically along $y = 0$. However, the strength of these sources is not prescribed: it has to be determined so as to satisfy the boundary condition

$$c(x=a, y=0, t) = C_\delta(\mathrm{T}) \qquad (25a)$$

which would be satisfied at the boundary of an actual precipitate of radius a $(<b)$ centred at the origin. It is noted that $C_\delta(\mathrm{T})$ denotes the solute concentration in equilibrium with the δ-phase, and this changes on going from T_1 to T_2.

The next important step in the formulation is to account for solute enrichment and faster diffusivity at the boundary. A convenient way of proceeding is to imagine a separate boundary phase of thickness $l << h$ in which the solute concentration c_b is enriched relative to the adjacent bulk concentration,

$$c_b(x, t) = \alpha\, c(x, y \to l+, t)\,, \qquad (25b)$$

where α (>1) denotes the enrichment factor. Let B, D denote respectively the boundary and bulk diffusivities. In the present physical context, it is reasonable to assume that $B>D$, but the following mathematical formulation is not limited to that case. The conservation of matter within this boundary layer implies

$$l\,\{-B\, \partial^2 c_b/\partial x^2 + \partial c_b/\partial t\} = D\, \partial c(x, y \to l+, t)/\partial y\,, \qquad (25c)$$

for a source-free region of the boundary. Using Eq.(25b) and considering l to be vanishingly small, one can represent the effect of the boundary layer by the following boundary condition, which only involves the bulk concentration c,

$$D\, \partial c/\partial y + \alpha l\{B\, \partial^2 c/\partial x^2 - \partial c/\partial t\} = 0\,, \qquad y = 0+\,. \qquad (25d)$$

It is noted that the layer thickness and the enrichment factor do not appear separately but only in the combination αl, which has dimensions of length, and which is directly related to the thermodynamic concept of a surface excess $\Gamma(=\alpha l c)$; *i.e.* the preceding formulation applies equally to any concentration profile in the immediate vicinity of the boundary, provided that $\alpha l c$ in Eq.(25d) is interpreted as the surface excess [15].

If the effect of precipitates is simulated by a periodic array of sinks, each of (unknown) strength $2S$, the full boundary condition on $y = 0+$ can be written as

$$D\,\partial c/\partial y + \alpha l\,\{B\,\partial^2 c/\partial x^2 - \partial c/\partial t\} = S(t)\,\{\delta(x) + \sum_{n=1}^{\infty} \delta(x \pm nb)\}\,, \qquad (25e)$$

where $\delta(x)$ denotes the Dirac delta function. The mathematical problem is then reduced to solving the diffusion equation in the strip $0<y\leq h$, subject to a specified initial condition and to the boundary condition (25e) on $y = 0+$ and on $y=h$,

$$c(x, y=h, t) = C_\delta{}'(\mathrm{T}), \qquad (25f)$$

where $C_\delta{}'$ denotes the solute concentration in equilibrium with the metastable δ'-phase which is present in the bulk, beyond the precipitate-free zone (*i.e.* for $y > h$).

This problem is linear, and therefore amenable to integral-transform techniques, but to the author's knowledge, the only previous treatment of diffusion problems involving the boundary condition (25e) appears in [14,§14.11] and in the original papers cited there. In the present context, there are four characteristic lengths: αl, a, b and h, so that the best choice for normalized variables is not immediately obvious. We present here, as a first result of continuing work, the *steady-state* solution for an isolated source at the origin, between two half-spaces (*i.e.* assuming $b, h \to \infty$). A convenient choice of normalized variables for this case is

$$\xi = x\,D/(\alpha l B)\,, \quad \eta = y\,D/(\alpha l \mathrm{B})\,, \qquad (26a)$$

$$u(\xi,\eta) = c(x,y)/C_\delta(\mathrm{T}). \qquad (26b)$$

Then u satisfies Laplace's equation in the half-space $\eta > 0$, subject to the following boundary condition on $y = 0$,

$$\partial u/\partial\eta + \partial^2 u/\partial\xi^2 = S/(DC_\delta)\ \delta(\xi)\,, \tag{26c}$$

where the sink-strength S has to be chosen so as to satisfy the condition (25a), *i.e.*

$$u[\xi = aD/(B\alpha l), \eta = 0] = 1\,. \tag{26d}$$

It is found that $u(\xi,\eta)$ can be expressed as the real part of a complex potential $\Omega(\zeta)$, $\zeta = \xi + i\eta$, as follows

$$u(\xi,\eta) = S/(DC_\delta)\ \mathrm{Re}[\Omega(\zeta)]\,, \tag{27a}$$

$$\Omega(\zeta) = \pi^{-1} \int_0^\infty \frac{e^{i\zeta t}}{t(1+t)}\, dt\,, \qquad \mathrm{Im}(\zeta) > 0\,. \tag{27b}$$

The corresponding asymptotic expansions

$$\pi\ \Omega(\zeta) \simeq \gamma + i\zeta + \ldots\,, \qquad \zeta \to 0,\ |\arg \zeta| < \pi\,, \tag{28a}$$

$$\simeq -\ln(-i\zeta) - i/\zeta + \ldots\,, \qquad \zeta \to \infty,\ |\arg \zeta| < \pi\,, \tag{28b}$$

indicate that the presence of a boundary diffusion path removes the logarithmic singularity at the origin, while retaining that singularity at infinity.

5. CONCLUSION

Some recent and continuing work on diffusion problems arising in connection with aircraft structural alloys has been presented, focussing mainly on analytical results. There is considerable scope for further work on these topics relying on analytical techniques. These generally require the formulation to be simplified so as to retain only the most significant features of the problem, which is a considerable advantage when it comes to interpreting the results and assessing the implications of the model. However, even a relatively simple-looking non-linearity, such as that arising in the McNabb-Foster theory of trapping, appears to be beyond the reach of analytical techniques, and numerical techniques are necessary if one wishes to predict the permeation transient [16], which is required for the purposes of addressing the important inverse problem of determining the trapping parameters from experimental permeation curves, although some progress has been made by asymptotic and dimensional analysis [17,18].

I am grateful to Dr W.J. Pollock and Dr S.P. Lynch for initiating the work reported above, and to Dr S.K. Burke for a critical reading of the manuscript.

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