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KINETICS OF DISSOLUTION OF ZIRCONIUM
IN MOLTEN URANIUM

by

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ABSTRACT

The dissolution of zirconium in molten uranium has been studied, employing a one-dimensional model that assumes the rate of dissolution to be purely diffusion-controlled. The theoretical study has proceeded in three stages of increasing complexity: first, dissolution into a solution of infinite depth was treated, assuming the solid-liquid interface to be stationary; secondly, dissolution into a solution of finite depth was studied, again keeping the interface stationary (it was found that the second model was approximated closely by the more simple first model); thirdly, dissolution into a solution of infinite depth was studied, assuming the interface to move with time. It was found that the moving interface model is approximated closely by the simpler stationary interface model at temperatures not greatly in excess of the uranium melting point. This approximation becomes increasingly erroneous as the solution temperature increases but then at the higher temperatures the dissolution rate may become solute phase-transfer controlled, invalidating the diffusion-controlling assumption.

Equations were derived that permit the dissolution rate and total amount of zirconium in solution to be determined from a knowledge of the diffusion coefficient and equilibrium solubility data. The derivations are sufficiently general that the equations are applicable to any one-dimensional dissolution system in which the rate of dissolution is diffusion-controlled.

An experiment has been proposed to test the diffusion-controlling assumption, and also to yield data from which the diffusion coefficient may be computed. In essence, in the experiment the movement with time of the solid-liquid interface is followed by means of gamma radiography.

NOMENCLATURE

$c(x,t)$ = concentration of zirconium in molten uranium at point x at time t , gm/cm^3 .

D = diffusion coefficient, cm^2/sec .

ρ_{Zr} = density of zirconium (assumed equal to 6.49), gm/cm^3 .

ρ_{U} = density of uranium (assumed equal to 19.1), gm/cm^3 .

$k(T)$ = ratio of concentration of zirconium in molten uranium at solid-liquid interface to density of solid zirconium, $(\text{gm}/\text{cm}^3)/(\text{gm}/\text{cm}^3)$.

$\text{erf } x = \left(2/\sqrt{\pi} \right) \int_0^x e^{-\lambda^2} d\lambda$, error function, dimensionless.

$\text{erfc } x = \left(2/\sqrt{\pi} \right) \int_x^\infty e^{-\lambda^2} d\lambda$, complementary error function, dimensionless.

h = distance from solid-liquid interface to bottom of molten uranium solution, cm .

$W(t)$ = the total mass of zirconium per unit area normal to the direction of diffusion in the solution at time t , gm/cm^2 .

$\alpha = h/2 \sqrt{Dt}$, dimensionless.

$X(t)$ = position of interface at time t in moving interface model, cm .

β = constant of proportionality, equals $X/\sqrt{t}$, $\text{cm}/\text{sec}^{1/2}$.

$\nu = \beta/2 \sqrt{D}$, dimensionless.

T = system temperature, $^\circ\text{C}$.

d = diameter of circular collimating hole, cm .

S_0 = cobalt-60 source strength, curies.

$\mu_{1,2}$ = total linear absorption coefficients of 1.17 and 1.33-Mev gamma photons in uranium, cm^{-1} .

$\mu_{3,4}$ = total linear absorption coefficients of 1.17 and 1.33-Mev gamma photons in zirconium, cm^{-1} .

$\mu_{5,6}$ = total linear absorption coefficients of 1.17 and 1.33-Mev gamma photons in sodium iodide, cm^{-1} .

$\dot{n}$ = count rate measured by detector, counts/min.

ϵ = counting efficiency of sodium iodide detector, dimensionless.

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I. INTRODUCTION

A. General Background

An increasing amount of effort has been devoted to the development of fast reactors in recent years, due to their potential as commercial sources of power. One phase has been concerned with fast reactor safety.⁽¹⁾ Since present designs of fast reactors envision cores that contain large amounts of concentrated fissile material, an accident resulting in the melting down of the core can give rise to a supercritical reassembly of the fissile material. Hence, an elucidation of the meltdown mechanism is of paramount importance in order to determine the nature of such a reassembly. This mechanism is extremely complex, involving the nature of the fuel elements comprising the core, the power distribution in the fuel elements and the condition of the coolant.

A program at Argonne National Laboratory undertakes to study the fast reactor meltdown problem. One phase is concerned with the mode of failure of fuel elements at temperatures significantly above normal operating temperatures. Such fuel elements may consist of a uranium alloy clad with a material that serves to isolate the alloy from the coolant stream. The cladding materials usually employed are chemically resistant, high melting point metals or alloys, such as zirconium (used in the Enrico Fermi Fast Breeder Reactor) and stainless steel (used in the Experimental Breeder Reactor-II). A transient increase in temperature may result in an interaction of the uranium alloy with the cladding material, leading to failure of the fuel element. Three types of interaction, depending upon the temperature and composition of the uranium and cladding alloys, have been postulated:

1. interaction of solid uranium and solid cladding (solid-phase interdiffusion);
2. interaction of solid uranium and solid cladding with liquid eutectic formation at the interface; and
3. interaction of liquid uranium and solid cladding (continuous liquid solution formation).

B. Preliminary Research

An experimental program has been undertaken by Nuclear Metals, Inc., under the sponsorship of Argonne National Laboratory, to study the interactions of uranium with cladding materials at elevated temperatures. One phase is concerned with studies of the dissolution of such materials in molten uranium. These studies were made initially by immersing a rod of the cladding material vertically in a bath of molten uranium for a given time, and then removing the rod to measure its decrease in volume.

However, it was discovered that analyses of these experiments were very complicated because of the experimental geometrical arrangements employed.⁽²⁾ First, the necessarily limited amount of uranium used in a given experiment (about 250 grams) led to rates of dissolution that depended upon the concentration of solute at each point in the solution at a given time. (The rate of dissolution was independent of the geometrical arrangement only at the instant when dissolution commenced.) Secondly, as the cladding rod dissolved in the molten uranium, convection currents arose around the rod due to density gradients in the solution. The experiments showed that, as material dissolved from the rod, the latter assumed the shape of an icicle, tapering down from the top. Since the rate of dissolution along the rod was not uniform, it was likely that convection rather than diffusion controlled the rate of dissolution. Thus, these results could only be used to predict dissolution rates in systems where the same convection currents are established, and as such, were of limited applicability.

A temperature gradient in the molten uranium solution can also lead to the establishment of convection. Such a gradient results from a heat effect at the solid-liquid interface. For example, as zirconium dissolves in molten uranium, a quantity of heat of the order of the heat of fusion of the zirconium (5500 cal/mole) flows to the interface. If the zirconium surface dissolves at the rate of one millimeter per hour, the temperature gradient at the interface is estimated to be of the order of $0.04^{\circ}\text{C}/\text{cm}$. Thus, temperature gradient-induced convection is not likely to be severe in this system.

As a result of the above problems associated with the "vertical dip" dissolution studies, an experiment was proposed in which density gradient-initiated convection in the solution should not occur. In this experiment a disc of the cladding material at a given temperature is brought down into contact with the free surface of a liquid uranium bath at the same temperature. If the density of the cladding material is much less than that of the molten uranium, appreciable convection should not occur in the liquid, since the density of the solution increases with increasing distance down from the interface. Therefore, if the experiment is suitably designed to minimize edge effects, the system may approximate closely a one-dimensional

rectangular model for diffusion-controlled dissolution. This report describes a theoretical study of such a model. Although the method of approach is general, the discussion is given in terms of the zirconium-liquid uranium system. This system has been chosen because of the availability of necessary data, and because this system is nearly ideal over the entire range of composition of the liquid solution; no eutectic or compound formation occurs.⁽³⁾

C. Scope of the Study

This study has proceeded in three stages. In the first, the solid-liquid interface is assumed to be stationary with time. Diffusion into a uranium solution of infinite depth is studied, and then diffusion into the solution of finite depth is studied. An expression is derived that permits the diffusion coefficient to be evaluated from a knowledge of the total amount of zirconium in solution at a given time and the equilibrium solubility of zirconium in molten uranium. The error in the total zirconium in solution, due to assuming the uranium solution of finite depth to be infinitely deep, is derived, and its value for a specific case is computed.

In the second state of the study the more realistic assumption is made that the solid zirconium-liquid uranium interface moves with time. Here expressions are derived that enable the diffusion coefficient to be evaluated from a knowledge of the movement of the interface or else the total amount of zirconium in solution as a function of time. (In order to evaluate the diffusion coefficient by either of the above methods, it is again necessary to make use of experimental data on the equilibrium solubility of zirconium in molten uranium.) Also, the fractional deviation between the total amount of zirconium in solution at a given time computed by the nonstationary and stationary interface models is evaluated as a function of solution temperature, between the uranium and zirconium melting points.

In the third stage of the study an experiment is proposed that serves to:

1. test the assumption that the dissolution rate is diffusion controlled;
2. test the self-consistency of the equations derived for the moving interface model; and
3. furnish data from which the space- and time-average diffusion coefficient can be computed.

In this experiment a collimated beam of cobalt-60 gamma photons is employed to follow the movement of the solid-liquid interface with time. Use is made of the fact that for the experimental geometrical arrangement, the

zirconium will transmit twenty times as much of the incident beam as will the uranium, thus permitting the accurate location of the interface. Finally, an estimate is made of the minimum activity required for the cobalt-60 source.

II. BACKGROUND OF THE PROBLEM

A. Historical

Moelwyn-Hughes has summarized the work on the macroscopic theory of the dissolution of solids in liquids.⁽⁴⁾ From the work of Noyes and Whitney and later of Nernst, the concept arose that such dissolution takes place in two steps. First, solute passes from the surface of the solid into an adjacent liquid layer, and secondly, solute diffuses from this liquid layer into the bulk of the solution. The overall rate of dissolution is controlled by the slower of these two steps. The liquid-film model was employed by Berthoud to derive the dissolution kinetic equation; Moelwyn-Hughes' treatment of Berthoud's analysis is now given. Let

S = surface area of the solid in contact with the liquid, cm^2

n_s = number of molecules in unit area of the surface of the solid

n = concentration of solute in the bulk of the solution, molecules/cc

n' = concentration of solute in the liquid layer at a point very near the solid-liquid interface

n_0 = saturation concentration of solute

δ = thickness of liquid layer, cm

V = volume of solution, cm^3 .

The net rate of dissolution is equal to the rate at which molecules leave the surface of the solid minus the rate at which they return. Thus,

$$V \frac{dn}{dt} = \bar{\nu} n_s S - k_s n S \quad ,$$

where $\bar{\nu}$ and k_s are constants of proportionality. At equilibrium,

$$\frac{dn}{dt} = 0 \quad .$$

Thus,

$$\bar{\nu} n_s = k_s n_0 \quad .$$

By means of this reaction, the previous equation may be written in the form

$$\frac{dn}{dt} = \frac{k_s S}{V} (n_0 - n) \quad . \quad \text{II.2}$$

If the rate of dissolution depends upon diffusion through the liquid layer adjacent to the surface of the solid, then n' is less than n_0 , as indicated by the diagram below:

Employing the one-dimensional form of Fick's first law, a mass flow balance at a distance δ from the interface gives (noting that the concentration gradient is zero for $X > \delta$):

$$V \frac{dn}{dt} = -DS \frac{dn}{dx} \quad .$$

Assume that

$$\frac{dn}{dx} = \frac{n - n'}{\delta} \quad .$$

Then:

$$\frac{dn}{dt} = \frac{DS}{V\delta} (n' - n) \quad . \quad \text{II.3}$$

From equation II.2 it is seen that

$$\frac{dn}{dt} = \frac{k_s S}{V} (n_0 - n') \quad . \quad \text{II.4}$$

Thus,

$$n' = n_0 \frac{k_s + \frac{n}{n_0} \frac{D}{\delta}}{k_s + \frac{D}{\delta}} \quad \text{II.5}$$

If, $k_s \gg \frac{D}{\delta}$, then $n' \rightarrow n_0$, and the overall rate of dissolution is controlled by the diffusion step. If $k_s \ll \frac{D}{\delta}$, then $n' \rightarrow n$ and the overall dissolution rate is controlled by the solute phase-transfer step.

Combining equations II.4 and II.5 gives

$$\frac{dn}{dt} = \frac{k_s S}{V \left[1 + \frac{k_s \delta}{D} \right]} (n_0 - n) \quad \text{II.6}$$

Upon integrating there is obtained

$$n(t) = n_0 \left[1 - e^{-\frac{k_s S}{V \left[1 + \frac{k_s \delta}{D} \right]} t} \right] \quad \text{II.7}$$

(It should be noted that in references 4 and 5 the $\left[1 + \frac{k_s \delta}{D} \right]$ term incorrectly appears in the numerator of the exponential.)

As stated earlier, the dissolution rate is diffusion-controlled for

$$k_s \gg \frac{D}{\delta} \text{ or } \delta \gg \frac{D}{k_s} \quad .$$

Since from equation II.1,

$$k_s = \bar{v}_{n_s} / n_0 \quad , \quad \text{II.8}$$

it is to be expected that the dissolution rate will be diffusion controlled if n_0 is small, i.e., the solute is relatively insoluble.

It is important to note that the liquid layer dissolution model assumes that the solute concentration gradient is zero in the bulk of the solution. This implies a mixing action in the latter, due either to mechanical stirring or the presence of convection currents. The liquid layer model thus has two extremes. If the mixing effect in the bulk of the solution is very small, the layer is very thick, and in the limit approaches the depth of the solution. If, on the other hand, the mixing effect is very great, the liquid layer becomes very thin, and in the limit vanishes.

The dissolution rate of copper in liquid lead and bismuth under static, isothermal conditions was investigated recently by Ward and Taylor.⁽⁵⁾ The salient results of their work were that the dissolution of copper in molten lead and bismuth does follow equation II.7, and that the rate of dissolution seems to be controlled by the diffusion step. The arguments used to support this latter point are taken from the observed variation with temperature of the dissolution rate constant, defined as follows:

$$K \equiv \frac{k_s}{1 + \frac{k_s \delta}{D}} = \frac{k_s \frac{D}{\delta}}{\frac{D}{\delta} + k_s} \quad \text{II.9}$$

From equation II.9 it is seen that for:

$$k_s \gg \frac{D}{\delta}, K \longrightarrow \frac{D}{\delta} \quad (\text{Diffusion controlling})$$

$$k_s \ll \frac{D}{\delta}, K \longrightarrow k_s \quad (\text{Solute phase-transfer controlling}).$$

The main arguments employed by Ward and Taylor are:

1. If the dissolution rate is controlled by the solute phase-transfer step, then from equation II.8:

$$K \longrightarrow k_s = \bar{\nu} n_s / n_0$$

Since $\bar{\nu}$ and n_s are constants, it is seen that K is inversely proportional to n_0 , which increases with increasing temperature. Hence, K should decrease with increasing temperature. Actually, for the dissolution of copper in both lead and bismuth, K was found to increase with increasing temperature.

2. If at a given temperature $\bar{\nu}$ is approximately the same for the Cu-Pb and Cu-Bi dissolution systems, then, since $n_{0\text{Pb}}$ is less than $n_{0\text{Bi}}$, it follows that K_{Bi} should be less than K_{Pb} . Actually, K_{Bi} was found to be greater than K_{Pb} .

3. If the dissolution rate is diffusion controlled, then

$$K \longrightarrow D/\delta$$

If δ is constant over a range of temperatures, then in this range K is directly proportional to D ; this implies that the activation energy of dissolution is equal to the activation energy of diffusion. In the absence of experimental diffusion data for the Cu-Pb and Cu-Bi systems, the diffusion energies of

activation were estimated from the Stokes-Einstein equation ($D = kT/6\pi\eta r$) by Ward and Taylor, using published data for the viscosities of the two pure liquids. The estimated and observed energies (in cal/mole) are:

	<u>Cu-Pb</u>	<u>Cu-Bi</u>
Stokes-Einstein	3950	3300
Observed	3500	6300

It is seen that, because of the poor agreement of the results for the Cu-Bi system, it is not possible to conclude decisively that diffusion controls dissolution in these systems.

B. Background Assumptions

In the present study the liquid film model is modified for the case of a one-dimensional dissolution system in which the liquid is postulated to be free of convection currents. The modified liquid film model implies that, because of the absence of convection, the film thickness is equal to the full depth of the liquid, and hence the concentration gradient may not be assumed to be linear in the liquid. On the basis of the preceding discussion and the fact that the film thickness, δ , is large for a convection-free liquid, it is assumed that in the Zr-U system described earlier the dissolution rate is diffusion controlled at temperatures not too far above the uranium melting point. (It is quite possible that the dissolution rate becomes solute phase-transfer controlled at temperatures approaching the zirconium melting point.)

The concentration of zirconium in the molten uranium is assumed to be described by the one-dimensional rectangular form of Fick's second law:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad \text{II.10}$$

It is further assumed that the diffusion coefficient, D , defined by equation II.10 is constant with respect to coordinate and time, which is equivalent to the assumption that the diffusion coefficient is independent of the zirconium concentration. This is true at the uranium melting point (zero concentration), but becomes increasingly erroneous as the temperature of the solution increases. Since the dissolution rate is assumed to be diffusion controlled, thermodynamic equilibrium is postulated to exist at the solid-liquid interface, that is, the partial molal free energy of the zirconium in solution at the interface is equal to the free energy of the solid zirconium. Hence, the ratio of the concentration of zirconium in solution at the interface to the density of the solid zirconium depends only upon the temperature of the system (see ref. 4, p. 368).

III. THE STATIONARY INTERFACE MODEL OF DISSOLUTION

A. Dissolution into Liquid of Infinite Depth

The solution of the exact model for diffusion-controlled dissolution involves the concept of a solid-liquid interface that moves with time. Before treating this model it is instructive to consider a model in which the interface is stationary; the latter model is thus an asymptotic form of the previous model for very low dissolution rates and times. In this section the stationary interface model is solved for the two cases of diffusion into the solution of infinite depth and the solution of finite depth.

Consider the one-dimensional rectangular, diffusion-controlled, stationary interface model shown in the diagram below:

(Note: Symbols employed in the following and subsequent derivations are defined in the Nomenclature)

For the above system,

$$c(x,t) = \rho_{Zr}; \quad x \leq 0^-, \quad t \geq 0 \quad . \quad \text{III.1}$$

$$c(0^+,t) = c(0^-,t) k(T) = \rho_{Zr} k(T); \quad x = 0, \quad t > 0 \quad . \quad \text{III.2}$$

$$c(x,t) = 0; \quad x \geq 0^+, \quad t = 0 \quad . \quad \text{III.3}$$

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}; \quad x \geq 0^+, \quad t \geq 0 \quad . \quad \text{III.4}$$

From the nature of the model proposed,

$$\lim_{x \rightarrow \infty} c(x,t) = 0; \quad x \rightarrow \infty, \quad t \geq 0 \quad . \quad \text{III.5}$$

Define the Laplace transform of $c(x,t)$ with respect to time as

$$L \{c(x,t)\} = \bar{c}(x,p) = \int_0^{\infty} c(x,t) e^{-pt} dt \quad . \quad \text{III.6}$$

Then, from equations III.3 and 4,

$$\frac{\partial^2 \bar{c}}{\partial x^2} = \frac{p}{D} \bar{c} \quad ;$$

$$\bar{c}(x,p) = A(p) e^{-\sqrt{\frac{p}{D}} x} + B(p) e^{\sqrt{\frac{p}{D}} x} \quad .$$

Now, from equation III.5,

$$\lim_{x \rightarrow \infty} \bar{c}(x,p) = 0 \implies B(p) = 0$$

Thus,

$$\bar{c}(x,p) = A(p) e^{-\sqrt{\frac{p}{D}} x} \quad .$$

Transforming equation III.2 yields

$$\bar{c}(0^+,p) = \rho_{zr} k(T)/p \quad .$$

Hence,

$$A(p) = \rho_{zr} k(T)/p$$

and

$$\bar{c}(x,p) = \frac{\rho_{zr} k(T)}{p} e^{-\sqrt{\frac{p}{D}} x} \quad .$$

Taking the inverse transform of the above yields

$$c(x,t) = \rho_{zr} k(T) \operatorname{erfc} \frac{x}{2\sqrt{Dt}} \quad . \quad \text{III.7}$$

Note that

$$c(0^+,t) = \rho_{zr} k(T) \operatorname{erfc} 0^+ = \rho_{zr} k(T)$$

and

$$\lim_{t \rightarrow 0} c(x,t) = 0, \quad x > 0 \quad .$$

Now, the total amount of zirconium in solution, per unit area normal to the direction of diffusion, is

$$\begin{aligned} W(t) &= \int_0^{\infty} c(x,t) dx = \int_0^{\infty} \rho_{Zr} k(T) \operatorname{erfc} \frac{x}{2\sqrt{Dt}} dx \\ &= \rho_{Zr} k(T) \int_0^{\infty} \operatorname{erfc} \frac{x}{2\sqrt{Dt}} dx \end{aligned}$$

Set

$$\frac{x}{2\sqrt{Dt}} = \phi; \quad dx = 2\sqrt{Dt} d\phi$$

Then,

$$\begin{aligned} W(t) &= 2\sqrt{Dt} \rho_{Zr} k(T) \int_0^{\infty} \operatorname{erfc} \phi d\phi \\ &= 2\sqrt{Dt} \rho_{Zr} k(T) \left[\phi \operatorname{erfc} \phi - \frac{e^{-\phi^2}}{\sqrt{\pi}} \right]_0^{\infty} \\ &= 2\rho_{Zr} k(T) \sqrt{\frac{Dt}{\pi}} \end{aligned} \quad \text{III.8}$$

(See Appendix A). Hence,

$$\frac{dw}{dt} = \rho_{Zr} k(T) \sqrt{\frac{D}{\pi t}} \quad \text{III.9}$$

B. Dissolution into Liquid of Finite Depth

Consider, next, the one-dimensional rectangular, diffusion-controlled stationary interface model shown below:

For this system:

$$c(x,t) = \rho_{zr}; \quad x < 0^-, \quad t \geq 0 \quad . \quad \text{III.10}$$

$$c(0^+,t) = c(0^-,t) \quad k(T) = \rho_{zr} \quad k(T); \quad x = 0, \quad t \geq 0. \quad \text{III.11}$$

$$c(x,t) = 0; \quad h \geq x > 0, \quad t = 0 \quad \text{III.12}$$

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}; \quad h \geq x \geq 0^+, \quad t \geq 0 \quad . \quad \text{III.13}$$

Also, since there is no net diffusion of the solute out of the system at the bottom of the solution,

$$\left. \frac{\partial c}{\partial x} \right|_{x=h} = 0 \quad . \quad \text{III.14}$$

Transforming equation III.13 as before yields:

$$\begin{aligned} \frac{\partial^2 \bar{c}}{\partial x^2} &= \frac{p}{D} \bar{c} \\ \bar{c} &= A(p) e^{-\sqrt{\frac{p}{D}} x} + B(p) e^{\sqrt{\frac{p}{D}} x} \end{aligned} \quad \text{III.15}$$

From equations III.11 and 15,

$$\bar{c}(0^+,p) = \frac{\rho_{zr} k(T)}{p} = A + B \quad ,$$

$$A = \frac{\rho_{zr} k(T)}{p} - B,$$

and

$$\bar{c} = \frac{\rho_{zr} k(T)}{p} e^{-\sqrt{\frac{p}{D}} x} + 2 B \sinh \sqrt{\frac{p}{D}} x \quad . \quad \text{III.16}$$

Now,

$$L \left\{ \left. \frac{\partial c}{\partial x} \right|_{x=h} \right\} = \left. \frac{\partial \bar{c}}{\partial x} \right|_{x=h} = 0 \quad . \quad \text{III.17}$$

But from equation III.16

$$\frac{\partial \bar{c}}{\partial x} = -\frac{\rho_{zr} k(T)}{p} \sqrt{\frac{p}{D}} e^{-\sqrt{\frac{p}{D}} x} + 2B \sqrt{\frac{p}{D}} \cosh \sqrt{\frac{p}{D}} x \quad . \quad \text{III.18}$$

Thus,

$$2B = \frac{\rho_{zr} k(T) e^{-\sqrt{\frac{p}{D}} h}}{p \cosh \sqrt{\frac{p}{D}} h},$$

and

$$\begin{aligned} \bar{c}(x,p) &= \frac{\rho_{zr} k(T)}{p} e^{-\sqrt{\frac{p}{D}} x} + \frac{\rho_{zr} k(T) \sinh \sqrt{\frac{p}{D}} x}{p e^{\sqrt{\frac{p}{D}} h} \cosh \sqrt{\frac{p}{D}} h} \\ &= \frac{\rho_{zr} k(T)}{p} e^{-\sqrt{\frac{p}{D}} x} + \frac{2 \rho_{zr} k(T) \sinh \sqrt{\frac{p}{D}} x}{p \left[e^{2\sqrt{\frac{p}{D}} h} + 1 \right]} \end{aligned} \quad \text{III.19}$$

Expanding the denominator of the second term on the right side of equation III.19 by means of the binomial theorem and then simplifying the result yields

$$\bar{c}(x,p) = \rho_{zr} k(T) \left[\frac{1}{p} e^{-\frac{x}{\sqrt{D}} \sqrt{p}} + \frac{1}{p} \sum_{n=1}^{\infty} (-1)^{n+1} \left(e^{-\frac{2nh-x}{\sqrt{D}} \sqrt{p}} - e^{-\frac{2nh+x}{\sqrt{D}} \sqrt{p}} \right) \right]. \quad \text{III.20}$$

The inverse transform of equation III.20 is

$$c(x,t) = \rho_{zr} k(T) \left\{ \operatorname{erfc} \frac{x}{2\sqrt{Dt}} + \sum_{n=1}^{\infty} (-1)^{n+1} \left[\operatorname{erfc} \left(\frac{2nh-x}{2\sqrt{Dt}} \right) - \operatorname{erfc} \left(\frac{2nh+x}{2\sqrt{Dt}} \right) \right] \right\} \quad \text{III.21}$$

C. Comparison of Infinite and Finite Models

Define the following:

$$c_f = c(x,t) \text{ given by III.21; } w_f = \int_0^h c_f dx \quad .$$

$$c_\infty = c(x,t) \text{ given by III.7; } w_\infty = \int_0^\infty c_\infty dx \quad .$$

The error in $c(x,t)$ due to approximating the finite model of dissolution by the infinite model is

$$c_f - c_\infty = \Delta c(x,t) = \rho_{zr} k(T) \sum_{n=1}^{\infty} (-1)^{n+1} \left[\operatorname{erfc} \left(\frac{2nh-x}{2\sqrt{Dt}} \right) - \operatorname{erfc} \left(\frac{2nh+x}{2\sqrt{Dt}} \right) \right]. \quad \text{III.22}$$

An analysis of this expression for $\Delta c(x,t)$ shows that $\Delta c(x,t) \geq 0$, being zero at $x = 0$ and increasing to a maximum at $x = h$. Setting $h/2\sqrt{Dt} \equiv \alpha$, there is obtained

$$\Delta c(h,t) = \rho_{Zr} k(T) \sum_{n=1}^{\infty} (-1)^{n+1} \left\{ \operatorname{erfc} [\alpha(2n-1)] - \operatorname{erfc} [\alpha(2n+1)] \right\} \quad \text{III.23}$$

The error in $W(t)$ due to approximating the finite model of dissolution by the infinite model is

$$W_f - W_{\infty} = \Delta W = \int_0^h c_f dx - \int_0^{\infty} c_{\infty} dx = \int_0^h \Delta c(x,t) dx - \int_h^{\infty} c_{\infty} dx, \quad \text{III.24}$$

but

$$\int_0^h \Delta c(x,t) dx < h \Delta c(h,t)$$

and

$$\int_h^{\infty} c_{\infty} dx = \rho_{Zr} k(T) \int_h^{\infty} \operatorname{erfc} \frac{x}{2\sqrt{Dt}} dx = 2 \rho_{Zr} k(T) \sqrt{Dt} \left[\frac{e^{-\alpha^2}}{\sqrt{\pi}} - \alpha \operatorname{erfc} \alpha \right]$$

(See Appendix A). Thus

$$\Delta W < h \Delta c(h,t) - 2 \rho_{Zr} k(T) \sqrt{Dt} \left[\frac{e^{-\alpha^2}}{\sqrt{\pi}} - \alpha \operatorname{erfc} \alpha \right]$$

or

$$\frac{\Delta W}{W_{\infty}} < \sqrt{\pi} \left\{ \alpha \sum_{n=1}^{\infty} (-1)^{n+1} \left(\operatorname{erfc} [\alpha(2n-1)] - \operatorname{erfc} [\alpha(2n+1)] \right) - \frac{e^{-\alpha^2}}{\sqrt{\pi}} + \alpha \operatorname{erfc} \alpha \right\} \quad \text{III.25}$$

Taking the first two terms of the series in equation III.25 yields

$$\frac{\Delta W}{W_{\infty}} < \sqrt{\pi} \left\{ \alpha [\operatorname{erfc} \alpha - 2 \operatorname{erfc} 3\alpha + \operatorname{erfc} 5\alpha] - \frac{e^{-\alpha^2}}{\sqrt{\pi}} + \alpha \operatorname{erfc} \alpha \right\}$$

It is instructive to evaluate the above expression for a specific value of $\alpha = h/2\sqrt{Dt}$. Smith⁽⁶⁾ determined the diffusion coefficient of zirconium in molten uranium to be $1.9 \times 10^{-4} \text{ cm}^2/\text{sec}$ at 1270°C . Assume $h = 10 \text{ cm}$ and $t = 10 \text{ hours} = 3.6 \times 10^4 \text{ sec}$; then

$$\alpha = \frac{h}{2\sqrt{Dt}} = \frac{10}{2\sqrt{1.9 \times 3.6}} = 1.912$$

and

$$\frac{\Delta W}{W_{\infty}} < 1.772 \left\{ 1.912 [6.852 \times 10^{-3}] - \frac{0.02583}{1.772} + 1.912 \times 6.852 \times 10^{-3} \right\} = 2.06 \times 10^{-2} .$$

Thus, for the above conditions the error due to replacing the finite by the infinite dissolution model is less than 2%.

For the same conditions, the value of W_{∞} (given by equation III.8) is

$$W_{\infty} = 2 \rho_{\text{Zr}} k(T) \sqrt{\frac{Dt}{\pi}} = (2) (6.49) (0.132) \sqrt{\frac{(1.9) (3.6)}{3.1416}} = 2.53 \frac{\text{grams}}{\text{cm}^2}$$

[(see Appendix B.1 for evaluation of $k(T)$]. This corresponds to an actual recession of the interface of magnitude

$$2.53/6.49 = 0.390 \text{ cm.}$$

The above computations indicate that even for relatively large amounts of zirconium in solution, the stationary interface-finite depth model is approximated closely by the infinite model.

IV. THE MOVING INTERFACE MODEL OF DISSOLUTION

A. Dissolution into Liquid of Infinite Depth

In this section the one-dimensional rectangular moving interface model is solved for the case of diffusion into the solution of infinite depth. Consider the system shown in the diagram below:

(In this diagram the zirconium is indicated by the sectioned area.)

For the above system,

$$c(x, t) = \rho_{Zr}; \quad x \leq X^-, \quad t \geq 0. \quad \text{IV.1}$$

$$c(X^+, t) = c(X^-, t) k(T) = \rho_{Zr} k(T); \quad x = X, \quad t > 0 \quad \text{IV.2}$$

$$c(x, t) = 0; \quad x > 0, \quad t = 0 \quad \text{IV.3}$$

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}; \quad x \geq X^+, \quad t \geq 0 \quad \text{IV.4}$$

From the nature of the model proposed,

$$\lim_{x \rightarrow \infty} c(x, t) = 0; \quad x \rightarrow \infty, \quad t \geq 0 \quad \text{IV.5}$$

At $x = X(t)$, a mass balance on the zirconium is written, based upon the following diagram:

(This diagram shows the relative positions of the interface at time t and $t + \Delta t$, and the corresponding concentration curves.)

At time t , the total zirconium in solution, per unit area normal to the direction of flow, is

$$\int_X^\infty c(x, t) dx, \quad x > X^+.$$

At time $t + \Delta t$, the total zirconium in solution is

$$\int_{X + \Delta X}^\infty c(x, t + \Delta t) dx = \int_{X + \Delta X}^X c(x, t + \Delta t) dx + \int_X^\infty c(x, t + \Delta t) dx.$$

Thus, the mass balance is given by the relation

$$\int_{X+\Delta X}^X c(x,t+\Delta t) dx + \int_X^{\infty} [c(x,t+\Delta t) - c(x,t)] dx = -c(X^-,t) \Delta X \quad .$$

In the interval $X + \Delta X \leq x \leq X$, it is seen that $c(x,t + \Delta t) \approx c(X^+,t)$. The error in this approximation appears as the crosshatched area in the above diagram. In the interval $x > X$, it is found that

$$c(x,t + \Delta t) - c(x,t) \approx \frac{\partial c}{\partial t} \Delta t \quad .$$

Hence,

$$c(X^+,t) \int_{X+\Delta X}^X dx + \int_X^{\infty} \frac{\partial c}{\partial t} \Delta t dx = -c(X^-,t) \Delta X;$$

or

$$\int_X^{\infty} \frac{\partial c}{\partial t} dx = -\frac{\Delta X}{\Delta t} [c(X^-,t) - c(X^+,t)] \quad .$$

Taking the limit of the above expression and using equation IV.4, there is obtained

$$-\frac{dX}{dt} [c(X^-,t) - c(X^+,t)] = D \int_{X^+}^{\infty} \frac{\partial^2 c}{\partial x^2} dx = -D \left. \frac{\partial c}{\partial x} \right|_{x=X^+} \quad . \quad \text{IV.6}$$

A solution of equation IV.4 is:

$$c(x,t) = A + B \operatorname{erf} \frac{x}{2\sqrt{Dt}} \quad . \quad \text{IV.7}$$

From equation IV.5,

$$\lim_{x \rightarrow \infty} c(x,t) = A + B \operatorname{erf}(\infty) = A + B = 0; \quad B = -A$$

$$c(x,t) = A - A \operatorname{erf} \frac{x}{2\sqrt{Dt}} = A \operatorname{erfc} \frac{x}{2\sqrt{Dt}} \quad . \quad \text{IV.8}$$

From equation IV.2,

$$\rho_{Zr} k(T) = A \operatorname{erfc} \frac{X^+}{2\sqrt{Dt}} \quad . \quad \text{IV.9}$$

Since the left side of the above expression is independent of time, the right side implies that

$$X = \beta \sqrt{t} \quad , \quad \text{IV.10}$$

or

$$\rho_{zr} k(T) = A \operatorname{erfc} \frac{\beta}{2\sqrt{D}} \quad . \quad \text{IV.11}$$

Substituting equations IV.2, 8 and 10 into 6 yields

$$\begin{aligned} -D \frac{\partial}{\partial x} \left[A \left(1 - \operatorname{erf} \frac{x}{2\sqrt{Dt}} \right) \right]_{x=X^+} &= -\rho_{zr} (1 - k) \frac{d}{dt} (\beta \sqrt{t}) \\ D A \frac{\partial}{\partial x} \operatorname{erf} \frac{x}{2\sqrt{Dt}} \Big|_{x=X^+} &= -\frac{\rho_{zr} \beta (1-k)}{2\sqrt{t}} \quad . \end{aligned}$$

Now

$$\frac{\partial}{\partial x} \operatorname{erf} \frac{x}{2\sqrt{Dt}} = \frac{\partial}{\partial x} \cdot \frac{2}{\sqrt{\pi}} \int_0^{x/2\sqrt{Dt}} e^{-\lambda^2} d\lambda = \frac{e^{-\left(\frac{x}{2\sqrt{Dt}}\right)^2}}{\sqrt{\pi Dt}} \quad .$$

Thus,

$$A e^{-\left(\frac{\beta}{2\sqrt{D}}\right)^2} \sqrt{\frac{D}{\pi}} = -\frac{\rho_{zr} \beta (1-k)}{2} \quad . \quad \text{IV.12}$$

It is instructive to consider equations IV.11 and 12 further. Since

$$\operatorname{erfc} (-z) = 1 - \operatorname{erf} (-z) = 1 + \operatorname{erf} z,$$

for

$$-\infty \leq \frac{\beta}{2\sqrt{D}} \leq \infty,$$

it follows that

$$2 \geq \operatorname{erfc} \frac{\beta}{2\sqrt{D}} \geq 0 \quad .$$

Therefore, since $0 \leq k(T) \leq 1$ and $\rho_{zr} > 0$, from IV.11, $A \geq 0$.

Then from equation IV.12, $\beta \leq 0$. Since the moving interface does move to the left with time in the coordinate system employed (see equation IV.10) this result is anticipated.

Equations IV.11 and 12 are combined to yield a transcendental equation in β :

$$e^{\left(\frac{\beta}{2\sqrt{D}}\right)^2} \operatorname{erfc}\left(\frac{\beta}{2\sqrt{D}}\right) = -\frac{2k}{\beta(1-k)}\sqrt{\frac{D}{\pi}} = -\left(\frac{2\sqrt{D}}{\beta}\right)\left(\frac{k}{1-k}\right)\frac{1}{\sqrt{\pi}} \quad \text{IV.13}$$

Setting $\beta/2\sqrt{D} = \nu$ gives

$$\nu e^{\nu^2} \operatorname{erfc} \nu = -\left(\frac{k}{1-k}\right)\frac{1}{\sqrt{\pi}} \quad \text{IV.13'}$$

Because $k(T)$ is a function of temperature only, equation IV.13' gives ν implicitly as a function of temperature. This relationship is determined in the following steps:

1. k is evaluated as a function of T (Appendix B.1).
2. $\nu e^{\nu^2} \operatorname{erfc} \nu$ is evaluated as a function of ν (Appendix B.2).
3. $-\left(\frac{k}{1-k}\right)\frac{1}{\sqrt{\pi}}$ is evaluated as a function of T ; reference to ν vs $\nu e^{\nu^2} \operatorname{erfc} \nu$ yields ν vs T (Appendix B.3).

Knowing ν as a function of temperature permits the evaluation of A as a function of temperature:

$$A = \frac{\rho_{\text{Zr}} k(T)}{\operatorname{erfc} \nu}; \quad \text{IV.14}$$

this is done in Appendix B.4.

B. Comparison of Stationary and Moving Interface Models

Given ν as a function of temperature, it becomes possible to compare the equations for $W(t)$ developed by the stationary and moving interface models of dissolution. For the stationary interface infinite model,

$$W(t) = 2 \rho_{\text{Zr}} k(T) \sqrt{\frac{Dt}{\pi}} \quad \text{IV.15}$$

For the moving interface infinite model,

$$X = \beta \sqrt{t} \quad \frac{dX}{dt} = \frac{\beta}{2\sqrt{t}}$$

and

$$\frac{dw}{dt} = -\rho_{zr} \frac{dX}{dt} = -\frac{\rho_{zr} \beta}{2\sqrt{t}} \quad .$$

Then,

$$W(t) = -\rho_{zr} \int_0^t \frac{dX}{dt} dt = -\rho_{zr} \beta \sqrt{t} \quad . \quad \text{IV.16}$$

(Note: This result is also obtained from $W(t) = \int_X^\infty c(x,t) dx$; see Appendix A)

If equations IV.15 and 16 are equated, it is seen that

$$2 \rho_{zr} k(T) \sqrt{\frac{Dt}{\pi}} = -\rho_{zr} \beta \sqrt{t}$$

and

$$\nu = \frac{\beta}{2\sqrt{D}} = -\frac{k}{\sqrt{\pi}} \quad . \quad \text{IV.17}$$

Equation IV.17 becomes exact only in the limit as $k \rightarrow 0$, since then, by equation IV.17, $\nu \rightarrow 0$. Hence $e^{\nu^2} \rightarrow 1$, $\text{erfc } \nu \rightarrow 1$, and from equation IV.13',

$$\nu \rightarrow -k/\sqrt{\pi} \quad .$$

Thus, the two models become equivalent for temperatures decreasing in the limit to the uranium melting point, 1133°C, and short diffusion times.

The fractional deviation between equations IV.16 and 15 (setting $\beta = 2\nu\sqrt{D}$) is

$$\epsilon = \frac{\Delta W}{W} = \frac{-\rho_{zr} \beta \sqrt{t} - 2\rho_{zr} k(T) \sqrt{\frac{Dt}{\pi}}}{-\rho_{zr} \beta \sqrt{t}} = \frac{-\nu - \frac{k}{\sqrt{\pi}}}{-\nu} \quad \text{IV.18}$$

100 ϵ is evaluated as a function of temperature in the following:

T°C	$-\nu$	k	$k/\sqrt{\pi}$	$-\nu - (k/\sqrt{\pi})$	100 ϵ	T°C	$-\nu$	k	$k/\sqrt{\pi}$	$-\nu - (k/\sqrt{\pi})$	100 ϵ
1133	0	0	0	0	0	1600	0.418	0.563	0.318	0.1000	23.92
1200	0.0345	0.061	0.0344	0.0001	0.29	1700	0.638	0.736	0.415	0.223	34.95
1300	0.0974	0.163	0.0920	0.0054	5.54	1800	1.183	0.942	0.531	0.652	55.11
1400	0.1780	0.280	0.1580	0.0200	11.24	1820	∞	1.000	0.564	∞	100.00
1500	0.2795	0.412	0.232	0.0475	16.99						

(These results are plotted in Fig. 5.)

The above computation shows that $\epsilon \geq 0$ and increases with increasing uranium solution temperature. This result may be explained by the fact that, at any temperature above the uranium melting point, the rate of dissolution of zirconium is greater for the moving interface model than it is for the stationary interface model;

$$\frac{\left(\frac{dw}{dt}\right)_{m.i.}}{\left(\frac{dw}{dt}\right)_{s.i.}} = \frac{-\frac{\rho_{Zr}\beta}{2\sqrt{t}}}{\rho_{Zr} k(T) \sqrt{\frac{D}{\pi t}}} = -\frac{\beta}{2\sqrt{D}} \frac{\sqrt{\pi}}{k} = \frac{-\nu}{k} \sqrt{\pi} \quad \text{IV.19}$$

This ratio is computed as a function of temperature in the following:

T, °C	$(-\nu)$	$(-\nu)\sqrt{\pi}$	k	$\left(\frac{dw}{dt}\right)_{m.i.} / \left(\frac{dw}{dt}\right)_{s.i.}$
1133	0	0	0.0610	1.000
1200	0.0345	0.0611	0.163	1.002
1300	0.0974	0.1725	0.280	1.058
1400	0.1780	0.3153	0.280	1.127
1500	0.2795	0.495	0.412	1.200
1600	0.418	0.741	0.563	1.317
1700	0.638	1.130	0.736	1.536
1800	1.183	2.097	0.942	2.225
1820	∞	∞	1.000	∞

It must be borne in mind that at the higher temperatures the diffusion-controlling assumption may become invalid.

V. PROPOSAL OF EXPERIMENT

A. Description

The dissolution model considered in the previous sections is based upon the assumption that the rate of dissolution of zirconium into molten uranium is diffusion controlled. In this section an experiment is proposed that tests both the above assumption and the self-consistency of the equations describing the moving interface model. The experiment also yields data from which the space-and-time averaged diffusion coefficient can be computed.

The experiment consists of determining the movement with time of the solid zirconium-liquid uranium solution interface in the system described in section I-B. If the dissolution rate is diffusion controlled,

the interface will move as the square root of time, that is, a plot of the interface position, X , vs $t^{1/2}$ will be linear (see Equation IV.10). No other known dissolution model will lead to this result.⁽²⁾ The slope of X vs $t^{1/2}$ is equal to the parameter β , which is a function of the diffusion coefficient and another parameter, ν (see Equations IV.13 and 13'). Thus, if the postulated model of dissolution is correct, measurement of the movement of the interface with time yields results from which the diffusion coefficient, D , can be evaluated. It is seen that this value of D does not come directly from measurements made upon the liquid phase; it is just an average for the dimensions and duration of the experiment being made. If the moving interface model is correct, the value of β may also be obtained by measuring the total amount of zirconium in solution, $W(t)$, as a function of time. In Appendix A it is shown that by integrating the moving interface expression for the concentration of zirconium in uranium over the depth of the solution, $W(t)$ is obtained as a function of β and t . Therefore, by determining $W(t)$ at time t , the parameter β and hence D can be evaluated. This value of D should be the same as that computed from the moving interface data.

B. Location of Interface

The movement of the solid-liquid interface with time can be determined in several ways. The simplest of these is to freeze the system at the end of the desired interaction time, cut it into suitable sections, and examine these under low-power magnification to determine the position of the interface. If freezing the entire system requires too long a time, the zirconium disc (and adhering uranium) can simply be removed from the solution, chilled and then treated as above. (A more elegant method, called electronic microsoundings, has been used to locate the interface in uranium-transition metal diffusion couples.⁽⁸⁾ In this method the sample section is bombarded with a highly focused electron beam and the resulting X-ray spectrum is studied to yield an element analysis.) The main disadvantages of the section examination method are that it gives only one measurement of X vs t per experiment, and this measurement requires careful averaging of the irregularities in the interface.

The movement of the interface can be followed continuously by means of gamma radiography, and thus one experiment can be made to yield a number of values of X vs t at a given temperature. The equipment employed in such an experiment consists of the following:

- (1) a suitable furnace containing the system under test;
- (2) a highly collimated gamma source;
- (3) a scintillation detector connected to a single-channel analyzer;
and
- (4) a yoke to hold the source and detector in line and indicate the relative motion of this line.

Such an arrangement is shown below:

It is important to note that this experiment does not require a determination of the relative or absolute count rates, but only the point at which a sharp discontinuity in the observed count rate occurs. Cobalt-60 is suggested as the gamma source; in each disintegration it emits a 1.17 and 1.33-Mev photon. The base setting of the analyzer corresponds to just less than 1.17 Mev, and the window is just larger than 0.16 Mev. This permits counting of essentially only the cobalt-60 primary gamma photons.

It is of interest to estimate the required activity of the cobalt-60 source and also the ratio of the count rate after passage through the zirconium to that after passage through the uranium. The symbols employed are defined in the preceding diagram and the Nomenclature.

Let:

$$a = \frac{1}{2} \text{ in.} = 1.270 \text{ cm}$$

$$\mu_1 = 19.1 \times 0.0700 = 1.337 \text{ cm}^{-1}$$

$$2a\mu_1 = 3.396$$

$$\mu_2 = 19.1 \times 0.0622 = 1.188 \text{ cm}^{-1}$$

$$2a\mu_2 = 3.018$$

The total rate of interaction of the gamma photons that have penetrated the uranium with the scintillator is

$$S_0 \times 3.70 \times 10^{10} \times 60 \times \frac{\pi \left(\frac{d}{2}\right)^2}{4\pi l^2} \left[\epsilon_1 e^{-2a\mu_1} + \epsilon_2 e^{-2a\mu_2} \right]$$

(The buildup due to secondary photon production is neglected because essentially only the primary photons are counted.) The values of ϵ_1 and ϵ_2 are estimated. The NaI(Tl) scintillation crystal is assumed to be 2.54 cm thick. From Price,(7)

$$\mu_5 = 0.20 \text{ cm}^{-1}; \mu_6 = 0.18 \text{ cm}^{-1}$$

$$\epsilon_1 = 1 - e^{-0.20 \times 2.54} = 0.3983$$

$$\epsilon_2 = 1 - e^{-0.18 \times 2.54} = 0.3669$$

Hence, the measured count rate is

$$\dot{n} = 4.342 \times 10^9 S_0 d^2 / \ell^2$$

As an estimate, set

$$S_0 = 10^{-2} \text{ curie} = 10 \text{ millicuries}$$

$$d = 0.1 \text{ cm}$$

$$\ell = 40 \text{ cm}$$

Then,

$$\dot{n} = 271 \text{ counts/min.}$$

Thus, a 10-millicurie cobalt-60 source will give a count rate, after passage through the uranium, that is well above the background count rate of the detector, with a resolution of approximately one millimeter. If it is desired to improve the resolution of the apparatus by decreasing d to 0.5 millimeter, then in order to hold the count rate constant it is necessary to increase the cobalt-60 activity to 40 millicuries. It may be recalled that for the experimental conditions postulated at the end of Section III, the interface was estimated to recede 3.9 millimeters in ten hours. It thus appears feasible to design this apparatus to yield sufficient resolution of the solid-liquid interface. If nonuniform dissolution of the interface occurs, the radiography technique will locate the mean interface position at a given time.

The ratio, R , of the count rate after passage through the zirconium to the count rate after passage through the uranium, is computed from the following:

$$\mu_3 = 0.0508 \text{ cm}^{-1}, 2a\mu_3 = 0.1290; \mu_4 = 0.0475 \text{ cm}^{-1}, 2a\mu_4 = 0.1207$$

$$R = \frac{e^{-2a\mu_3} + e^{-2a\mu_4}}{e^{-2a\mu_1} + e^{-2a\mu_2}} = 21.42$$

The count rate after passage through the zirconium is:

$$271 \times 21.42 = 5,805 \text{ counts/min.}$$

The relatively large magnitude of R indicates that this technique is well suited for locating the uranium-zirconium interface.

VI. CONCLUSIONS

A model has been presented for the dissolution of zirconium into molten uranium, based upon the assumption that the rate of dissolution is diffusion controlled. It has been shown that at temperatures not greatly in excess of the uranium melting point the stationary interface-finite depth model is approximated closely by the stationary interface-infinite depth model. Also, at these temperatures the moving interface-infinite depth model is approximated closely by the stationary interface-infinite depth model. It may be concluded from these results that if dissolution is diffusion-controlled at temperatures not too far above the uranium melting point, the stationary interface-infinite depth model can be used to predict the recession of the solid-liquid interface with time. It must be borne in mind that at temperatures significantly above the uranium melting point, even the moving interface model becomes inadequate in predicting the movement of the interface. This is because at higher temperatures the rate of dissolution may become solute phase-transfer controlled, as was pointed out in Section II.

The equations derived in this study are applicable to any dissolution system in which the rate of dissolution is diffusion controlled and the equilibrium solubility is a smooth function of the system temperature. This suggests the possibility of using these equations to predict the dissolution of niobium, tantalum, titanium, and tungsten in molten uranium. Further experimental work, along the lines outlined in Section V, would be required to check this possibility.

FIG 1
COMPUTED k VS T

FIG 2a
 $\nu e^{\nu^2} \operatorname{erfc} \nu$ VS ν

FIG 2b
 $\nu e^{\nu^2} \operatorname{erfc} \nu$ VS ν

FIG 3
 ν VS T

FIG 4
 $k\rho_{2r}$ & A VS T

FIG 5
 100ϵ VS T

APPENDIX A

ALTERNATE DERIVATION OF MOVING BOUNDARY EQUATION

By definition,

$$w(t) = \int_X^\infty c(x,t) dx = \int_X^\infty A \operatorname{erfc} \frac{x}{2\sqrt{Dt}} dx = A \int_X^\infty \operatorname{erfc} \frac{x}{2\sqrt{Dt}} dx.$$

Set

$$x/2\sqrt{Dt} = \phi$$

so that

$$x = 2\sqrt{Dt} \phi$$

$$dx = 2\sqrt{Dt} d\phi.$$

Then

$$w(t) = 2A\sqrt{Dt} \int_{X/2\sqrt{Dt}}^\infty \operatorname{erfc} \phi d\phi = 2A\sqrt{Dt} \int_\nu^\infty \operatorname{erfc} \phi d\phi.$$

But

$$\int \operatorname{erfc} \phi d\phi = \phi \operatorname{erfc} \phi - \frac{e^{-\phi^2}}{\sqrt{\pi}}.$$

Thus,

$$W(t) = 2A\sqrt{Dt} \left[\lim_{\phi \rightarrow \infty} \phi \operatorname{erfc} \phi - \nu \operatorname{erfc} \nu + \frac{e^{-\nu^2}}{\sqrt{\pi}} \right].$$

But,

$$\lim_{\phi \rightarrow \infty} \phi \operatorname{erfc} \phi = \lim_{\phi \rightarrow \infty} \frac{\operatorname{erfc} \phi}{\frac{1}{\phi}} = \lim_{\phi \rightarrow \infty} \frac{\frac{-2}{\sqrt{\pi}} e^{-\phi^2}}{-\frac{1}{\phi^2}} = \frac{2}{\sqrt{\pi}} \lim_{\phi \rightarrow \infty} \frac{\phi^2}{e^{\phi^2}} = 0.$$

Therefore:

$$W(t) = 2A\sqrt{Dt} \left[-\nu \operatorname{erfc} \nu + \frac{e^{-\nu^2}}{\sqrt{\pi}} \right].$$

Employing equation IV.11 to eliminate A, there is obtained

$$\begin{aligned}
 W(t) &= \frac{2\sqrt{Dt} \rho_{zr} k(T)}{\operatorname{erfc} \nu} \left[-\nu \operatorname{erfc} \nu + e^{-\nu^2/\sqrt{\pi}} \right] \\
 &= \frac{2\sqrt{Dt} \rho_{zr} k(T)}{e^{\nu^2} \operatorname{erfc} \nu} \left[-\nu e^{\nu^2} \operatorname{erfc} \nu + \frac{1}{\sqrt{\pi}} \right] .
 \end{aligned}$$

Equation IV.13' may be used to simplify the above expression:

$$\begin{aligned}
 W(t) &= \frac{2\sqrt{Dt} \rho_{zr} k(T)}{e^{\nu^2} \operatorname{erfc} \nu} \left[\frac{k}{1-k} \cdot \frac{1}{\sqrt{\pi}} + \frac{1}{\sqrt{\pi}} \right] \\
 &= 2\sqrt{\frac{Dt}{\pi}} \left(\frac{k}{1-k} \right) \rho_{zr} \frac{1}{e^{\nu^2} \operatorname{erfc} \nu} = -2\sqrt{\frac{Dt}{\pi}} \left(\frac{k}{1-k} \right) \rho_{zr} \frac{\nu(1-k)}{k} \sqrt{\pi} \\
 &= -2 \rho_{zr} \nu \sqrt{Dt} = -\rho_{zr} \beta \sqrt{t} .
 \end{aligned}$$

APPENDIX B

I. EVALUATION OF $k(T)$ vs T .

By definition:

$$k(T) = c(X^+, t) / \rho_{Zr} \quad .$$

Employing the data from BMI-1300,⁽²⁾ $k(T)$ is computed upon the basis of one gram of a mixture of uranium and zirconium. This computation depends upon the following assumptions:

1. $\rho_{Zr} = 6.49 \text{ gm/cm}^3$; $\rho_u = 19.1 \text{ gm/cm}^3$.
2. The solution is ideal, i.e., $v_{Zr} + v_u = v_{\text{solution}}$.

Then,

$T, ^\circ\text{C}$	Wt % Zr	Mass Zr, gm	Mass U, gm	Volume Zr, cm^3	Volume U, cm^3	Total Volume, cm^3	$\frac{\text{gm Zr}}{\text{cm}^3}$	$k(T)$
1133	0	0	1.000	0	19.1	19.1	0	0
1190	2	0.02	0.98	0.0031	0.0513	0.0544	0.368	0.0567
1290	5	0.05	0.95	0.0077	0.0497	0.0574	0.871	0.1342
1370	10	0.10	0.90	0.0154	0.0471	0.0625	1.600	0.247
1500	20	0.20	0.80	0.0308	0.0419	0.0727	2.751	0.424
1590	30	0.30	0.70	0.0462	0.0366	0.0828	3.623	0.558
1670	40	0.40	0.60	0.0616	0.0314	0.0930	4.301	0.663
1740	60	0.60	0.40	0.0924	0.0209	0.1133	5.296	0.816
1790	80	0.80	0.20	0.1233	0.0105	0.1338	5.979	0.921
1820	100	1.00	0.00	0.1541	0.000	0.1541	6.49	1.000

$k(T)$ vs T is plotted in Fig. 1.

II. EVALUATION OF $\nu e^{\nu^2} \text{erfc } \nu$ VS ν .

For

$$0 \leq k(T) \leq 1,$$

it is seen that

$$0 \geq \nu e^{\nu^2} \text{erfc } \nu \geq -\infty.$$

Then:

$(-\nu)$	ν^2	e^{ν^2}	$-\operatorname{erf} \nu$	$\operatorname{erfc} \nu$	$-\nu e^{\nu^2} \operatorname{erfc} \nu$
0	0	1.0000	0	1.0000	0
0.03	0.0009	1.0009	0.0338	1.0338	0.0310
0.06	0.0036	1.0036	0.0676	1.0676	0.0643
0.09	0.0081	1.0081	0.1013	1.1013	0.0999
0.12	0.0144	1.0145	0.1348	1.1348	0.1382
0.15	0.0225	1.0227	0.1680	1.1680	0.1792
0.18	0.0324	1.0329	0.2009	1.2009	0.2233
0.21	0.0441	1.0451	0.2335	1.2335	0.2707
0.24	0.0576	1.0593	0.2657	1.2657	0.3218
0.27	0.0729	1.0756	0.2974	1.2974	0.3768
0.30	0.0900	1.0942	0.3286	1.3286	0.4361
0.33	0.1089	1.1150	0.3593	1.3593	0.5002
0.35	0.1225	1.1304	0.3794	1.3794	0.5457
0.36	0.1296	1.1384	0.3893	1.3893	0.5694
0.45	0.2025	1.2245	0.4755	1.4755	0.8130
0.60	0.3600	1.4333	0.6039	1.6039	1.3793
0.80	0.6400	1.8965	0.7421	1.7421	2.6431
1.00	1.0000	2.7183	0.8427	1.8427	5.0090
1.10	1.2100	3.3530	0.8802	1.8802	6.9347
1.20	1.4400	4.2210	0.9103	1.9103	9.6761
1.30	1.6900	5.4190	0.9340	1.9340	13.624

$\nu e^{\nu^2} \operatorname{erfc} \nu$ vs ν is plotted in Fig. 2.

III. EVALUATION OF $\nu(T)$ VS T.

By referring to Figs. 1 and 2, $\nu(T)$ vs T is evaluated:

T, °C	k	1-k	$k/(1-k)$	$(-\nu e^{\nu^2} \operatorname{erfc} \nu)$	$(-\nu)$
1133	0	1.000	0	0	0
1200	0.061	0.939	0.0650	0.0367	0.0345
1250	0.111	0.889	0.1249	0.0705	0.0643
1300	0.163	0.837	0.1947	0.1098	0.0974
1350	0.221	0.779	0.2837	0.1601	0.1366
1400	0.280	0.720	0.3889	0.2194	0.1780
1450	0.343	0.657	0.5221	0.2946	0.2242
1500	0.412	0.588	0.7007	0.3953	0.2795
1550	0.486	0.514	0.9455	0.5335	0.345
1600	0.563	0.437	1.288	0.7267	0.418
1650	0.647	0.353	1.833	1.0342	0.516
1700	0.736	0.264	2.788	1.573	0.638
1750	0.831	0.169	4.917	2.774	0.812
1800	0.942	0.058	16.241	9.163	1.183
1820	1.000	0	∞	∞	∞

$\nu(T)$ vs T is plotted in Fig. 3.

IV. EVALUATION OF $A(T)$ vs T .

$T, ^\circ\text{C}$	$(-\nu)$	$\text{erfc } \nu$	$k(T)$	$\rho_{\text{Zr}} k(T)$	A
1133	0	1.0000	0	0	0
1197	0.03	1.0338	0.059	0.383	0.370
1244	0.06	1.0676	0.105	0.681	0.638
1290	0.09	1.1013	0.153	0.993	0.902
1330	0.12	1.1348	0.198	1.285	1.132
1367	0.15	1.1680	0.239	1.551	1.328
1403	0.18	1.2009	0.284	1.843	1.535
1437	0.21	1.2335	0.327	2.122	1.720
1466	0.24	1.2657	0.363	2.356	1.861
1492	0.27	1.2974	0.399	2.590	1.996
1517	0.30	1.3286	0.434	2.817	2.120
1539	0.33	1.3593	0.468	3.037	2.234
1562	0.36	1.3893	0.502	3.258	2.345
1617	0.45	1.4755	0.592	3.842	2.604
1686	0.60	1.6039	0.710	4.608	2.873
1747	0.80	1.7421	0.823	5.341	3.066
1783	1.00	1.8427	0.903	5.860	3.180
1793	1.10	1.8802	0.927	6.016	3.200
1802	1.20	1.9103	0.942	6.114	3.201

k , ρ_{Zr} and A vs T are plotted in Fig. 4.

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