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MATHEMATICS OF THE THERMAL DIFFUSION OF HYDROGEN IN ZIRCALOY-2

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by

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Chalk River, Ontario

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By means of mathematical solutions to the appropriate diffusion equations we describe the kinetics of the thermal diffusion of hydrogen in Zircaloy-2 for the various temperatures and concentrations encountered in a heavy water moderated reactor. When the hydrogen concentration is below terminal solid solubility hydrogen is present only in the α-phase. Redistributions are then described in terms of the characteristic functions of the diffusion equation. For higher concentrations both the α- and δ-phases are present. We assume the two phases to be always in equilibrium. For moderately small hydrogen concentrations exact solutions of the two-phase equation approach the approximate solutions derived by Sawatzky and for all concentrations the exact solutions exhibit the qualitative features of his result: the two-phase concentration increases with time, everywhere; in the absence of a hydrogen current at the hot end of the sample an α-phase region always exists there; the interface of the α+δ, α-phase boundary moves toward the cold end of the sample and the hydrogen concentration is discontinuous at the interface. Simultaneous solutions of the α- and α+δ hydrogen distributions and of the concomitant interface motion are obtained and compared to the observations of Sawatzky and Markowitz. The kinetics of the hydrogen diffusion process are shown to lead to an apparent heat of transport of the α-phase which is lower than the actual value (even for samples with long anneals) thus resolving at least partially the disparity between experimental measurements of this quantity.

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I INTRODUCTION

A number of recent papers[1-4] have reported measurements on the diffusion and redistribution of hydrogen in Zircaloy -2 under temperature and concentration gradients. These studies were instigated by problems arising from increasing use of Zircaloy-2 as a fuel element cladding material in pressurized-water power reactors. The Zircaloy-2 picks up hydrogen during the operation of the reactor: the consequent precipitation of zirconium hydride in the Zircaloy-2 has pronounced effects on its mechanical properties.

The purpose of the present paper is to describe the kinetics of the thermal diffusion of hydrogen in Zircaloy-2 for the various hydrogen concentrations and temperatures likely to be encountered in reactors.

When the hydrogen in the Zircaloy-2 is entirely in the solid solution phase (α-phase) - that is the hydrogen concentration everywhere is below terminal solid solubility - then the differential equation for thermal diffusion is a well known one and the redistribution can be described by standard mathematical methods some of which are given in section III below. For larger hydrogen concentrations (above terminal solid solubility) the hydrid phase (δ-phase) is present as well.

When both the α and δ phases are present we follow previous authors in assuming that the two phases are always in equilibrium with each other. However, the hydrogen diffusion in both phases is fully taken into account. Shewmon[5] first pointed

out that for small hydride concentrations the $\alpha+\delta$ thermal diffusion takes place predominantly in the α-phase. Using this idea Sawatzky[3] solved the two-phase diffusion equation, in the linear geometry appropriate to his measurements, neglecting both the diffusion in the hydride phase and the reduction in the volume of the α-phase due to the presence of hydride. Modifications of Sawatzky's diffusion equation to take into account these effects were first suggested to us by Kidson[6]. The modified equation in linear geometry, has been published recently by Markowitz[4], although he does not attempt to solve it.

For the moderately small hydrogen concentrations which he used, Sawatzky found good agreement between his measurements and his approximate solution of the $\alpha+\delta$ diffusion kinetics. On the basis of his own measurements with cylindrical geometry Markowitz[4] has strongly attacked Sawatzky's approximate $\alpha+\delta$ solutions. Apparently he has neither understood the principal features of Sawatzky's solutions nor appreciated the importance of the difference between the solutions appropriate to cylindrical and to plane geometry.

Taking into the account the change in geometry, Sawatzky's approximate two-phase results are shown below to agree well with Markowitz's observed redistributions even though the initial hydrogen concentrations are far above terminal solid solubility.

In the next section we derive the modified two-phase equation for arbitrary geometry. The exact solution of this equation is given in section IV for linear and cylindrical geometry. It is shown that Sawatzky's approximate solution is quite accurate for almost all the temperatures and hydrogen concentrations which are actually encountered.

In Sawatzky's approximate theory the hydrogen concentration everywhere in the two-phase region increases continuously. As his paper pointed out, this result, together with hydrogen conservation, implies that in a sample with no hydrogen current flowing into the hot end a two-phase region is always accompanied by a single-phase region at the hot end of the sample. The net hydrogen gain in the two-phase region is supplied by the decrease of hydrogen in the single-phase region and by the movement of the (α, $\alpha+\delta$) boundary toward the cold end of the sample. Hydrogen conservation at the (α, $\alpha+\delta$) boundary leads to a discontinuity in the concentration and its derivative there. In Section VI it is shown how these qualitative features of the thermal diffusion kinetics arise from the simultaneous solution of the α-phase differential equation and $\alpha+\delta$ phase equation. Methods are derived for the solution of the redistribution in both phases and the accompanying motion of the boundary: approximate solutions valid for small and large times are given. The solutions account well for the observed redistributions of Sawatzky and Markowitz. It is shown how the continuing motion of the (α, $\alpha+\delta$) boundary leads to measured values of the heat of transport lower than the actual value, even for specimens with relatively long anneals.

II THE BASIC DIFFUSION EQUATIONS

At each temperature in Zircaloy-2, the maximum amount of hydrogen which can be in the solid solution phase (α-phase) is called the terminal solid solubility, N_α, given by

$$N_\alpha = N_\alpha^{(o)} e^{-\Delta H/RT} \tag{1}$$

where $N_\alpha^{(o)}$ is a constant, T the temperature in ^oK, R the gas constant and ΔH the heat of mixing. Values of $N_\alpha^{(o)}$ and ΔH have been measured by Sawatzky[2]. Hydrogen in excess of N_α precipates out as hydride (δ-phase).

When only the solid-solution phase is present the hydrogen current J, is simply

$$J = -D_\alpha \{\vec{\nabla} N + \frac{Q_\alpha{}^* N}{RT^2} \vec{\nabla} T\} \tag{2}$$

where D_α is the diffusivity, $Q_\alpha{}^*$ the heat of transport, N the hydrogen concentration and $\vec{\nabla}$ the gradient operator. The expression (2) for the α-phase current is strictly valid only for the case of isotropic diffusion. Hence it does not hold for single Zr crystals but is valid for polycrystals. The diffusivity is temperature dependent:

$$D_\alpha = D_\alpha^{(o)} e^{-Q_\alpha/RT} \tag{3}$$

where $D_\alpha{}^{(o)}$ is the frequency factor and Q_α the activation energy of the alpha phase. Measurements of $D_\alpha{}^{(o)}$ and Q_α have been given by a number of workers[7]. The measurements of $Q_\alpha{}^*$[8] are not in good agreement with each other. However, as shown below, the disagree-

ment between the various measurements may be at least partially resolved by properly taking into account the kinetics of the thermal diffusion of hydrogen.

In (2), the first term on the right gives the hydrogen current arising from the concentration gradient; the second term arises from the temperature gradient. The change of hydrogen concentration with time is obtained from (2) by means of the continuity equation.

$$\frac{dN}{dt} = -\vec{\nabla}.\vec{J} = D_\alpha \nabla^2 N + \vec{\nabla}N.\left(\vec{\nabla}D_\alpha + \frac{D_\alpha Q_\alpha^*}{RT^2}\vec{\nabla}T\right) + N\vec{\nabla}\cdot\left(\frac{D_\alpha Q_\alpha^*}{RT^2}\vec{\nabla}T\right) \quad (4)$$

Given a sample with an initial (t=0) distribution of hydrogen and with a given hydrogen current at each boundary of the sample, (4) may be used to solve for the hydrogen distribution at all times t subsequent to t=0. In Section III a method of solving (4) is discussed and applied to observed redistributions.

In the two-phase region, where N exceeds N_α, we assume that at every point the α and δ phases are in equilibrium with each other so that the concentration of the solid solution is N_α. Sawatzky's treatment of the two-phase region followed Shewmon[7] in assuming that the diffusion of hydrogen occured primarily in the α-phase rather than in the hydride: both the diffusion through the hydride and the reduction of the α-phase volume caused by the presence of the hydride are neglected. Then the solution for the hydrogen concentration in the two-phase region is simple. We use (2) above, for the current replacing the actual hydrogen

concentration by the solid solution concentration N_α, obtaining

$$\vec{J}_\alpha = -D_\alpha \{\vec{\nabla} N_\alpha + (Q_\alpha^* N_\alpha / RT^2) \vec{\nabla} T\} \qquad (5)$$

Using $\vec{J}_\alpha$ in the continuity equation (4) we obtain

$$\frac{dN}{dt} = -\vec{\nabla} \cdot \vec{J}_\alpha = \vec{\nabla} \cdot D_\alpha (\vec{\nabla} N_\alpha + \frac{Q_\alpha^* N_\alpha}{RT^2} \vec{\nabla} T) \qquad (6)$$

The $\alpha+\delta$ results of Sawatzky correspond to solutions of the approximate two-phase equation (6) specialized to the linear geometry of his measurements. The important features of his results are independent of geometry. Thus, since the right side of (6) is independent of N the total hydrogen concentration of (6) increases linearly with the time everywhere in the two-phase region. This fact together with hydrogen conservation is sufficient to yield the other important features of the redistribution discussed in the introduction and below, that is, the development of an α-phase region at the hot end of the sample, the movement of the $\alpha+\delta$, α interface toward the cold end of the sample and the development of a hydrogen concentration discontinuity at the $\alpha+\delta,\alpha$ interface.

The modifications of (6) to take into account the effects of the hydride were pointed out to us by Kidson[6] and have been published independently by Markowitz[4] (for the special case of linear geometry). They are based on the following expression for the current $\vec{J}$,

$$\vec{J} = \vec{J}_\alpha A_\alpha + \vec{J}_\delta A_\delta \tag{7}$$

where $\vec{J}_\alpha$ is the α-phase flux, (5), above, $\vec{J}_\delta$ is the δ-phase flux while A_α and A_δ are the fractional areas occupied by each component at a cross section normal to the flux. The areas are taken as equal to the relative amounts of α- and δ- phases present at each temperature, that is

$$A_\alpha = (N_\delta - N)/(N_\delta - N_\alpha) , \tag{8}$$

$$A_\delta = (N - N_\alpha)/(N_\delta - N_\alpha) , \tag{9}$$

where N_δ is the $(\alpha+\delta,\delta)$ phase boundary hydrogen concentration. The areas (8) and (9) are based on the assumption that the densities of the α and δ phases are equal. The hydrogen current in the hydride phase, J_δ, is similar to (2)

$$\vec{J}_\delta = -D_\delta \{\vec{\nabla} N_\delta + \frac{Q_\delta^* N_\delta}{RT^2} \vec{\nabla} T\} , \tag{10}$$

where Q_δ^* is the δ-phase heat of transport, D_δ is the δ-phase diffusivity,

$$D_\delta = D_\delta^{(o)} \; e^{-Q_\delta/RT} , \tag{11}$$

$D_\delta^{(o)}$ is the frequency factor and Q_δ the activation energy of the δ-phase. Below 450°C, N_δ is roughly temperature independent[8] so that we can neglect the gradient $\vec{\nabla} N_\delta$ in (10).

Using the current (7) in the continuity equation (4) yields the following general differential equation for the two-phase hydrogen concentration, applicable to any geometry:

$$\frac{dN}{dt} = \vec{\nabla}N \cdot \frac{1}{N_\delta - N_\alpha}\left[-D_\alpha \vec{\nabla}N_\alpha - \frac{D_\alpha Q_\alpha{}^* N_\alpha}{RT^2}\vec{\nabla}T + \frac{D_\delta Q_\delta{}^* N_\delta}{RT^2}\vec{\nabla}T\right]$$

$$+ N\vec{\nabla} \cdot \frac{1}{N_\delta - N_\alpha}\left[-D_\alpha \vec{\nabla}N_\alpha - \frac{D_\alpha Q_\alpha{}^* N_\alpha}{RT^2}\vec{\nabla}T + \frac{D_\delta Q_\delta{}^* N_\delta}{RT^2}\vec{\nabla}T\right] \tag{12}$$

$$+ \vec{\nabla} \cdot \frac{1}{N_\delta - N_\alpha}\left[N_\delta D_\alpha \vec{\nabla}N_\alpha + \frac{N_\alpha N_\delta D_\alpha Q_\alpha{}^*}{RT^2}\vec{\nabla}T - \frac{N_\delta N_\alpha D_\delta Q_\delta{}^*}{RT^2}\vec{\nabla}T\right]$$

The right side of (12) has three terms, one proportional to the gradient $\vec{\nabla}N$, of the total hydrogen concentration, another proportional to N and the other independent of N. Although (12) is not as simple as the approximate two-phase equation (6), employed by Sawatzky, we give exact solutions of (12) in Section IV below and compare them to the solutions of (6). The exact solutions of (12) are not too difficult because (12) contains only first order time and position derivatives of N, - unlike the single-phase equation (4) which contains second-order position derivatives.

In the following sections we give solutions not only for the α-phase equation separately and the $\alpha+\delta$ equation separately but also for the more general case in which a sample contains regions of both types separated by a moving interface. As will be shown an $\alpha+\delta$ region is almost always accompanied by an α-phase region so that in most problems of practical interest one must actually take both regions into account. The results obtained are compared to the redistributions observed by Sawatzky[3] and Markowitz[4].

III REDISTRIBUTION IN THE ALPHA-PHASE

We shall specialize the single-phase differential equation (4), to the linear geometry used by Sawatzky[3] and to the cylindrical geometry of Markowitz[4]. To facilitate the computations given below we change variables

$$y = 1/T \tag{13}$$

In the linear geometry the temperature varies only in the one direction, $\vec{r}$, and all quantities including the concentration are assumed to be constant in directions perpendicular to $\vec{r}$. The heat conductivity of Zircaloy-2 is assumed to be temperature independent so that the temperature gradient along $\vec{r}$ is assumed to have a constant value K,

$$\frac{dT}{dr} = K, \tag{14}$$

Noting that, for the linear geometry, $\vec{\nabla}N = -Ky^2\ dN/dy$ along $\vec{r}$ and that $\vec{\nabla}.\vec{J} = -Ky^2\ dJ/dy$ for a $\vec{J}$ along $\vec{r}$, the differential equation (4) reduces to

$$\frac{dN}{dt} = K^2 D_\alpha y^4 \left[\frac{d^2N}{dy^2} + \left(\frac{2}{y} - \frac{Q_\alpha + Q_\alpha^*}{R}\right)\frac{dN}{dy} - \frac{Q_\alpha^*}{R}\left(\frac{2}{y} - \frac{Q_\alpha}{R}\right)N\right] \tag{15}$$

For the cylindrical geometry of Markowitz the temperature varies in cylindrical coordinates, only with the radius parameter, r. If the temperature dependence of the conductivity is again neglected we have

$$\frac{dT}{dr} = K'/r \tag{16}$$

where K' is a constant. The gradient and divergence are different in this geometry: $\vec{\nabla}N = dN/dr = -\frac{K'y^2}{r}\frac{dN}{dy}$ along the radius vector and $\vec{\nabla}.\vec{J} = \frac{1}{r}\, d(rJ)/dr = -\frac{K'}{r^2}\, y^2 \frac{d}{dy}\,(rJ)$ for a current along the radius vector. The resulting differential equation for cylindrical geometry is identical to (15) if, on the right side of (15), we replace K^2 by $(K'/r)^2$. In this section we shall develop the solutions of (15) and mention only briefly the modifications which occur when cylindrical geometry is used.

To solve (15) we need to specify an initial distribution of hydrogen (at t=0) and boundary conditions at the cold end, y_2, and hot end, y_1, of the sample. The boundary condition at the ends of the sample are given by the hydrogen current there. We develop, first, the solution for zero current at both ends of the sample and then give the modifications in the solution when a constant current flows through the sample. For linear geometry the hydrogen current, (2), reduces to

$$J = KD_\alpha\, y^2 \left[\frac{dN}{dy} - \frac{Q_\alpha^*}{R}\, N\right] \tag{17}$$

and the boundary conditions are

$$J(y_1) = J(y_2) = 0 \tag{18}$$

The method of solution which we employ is very closely analogous to the Fourier series solution of heat flow

problems. We look for solutions of the following form:

$$N(y,t) = \Sigma_\lambda a_\lambda \; e^{-E_\lambda t} \; N_\lambda(y) \tag{19}$$

where the a_λ are a set of expansion coefficients, and where each eigenfunction, N_λ, satisfies the equation

$$K^2 y^4 D_\alpha \left\{ \frac{d^2 N_\lambda}{dy^2} + \left(\frac{2}{y} - \frac{Q_\alpha + Q_\alpha^*}{R} \right) \frac{dN_\lambda}{dy} - \left(\frac{2}{y} - \frac{Q_\alpha}{R} \right) \frac{Q_\alpha^*}{R} N_\lambda \right\} = -E_\lambda N_\lambda \tag{20}$$

with an eigenvalue E_λ and the following boundary conditions at y_1, y_2.

$$\frac{dN_\lambda}{dy} = \frac{Q_\alpha^*}{R} \; N_\lambda \qquad \Big|_{y=y_1,\; y_2} \tag{21}$$

The eigenvalues, E_λ, of (20) are assumed to be real, non-degenerate, and non-negative and the eigenfunctions, N_λ, are assumed to form a complete orthonormal set of functions, that is

$$\int_{y_1}^{y_2} N_\lambda(y) \; N_\lambda'(y) \; f\,(y) \; dy = \delta_{\lambda\lambda'} \tag{22}$$

where f(y) is an appropriate weight function.

By substitution of the suggested solution, (19) into the differential equation (15) it is easily verified that (19) is indeed a solution of (15). Also since each N_λ satisfies the boundary conditions (18) the whole sum does also. Further more, if $N^{(o)}(y)$ is the initial distribution of hydrogen and if the N_λ are a complete orthonormal set of functions, as implied

by (22), then the expansion coefficients a_λ can be found by multiplying both sides of (19), for t=0, by $N_{\lambda'}(y)\ f(y)$ and integrating over all values of y between y_1 and y_2. The result is

$$a_{\lambda'} = \int_{y_1}^{y_2} N^{(o)}(y)\ N_{\lambda'}(y)\ f(y)\ dy \tag{23}$$

Therefore all we need to do to complete the solution is to find the weight function f(y) which makes the eigenfunctions $N_\lambda(y)$ orthogonal to each other.

To construct the weight function*, f(y) we begin by writing each N_λ as a product

$$N_\lambda \equiv H(y)\ G_\lambda(y) \tag{24}$$

where H(y) is independent of λ and chosen so that the differential equation for G_λ, derived from (20) contains no first-order derivatives of G_λ with respect to y. The removal of the first order derivatives will make it simpler for us to establish the desired orthogonality properties of the eigenfunctions. The H(y) which has this property is

$$H(y) = \frac{1}{y}\ e^{\frac{1}{2}\left(\frac{Q_\alpha}{R} + \frac{Q_\alpha^*}{R}\right) y} \tag{25}$$

although any constant multiple of (25) would serve as well. Then equation (20) changes to (after dividing both sides of (20) by $K^2 y^4\ D_\alpha\ H$)

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* The reader who is willing to accept the result ((32), below) for the weight function, without going through the intervening mathe- may proceed to the middle of page 14.

$$\frac{d^2G_\lambda}{dy^2} + \left(\frac{Q_\alpha - Q_\alpha^*}{R}\right)^2 \left[\frac{1}{\left(\frac{Q_\alpha - Q_\alpha^*}{R}\right)y} - \frac{1}{4}\right] G_\lambda = -K^{-2}y^{-4}D_\alpha^{-1}\, E_\lambda G_\lambda \qquad (26)$$

We write down the same equation for $G_{\lambda'}$, that is

$$\frac{d^2G_{\lambda'}}{dy^2} + \left(\frac{Q_\alpha - Q_\alpha^*}{R}\right)^2 \left[\frac{1}{\left(\frac{Q_\alpha - Q_\alpha^*}{R}\right)y} - \frac{1}{4}\right] G_{\lambda'} = -K^{-2}y^{-4}D_\alpha^{-1}\, E_{\lambda'}G_{\lambda'} \qquad (27)$$

We multiply (26) by $G_{\lambda'}$, (27) by G_λ, subtract and integrate to obtain

$$\int_{y_1}^{y_2} \left(G_{\lambda'} \frac{d^2G_\lambda}{dy^2} - G_\lambda \frac{d^2G_{\lambda'}}{dy^2}\right) dy = (E_\lambda - E_{\lambda'}) \int_{y_1}^{y_2} K^{-4}D_\alpha^{-1} G_\lambda G_{\lambda'} dy \qquad (28)$$

The boundary condition (21) for G_λ is

$$\frac{dG_\lambda}{dy} = \left(\frac{1}{y} - \frac{1}{2}\,\frac{Q_\alpha - Q_\alpha^*}{R}\right) G_\lambda \Big|_{y=y_1,\ y_2} \qquad (29)$$

If we integrate both terms on the left side of (28) partially we obtain

$$\int_{y_1}^{y_2} \left(G_{\lambda'} \frac{d^2G_\lambda}{dy^2} - G_\lambda \frac{d^2G_{\lambda'}}{dy^2}\right) dy = G_{\lambda'} \frac{dG_\lambda}{dy} - G_\lambda \frac{dG_{\lambda'}}{dy} \Big|_{y = y_1} \qquad (30)$$

which vanishes according to the boundary condition (29). Hence (28) becomes

$$0 = (E_\lambda - E_{\lambda'}) \int_{y_1}^{y_2} K^{-2}\, y^{-4}\, D_\alpha^{-1}\, G_\lambda G_{\lambda'}\, dy$$

$$= (E_\lambda - E_{\lambda'}) \int_{y_1}^{y_2} f(y)\, N_\lambda(y)\, N_{\lambda'}(y)\, dy \tag{31}$$

where

$$f(y) = K^{-2}\, y^{-4}\, D_\alpha^{-1}\, H^{-2} = \left(K^2 y^2\, D_\alpha(o)\, e^{\frac{Q_\alpha^*}{R} y}\right)^{-1} \tag{32}$$

Since the eigenvalues are assumed to be non-degenerate (that is $E_\lambda \neq E_{\lambda'}$ for $\lambda \neq \lambda'$) (31) shows that the orthogonality conditions (22) holds if the weight function is defined as in (32). This completes the proof that (19) is a satisfactory solution of the alpha-phase differential equation.

The lowest eigenvalue, E_o, is identically zero and the corresponding eigenfunction N_o corresponds to zero current everywhere. From (17) we find

$$N_o = c_o\, e^{Q_\alpha^*\, y/R} \tag{33}$$

where c_o is a normalizing coefficient,

$$c_o = \left[\int_{y_1}^{y_2} e^{2Q_\alpha^*\, y/R}\, f(y)\, dy\right]^{-\frac{1}{2}}$$

$$= (K^2 D_\alpha(o))^{\frac{1}{2}} \left[\frac{e^{Q_\alpha^* y_1/R}}{y_1} - \frac{e^{Q_\alpha^* y_2/R}}{y_2} + \frac{Q_\alpha^*}{R}\left\{E_i\left(\frac{Q_\alpha^*}{R}\, y_2\right) - E_i\left(\frac{Q_\alpha^*}{R}\, y_1\right)\right\}\right]^{-\frac{1}{2}} \tag{34}$$

The exponential integral, $E_i(x)$, in (34) is defined by

$$E_i(x) = \int_{-\infty}^{x} e^{-t} dt/t \tag{35}$$

and numerous tables of it exist.

The expansion coefficient, for the mode $\lambda = 0$ is easily found if the initial hydrogen concentration, $N^{(o)}$, is constant. We then find, from (23)

$$a_o = (N^{(o)} c_o / K^2 D_\alpha{}^{(o)}) \left(\frac{1}{y_1} - \frac{1}{y_2}\right) \tag{36}$$

For $\lambda > 0$ the eigenvalues E_λ are all positive. The solution (19) has, therefore, a very plausible behaviour: as the time increases from $t = 0$ all of the modes other than $\lambda = 0$ decay exponentially. The zero current mode ($\lambda = 0$) is the final equilibrium distribution of hydrogen attained by (19) at large values of t. It is easily verified that this final distribution, $a_o\ c_o\ e^{Q_\alpha{}^* y/R}$, contains the same amount of hydrogen as present initially.

Unfortunately the higher modes ($\lambda > 0$) cannot be evaluated, as was that for $\lambda = 0$, in terms of simple transcendental functions. Some of the higher eigenvalues, E_λ, and eigenfunctions, N_λ, were computed directly from (20) by Dr. J.M. Kennedy with the Chalk River Datatron Computer, for a temperature range and gradient typical of Sawatzky's experiments. The constants used in this calculation were $Q_\alpha{}^*/R = 3050°K$, $D_\alpha{}^o = 2.17 \times 10^{-3}$ cm^2/sec,

$Q_\alpha/R = 4180°K$, temperature gradient 80 deg/cm, hot end temperature 500°C and cold end temperature 300°C. It was found that the lower eigenvalues are all very nearly given by $E_\lambda = \lambda^2/46$ hours^{-7}. Thus even at 1 hour all modes higher than the sixth or seventh have substantially decayed. In addition the initial constant distribution itself is quite well fitted when only the terms with $\lambda = 0, 1, 2, 3$ are retained, the error being only 7% at the ends of the sample and 3% elsewhere. This error itself, being due to neglect of higher terms, is rapidly damped out with time. The shape of the resulting distributions, at several times, is shown in Figure 1.

The difference between the slope and value of the curves on Figure 1 for finite t from that for $t = \infty$ leads to an error in the heat of transport estimated from these curves. Unless t is more than 4 days this error may be as large as 10%.

Although the exact eigenfunction (other than $\lambda = 0$) cannot be expressed analytically there is an acceptable approximation method which makes these functions more tractable. We make the following three approximations:

1) In (27) we ignore the second term on the left because it happens to be small (for $\lambda \neq 0$ and with the constants appropriate to Zircaloy-2) compared to the right side of (27). This approximation is also valid for cylindrical geometry.

2) On the right side of (27) and in (32) we regard $y^{-4} D_\alpha^{-1}$ as independent of y. For the temperature range of Figure 1

this quantity in fact varies only by about 30% for Zircaloy-2. However for cylindrical geometry the corresponding approximation would be untenable, except for very small temperature ranges.

3) In the boundary conditions, (29), the bracket on the right side of (29) is very small compared to the reciprocal of the period of oscillation of the eigenfunctions so that we can approximate (29) by setting $dG_\lambda/dy = 0$. This approximation depends again on the particular constants of Zircaloy-2 but will also hold for cylindrical geometry.

The first two approximations makes the eigenfunctions trigonometric ones. The third states that they have zero derivative at both y_1 and y_2. Therefore they are

$$N_\lambda = c\ H(y)\ \cos\left(\lambda\pi\ \frac{y-y_1}{y_2-y_1}\right) \tag{37}$$

where c is a constant independent of λ and y. The value of c can be determined from the orthogonality condition (22) to be

$$c = \left(K^2\ y^4\ D_\alpha\ \frac{2}{y_2-y_1}\right)^{\frac{1}{2}} \tag{38}$$

In (37) λ takes on all integral values from 0 upwards. To show how good these approximate eigenfunctions are, the calculations shown on Fig. 1 have been repeated, on Fig. 2, using the approximate eigenfunctions. The approximate redistributions differ only slightly from the exact ones. It should be noted that the

most critical approximation made above is the second one: this approximation becomes better as the temperature range, y_2-y_1, is decreased. The eigenvalues, E_λ, corresponding to the approximate eigenfunctions are proportional to λ^2.

$$E_\lambda \equiv \lambda^2 E = \frac{\lambda^2\pi^2}{(y_2-y_1)^2} K^2 D_\alpha y^4 \tag{39}$$

where the constant of proportionality, E, is 1/46 hours^{-1} for the case discussed on Fig. 2. The first ten approximate eigenvalues for this case differ from the corresponding exact values by less than 1%.

No calculations have been carried out for cylindrical geometry although the exact solution developed above holds for that geometry if we replace K^2, in the weight function (32), by $(K'/r)^2$.

The solutions discussed thus far correspond to zero current at the boundaries of the sample. A constant current, J_o, flowing into one boundary and out of the other is easily accommodated in the solution. We describe first the equilibrium solution, N', with constant current J_o, everywhere. According to (17) we then have

$$\frac{dN'}{dy} - \frac{Q_\alpha^* N'}{R} = J_o(K D_\alpha^{(o)} y^2)^{-1} e^{Q_\alpha y/R} \tag{40}$$

We solve (40) by writing, first

$$N'(y) = e^{+Q_\alpha^* y/R} M(y) \tag{41}$$

so that M(y) satisfies the equation

$$\frac{dM}{dy} = J_o(KD_\alpha^{(o)}\ y^2)^{-1}\ e^{(Q_\alpha - Q_\alpha^*)\ y/R} \tag{42}$$

which can be integrated directly, in the same way as (34) above, to yield

$$N'(y) = J_o(KD_\alpha^{(o)})^{-1}\left[-\frac{1}{y}\ e^{Q_\alpha y/R} + \frac{Q_\alpha - Q_\alpha^*}{R}\ e^{Q_\alpha^* y/R}\ E_i\left(\frac{Q_\alpha - Q_\alpha^*}{R}\ y\right)\right] + A\ e^{Q_\alpha^*\ y/R} \tag{43}$$

where A is an integrating constant determined, for example by the value of N'(y) at any one given point.

The redistribution of hydrogen in a sample with constant current at both boundaries will, for large time t, approach the equilibrium solution (43). If the initial hydrogen distribution is $N^{(0)}$ then we choose the constant A, in (43) so that the final hydrogen distribution contains the same amount of hydrogen as the initial distribution, that is

$$\int_{y_1}^{y_2} N^{(0)}\ dy/y^2 = \int_{y_1}^{y_2} N'\ dy/y^2 \tag{44}$$

To find the hydrogen distribution at any finite time we write N = N' + (N-N') and analyze the difference (N-N') in a series of eigenfunctions corresponding to zero current at the boundary as it was done above. It follows at once from the choice

of the constant A that the coefficient, a_o, of the lowest eigenfunction vanishes identically. The higher modes decay exponentially to yield the asymptotic solution $N \rightarrow N'$. Since N' carries a current J_o everywhere and since N-N' has zero current at the ends of the sample the superposition of N' and (N-N') has the desired behaviour at the boundary.

An illustration of the constant current solution, N', is given on Fig. 3 for a case which is used below to discuss the diffusion kinetics when both α-phase and α+δ regions exist. In the alpha phase part of the figure (above 245°C) the solid line is the constant current solution with $J_o = 1.12 \times 10^{-4}$ ppm cm/sec. The constant A of (43) is chosen so that the hydrogen concentration at 245°C is equal to terminal solid solubility. For comparison the figure also shows a zero current distribution normalized to the same hydrogen concentration at 245°C.

IV REDISTRIBUTION IN THE TWO-PHASE REGION

In the linear geometry of Sawatzky the two-phase equation (12) reduces to

$$\frac{dN}{dt} = - K^2 y^2 \frac{d}{dy} \{g(y)\ N + h(y)\ N_\delta\} \tag{45}$$

where

$$g(y) = y^2 (N_\delta - N_\alpha)^{-1} \left[N_\delta D_\delta \frac{Q_\alpha{}^*}{R} - N_\alpha D_\alpha \left(\frac{\Delta H}{R} + \frac{Q_\alpha{}^*}{R} \right) \right] \tag{46}$$

$$h(y) = y^2 (N_\delta - N_\alpha)^{-1} \left[N_\alpha D_\alpha \left(\frac{\Delta H}{R} + \frac{Q_\alpha{}^*}{R} \right) - N_\alpha D_\delta \frac{Q_\alpha{}^*}{R} \right] \tag{47}$$

We have used the fact that N_δ is approximately constant. Again, for cylindrical geometry the equation (45) applies if we replace K^2 by $(K'/r)^2$. The differential equation (45) was written down by Markowitz[4] and he asserts that its solution is either difficult or impossible. In fact (45) is easily solved in several ways. One method of solution consists in recognizing that the term $\frac{d}{dy} \{g(y)N\}$ of (45) is small compared to $\frac{d}{dy}$ (h(y)) unless N is close to N_δ. Because of this fact we can treat the term arising from $\frac{d}{dy}$ (g N) as a perturbation and write N as a series:

$$N(y,t) = \sum_{n=o}^{\infty} N^{(n)}(y)\ t^n \tag{48}$$

where $N^{(o)}$ is the initial hydrogen distribution. Inserting the series (48) into (45) and equating equal powers of t on both sides yields recursion relations for the higher functions $N^{(n)}$.

$$N^{(1)} = - K^2 y^2 \left\{ g \frac{dN^{(0)}}{dy} + N^{(0)} \frac{dg}{dy} + \frac{dh}{dy} N_\delta \right\} \tag{49}$$

$$N^{(n)} = - \frac{K^2 y^2}{n} \left\{ g \frac{dN^{(n-1)}}{dy} + N^{(n-1)} \frac{dg}{dy} \right\}, \quad n \geqslant 2 \tag{50}$$

In all cases of practical interest the series (48) appears to converge very rapidly. The first two terms on the right side of (48) correspond, very nearly, to the approximate solution for the two-phase region given by Sawatzky[3].

An exact solution of (45) not involving an infinite series can also be given and is used in the computations described below. To derive the solution we define a new function $H(y,t)$ to replace $N(y,t)$ and a new variable, z, to replace y:

$$H(y,t) \equiv (Ng + N_\delta h) \tag{51}$$

and

$$z \equiv - \int_{y_1}^{y} \frac{dy'}{(y')^2 \, g(y')} \tag{52}$$

where y_1 is an arbitrary point, e.g., the hot end of the two phase region at $t = 0$. Then (45) reduces to

$$\frac{dH}{dt} = - K^2 \, g y^2 \frac{dH}{dy} = K^2 \frac{dH}{dz} \tag{53}$$

We change variables again in the following way

$$u \equiv K^2 t + z$$
$$v \equiv K^2 t - z \tag{54}$$

in terms of which (53) may be written

$$\frac{dH}{dv} = 0 \tag{55}$$

Consequently H(u,v) must be independent of v but it may be an arbitrary function of u. The arbitrariness is removed by the initial condition. For t = 0 we have

$$H(y,o) = [N^{(o)} g + N_\delta h] \tag{56}$$

where $N^{(o)}$ is the initial hydrogen concentration. By means of the transformation (52) we can write

$$H(y,o) \equiv S(z) \tag{57}$$

where S(z) is the initial value of H as a function of z. According to (54) and (55), however, at all later times we must have

$$H(y,t) = S(z + K^2 t) \tag{58}$$

and, from (51),

$$N(y,t) = g^{-1} [H(y,t) - hN_\delta]$$
$$= g^{-1} [S(z+K^2 t) - hN_\delta] \tag{59}$$

which completes the exact solution.

The only computational difficulty arises in the connection between z and y, given by (52) which must be integrated numerically. The function g may have a singularity in which case the principal value of the integral in (52) must be taken. For cylindrical geometry the only change in the above procedure is to change K^2 to $(K')^2$ everywhere and to multiply the integrand on the right side of (52) by r^2.

The practical application of the above method is illustrated by means of Fig. 4 which shows h, g, and z plotted against y. The values of z shown on Fig. 4 were obtained from (52) by numerical integration for a choice of y_1, in (52) of $(800^\circ K)^{-1}$. To obtain N(y,t), for a given y,t, from a given initial hydrogen distribution $N^{(o)}(y)$ we first look up the value of z corresponding to y. We then augment z by K^2t, to $z'' = z + K^2t$, and look up the value, y", corresponding to z". From (57) we get

$$S(z + K^2t) \equiv S(z'') = N^{(o)}(y'')\ g(y'') + h(y'')\ N_\delta \tag{60}$$

yielding

$$N(y,t) = \frac{g(y'')}{g(y)} N^{(o)}(y'') + N_\delta \frac{h(y)}{g(y)} \left[\frac{h(y'')}{h(y)} - 1\right] \tag{61}$$

Knowing y,y" we merely need to look up the values of g and h at both points and to look up $N^{(o)}$ at y" in order to obtain N(y,t).

The second term on the right side of (61) is always positive. To prove this, for example, we observe, from Figure 4, that h/g is negative for $T > 480^\circ K$. However, since h increases

monotonically with T and z decreases monotonically with T ($T > 480^{\circ}$) we have $[h(y'')/h(y)] < 1$ so that the whole term is indeed positive. A similar proof may be given for temperatures below 480°K. Most of the increase in the hydrogen concentration arises from this term in (61). For moderate hydrogen concentrations this second term corresponds very closely to the approximate solution of Sawatzky. The first term contains modifications in the solution arising from the presence of hydride in the two-phase region.

The dominant features of the kinetics of hydrogen diffusion in $\alpha+\delta$ Zircaloy-2 are the tendency of the hydrogen concentration to increase everywhere in the two-phase region and the impossibility of achieving zero-current anywhere in the two-phase region. By choosing $N^{(o)}(y)$ to be an appropriate function of y it is possible to have the concentration at y decrease initially. This is not typical. For example, for a distribution which is initially constant we find, independent of the constant value

$$N(y,t) \geqslant N^{(o)}(y) \qquad t > 0 \tag{62}$$

Consequently, either a net hydrogen current flows into the two-phase region or the size of the two-phase region shrinks with time.

In the two phase region the hydrogen current for linear geometry, is given by

$$J(y) = K[g(y)\ N(y,t) + h(y)N_{\delta}] \tag{63}$$

If we wish to have a zero current at y we find

$$J(y) = 0 = K(g\ N + hN_\delta) \tag{64}$$

$$\text{or} \qquad N = -\ hN_\delta/g \tag{65}$$

a result which also holds for cylindrical geometry. However it is obvious from Fig. 4 that the concentration $-\ hN_\delta/g$ is everywhere unphysical. Above 480°K it lies above N_δ, below 480°K it is negative. In particular no boundary with zero current can exist for a two-phase region. Even if a hydrogen current is fed into the sample in order to maintain a two-phase region at the boundary the current J will have to vary with time, as N varies, precisely so that (63) is satisfied. In general, therefore, a two-phase region will not exist at the boundary of a sample. If it exists there initially it will immediately begin shrinking from the boundary. Even more, because zero current in the two-phase region cannot be attained, anywhere, for any hydrogen distribution in the two-phase region, the equilibrium distribution attained at large times by a sample with no hydrogen current at its boundaries cannot possibly contain a two-phase region.

It is interesting to note the simple way in which the temperature gradient enters into the exact solution (see equation (59)). If a calculation is made for a definite value of K and t and if we choose a new temperature gradient, K" the original solution will now hold for a new time t" such that $(K'')^2\ t'' = K^2 t$.

Figure 5 shows calculations of the two-phase hydrogen distribution made with (61) for K = 100 deg/cm. and t = 10, 30 and 100 days (or, more correctly, for $K^2t = 10^5$, 3×10^5 and 10^6 (deg./^{2} days/(cm)^2). The gain in hydrogen distribution is plotted against temperature for an initial constant concentration which is small ($N^{(o)} = 0$ in (61)) and for $N^{(o)} = 5000$ p.p.m. All the computed curves are compared withones obtained with Sawatzky's simple model. The constants used in the calculations are $N_\delta = 1.6 \times 10^4$ p.p.m., $N_\alpha^{(o)} = 8.5 \times 10^4$ p.p.m., $\Delta H/R = 3820^oK$, $D_\alpha^{(o)} = 2.17 \times 10^{-3}$ cm^2/sec, $Q_\alpha/R = 4170^oK$, $Q_\alpha^*/R = 3015^oK$, $D_\delta^{(o)} = 1.09 \times 10^{-3}$ cm^2/sec, $Q_\delta/R = 5730^oK$, $Q_\delta^*/R = 653^oK$.

It is quite evident from the figure that Sawatzky's model is quite accurate for all moderate concentrations (say $N < 1000$ p.p.m.). At higher concentrations two kinds of deviations from Sawatzky's approximate result occur. The first, which is most important, is the reduction of the alpha phase diffusion caused by the presence of hydride. This purely geometric effect is seen on the figure at high temperatures where the hydride concentration is largest. At the lowest temperatures shown on the figure a second effect - the actual diffusion in the hydride phase - becomes important, illustrated on the figure by the increased gain of the curve for $N^{(o)} = 5000$ p.p.m. It is quite possible that at these low temperatures the hydride diffusivity is much smaller than assumed on Figure 5 so that the diffusion in the hydride is always negligible.

More illustrations of two-phase solutions will be given in the next section in which the redistribution in the two-phase region and the single-phase region are treated simultaneously.

V SIMULTANEOUS REDISTRIBUTION IN THE α, δ AND $\alpha+\delta$ PHASES

A - Qualitative Features Of The Solution

In the last section it was shown that zero current or even a constant current was an impossibility in the $\alpha+\delta$ phase. Therefore any sample of Zircaloy-2 which has a temperature gradient will in general have a single phase region at its hot boundary. For example, if we take a sample whose initial hydrogen concentration is everywhere larger than terminal solid solubility and if we prevent hydrogen from flowing into the hot end of the sample then an α-phase region begins to develop at the hot end from time $t = 0$ onwards.

The non-zero current at the cold end of the two-phase region is taken care of by the continuing deposition of solid hydride there. Consequently any sample containing a region of $\alpha+\delta$ phase will involve both a region of δ-phase only and a region of α-phase only. The proper description of the kinetics of the diffusion process for such a sample must then take the redistribution in all three regions into account simultaneously. In general the interfaces separating the three regions will change with time. Before developing a detailed treatment of the redistribution of hydrogen in all three regions simultaneously we discuss a few of its qualitative features and of the interface motion.

The $\alpha, \alpha+\delta$ interface will, in general, move toward the cold end of the sample. The reason for this fact is the following. The hydrogen current on the $\alpha+\delta$ side of the interface is

negative (i.e. hydrogen flows toward the cold end) and large (except for large hydride concentrations it is roughly equal to the solid-solution current, J_α, augmented by the steep gradient of the terminal-solid-solubility curve). On the other hand, in the single-phase region the distribution decays rapidly into the lowest eigenfunction which has a small current everywhere, even at the interface. In general the slope of the single-phase hydrogen distribution at the interface will be much smaller than the slope of the terminal-solid-solubility curve so that the hydrogen current flowing into the interface from the α-phase will be much smaller than the hydrogen current flowing from the interface into the two-phase region. Hydrogen conservation at the interface can be accomplished only by the motion of the interface toward the cold end with the accompanying transfer of the hydride at the interface into the $\alpha+\delta$ region.

Because the hydrogen concentration in the two-phase region increases with time everywhere and because the $\alpha+\delta,\alpha$ interface moves toward the cold end the hydrogen concentration on the two-phase side of the interface will, in general, be larger than terminal solid solubility, N_α. On the single-phase side of the interface the concentration is N_α. Therefore a discontinuity in the hydrogen concentration exists at the interface. Moreover the discontinuity grows with time. The $\alpha+\delta,\alpha$ interface motion, the concentration discontinuity at the interface, and the continuing growth of the two-phase region were the fundamental features of Sawatzky's approximate treatment of the thermal diffusion of

hydrogen in Zircaloy-2. These features also occur in more exact treatment. They arise from the simple properties of the general two-phase diffusion equation. The detailed calculation of the hydrogen redistribution to illustrate these features is carried out below. It should be emphasized that the existence of $\alpha+\delta,\alpha$ interface motion and of the hydrogen discontinuity there rely on the assumption of constant equilibrium between the α and δ phases. If the equilibrium is not instantaneous the discontinuity may not be infinitely sharp. For simplicity the calculations carried out below always assume phase equilibrium.

If a hydrogen current flows into the hot end of a Zircaloy-2 specimen then the motion of the $(\alpha,\alpha+\delta)$ interface can be approximately stopped. As was shown in section III (see Fig. 3), the single-phase region has an equilibrium solution with constant current flowing through it. If we choose J_o, of (40), so that the single-phase current at the interface is equal to the two-phase current there then the interface will no longer move. As Fig. 3 shows this condition requires that both the slope and the value of the hydrogen distribution on the α-phase side of this interface are approximately the same as those of the terminal-solid-solubility curve. (The correspondence is exact for zero hydride concentration on the two-phase side of the interface.) The J_o of Fig. 3 achieves this condition. However, as the hydrogen concentration in the two-phase region builds up the two-phase current changes slightly and J_o would have to be adjusted appropriately with time to fix the position of the interface.

It is possible to have a hydride layer at the hot end of the sample if the hydrogen current there is large enough. Thus if the hydrogen pickup yields a slope of N greater than the the slope of N_α at the hot end, a hydride layer will develop there.

The deposition of hydride at the cold end of a Zircaloy-2 specimen leads to a hydride layer of increasing thickness. Eventually the $\alpha+\delta,\delta$ and $\alpha+\delta,\alpha$ interfaces will merge and no two-phase region will exist. Of course hydrogen redistribution will also occur in the hydride layer. However, this redistribution occurs very slowly and will be ignored in the calculations given below. With this approximation, the ultimate fate of a hydrogen distribution in a Zircaloy-2 specimen with temperature gradients is the formation of a solid-hydride layer at the cold end together with a zero current α-phase distribution in the remainder of the specimen.

If the slow δ-phase redistribution were considered the final equilibrium distribution would have zero current in both the hydride layer and the α-phase region. Zero current in the hydride layer implies a distribution of the form

$$N = A\ e^{Q_\delta^*/RT} \tag{66}$$

in the hydride layer. Moreover such a zero current hydride layer has a finite thickness because the concentration at both boundaries is either fixed or limited. At the δ,α interface the concentration, $N(T_2)$, of the hydride phase will be determined by the requirement of equilibrium with the solid solution phase. At the outer cold surface of the δ-phase the hydrogen concentration, $N(T_3)$, is limited by the maximum amount of hydrogen which can occur in the δ-phase. The maximum amount, in p.p.m., is no more than 25% larger than $N(T_2)$.

From (66) we find

$$T_2 = T_3 \left[1 + \frac{T_3 R}{Q_\delta^*} \ln \left(\frac{N(T_2)}{N(T_3)} \right) \right]^{-1} \tag{67}$$

from which the finite thickness, d, of the hydride layer is found to be

$$d \equiv \frac{1}{K} [T_2 - T_3] = - \frac{RT_3^{\,2} \ln [N(T_2)/N(T_3)]}{K(Q_\delta^* + RT_3 \ln [N(T_2)/N(T_3)]} \tag{68}$$

In problems involving the redistribution of a two-phase region we do not need to take redistribution in the δ-phase into account because of the small diffusivity of the δ-phase. The two-phase region disappears long before any substantial redistribution in the δ-phase occurs. Therefore we can assume that the hydride layer at the cold end of the two-phase region continues to grow even if the hydride layer exceeds the limiting thickness d at the time when the two-phase region has just disappeared. The ultimate thickness, d, to which the hydride layer attains at much larger times will be determined by the effective hydrogen pressure of the medium in contact with the surface.

The maximum hydride thickness, (68), may be of great practical importance for problems in which hydrogen enters the Zircaloy-2 specimen from the cold surface. Then $N(T_3)$ is determined by the hydrogen pressure of the gas in contact with the

surface. At no time, under these conditions, can the thickness of the hydride layer exceed d. For example, non-defected fuel rods exposed in a reactor for a long time will never become completely hydrided if the origin of the hydrogen is at the cold surface and if the thickness of the Zircaloy-2 sheathing is larger than d.

In part B of this section methods are derived for solving the general problem of the simultaneous redistribution in the α and $\alpha+\delta$ regions. Parts C and D give approximate solutions valid for small and large times respectively. The final part, E, applies the solutions to various observed hydrogen distributions and shows the effect of the diffusion kinetics on the measurements of the α-phase heat of transport.

B - General Solution of the α and $\alpha+\delta$ Equations and of the Interface Motion

Because the entire two-phase region shrinks with time the solution for it can be given without reference to the single-phase region. The build-up of hydrogen concentration in the two-phase region is given by (61); and the two-phase hydrogen current by (3). With the known two-phase current at the interface we must use hydrogen concentration at the boundary to solve simultaneously for the motion of the boundary and for the distribution of hydrogen in the single phase region.

To determine the redistribution in the single-phase region while the boundary, y_2, is moving we use the "Fourier series" method developed in section III. However we can no longer build the eigenfunctions with a zero-current

boundary condition at y_2. The most general boundary condition which is suitable for the construction of a complete set of orthonormal functions is

$$[dN_\lambda/dy]/N_\lambda \Big|_{y = y_2} = B \tag{69}$$

where B is a constant. Without a boundary condition of this form the orthogonality condition, as proved in Section III, (29) and (30), would not hold. The zero-current boundary condition (21) corresponds to the special choice of the logarithmic derivative, ($B = Q_\alpha^*/R$). Other choices of B will correspond to non-zero current at the boundary. However, as the boundary, y_2 moves toward the cold-end there is a net flow of hydrogen from the single-phase region and hence a non-zero current at y_2. $B(y_2)$ is chosen to be equal to $[dN/dy]/N$ at y_2. As y_2 changes with time we must adjust $B(y_2)$ to correspond to the change of the single-phase current at the interface. The boundary condition, $B(y_2)$ depends implicitly on the time through its dependence on y_2. The evaluation of B for each y_2 will accompany the general solution. At the hot end, y_1, of the single-phase region we assume the zero-current time-independent boundary condition used in section III[9].

We write the hydrogen distribution in the single phase region as

$$N(y,t) = \Sigma_\lambda A_\lambda(t) N_\lambda (y, B, y_2) \tag{70}$$

where each N_λ is a solution of (20) which depends parametrically on B and on y_2 both of which are functions of the time. Because the dependence on time through B and y_2 is only parametric the orthogonality condition (22) and the completeness of the set of functions, N_λ, holds as before and the weight function is still given by (32). However, the solution for the functions $A_\lambda(t)$ is no longer given by $a_\lambda e^{-E_\lambda t}$, where a_λ is a constant. Rather we must find $A_\lambda(t)$ by substituting (70) into the single-phase equation (15). Making this substitution we obtain

$$\Sigma_{\lambda'} \frac{dA_{\lambda'}}{dt} N_{\lambda'} + \Sigma_{\lambda'} A_{\lambda'} \left(\frac{dN_{\lambda'}}{dy_2} \frac{dy_2}{dt} + \frac{dN_{\lambda'}}{dB} \frac{dB}{dt}\right) = - \Sigma_{\lambda'} A_{\lambda'} E_{\lambda'} N_{\lambda'} \quad (71)$$

Multiplying both sides by $N_\lambda f$ and integrating we find

$$- \frac{dA_\lambda}{dt} = E_\lambda A_\lambda + \Sigma_{\lambda'} A_{\lambda'} \left(S_{\lambda\lambda'} \frac{dy_2}{dt} + T_{\lambda\lambda'} \frac{dB}{dt}\right) \quad (72)$$

where

$$S_{\lambda\lambda'} = \int_{y_1}^{y_2} \frac{dN_{\lambda'}}{dy_2} N_\lambda f \, dy \quad (73)$$

and

$$T_{\lambda\lambda'} = \int_{y_1}^{y_2} \frac{dN_{\lambda'}}{dB} N_\lambda f \, dy \quad (74)$$

Both $S_{\lambda\lambda'}$ and $T_{\lambda\lambda'}$ as well as the eigenvalues E_λ are functions of y_2 and B.

To complete the solution we still need to satisfy two conditions at y_2. The first condition states the fact that at the interface the single phase concentration is equal to terminal solid solubility, i.e.

$$N(y_2) = N_\alpha (y_2) \tag{75}$$

(75) must always hold if the interface is moving toward the cold end. The second condition states the conservation of hydrogen at the interface and may be written

$$\begin{aligned} J^{(2)} - J^{(1)} &= [N^{(2)} - N^{(1)}]\, v \\ &= [N^{(2)} - N_\alpha]\, (Ky_2{}^2)^{-1} \frac{dy_2}{dt} \end{aligned} \tag{76}$$

where $J^{(2)}$ is the two-phase hydrogen current, (64) at y_2, $J^{(1)}$ is the single-phase hydrogen current, $N^{(2)}$ the hydrogen concentration on the two-phase side of the interface, $N^{(1)}$ the hydrogen concentration on the single-phase side of the interface and v the velocity of the interface.

Together (76), (75) and (72) can be solved for the time dependence of y_2, B and the set of functions A_λ. We begin by expanding each of these functions as a Taylor series in an appropriate time variable. We define

$$w \equiv t^m \tag{77}$$

where m will turn out to be 1/2 or 1, depending on whether or

not the initial hydrogen concentration at the hot end of the specimen is below or above terminal-solid-solubility. Then we write

$$y_2 \equiv \Sigma_n \, y_2^{(n)} \, w^n \tag{78}$$

$$B \equiv \Sigma_n \, B^{(n)} \, w^n \tag{79}$$

$$A_\lambda \equiv \Sigma_n \, A_\lambda^{(n)} \, w^n \tag{80}$$

The first term in each of (78), (79) (80) can be found independently of the differential equation (72) or of the two conditions (75), (76) at y_2. Thus $y_2^{(o)}$ is the intersection of the initial hydrogen distribution with the terminal-solid-solubility curve. The value of $B^{(o)}$ is derived in the next part of this section where the initial motion of the interface is considered. We find each $A_\lambda^{(o)}$ from the initial distribution, $N^{(o)}(y)$ in terms of the eigenfunctions $N_\lambda(y, y_2^{(o)}, B^{(o)})$ derived from (20):

$$A_\lambda^{(0)} = \int_{y_1}^{y_2} N^{(0)}(y) \, N_\lambda(y, y_2^{(0)}, B^{(0)}) \, f(y) \, dy \tag{81}$$

The boundary condition (76) gives us $y_2^{(1)}$ from $B^{(0)}$. Now the differential equation, (72), is used to give $A_\lambda^{(1)}$ in terms of $y_2^{(1)}$, $B^{(0)}$ and the $A_\lambda^{(0)}$. Finally $B^{(1)}$ is obtained from (72). The steps are repeated to obtain the higher coefficients in the Taylor's series, (78), (79) and (80) - taking care in each step to retain all the necessary powers of w in each of the equations at each stage. Although the process is messy it is straightforward.

The initial conservation of hydrogen at $y_2^{(0)}$, as expressed by (76) determines whether w is $t^{1/2}$ or t. Thus, in general, the left hand side of (76) will have a finite value, initially. The lowest order of $(K\, y_2^{\,2})^{-1}$ is, of course, $[K(y_2^{(0)})^2]^{-1}$ which is also finite. If $N^{(2)}(y_2^{(0)}) = N_\alpha(y_2^{(0)})$ as will happen if the initial hydrogen distribution cuts across the terminal-solid-solubility curve then, for small times, $[N^{(2)} - N_\alpha]$ will be proportional to w. On the other hand dy_2/dt is initially proportional to t^{m-1} according to (77). If wt^{m-1} is to be finite in the limit as $t \to 0$ then m must be 1/2 and therefore w is $t^{\frac{1}{2}}$. When the initial hydrogen concentration lies everywhere above N_α then $[N^{(2)} - N_\alpha]$ is finite as $t \to 0$ so that $w = t$.

The general solution developed in this part is used in part D below to establish the validity of an asymptotic solution valid for large times.

C - Initial Single-Phase Solution and Interface Motion

When $N^{(2)}(y_2)$ is initially larger than $N_\alpha(y_2)$ [e.g. when the initial hydrogen concentration, even at the hot end, is above terminal solid solubility] then the initial solution is simple: the interface velocity is finite and is given by (76).

In this section we explore the more interesting case where the initial constant hydrogen concentration, $N^{(0)}$, bisects the terminal solid solubility curve, that is $N_\alpha(y_3) < N^{(0)} < N_\alpha(y_1)$, where y_3 is the temperature of the cold end of the specimen. As was pointed out in the preceding part the initial velocity of the boundary is infinite for this case, or more precisely, v is

proportional to $t^{-1/2}$. The infinite velocity arises from the simultaneous continuity in the value and discontinuity of the slope of the solid solution concentration. For $y > y_2$ the solid solution concentration is initially N_α, for $y < y_2$ it is $N^{(0)}$. In investigating the initial infinite velocity of the interface arising from this discontinuity we are, of course, carrying the assumption of equilibrium between solid solution and hydride to an extreme. We do so, however, to keep the model of the present paper mathematically consistent.

Because the first derivative of the solid-solution concentration is discontinuous at $y_2^{(0)}$ the second derivative must become infinite at $y_2^{(0)}$ in the limit $t \to 0$. Therefore we can approximate (15) by

$$\frac{dN}{dt} \approx \theta^2 \frac{d^2N}{dy^2} \tag{82}$$

where

$$\theta^2 \approx K^2 D_\alpha y^4 \Big|_{y = y_2^{(0)}} \tag{83}$$

in which θ^2 is treated as a constant. This latter approximation is strictly valid only very near to $y_2^{(0)}$ - initially the region in which the second derivative tends to infinity is arbitrarily small so that all functions other than N can be treated as constant. [For Zircaloy-2 however, an approximation similar to (82) is valid over more extended regions. If we write $N \equiv HG$ as in

Section III then G satisfies (82), approximately, in the entire single-phase region, as was shown by the discussion preceding equation (37)].

If $\frac{d^2N}{dy^2}$ tends to infinity, at $y-y_2^{(0)}$ as any negative power of y then higher derivatives approach infinity even more rapidly. Hence we can take derivatives of (82) to obtain

$$\frac{d}{dt}\left[\frac{d^2N}{dy^2}\right] \approx \theta^2 \frac{d^2}{dy^2}\left[\frac{d^2N}{dy^2}\right] \tag{84}$$

A particular solution of (84) which has the appropriate properties at the discontinuity is given by

$$\frac{d^2N}{dy^2} = c_o t^{-1/2} e^{-(y-y_2^{(0)})^2/4\theta^2 t} \tag{85}$$

where c_o is an arbitrary constant. It is easily verified that (85) satisfies (84) and, moreover, d^2N/dy^2 given by (85) tends to infinity at $y_2^{(0)}$ as $t \to 0$. We obtain the hydrogen concentration N, from (85) and (82) by one integration.

$$N = \theta^2 c_o \int_o^t (t')^{-1/2} e^{-(y-y_2^{(0)})^2/4\theta^2 t'} dt' \tag{86}$$

Again it is easily verified that (86) satisfies (82). One can also show that the slope of (86) is discontinuous in the limit $y \to y_2^{(0)}$, $t \to 0$. However the hydrogen concentration (86) is finite and continuous. Thus the solution (86) has all the required properties. The value of c_o is determined simultaneously

with the interface velocity from the discontinuity in the solid solution concentration at the interface.

Figure 6 shows the qualitative features of the initial solution in the immediate neighbourhood of $y_2^{(0)}$ for infinitesmal times. The interface, y_2, between the single phase and two phase regions moves along the terminal solid solubility curve, N_α, with a velocity proportional to $t^{-1/2}$

$$y_2 - y_2^{(0)} = y_2^{(1)} \; t^{1/2} \tag{87}$$

At y_2 the slope of N has a value, $B^{(0)} \; N^{(0)}$, which is constant and intermediate between the slopes of $N^{(0)}$ and N_α. Because of our assumption of equilibrium between the two phases the hydride between y_2 and y_2^{0} disappears. For $y > y_2$ the hydrogen concentration remains approximately fixed at $N^{(0)}$ because the increase in concentration in the two-phase region is initially proportional to t, not to $t^{1/2}$ so that the initial motion of the interface all takes place before any substantial increase of N in the two-phase region can occur. Total hydrogen conservation takes place over the whole sample, not in the infinitesmal region near $y_2^{(0)}$. Although the slope of N at the interface does not change the departure of N from $N^{(0)}$ spreads rapidly with increasing time as the figure shows.

The connection between $B^{(0)}N^{(0)}$ and c_o can be found by integrating d^2N/dy^2 from y' to y_2 where $(y_2^{(0)}-y') >> (4\theta^2 t)^{1/2}$. If we recognize that $dN/dy \; |_{y'}$ approaches zero for an initially constant hydrogen distribution we can write

$$\int_{y'}^{y_2} \frac{d^2N}{dy^2}\, dy = B^{(0)}N^{(0)} \tag{88}$$

On the other hand, we find, from (85)

$$B^{(0)}N^{(0)} = \int_{y'}^{y_2} \frac{d^2N}{dy^2}\, dy \approx \frac{c_o}{t^{1/2}} \int_{-\infty}^{(y_2 - y_2^{(0)})} e^{-y^2/4\theta^2 t}\, dy \tag{89}$$

$$= (c_o 2\theta\pi^{1/2})\ E\ (y_2^{(1)}/2\theta)$$

where

$$E(x) \equiv \pi^{-1/2} \int_{-\infty}^{x} e^{-z^2}\, dz \tag{90}$$

is a well tabulated function. The boundary condition (76) yields a second relation between $B^{(0)}N^{(0)}$ and $y_2^{(1)}$, namely

$$K[g(y_2^{(0)})N^{(0)} + h(y_2^{(0)}N_\delta)] - KD_\alpha[y_2^{(0)}]^2\ N^{(0)} \left[B^{(0)} - \frac{Q_\alpha^*}{R}\right]$$

$$= \frac{1}{2}\frac{\Delta H}{R}\ N_\alpha(y_2^{(0)})\ K^{-1}\ [y_2^{(0)}]^{-2}\ [y_2^{(1)}]^2 \tag{91}$$

Together (91) and (89) can be solved simultaneously for $B^{(0)}$ and $y_2^{(1)}$.

To illustrate the calculation of the initial motion we take an initial hydrogen concentration of $N^{(0)} = 130$ p.p.m.

Then the interface occurs initially at 590°K, using the same constants for Zircaloy-2 as in Fig. 1. The simultaneous solution of (89) and (91) yields an initial motion of the interface given by

$$y_2^{(1)} = 4.82 \times 10^{-7} \ (\text{sec})^{-1/2} \ (\text{deg})^{-1}$$

After one day this motion if it continued unchanged, would take the interface to a temperature of 544°K. However the $t^{-1/2}$ velocity is probably no longer accurate for times as long as one day. As we shall see in the next part the later motion of the interface is considerably slower.

The methods of the present part give the correct initial motion of the interface, which is required to begin the general analysis of the motion as described in the preceding part.

D - Interface Motion and Single-Phase Solution for Large Times

In part B it was shown that for the case of a moving boundary both the normal modes, N_λ, and the corresponding eigenvalues, E_λ, depend parametrically on y_2 and therefore on the time. The non-zero value of the single-phase hydrogen current at the interface has the effect of raising the value of each of the eigenvalues from that which holds for zero current at the interface. The increase in the eigenvalues is limited - if we call E_λ the eigenvalues for zero current and E'_λ those for any finite current the following relationship can be shown to hold

$$E_\lambda \leq E'_\lambda \leq E_{\lambda+1} \qquad (92)$$

When the interface is moving the terms in (72) containing $S_{\lambda\lambda'}$ and $T_{\lambda\lambda'}$ give rise to a "feeding" of each normal mode and counteract its exponential decay. However, as (39) shows, the eigenvalues of the higher normal modes are very large so it might be expected that the very rapid exponential decay corresponding to these high eigenvalues might overwhelm any "feeding" which does occur. This expectation forms the starting point of the approximation to be developed here.

We assume that for large times the terms in (72) containing $S_{\lambda\lambda'}$ and $T_{\lambda\lambda'}$ may be neglected and that only the lowest normal mode of the single phase region needs to be retained, that is

$$N(y,t) \approx A_o \, N_o \, (y,y_2) = A_o \, H(y) \, G_o \, (y,y_2) \tag{93}$$

where H(y) is defined by (25). Now, from the boundary condition (75) we find

$$A_o = N_\alpha(y_2)/H(y_2) \, G_o \, (y_2,y_2) \tag{94}$$

The differential equation (72) is approximated as it was for (93), to obtain

$$\frac{dA_o}{dt} = -E_o \, A_o \tag{95}$$

However, according to (94)

$$\frac{dA_o}{dt} = A_o \left[\frac{H(y_2)}{N_\alpha(y_2)} \frac{d}{dt}\left(\frac{N_\alpha(y_2)}{H(y_2)}\right) + G_o(y_2,y_2) \frac{d}{dt} \frac{1}{G_o(y_2,y_2)}\right] \tag{96}$$

The approximate eigenfunctions of Section III may be used to show that the last term in the square bracket is negligible. The appropriate approximate form of G_o for this demonstration is simply:

$$G_o \approx c_o \cos k_o (y-y_1) \tag{97}$$

where c_o is a normalization coefficient (dependent on y_2) and k_o is determined below. The eigenvalue, E_o, is related to k_o by

$$E_o \approx K^2 D_\alpha y^4 k_o^2 \tag{98}$$

where $D_\alpha y^4$ is again regarded as a constant, as in the derivation of the approximate eigenfunctions. Combining (95) and (96) we find

$$-E_o \approx \frac{H(y_2)}{N_\alpha(y_2)} \frac{d}{dy_2} \left[\frac{N_\alpha(y_2)}{H(y_2)}\right] \frac{dy_2}{dt} = p \frac{dy_2}{dt} \tag{99}$$

$$\text{where} \quad p \equiv \frac{1}{y_2} - \frac{1}{2}\left(\frac{Q_\alpha + Q_\alpha^*}{R}\right) - \frac{\Delta H}{R} \tag{100}$$

p depends so slightly on y_2, for Zircaloy-2, that we may regard it as a constant.

A second connection between E_o and dy_2/dt is found from the boundary condition (76) which expresses hydrogen conservation at y_2. For simplicity we approximate the two-phase

current $J^{(2)}$ by neglecting both the hydride current and the hydride volume. Hence we have, for the right side of (76)

$$J^{(2)} - J^{(1)} = \left[y^2 D_\alpha \left(\frac{dN_\alpha}{dy} - \frac{dN}{dy}\right)\right]_{y = y_2} \tag{101}$$

where N is the single phase concentration given by (93) and (94). Therefore

$$J^{(2)} - J^{(1)} = \left[y^2 D_\alpha N_\alpha \left(p - \frac{1}{G_o}\frac{dG_o}{dy}\right)\right]_{y = y_2} \tag{102}$$

Equating the right side of (102) to the right side of (76) we obtain

$$-\frac{1}{G_o}\frac{dG_o}{dy}\bigg|_{y = y_2} = -p + \epsilon \frac{dy_2}{dt} (D_\alpha y^4 K)^{-1} \tag{103}$$

$$= -p - \epsilon \frac{E_o}{p} (D_\alpha y^4 K)^{-1} \tag{104}$$

where

$$\epsilon = \left(\frac{N^{(2)}(y_2)}{N_\alpha(y_2)} - 1\right) \tag{105}$$

depends on the ratio of the two-phase concentration and the single-phase concentration at the interface. Finally we evaluate $-G_o^{-1}\, dG_o/dy$ with the approximate eigenfunction (97) to obtain

$$k_o \tan k_o (y_2 - y_1) = -p - \epsilon \frac{k_o^2}{p} \tag{106}$$

This result, with the value of p known from (100), gives us k_o in terms of ϵ and y_2-y_1. Fig. 7 shows the value of $k_o(y_2-y_1)$ as a function of both of these parameters.

To determine at a time t the value of y_2 and k_o arising from an initial constant hydrogen distribution $N^{(0)}$ we proceed in the following way. We choose a value of y_2 and then use the methods of section IV to determine $N^{(2)}(y_2)$ and hence ϵ. From the known value of ϵ and of y_2-y_1 we then find $k_o(y_2-y_1)$ from Figure 7. Having found k_o we can next determine the total hydrogen concentration in the sample by integration. We check this value of total hydrogen against the initial total hydrogen. The procedure is repeated for different y_2 until self-consistency in the total hydrogen is attained. The corresponding values of y_2 and k_o give the asymptotic solution. The next part gives examples in which the asymptotic solution is calculated.

It remains to be shown that the approximations made in deriving (93) and (95) are valid for large times. If the approximate normal modes (37) are used the evaluation of $S_{\lambda\lambda'}$ and $T_{\lambda\lambda'}$ is quite simple. We have used this method in a number of calculations which show that the neglected terms are indeed small. The results of these calculations can, perhaps, be summed up in the following way: the approximations made in the asymptotic solution are valid for times such that $tE_1 \gg 1$. This result is also very plausible. For Zircaloy-2 tE_1 will generally be greater than unity in a small fraction of a day so that the asymptotic solution is usually valid within a day or two.

E - Comparison of the Calculated Distributions with Data

The asymptotic single-phase distribution calculated in the preceeding part has a very plausible behavior. It differs from the distribution with zero current everywhere in the following way. Because the interface moves toward the cold end and because the single-phase concentration at the interface, y_2, is equal to $N_\alpha(y_2)$ - and therefore decreasing continuously - the amplitude of the zeroth normal mode decreases continuously. This decrease implies a hydrogen current which builds up from the hot end to the interface y_2 - the current building up gives an increasing curvature to the hydrogen distribution. In the solution this curvature is contained in the term $\cos k_o(y-y_1)$. The zeroth normal mode, (97), is in fact approximately equal to the zero-current distribution multiplied by $\cos k_o(y-y_1)$. Figure 7 shows that for a wide range of interface positions and two-phase concentrations the "curvature factor" at the interface, $\cos k_o(y_2-y_1)$ has a value near 0.5. The curvature of the hydrogen distribution from its zero current value persists for a long time - much longer than the time in which a sample containing only the solid solution phase, as in Fig. 1, requires to reach its final distribution.

Figure 8 shows a comparison of the calculated hydrogen distribution with data of Sawatzky[4]. The data are for a 34 day anneal of a 2.5 cm. sample of Zircaloy-2 whose end temperatures were maintained at 403°K and 750°K respectively. The initial hydrogen concentration was 130 p.p.m. As already pointed

out by Sawatzky, this sample clearly shows both a two-phase and a single-phase region separated by a moving interface at which the hydrogen concentration is not continuous. The computed curve indicated by the broken line was obtained with the usual constants, given on page 27. In Sawatzky's paper[3] a better fit to the same date was found with a lower value of Q_α*. At the low hydrogen concentrations of Fig. 7 the effect of the hydride on the diffusion in the two phase region can be neglected.

The dotted curve shown on Fig. 8 does not fit the data very well - largely because it implies a larger increase in the two-phase region than is observed. The gain in concentration of the two-phase region can be reduced only by decreasing N_α, D_α or Q_α*. As shown below we believe that Q_α* has a value very close to 6×10^3 k-cal/mole. The situation with regards to N_α and D_α is not so certain. We must remember that the temperature region of the two-phase region shown on Fig. 7 is below that for which N_α and D_α have been measured. The data on the figure suggests that the value of N_α should not be reduced - the single-phase concentration at the interface must be equal to N_α so that decreasing N_α would lower the entire computed curve in the single phase region. The solid curve on the figure was computed with all the constants the same as for the broken curve, except for $D_\alpha^{(0)}$ which was reduced by a factor of two. The agreement of this curve with the data is quite good. It seems quite possible that measurements of the kind shown on Fig. 8 could be used to obtain values of D_α and N_α at temperatures below 500°K.

The "curvature" of the single-phase solution from the zero current solution is only slight on Fig. 8 - the value of cos $k_o(y_2-y_1)$ is 0.84. The sample of the Figure has been annealed for a sufficiently long time so that the hydrogen discontinuity at the interface is very large. The large discontinuity, in turn, slows down the motion of the interface and reduces the "curvature".

When cylindrical geometry is employed the shape of the two-phase and single-phase distributions will be very much different than those corresponding to linear geometry (as on Fig. 8). Qualitatively the problem is still the same: in general a moving interface will occur and the hydrogen concentration will be discontinuous at the interface. Fig. 9 shows some measurements of Markowitz (4) employing cylindrical geometry. Data for three initial concentrations are given and we show on the figure the computed two-phase distributions corresponding to two of these. For curve 2 both the approximate two phase distribution of Sawatzky and our more exact one are given. Unlike that of Fig. 8, the two-phase distribution increases with decreasing temperature, an effect which arises entirely from the temperature dependence of the temperature gradient in cylindrical geometry (K is replaced by K'/r). It is seen that the computed curve 2 is in moderate agreement with the corresponding data. The data of curve 3 departs from solid hydride concentration much more rapidly than the computed curve. A slope in the concentration as steep as that of the observed curve 3 cannot arise from an

initially constant distribution by diffusion perpendicular to the axis. Undoubtedly much diffusion along the axis occurs in Markowitz's samples. This effect has not been taken into account in the computations and will undoubtedly distort our simple results. Thus the curve labelled 1 on Fig. 9 probably has a single-phase and a two-phase region whose interface is not clearly defined because of longtitudinal diffusion.

The "curvature" of the single-phase hydrogen distribution means that a measurement of the heat of transport, Q_α^*/R, from the slope and value of the single phase data will be in error. As (33) shows, with zero current in the single-phase region one obtains Q_α^*/R from the following relationship

$$Q_\alpha^*/R = d \ \ell n \ N/dy \tag{107}$$

In the presence of a single-phase current and the consequent "curvature" of the hydrogen distribution (107) no longer holds. In general one will find

$$d \ \ell n \ N/dy = (Q_\alpha^*/R)_{eff} \tag{108}$$

where the "effective" value of the heat of transport, $(Q_\alpha^*/R)_{eff}$ will approach Q_α^*/R only after the motion of the interface has become small.

Figure 10 shows a measurement recently made by one of us (A.S.) of $(Q_\alpha^*/R)_{eff}$. The measurement was made by averaging $d \ \ell n \ N/dy$ over most of the single phase region for samples of

Zircaloy-2 annealed for various times. For each sample the initial hydrogen concentration was 150 p.p.m., the length was 2.5 cm. and the end temperatures were 473°K and 723°K respectively. We have computed the hydrogen distribution of these samples, including the single-phase "curvature". The computed value of $(Q_\alpha^*/R)_{eff}$ is also shown on Fig. 10. In order to obtain the good agreement shown there it was again necessary to reduce $D_\alpha^{(0)}$ by about the same amount as on Fig. 8 so that the calculated positions of the interface coincided with the observed ones. Without this adjustment the calculated values of $(Q_\alpha^*/R)_{eff}$ would differ from (Q_α^*/R) even more than is shown. It is quite apparent from the figure that measurements of the heat of transport made from samples containing a two-phase region can give values which are much too low even when the samples are annealed for a long time.

The effect of the diffusion kinetics on the logarithmic derivative of the single-phase hydrogen distribution may well account for the discrepancy between various measured values of the heat of transport. Reported values lie in the range 3 to 6 k-cal/mole. The results of Fig. 10 suggest that 6 k-cal/mole may be the correct value and show the size of the "error" arising from the kinetics for typical cases in linear geometry. For cylindrical geometry the temperature gradient in the single-phase region is often much smaller so that the effective heat of transport approaches its asymptotic value even more slowly. The "error" arising from the kinetics will tend to give a heat of transport

which is too low. So will a hydrogen current entering the sample at the hot end. We have calculated the effect of such a hydrogen current on the measurement of the heat of transport. For the samples whose results are given on Fig. 10 the current required to account for the observed variation of the effective heat of transport is too large - it would increase the total amount of hydrogen in the specimens by a few per cent per day which is not compatible with the observations. In any case, the kinetics already account adequately for the experimental results shown on Fig. 10.

VI CONCLUSIONS

We have given the thermal diffusion equations for Zircaloy-2 for a model based on the assumption of constant equilibrium between the α and δ phases in regions where both phases are present. The diffusion equations are solved and the solutions used to describe the kinetics of the diffusion process. Results are found for diffusion in the α phase alone, in the $\alpha+\delta$ region alone and for cases involving simultaneous redistribution in the two regions.

The case of single-phase thermal diffusion involves a second order diffusion equation. Our solution for this case is similar to that previously applied by DeGroot[10] to the thermal diffusion of gases in gases. The only new feature of our solution in this case is that we take into account the temperature dependence of the diffusivity.

For the case of thermal diffusion in the $\alpha+\delta$ region the diffusion equation of our model is first order in both time and position. The dominant features of the solution are twofold: (1) the tendency of the hydrogen concentration to increase everywhere in the two-phase region; (2) the impossibility of zero current in the $\alpha+\delta$ region making this region essentially unstable. The two-phase region is shown, in general, to be accompanied by both an α and a δ-phase region.

Redistribution simultaneously in the α, δ and $\alpha+\delta$ regions is dominated by the fundamental features of the two-phase solution. We show that the qualitative features of the

redistribution are those given in an earlier paper by Sawatzky[3]: (a) the δ-phase region at the cold end of the specimen and the α-phase region at the hot end both grow with time; (b) the motion of the α, α+δ interface is accompanied by the development of a hydrogen concentration discontinuity at the interface. The sharpness of this discontinuity is perhaps the only feature of our results which depends critically on our assumption of constant equilibrium of the two-phases in the α+δ region.

The solutions of the thermal diffusion equations are used to describe observed hydrogen redistributions and appear to account for these adequately. The influence of the kinetics on the measurement of Zircaloy-2 parameters is discussed.

ACKNOWLEDGMENTS

We wish to thank J.M. Kennedy for carrying out the calculation of the α-phase eigenfunctions on the Chalk River Datatron computer. Many of the detailed calculations carried out in this paper were stimulated by the tardy acceptance of the results obtained by Sawatzky in an earlier paper[3]. That paper used more approximate solutions of the diffusion equations to obtain, at least qualitatively, the principal results of the present work.

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7) See reference 1 and also C.M. Schwartz and M.W. Mallett, Trans. A.S.M. 46, p. 640 (1954), as well as M.W. Mallett and W.M. Albrecht, Journ. Electro chem. Soc. 104, p. 142 (1957).

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9) It may be noted that at the interface the hydrogen concentration of the single-phase region must be equal to N_α, the terminal solid-solubility. Although this condition at y_2 cannot be ignored it is not a suitable condition for the construction of a complete orthonormal set of functions - only a condition of the form (69) serves that purpose.

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FIGURE CAPTIONS

Figure 1 - The calculated change with time of an initially constant hydrogen distribution in the α-phase of Zircaloy-2. In addition to the initial distribution and the final equilibrium distributions curves are shown for a number of intermediate times in hours. The curves correspond to a specimen with end temperatures of 300° C and 500°C and a temperature gradient of 80 deg/cm. The exact eigenfunctions of the α-phase diffusion equation were used in the calculation. The Zircaloy-2 parameters of the calculation are given in the text.

Figure 2 - The calculated change with time of an initially constant hydrogen distribution in the α-phase of Zircaloy-2. The calculations are exactly like those of Fig. 1 except that the approximate eigenfunctions, (37), were used in place of the exact ones.

Figure 3 - The calculated hydrogen distribution (solid line) in a Zircaloy-2 specimen with hydrogen pickup at the hot surface. In the two-phase region ($T < 245^{\circ}$) the distribution is of the kind discussed in Section IV. In the α-phase region ($T > 245^{\circ}$) two hydrogen distributions are shown. The solid line is a constant current solution, (43), with a current $J_o = -1.12 \times 10^{-4}$ p.p.m. cm/sec., such that the slope of the α-phase hydrogen distribution at the α,α+δ interface is equal to the slope of N_α there. As discussed in Section V the position of the interface is approximately fixed under these conditions. For comparison

a zero-current distribution in the α-phase (the broken line) is also shown on the figure. The terminal solid-solubility curve is labelled N_α.

Figure 4 - The functions used in calculating the hydrogen distribution in α+δ Zircaloy-2. The top part of the figure gives h(y) and g(y) which are defined in the text. The bottom part of the figure gives the variable z which is also defined in the text. The abscissa is labelled both in terms of T^oK and in terms of the variable $y \equiv 1/T$.

Figure 5 - The hydrogen gain in α+δ Zircaloy-2 for various times and various initial hydrogen concentrations. The gain is calculated both by Sawatzky's approximate method and by the more exact methods using (61) and the functions of Fig.4.

Figure 6 - The calculated change with time of an initially constant hydrogen distribution in the neighborhood of the α,α+δ interface of Zircaloy-2 for very short times after t = 0. The initial concentration is labelled $N^{(0)}$. As discussed in the text, the interface moves with an initial velocity proportional to $t^{-1/2}$. Subsequent to t = 0 each distribution has a fixed slope at the interface. The only change in the two phase region is the development of a step in the hydride concentration. The calculations hold only in the infinitesimal region near the interface and they are extremely dependent on our assumption of constant equilibrium between the α and δ phases in the two-phase region.

Figure 7 - The "curvature" factor, $k_o(y_2-y_1)$, of the α-phase region of a Zircaloy-2 specimen yielding the single-phase distribution in the presence of a slowly moving $\alpha,\alpha+\delta$ interface. $k_o(y_2-y_1)$ is given as a function of y_2-y_1 and of second parameter, ϵ (defined in the text) which is determined by the ratio of hydride concentration to solid solution concentration on the two-phase side of the interface.

Figure 8 - Comparison of the calculated and observed redistribution of hydrogen in a specimen of Zircaloy-2. The measurements (points) were made by Sawatzky with linear geometry and correspond to a 34-day anneal under a temperature difference of 130°C - 477°C. The initial concentration was 130 p.p.m. Two calculated curves are shown corresponding to different choices of the Zircaloy-2 (α-phase) diffusivity. The solid curve corresponds to the lower value of $D_\alpha^{(0)}$ and is in better agreement with the experimental points.

Figure 9 - Comparison of calculated hydrogen distributions with the experiments of Markowitz using cylindrical specimens of Zircaloy-2. The points and solid curves are three different sets of experimental results. The broken and dotted curves give our calculations for the hydrogen distribution. The dotted curve 2 was calculated by Sawatzky's approximate treatment of the two-phase region. The broken curves 2 and 3 were obtained with our more exact treatment of the two-phase hydrogen gain.

Figure 10 - Effect of the diffusion kinetics on the apparent heat of transport. The experimental estimates (points) of Q_α^* were made from most of the single-phase region for specimens which began with conditions like that of Figure 8. The calculated curve (solid line) shows how the single-phase hydrogen current arising from the diffusion kinetics leads to apparent heats of transport in good agreement with the observed values. The broken line is the assumed true value of Q_α^*.

A.E.C.L. Ref. # A-2731-C

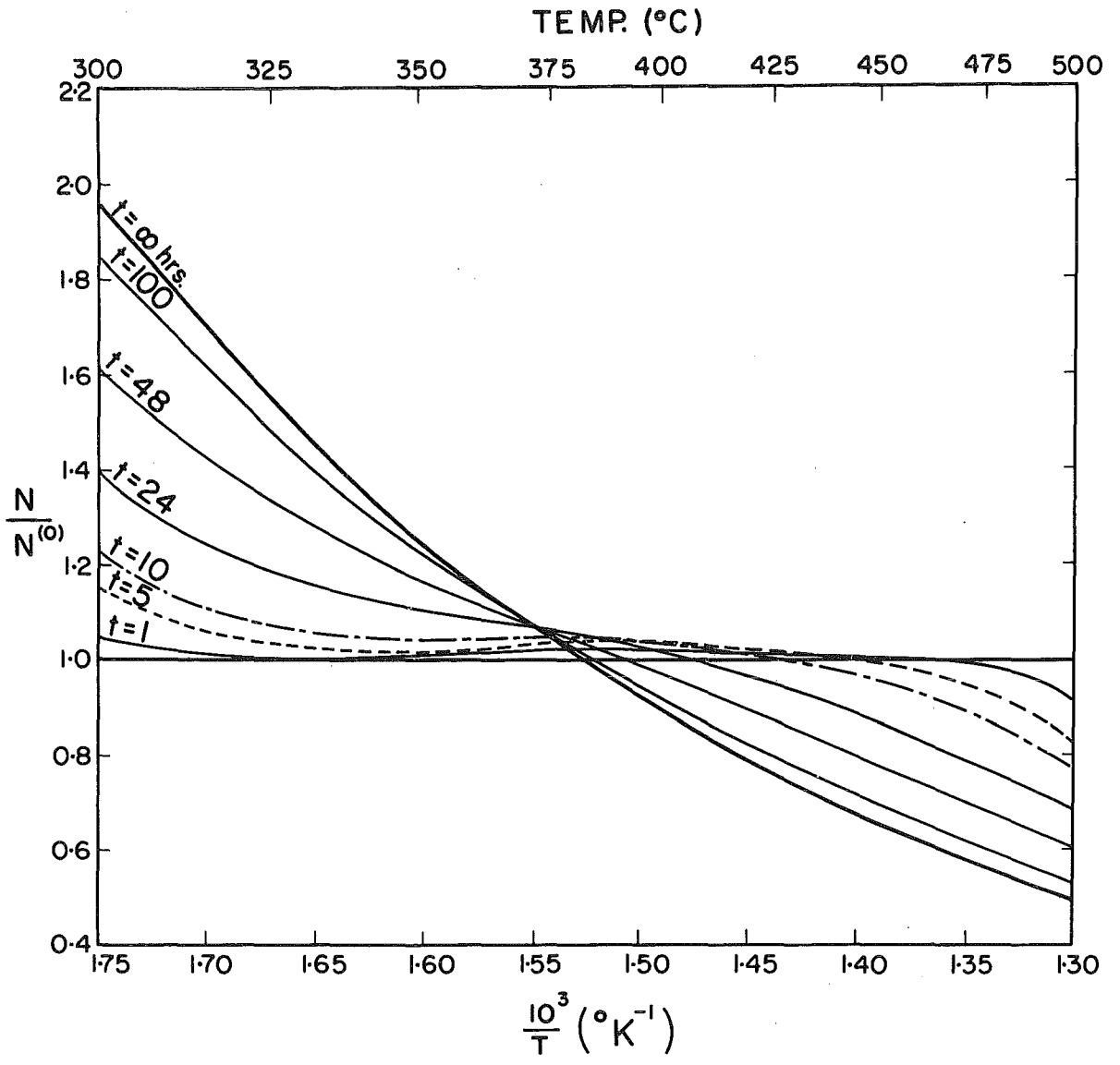


Figure 1

A.E.C.L. Ref. # A-2731-D

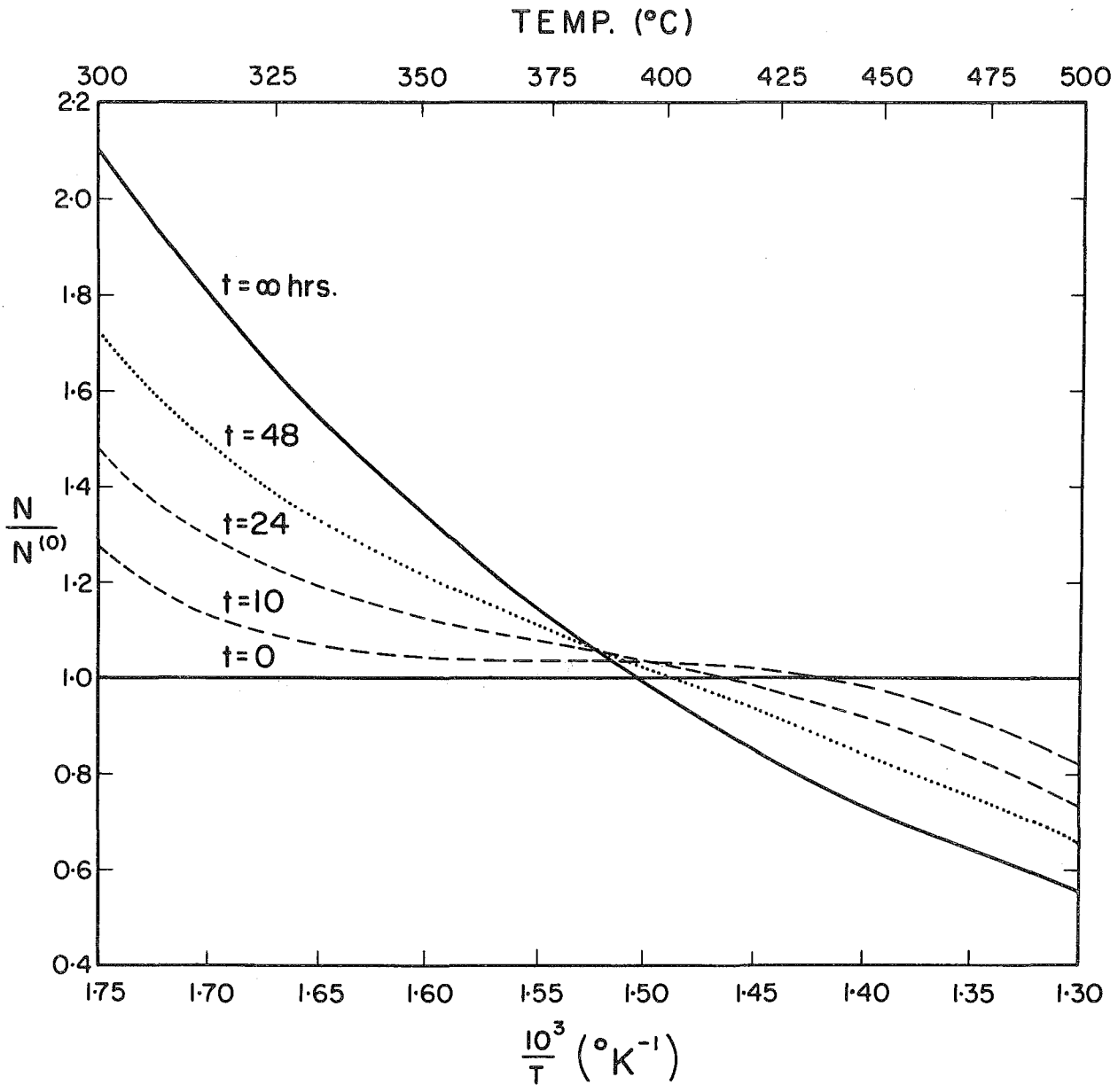
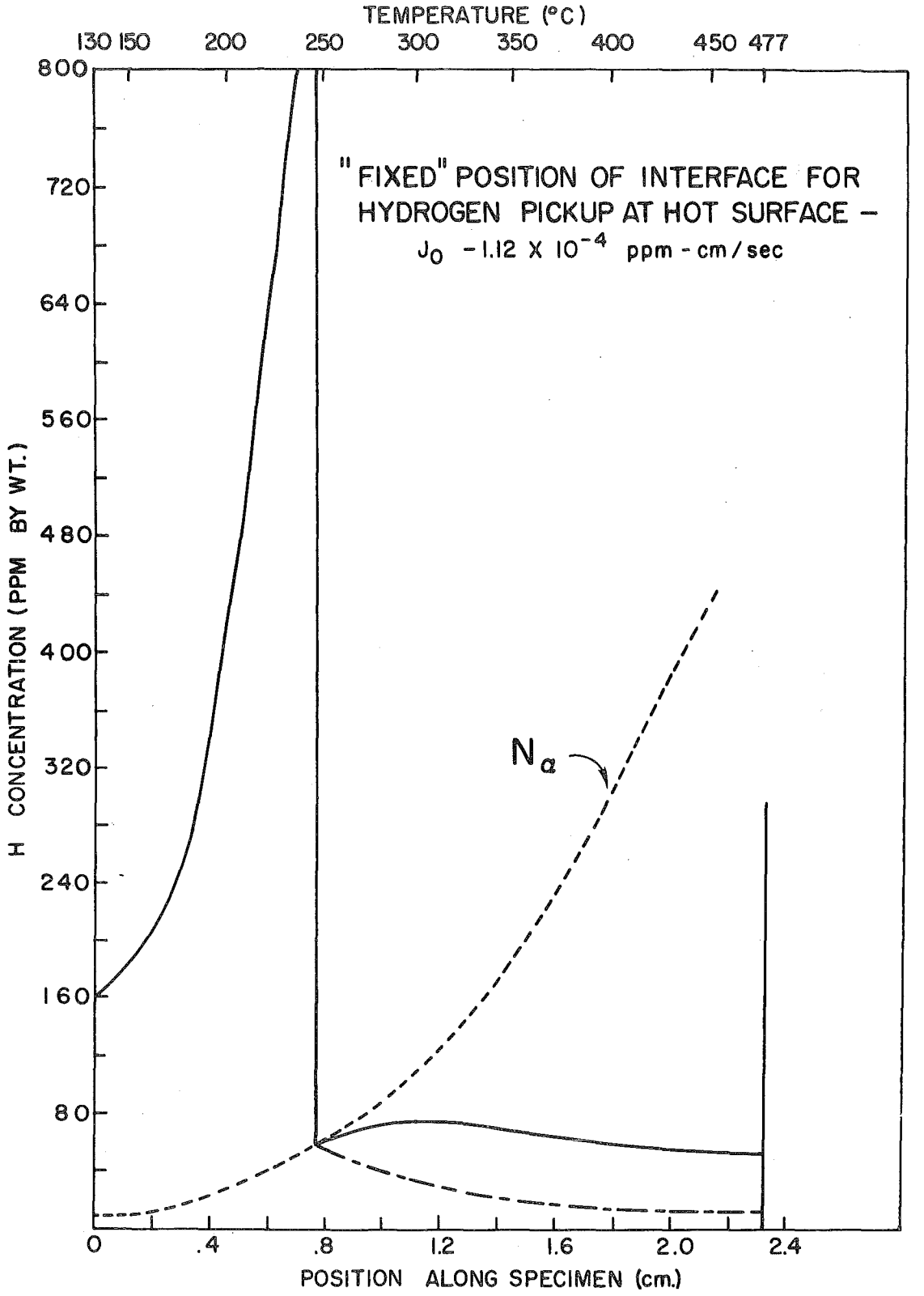


Figure 2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400
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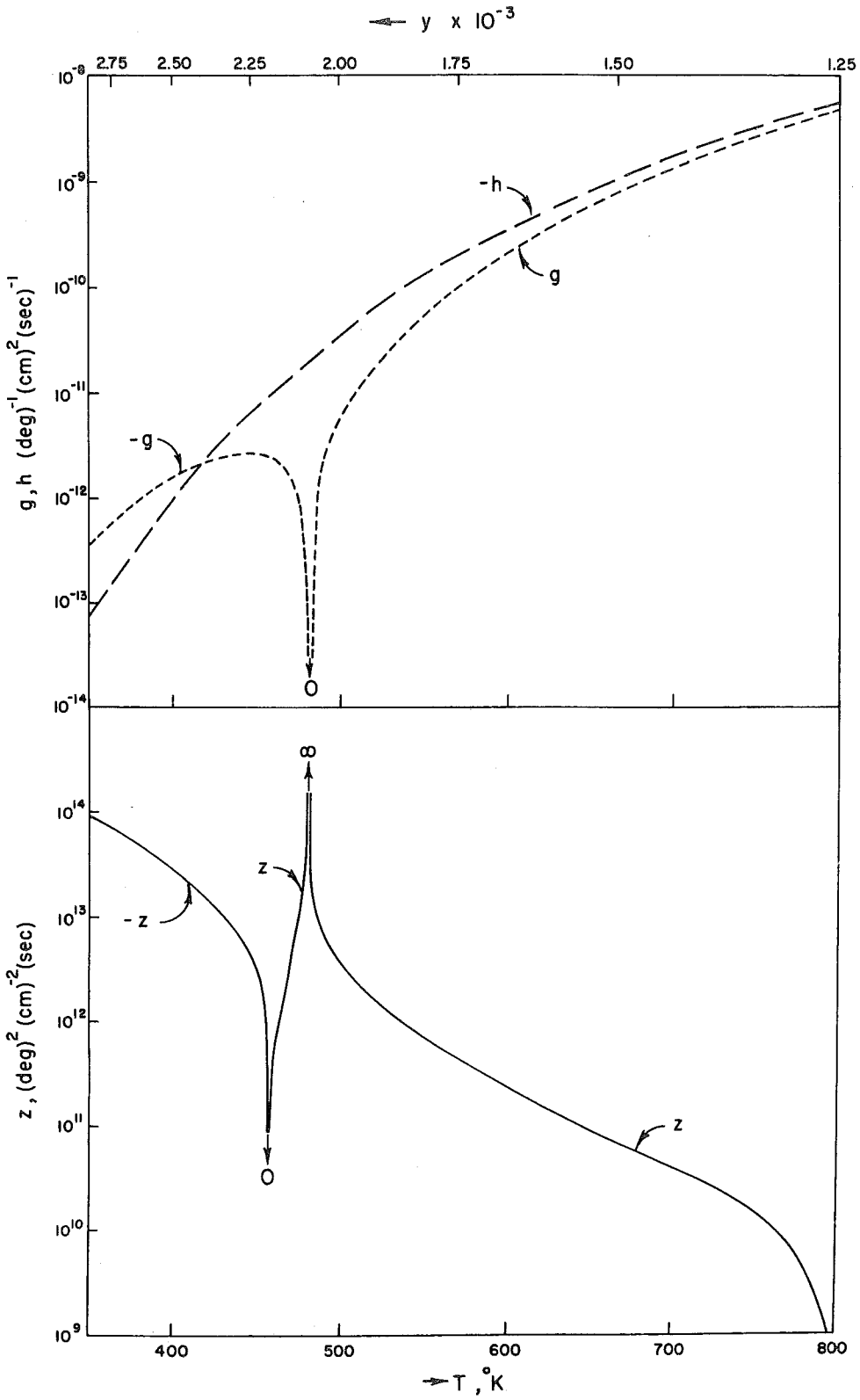
240
160
80
H CONCENTRATION (PPM BY WT.)
"FIXED" POSITION OF INTERFACE FOR HYDROGEN PICKUP AT HOT SURFACE –
J_0 -1.12 X 10^{-4} ppm - cm / sec
N_α
0 .4 .8 1.2 1.6 2.0 2.4
POSITION ALONG SPECIMEN (cm.)

Figure 3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2.50
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g, h (deg)^-1 (cm)^2 (sec)^-1
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T, °K

Figure 4

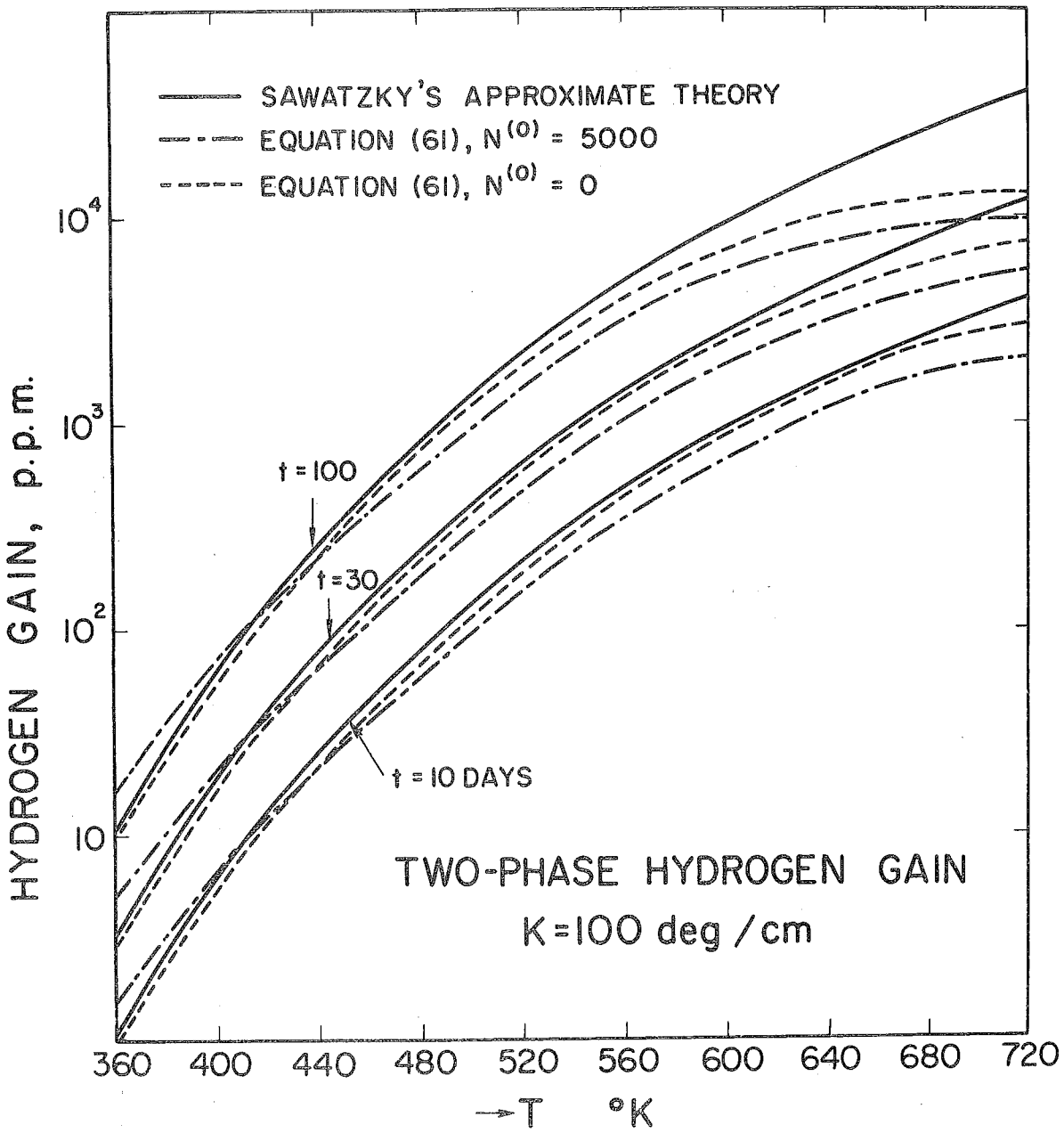
SAWATZKY'S APPROXIMATE THEORY
EQUATION (61), N(0) = 5000
EQUATION (61), N(0) = 0
t = 100
t = 30
t = 10 DAYS
TWO-PHASE HYDROGEN GAIN
K = 100 deg / cm
HYDROGEN GAIN, p.p.m.
10
10²
10³
10⁴
360
400
440
480
520
560
600
640
680
720
→T °K

Figure 5

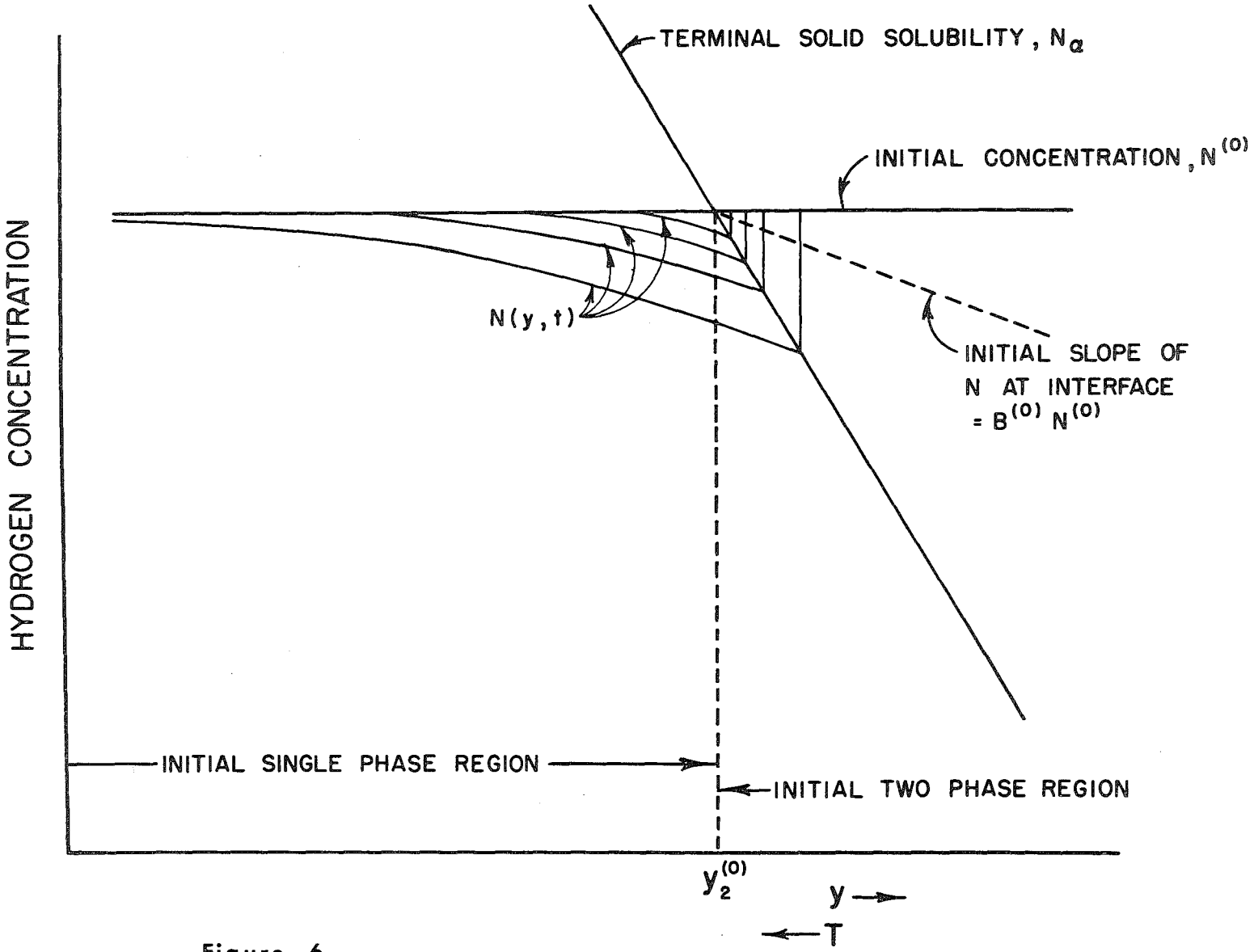
TERMINAL SOLID SOLUBILITY, N_α
INITIAL CONCENTRATION, $N^{(0)}$
HYDROGEN CONCENTRATION
$N(y,t)$
INITIAL SLOPE OF N AT INTERFACE $= B^{(0)} N^{(0)}$
INITIAL SINGLE PHASE REGION
INITIAL TWO PHASE REGION
$y_2^{(0)}$
y
T

Figure 6

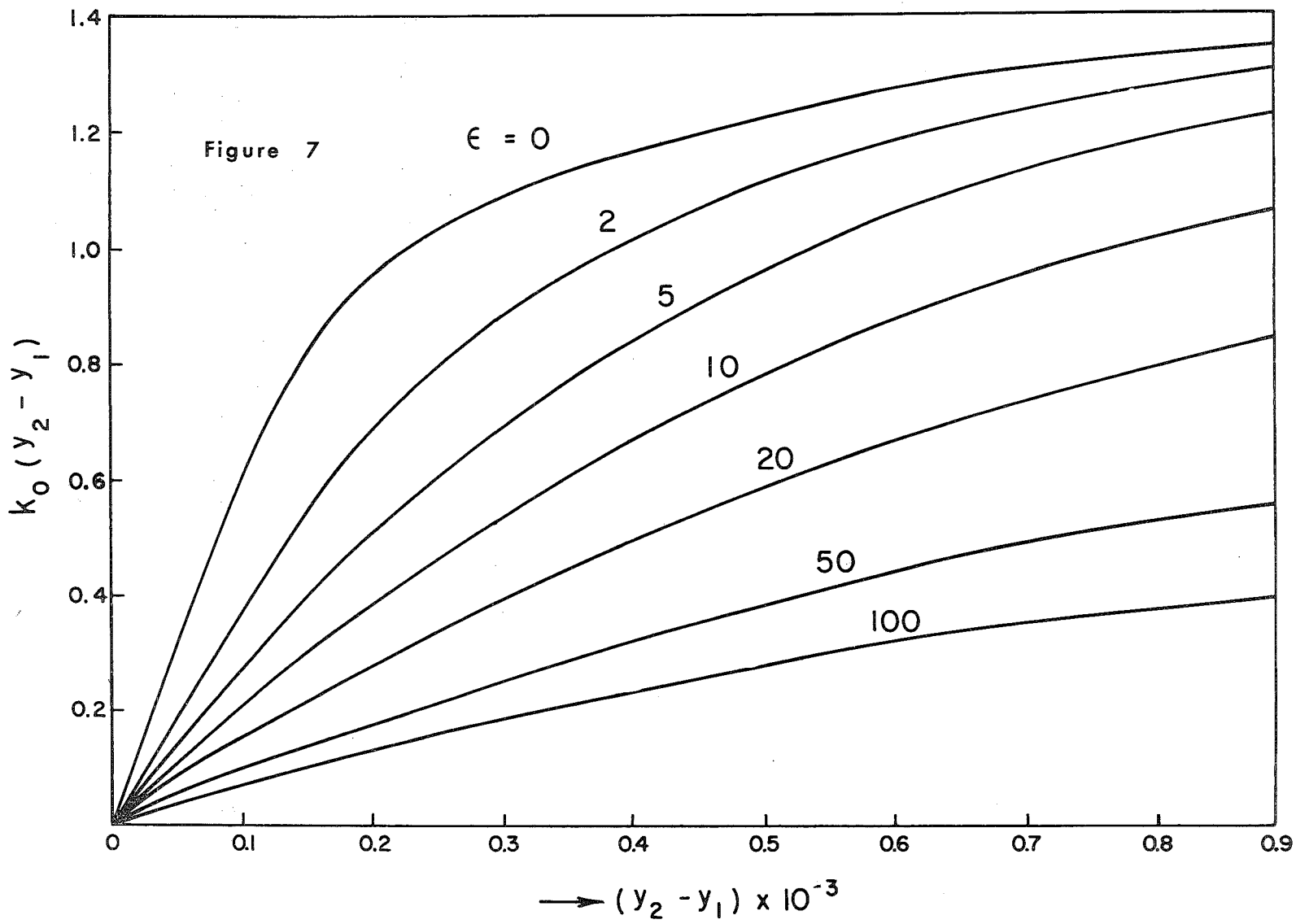
Figure 7
ϵ = 0
2
5
10
20
50
100
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
$k_o (y_2 - y_1)$
$(y_2 - y_1) \times 10^{-3}$

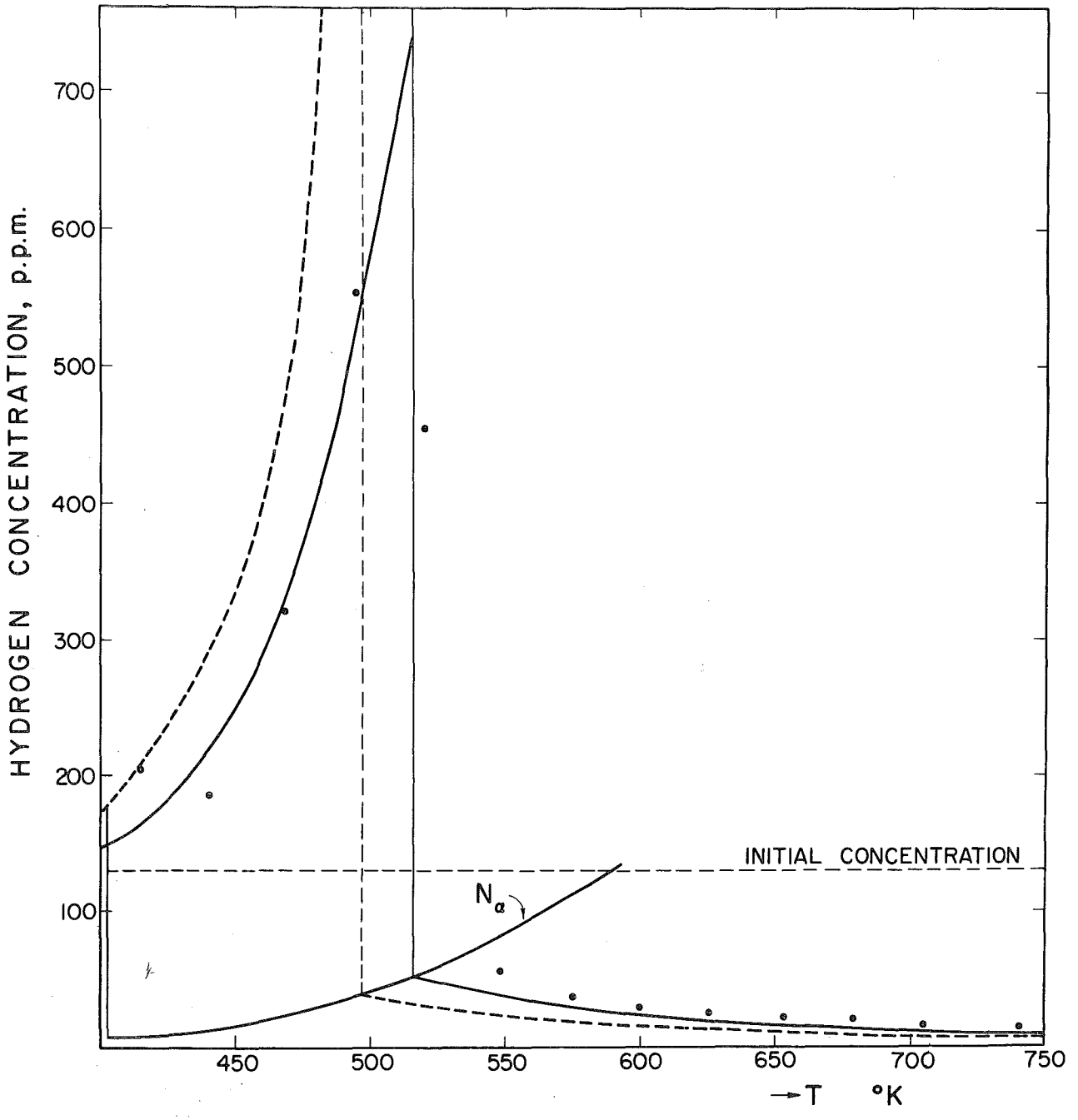
HYDROGEN CONCENTRATION, p.p.m.
700
600
500
400
300
200
100
INITIAL CONCENTRATION
N_α
450
500
550
600
650
700
750
→T °K

Figure 8

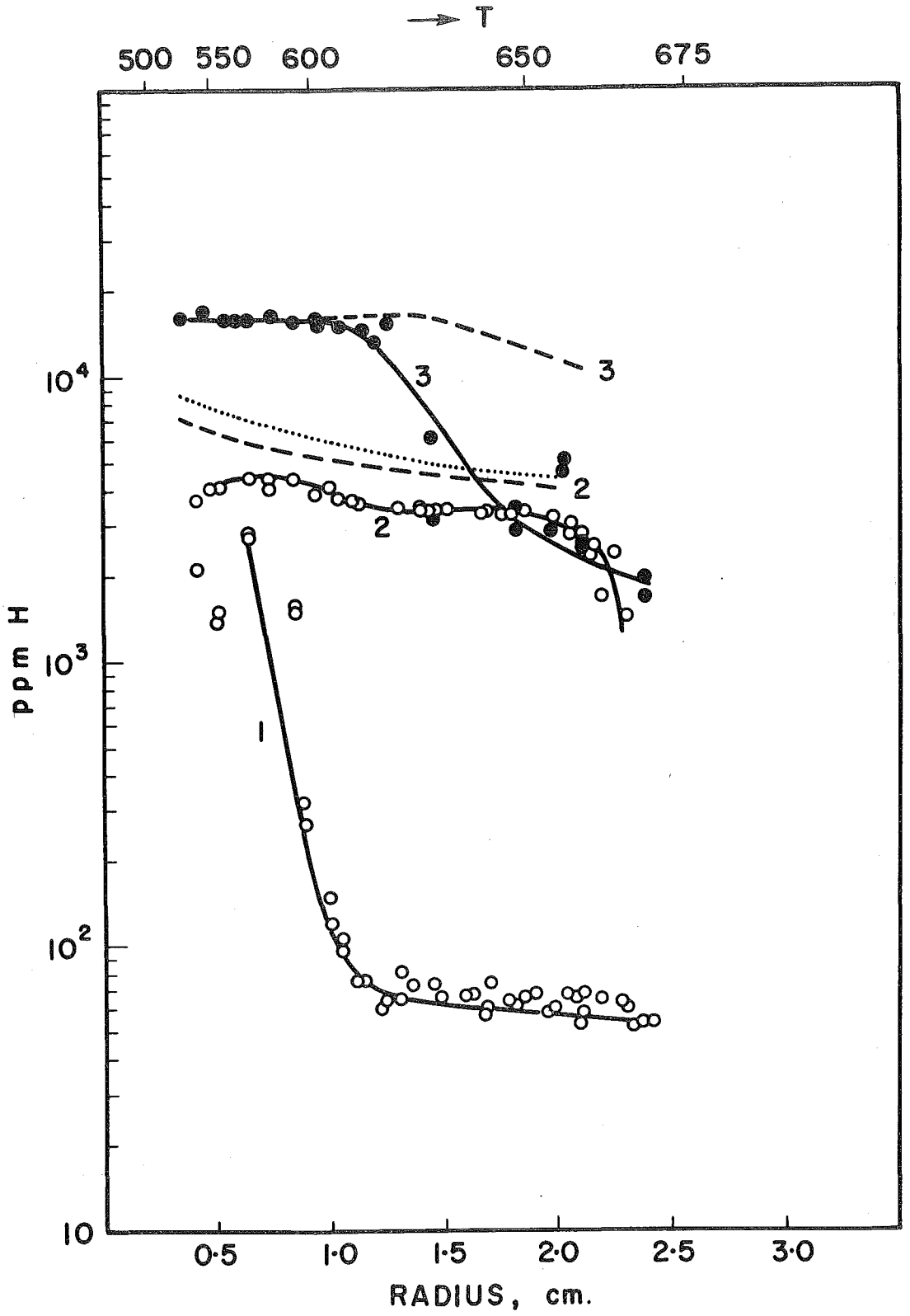
→ T
500
550
600
650
675
10^4
10^3
10^2
10
ppm H
3
3
2
2
8
8
1
0·5
1·0
1·5
2·0
2·5
3·0
RADIUS, cm.

Figure 9

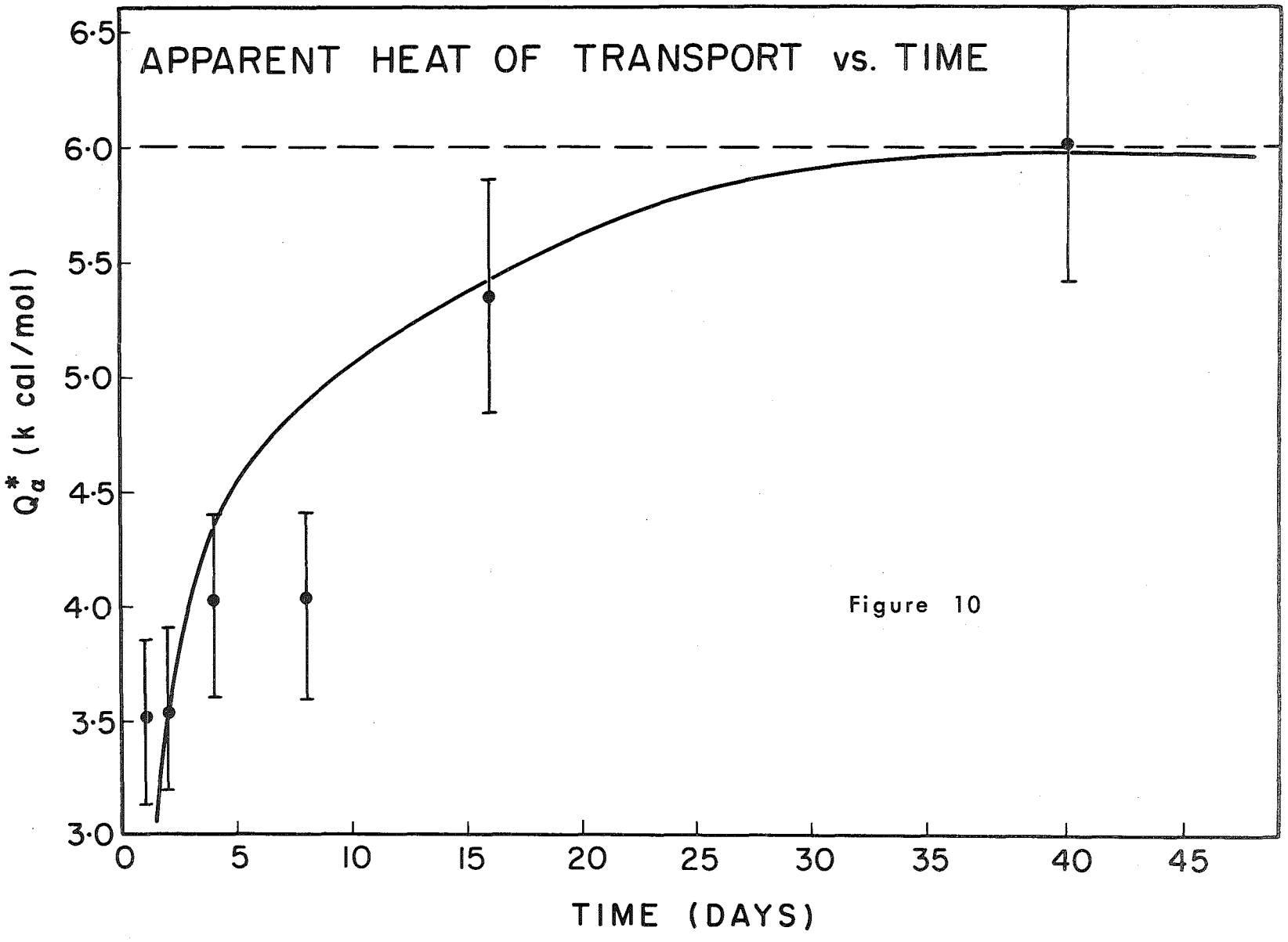
APPARENT HEAT OF TRANSPORT vs. TIME
Q_a^* (k cal/mol)
6·5
6·0
5·5
5·0
4·5
4·0
3·5
3·0
0
5
10
15
20
25
30
35
40
45
TIME (DAYS)

Figure 10