Transmutation Products May Influence Radiotracer Diffusion Rates in an Ionic Solid

Abstract. *An inherent aspect of radiotracer diffusion is that α, β^+, or β^- emission produces a daughter element of different ionization state. This process must either cause a change in the vacancy concentrations or create space charge, depending on the effectiveness of the internal sources or sinks. Four coupled equations established to model the kinetics, when solved by numerical methods, predict that the apparent tracer diffusion rate may easily be in error by a factor of 2 or 3 and, under certain conditions, by as much as an order of magnitude.*

Many high-temperature processes in solids are determined by the diffusion rates of the constituent ions. Examples are oxidation behavior, reaction rates, creep, sintering, and ionic electrical conductivity. Measurement of diffusion rates also provides insight into the concentration of imperfections and the energies for defect formation and motion in a crystalline solid. The most direct and widely used procedure for measuring diffusion rates is to follow the migration of a radioactive tracer isotope. Typically, an initial thin film of tracer is placed upon the planar surface of a host crystal. The sample is then annealed at elevated temperature for a period t during which the tracer diffuses into the crystal. The subsequent concentration distribution, which one determines by counting the radioactivity of sequential sections ground from the sample, is Gaussian: A plot of the logarithm of activity as a function of the square of solute penetration is linear and has a slope equal to $(-4D_t t)^{-1}$, where D_t is the tracer diffusion coefficient. Typical initial specific activities, $(SpA)_0$, are much less than 1 c/g; expressed in other terms, the initial concentration of tracer, $C_{t,0}$, is of the order of 10 to 10^3 atomic parts per million (ppm). It has universally been assumed that such concentrations are sufficiently small that the electrochemical equilibrium state of the crystal remains unperturbed. We examine that assumption in the work reported here and conclude that significant error may result under normal experimental conditions.

There are five modes of radioactive decay: α emission, β^+ emission, β^- emission, electron capture, and γ-ray emission. Charge is lost in the first three mechanisms. The radioisotope transmutes into a daughter product whose atomic number differs from that of the parent element by -2, -1, or $+1$, respectively, for α, β^+, and β^- decay. The inherent nature of studies carried out with such radioisotopes is that a sample will be continuously doped with an aliovalent impurity. Two effects are then possible. Internal sources and sinks for defects may create vacancies in concentrations sufficient to maintain electroneutrality. Alternatively, if this does not happen at a rate which keeps pace with the production of daughter, a space charge and electric field will develop. Either process will influence the diffusion rate of an ionic species and could conceivably produce an erroneous apparent value for the tracer diffusion coefficient.

Intuition suggests that the low tracer concentration should cause the transmutation effect to be insignificant except in special circumstances—perhaps, for example, in the rapid decay of an isotope of very short half-life. This turns out not to be the case. In practical diffusion experiments the activity and not the concentration of the isotope is maintained within narrow bounds determined by expense and radiation hazard on the one hand and acceptably high counting rates in sections of the annealed sample on the other. In actual experiments, then, the rate at which the daughter element is produced is essentially independent of the half-life of the particular tracer used.

The total amount of daughter impurity formed within a sample of radioisotope after an elapsed time typical of that of a diffusion annealing is readily estimated. For an initial specific activity of 0.3 mc/mg, for example, the concentration of daughter is 10 ppm after 10 days for half-lives in the range $10^{-2} < \tau < 10^4$ years. Vacancy concentrations in a typical alkali halide are, in comparison, of the order of 5 ppm at the transition from extrinsic, impurity-controlled mass transport to the intrinsic, high-temperature regime controlled by equilibrium defect concentrations. For an oxide with an energy for Schottky defect formation, E, of 6 ev, the equilibrium vacancy concentration, $\exp(-E/2kT)$ (where k is the Boltzmann constant and T is temperature), is of the order of 0.2 ppm at 2000°C. The daughter element will be diluted by diffusion during the course of an actual experiment, but the preceding estimate demonstrates that the concentrations are not necessarily negligible as compared to native defect concentrations. The influence of the vacancies or space charge created by transmutation should therefore be considered for the full range of

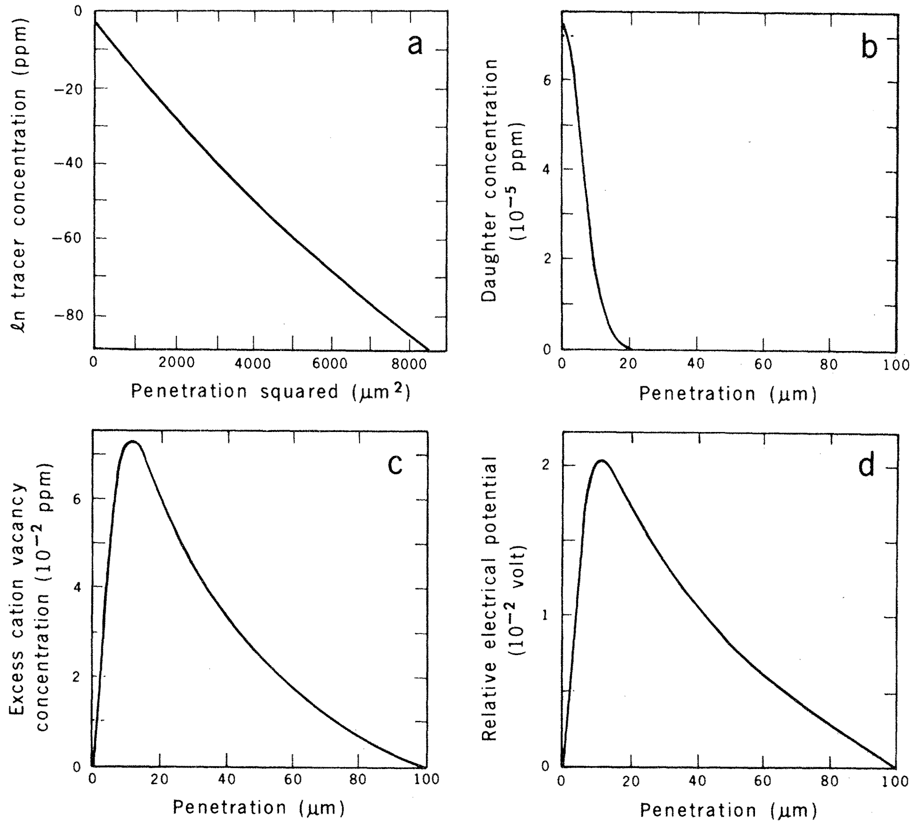

Fig. 1. A predicted distribution of (a) tracer concentration, (b) daughter concentration, (c) cation vacancy concentration, and (d) electric field in a thin-film diffusion specimen.

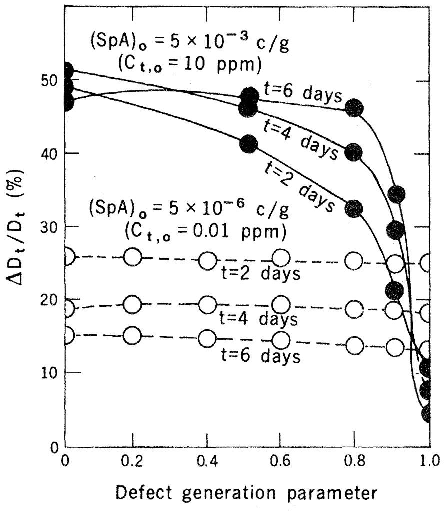

Fig. 2. Error in the apparent diffusion coefficient as a function of time and defect generation parameter, g, for two different initial specific activities, $(SpA)_0$. (The latter are also expressed as tracer concentration, $C_{t,0}$, in the initial thin film.)

useful half-lives for radioisotopes with commonly employed activities.

We have modeled the kinetics of radiotracer diffusion in the presence of continuous transmutation (*1*). We considered the case of an ionic solid in which only cation and anion vacancies may neutralize the space charge created by the aliovalent daughter ion. Electrons and holes, although they have high mobility, are assumed to be present in concentrations that are too low to contribute effectively to the process. Four flux equations of the form

$$J_i = -D_i \partial C_i/\partial x - D_i/kT \, C_i Z_i e \partial \phi/\partial x \quad (1)$$

may be written as a function of position, x, and time, t, for tracer, daughter, cation vacancies, and anion vacancies. In Eq. 1, J is the flux (in particles per unit area per unit time for each species), C is the concentration, Z is the valence, e is the electronic charge, and ϕ is the electric potential. A fifth relation is given by the Maxwell field equation

$$\nabla^2 \phi = -\rho/\epsilon \quad (2)$$

where ϵ is the permittivity of the host crystal. Space charge density, ρ, may be defined in terms of effective charge

$$\rho = (Z_d - Z_t)eC_d - Z_c eC_{vc} - Z_{va} eC_{va} + (Z_I - Z_t)eC_I \quad (3)$$

The subscripts t, d, vc, va, and I pertain to tracer, daughter, cation vacancy, anion vacancy, and native aliovalent impurity, respectively. From each flux equation a corresponding equation of continuity may be established:

$$\partial C_i/\partial t = -\nabla \cdot J_i + R_i \quad (4)$$

where R_i is the rate of production or destruction of the ith species. The latter term is $-\lambda C_t$ for tracer and $+\lambda C_t$ for daughter, where λ, the disintegration constant, is $0.693/\tau$.

To this point the formalism has been rigorous. An expression for R is difficult to specify for vacancy production since the term requires a description of the geometry and kinetics of defect production at internal sources and sinks (for example, dislocations and subgrain boundaries). Moreover, in addition to such "static" sources, there exist "dynamic" transient sources. Both the radiation emitted by decay and the recoil of the daughter interact with the host crystal to produce electronic and ionic defects (*2*). Such damage, although it quickly anneals out, provides a source of charged species to locally neutralize the daughter.

If thermal equilibrium holds,

$$C_{vc} C_{va} = \beta(T) \quad (5)$$

where β is a constant (*3*). Electroneutrality further requires, prior to any transmutation,

$$C_{vc} = C_{va} + C_I \quad (6a)$$

Let us consider two extreme cases. First, suppose that internal sources do not operate after transmutation to change defect concentrations. The vacancy concentrations then remain fixed at the values given by Eqs. 5 and 6a and, from Eq. 3, every daughter atom contributes to a space charge density $\rho = (Z_d - Z_t)eC_d$. Conversely, if internal sources are fully effective in maintaining electroneutrality, vacancy concentrations will adjust to new values such that

$$C_{vc} = C_{va} + C_I + C_d \quad (6b)$$

and $\rho = 0$. Intermediate, partially neutralized states between these extremes are conceivable. To be able to describe the full spectrum of states, we introduce an ad hoc defect generation parameter, g, such that

$$C_{vc} \equiv C_{va} + C_I + gC_d \quad (6c)$$

and g may vary between 0 and 1. For these extremes the relation reduces to Eq. 6a or 6b. The defect generation parameter is introduced to account for a variety of transient phenomena and microstructural influences that are impossible to model in a rigorous or general way. The parameter is a function at least of temperature, dislocation density, specific activity, and radiation characteristics, but it will be assumed to be independent of time. If this assumption is correct, then differentiation of Eq. 6c with respect to time and combination with the time derivative of Eq. 5 (which is zero) provides

$$\partial C_{vc}/\partial t = gC_{vc}/(2\,C_{vc} - C_I - gC_d)\, \partial C_d/\partial t \quad (7)$$

which is the rate term for vacancies needed in Eq. 4.

The set of equations of the form Eq. 4 for tracer, daughter, and cation vacancies plus the field equation (Eq. 2) provide a set of coupled, nonlinear, inhomogeneous partial differential equations which give a phenomenological description of the problem. No analytic solution is possible, but we have solved the equations numerically with finite difference methods (*4*) for a wide range of experimental parameters. Figure 1 provides an example of the results of one computation and presents plots, as a function of penetration, of tracer concentration, daughter concentration, cation vacancy concentration, and electrical potential. This calculation was carried out specifically for an initial thin film 1 μm thick containing a β^- emitter with an activity of 5×10^{-4} mc/mg with $\tau = 3.75$ years, $D_t = D_d = 10^{-12}$ cm²/sec, $D_{vc} = D_{va} = 10^{-6}$ cm²/sec, an initial cation vacancy concentration of 10^{-6}, $g = 0.8$, and an annealing time of 45 hours at 500°C. The material parameters necessary for the calculation were taken as those of KCl.

A surprising result of the calculations is that the tracer gradients remained remarkably close to the anticipated Gaussian distribution. The shape of a tracer gradient will therefore provide no indication of a transmutation effect. The excess cation vacancies are distributed over a larger range than the daughter product because of their higher mobility in response to the internal electric field. The excess cation vacancy concentration greatly exceeds that of the daughter because, from Eq. 6c, it is the excess cation vacancy concentration less the excess anion vacancy concentration which should be comparable to the daughter concentration. The tracer diffusion coefficient is everywhere enhanced as a result of increased cation vacancy concentrations, but the electric field acts to retard diffusion in the near-surface region and enhance it at large penetrations. The apparent diffusion coefficient deduced from the tracer gradient in Fig. 1 is larger than the true value by 9.5 percent.

Calculations similar to those shown in Fig. 1 have been made for a range of experimental parameters. Figure 2, for example, summarizes discrepancies as a function of g for diffusion annealings of different duration and for two different initial specific activities. The parameters for the calculations are the same as given above except that the initial cation vacancy concentration was 10^{-5} and the initial specific activities were 5×10^{-3} or 5×10^{-6} mc/mg. These activities are much smaller than usually employed and represent conditions under which transmutation might be expected to have a minimal effect. Errors of the order of 10 to 30 percent may occur even for these low specific activities. Because of a slight departure from a true Gaussian distribution, the error was also found to depend on the sensitivity of an experiment, that is, the lower limit to which tracer concentration may be measured. Higher defect diffusivities, as might be anticipated, acted to reduce the influence of the effect. (The gradient of Fig. 1, for example, provides an error which is roughly one-third of that plotted for bracketing activities at $g = 0.8$ in Fig. 2. The value employed for D_t was the same in both calculations and, since $D_{vc} = D_t/C_{vc}$, the higher mobility of the vacancies in the calculation for Fig. 1 resulted in a diminished effect.) The tracer half-life had very little influence for a given activity. The effect of daughter-vacancy association had little influence for typical association energies and was accordingly neglected in most computations. The importance of variables and parameters in the numerical calculations may be summarized as decreasing in approximately the following order: $g > t > (SpA)_0 > D_t >$ sensitivity $> D_{vc} > \tau$.

Our model predicts that the apparent tracer diffusion coefficient may differ from the true value by an amount which is a strong function of annealing time, initial activity, and the effectiveness of internal defect sources for the experimental conditions customarily used. The influence of transmutation must clearly be given attention in careful diffusion measurements with ionic solids. Several potential consequences are immediately apparent. The effect is a strong function of time and will therefore influence low-temperature and high-temperature measurements to a different extent, because of the different durations of the annealings which are employed. This effect will introduce a systematic error in the experimentally measured activation energy for diffusion. If the apparent diffusion coefficient is larger than the true tracer diffusion coefficient, a comparison of diffusion data with conductivity measurements may incorrectly imply the existence of neutral complexes. Finally, the transmutation effect could conceivably suppress entirely the onset of a regime of intrinsic diffusion in materials which have high energies for defect formation and in which the equilibrium concentration of vacancies is very small.

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References and Notes

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3. The electroneutrality condition expressed by Eq. 5 holds for an ionic compound of composition MX. Similarly, Eq. 6 applies specifically to divalent cation impurity in a monovalent compound such as an alkali halide. The modification of these expressions to a form applicable to a crystal of more complex composition or higher valence states is straightforward.
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5. This work was supported by the U.S. Atomic Energy Commission under contract AT(11-1)-2390.

5 October 1976; revised 4 February 1977

Comparison of Radioactive and Stable Tl^+ Diffusion in Potassium Chloride: Demonstration of a Transmutation Effect

Abstract. *Radioactive $^{204}Tl^+$ was found to diffuse in potassium chloride up to three times more rapidly than stable Tl^+. The difference is attributed to the $^{204}Pb^{2+}$ daughter element produced by β^- emission. A theoretical model accounts satisfactorily for the discrepancy and indicates that internal sources of cation vacancies are effective in maintaining electroneutrality at all but low temperatures.*

The technique usually used to measure diffusion rates in solids consists of following the migration of a radioactive tracer isotope. However, radioactive decay produces an aliovalent daughter element when charge is lost from the system by α, β^+, or β^- emission. This process may produce space charge and an internal electric field or, alternatively, vacancies may be internally created in the solid to maintain electroneutrality. Either process may cause an apparent tracer diffusion rate in an ionic solid which differs appreciably from the true value. In a companion report (*1*) we describe a theory which predicted that errors of a factor of 2 to 3 or even up to an order of magnitude may result under conditions commonly used in sample preparation. This result was quite unexpected for a procedure which has been widely employed with apparent success, and experimental evidence is necessary to substantiate the existence of a transmutation effect.

There are at least two ionic systems for which one investigator has made measurements with a radioisotope and another with a stable tracer. The diffusion rates reported for radioactive $^{204}Tl^+$ in KCl (*2*) are seven times more rapid than those later measured for stable Tl (*3*) with the aid of electron microprobe analysis. The disparity was present in both the extrinsic and intrinsic regimes of transport. The disparity in the extrinsic regime might be interpreted in terms of differences in sample purity, but we know of no obvious explanation for different behaviors in the supposed intrinsic region. The effect may be due to doping by the $^{204}Pb^{2+}$ daughter produced by the decay of the radiotracer. Similarly, measurements of $^{28}Mg^{2+}$ self-diffusion in MgO (*4*) provided diffusion coefficients larger by a factor of 8 than data obtained (*5*) with the stable isotope ^{26}Mg. The isotope $^{28}Mg^{2+}$ decays with a half-life of 21.3 hours to $^{28}Al^{3+}$ which, in turn, transmutes to $^{28}Si^{4+}$ (stable) with a half-life of 2.3 minutes. An aliovalent daughter may therefore be responsible for the discrepancy but, as with KCl, one is comparing measurements made on different host crystals with different procedures by separate investigators. Convincing evidence for a transmutation effect can be provided only on the basis of measurements made with a single well-characterized host material in experiments which differ only in the nature of the tracer used. We selected KCl as an ionic host crystal and decided to examine impurity rather than self-diffusion so that tracer gradients could be conveniently measured by chemical as well as radiometric methods. Thallium is unusual in displaying appreciable solid solubility in KCl; moreover, the literature (*2, 3*) suggests the existence of a transmutation