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**Processing of Plutonium by Ion Exchange VIII.
Self-Diffusion Studies in Anion-Exchange Resin**



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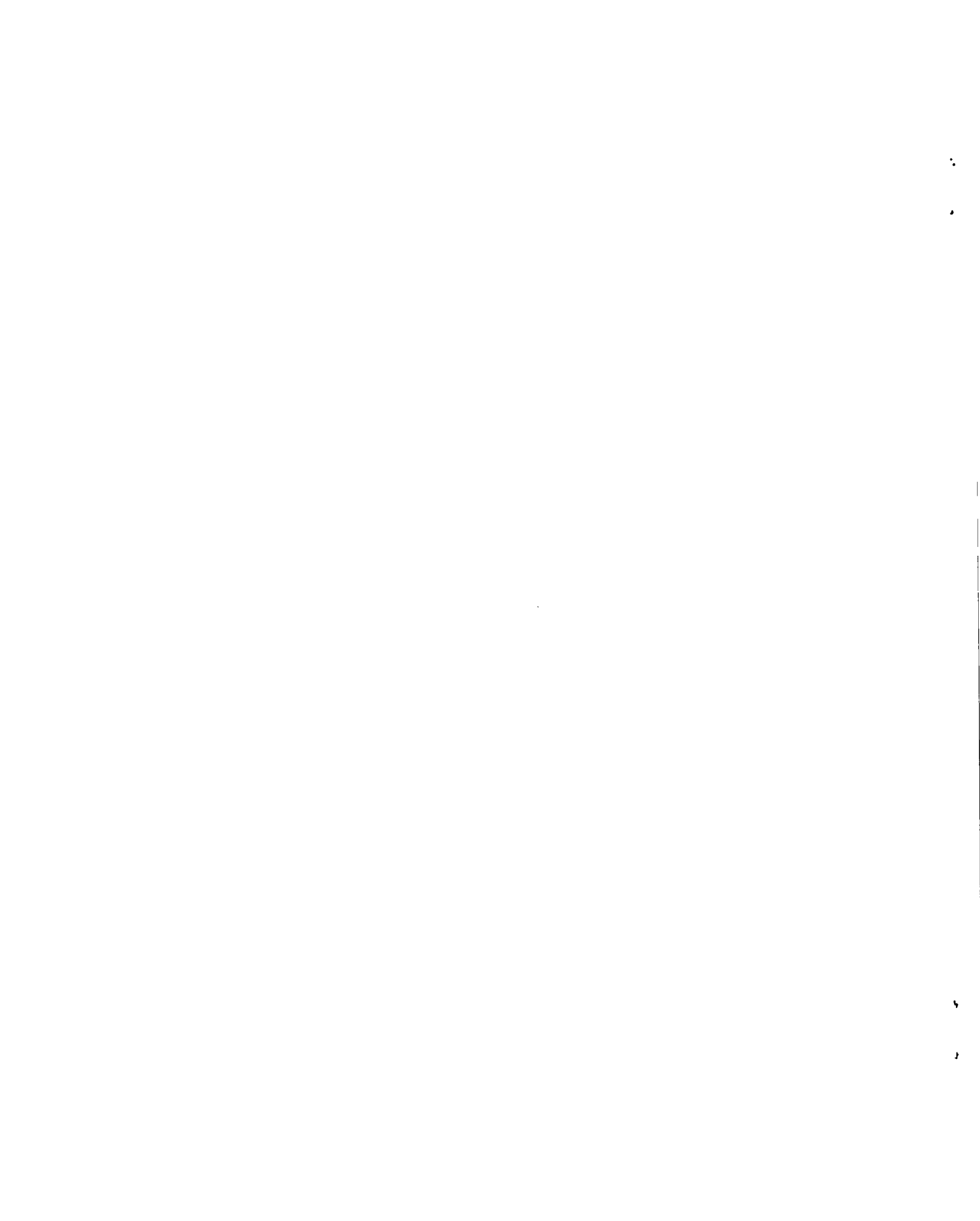
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Processing of Plutonium by Ion Exchange VIII.
Self-Diffusion Studies in Anion-Exchange Resin

by

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ABSTRACT

The isotopic migration rate of plutonium(IV) in Dowex 1 anion-exchange resin was studied with varying temperature, nominal percent cross-linking, and fractional equilibrium loading with plutonium. The diffusion coefficient decreases very rapidly with increasing loading. A diffusional model that is suggested by these results is qualitatively discussed.

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INTRODUCTION

The previous two papers in this series considered the kinetics of the sorption and the desorption of plutonium(IV) with anion-exchange resin from nitrate solutions.^{1,2} This and earlier work³ showed both processes to be controlled by the rate of diffusion of plutonium(IV) within the spherical resin particles. From Fick's laws of diffusion it can be shown⁴ that radial diffusion in a sphere is described by

$$\frac{\partial x(r)}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 \bar{D}(r, x) \frac{\partial x(r)}{\partial r} \right] . \quad (1)$$

The concentration of the diffusing plutonium at fractional radial distance r is $x(r)$; and $\bar{D}(r, x)$ is the local, intraspherical diffusion coefficient at r .

The only significant systems where equation (1) has been integrated exactly are those where it has been assumed that $\bar{D}(r, x)$ is independent of r and x and constant throughout the process. The desorption of plutonium(IV) from resin with x initially a nonzero constant follows such a treatment,² but sorption with x initially zero does not. The migration of isotopes in a system otherwise at equilibrium is described by the simple theory.

It was the purpose of the work reported here to study the diffusion of plutonium isotopes in anion-exchange systems at chemical and physical equilibrium in order to provide further information regarding this complicated diffusional system. A plutonium-239-rich resin phase was contacted with a plutonium-238-rich aqueous phase, and the plutonium-238 concentration in the aqueous phase was measured at timed intervals.

EXPERIMENTAL

A weighed amount (on an "oven-dry" basis) of resin was equilibrated with an appropriate nitric acid solution of plutonium-239 for sufficient time¹ to ensure that during the duration of the subsequent isotopic-diffusion experiment the chemical composition of the resin would not change significantly. After equilibration the aqueous phase was analyzed; a new aqueous phase was prepared with exactly the same chemical composition, but containing about five mole-percent plutonium-238, an optimal percentage for an alpha-particle, pulse-height analysis. A volume of this solution, such that the total plutonium in each phase was nearly equal, was added to the equilibrated resin phase at time zero.

The experimental technique was described before.¹ Samples of the aqueous phase, sufficiently small so that the total plutonium removed was insignificant, were removed from the stirred mixture at timed intervals. The sampling time was about 15 sec as was the initial mixing time. The fraction of isotopic equilibrium, Y, was calculated from

$$Y = \frac{1+w}{w} \cdot \frac{P_0 - P}{P_0 - \bar{P}_0}, \quad (2)$$

where w is the total equilibrium mole ratio of plutonium in the resin to that in the solution, P is the mole-percent plutonium-238 in the solution, and P₀ its initial value. The initial mole-percent plutonium-238 in the resin phase, \bar{P}_0 ,

was always 6.9×10^{-3} due to a small amount of plutonium-238 in the plutonium-239 stock solution.

RESULTS AND CONCLUSIONS

With a finite volume of aqueous phase an approximation (for $\tau \leq 0.1$) to the exact solution for $Y(t)$ resulting from equation (1) is given by⁵

$$Y(t) = \frac{w+1}{w} \left\{ 1 - \frac{1}{\alpha-\beta} \left[\alpha \exp(\alpha^2\tau)(1 + \operatorname{erf} \alpha\tau^{\frac{1}{2}}) - \beta \exp(\beta^2\tau)(1 + \operatorname{erf} \beta\tau^{\frac{1}{2}}) \right] \right\}, \quad (3)$$

where α and β are the roots of the equation

$$y^2 + 3wy - 3w = 0, \quad (4)$$

and $\tau \equiv \bar{D} t/R^2$ is a dimensionless time parameter with R the spherical particle radius. The function (3) is tabulated in reference (5) for various τ and w .

Values of \bar{D} were extracted from the experimental determinations of Y vs. the logarithm of t by obtaining a best fit with theoretical Y vs. the logarithm of τ . A representative result is shown in Fig. 1; the line indicates the theoretical fit. This experiment was conducted at $25 \pm 1^\circ\text{C}$ with Dowex 1X4(100-200) NO_3^- from a 7M nitric acid solution with an equilibrium fractional plutonium loading, \bar{x}^*/\bar{x}_m , of 0.4 (0.2 moles/equivalent).

Figure 2 demonstrates the very strong dependence of \bar{D} on \bar{x}^*/\bar{x}_m for three Dowex 1, 100-200 mesh resins with varying nominal percent cross-linking. The values at $\bar{x}^*/\bar{x}_m = 0$ are extrapolations which were taken from the sorption data of reference (1). The open circle at $\bar{x}^*/\bar{x}_m = 0.5$ corresponds to an experiment with Dowex 1X4(100-200) NO_3^- from 7M nitric acid at $60 \pm 1^\circ\text{C}$.

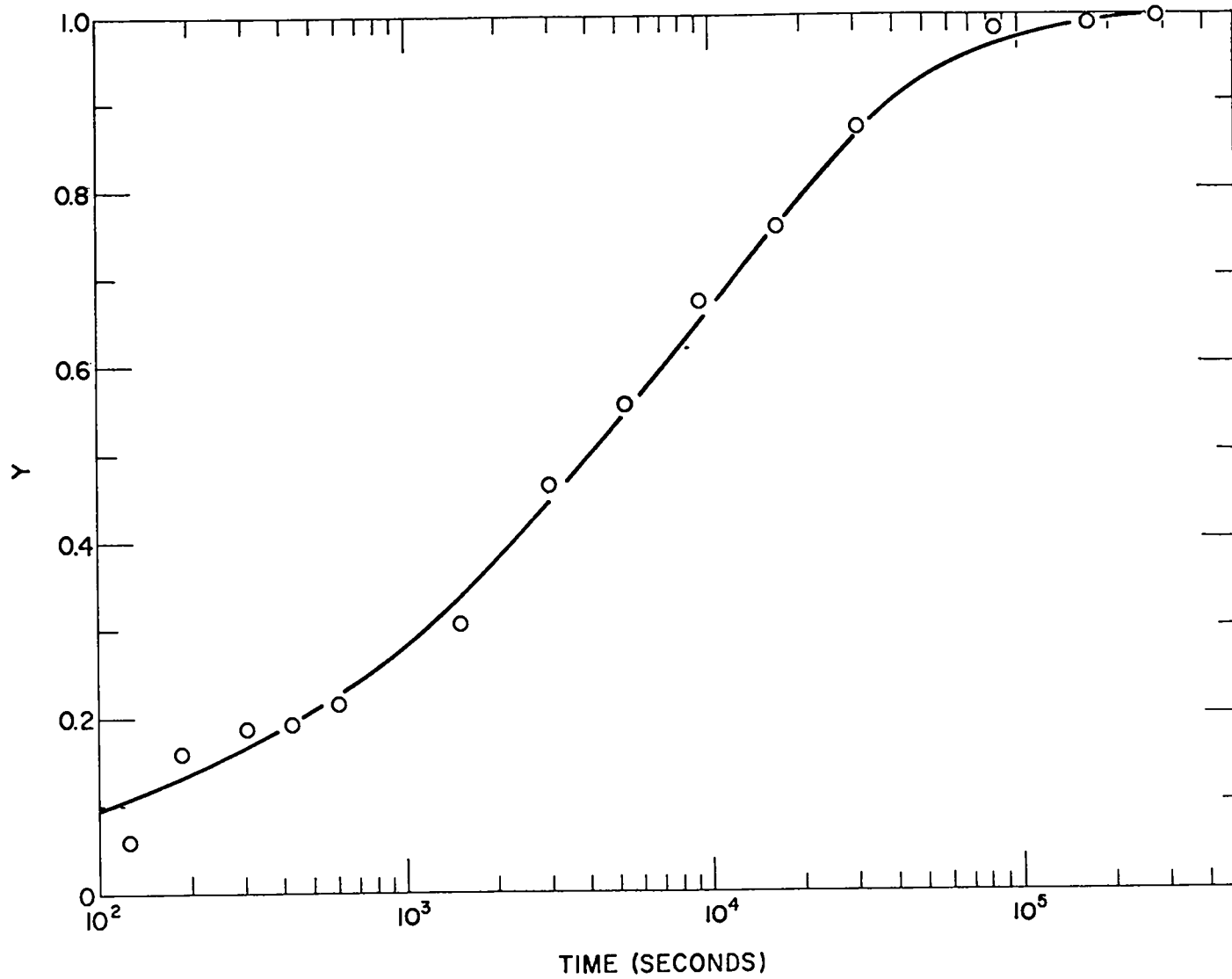


Fig. 1. Fraction of isotopic equilibrium Y as a function of time for Dowex 1X4(100-200)NO₃⁻ at 25^oC and $\bar{x}^*/\bar{x}_m = 0.4$

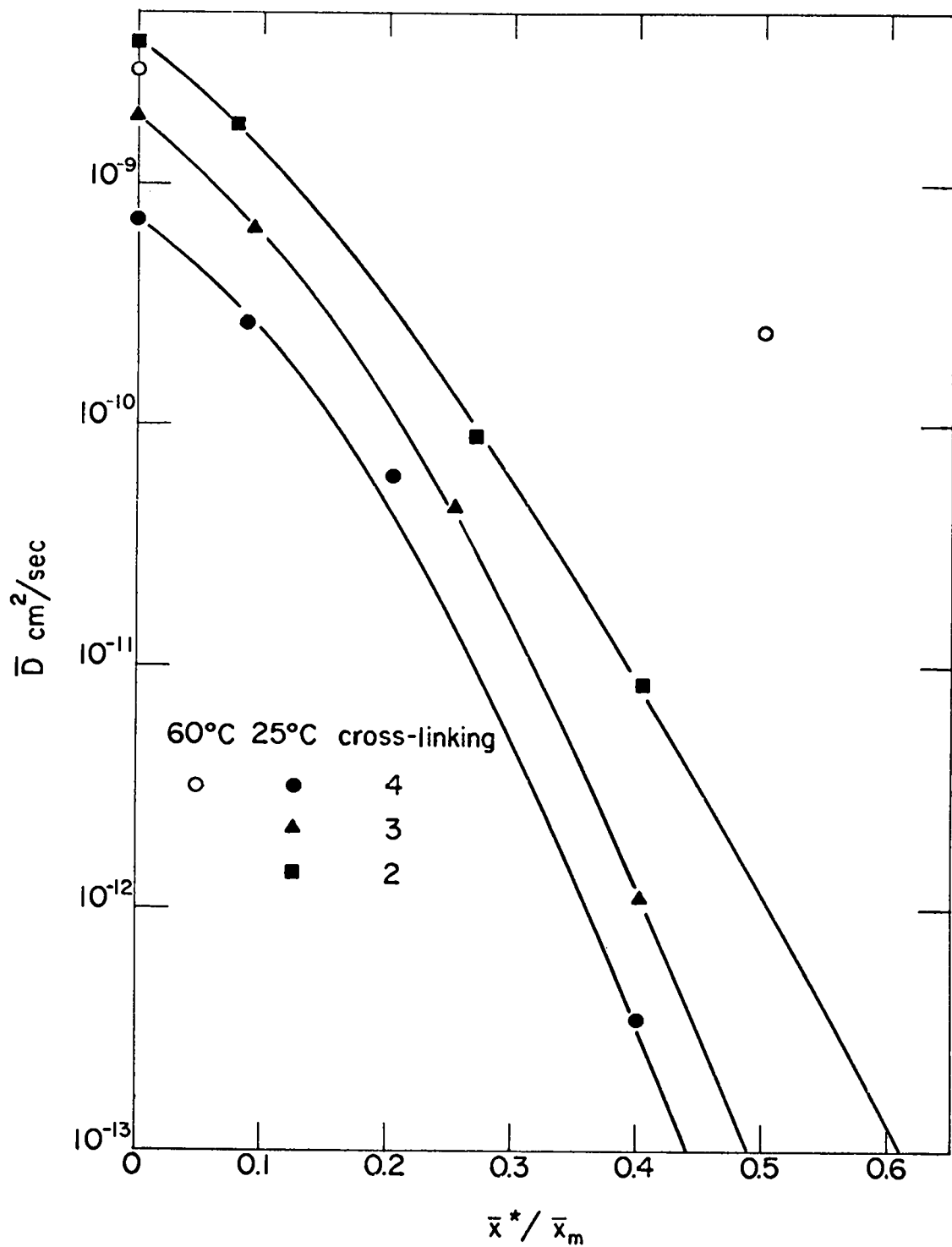


Fig. 2. \bar{D} as a function of equilibrium fractional plutonium loading

A log \bar{D} vs. reciprocal temperature treatment of this point and an extrapolation to $\bar{D} < 10^{-13} \text{cm}^2/\text{sec}$ of the data at $25 \pm 1^\circ \text{C}$ yields a diffusional activation energy of $> 50 \text{ kcal/mole}$ at $\bar{x}^*/\bar{x}_m = 0.5$. Since equilibrium is reached at about unit τ and R^2 is $2.4 \times 10^{-5} \text{cm}^2$,¹ isotopic equilibrium in half loaded Dowex 1X4(100-200) NO_3^- would not be reached for $> 2.4 \times 10^8 \text{ sec}$ or $> 7.6 \text{ yr!}$ However, sorption of plutonium(IV) on this resin to over 90 percent equilibrium loading takes only a week.¹

Of course, one would not expect isotopic redistribution to exhibit the same kinetic behavior as sorption or desorption. With isotopic redistribution, absent are all the perturbations due to changes in swelling, solvent content, and ionic composition and due to changes in electrical and chemical interactions of the exchanging species that are present during sorption and desorption. Nevertheless, it is difficult to attribute three orders of magnitude to such perturbations.

The slight decrease, relative to the isotopic diffusion data in Fig. 2, in the apparent sorption diffusion coefficient was attributed to the loss of imbibed solvent during sorption by Ryan and Wheelwright.³ They speculate that as the resin shrinks the intraparticle "pore diameter" approaches the size of the diffusing species. This was extended¹ to include the effect of the size of the sorbed plutonium. It was shown that by substituting

$$\bar{D}(r, x) = \bar{D}^0 \left\{ \frac{1-x(r)}{\bar{x}_m} \right\} \quad (5)$$

into equation (1) and integrating numerically, reasonable agreement with experimental sorption data is obtained. This proportionality of the local, intraparticle, sorption diffusion coefficient to the local fraction of unoccupied exchange sites may indicate that the large sorbed $\text{Pu}(\text{NO}_3)_6^-$ ion blocks the diffusional paths.

If this blocking model were the entire answer, the results of the isotopic diffusion studies as shown in Fig. 2 should vary approximately as equation (5), which they obviously do not. But fractional "pore volume" at r cannot depend solely upon the concentration of sorbed plutonium at r . During sorption the plutonium-free, expanded, inner regions of the sphere certainly must inhibit the contraction of the plutonium-laden outer regions. Possibly contraction occurs near the end of the sorption process when the integral plutonium concentration is significant, allowing fast sorption rates but slow isotopic-diffusion rates in systems at chemical and swelling equilibrium. With similar elastic interaction between regions during desorption, diffusion through contracted, but plutonium free, outer regions would be rate controlling. Such a mechanism would lead to the observed,² apparently constant, but reduced, desorption diffusion coefficients, which decrease with increasing initial loading. In order to simulate this strained-shell model, modern theory of elasticity must be employed to calculate numerically the fractional, local pore volume as a function of $x(r, t)$. Investigations at Los Alamos are proceeding toward this end.

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