dient 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.

G. C. T. Wei, B. J. Wuensch
Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge 02139

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

Abstract. *Radioactive* $^{204}\text{Tl}^+$ *was found to diffuse in potassium chloride up to three times more rapidly than stable* Tl^+*. The difference is attributed to the* $^{204}\text{Pb}^{2+}$ *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 $^{204}\text{Tl}^+$ 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 $^{204}\text{Pb}^{2+}$ daughter produced by the decay of the radiotracer. Similarly, measurements of $^{28}\text{Mg}^{2+}$ 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 $^{28}\text{Mg}^{2+}$ decays with a half-life of 21.3 hours to $^{28}\text{Al}^{3+}$ which, in turn, transmutes to $^{28}\text{Si}^{4+}$ (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

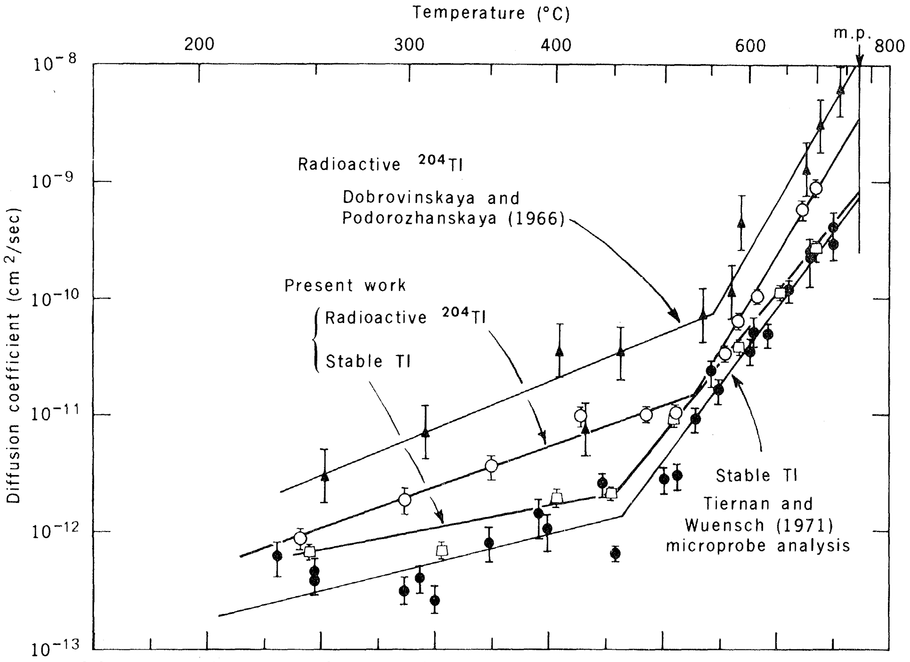

Fig. 1. Diffusion coefficients for radioactive and stable Tl^+ in single crystal KCl plotted as a function of reciprocal temperature; m.p., melting point.

effect. Accordingly, we selected the system Tl/KCl for reexamination.

We used single crystals of KCl which contained less than 23 parts per million cation impurity ($Ca < 10$, $Si < 7$, $Al < 5$, and $Fe < 3$) and a dislocation density of 4×10^5 to 8×10^5 cm^{-2}. Cleaved (100) surfaces were mechanically polished to achieve flatness. This procedure introduced mechanical damage in the form of excess dislocations to a depth of 50 μm, and this layer was removed by dissolution in acetone prior to the preparation of samples. The radiotracer ^{204}Tl was obtained in 0.5*N* HCl and, in solid form, had a specific activity of 2.38 c/g with a radiometric purity of 99 percent. The principal decay mode (98 percent probability) is emission of a 0.765-Mev β^- (half-life, 3.75 years) to produce $^{204}Pb^{2+}$ which, with a half-life of 10^{17} years, is essentially stable. In other samples we used stable TlCl (purity, 99 percent), which consists of the stable isotopes ^{203}Tl and ^{205}Tl in natural abundance 29.5 and 70.5 percent, respectively.

We used two types of specimens since TlCl has a very high vapor pressure. Crystals annealed at high temperature were tightly bound over an Al_2O_3 well which contained either TlCl powder or a TlCl-KCl mixture. The crystal surface was thus in equilibrium with a vapor of constant concentration during the annealing. The distribution of solute produced in the sample is such that a plot of the inverse complementary error function of concentration divided by the surface concentration varies linearly with penetration into the sample, and has slope equal to $(4D^*t)^{-1/2}$, where D^* is the diffusion coefficient and t is the time. At lower temperatures the solute was instead supplied from an initial thin film of TlCl which had been deposited on the surface of a crystal by evaporation in a vacuum from a heated tungsten filament. Annealing of this type of specimen for time t produces a Gaussian distribution of solute so that a plot of the logarithm of concentration as a function of the square of solute penetration is linear with a slope of $-1/4D^*t$.

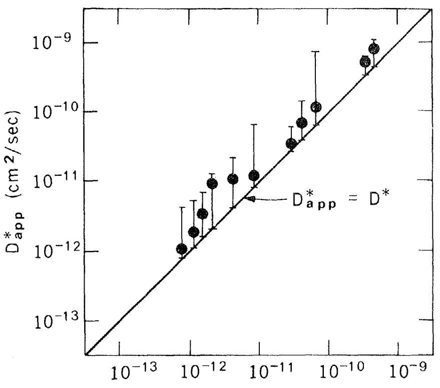

Fig. 2. Plot of the apparent diffusion coefficient for radioactive $^{204}Tl^+$ as a function of the "true" value obtained with stable Tl^+. The bar through each data point gives the range of theoretical values for an apparent diffusion coefficient as computed for the conditions of each experiment and for values of the defect generation parameter, g, ranging between 0 and 1.

Diffusion anneals were carried out in air over a temperature range from 245° to 700°C. After annealing, the samples were mechanically sectioned by hand-lapping on an Al planchet. We determined the concentration of ^{204}Tl in each section by counting β^- emission in a gas-flow proportional counter with 2π geometry. Stable Tl concentrations were measured with the aid of atomic absorption analysis. The diffusion coefficients so obtained are plotted as a function of reciprocal temperature in Fig. 1. The results, in square centimeters per second, may be represented as follows: for ^{204}Tl at 245° to 510°C,

$$D^* = 2.38 \times 10^{-9} \exp(-0.35 \pm 0.03 \text{ ev}/kT)$$

for ^{204}Tl at 510° to 690°C,

$$D^* = 6.09 \times 10^{-2} \exp(-1.53 \pm 0.12 \text{ ev}/kT)$$

for stable Tl at 247° to 446°C,

$$D^* = 2.33 \times 10^{-11} \exp(-0.15 \pm 0.01 \text{ ev}/kT)$$

and for stable Tl at 446° to 697°C,

$$D^* = 5.32 \times 10^{-4} \exp(-1.20 \pm 0.13 \text{ ev}/kT)$$

Where k is the Boltzmann constant and T is the temperature. The values of the logarithm of the preexponential term in these four expressions, and their standard deviations, are -8.62 ± 1.01, -1.22 ± 0.11, -10.63 ± 1.45, and -3.27 ± 0.40, respectively. The two ranges of different dependence upon temperature are taken, as usual, to represent an extrinsic region in which vacancies created by chemical impurities predominate and a high-temperature intrinsic region controlled by equilibrium defect concentrations. The apparent activation energies are slightly different for radioactive and stable Tl, and the radioisotope has clearly diffused at rates that are up to three times larger, an amount which exceeds the standard deviation of the measurements. Also included in Fig. 1 are the earlier data (*2, 3*). These results replicate the slightly different activation energies that we obtained. Our results for stable Tl diffusion agree, within experimental error, with those obtained earlier (*3*) through microprobe analysis. Our measured rates for $^{204}Tl^+$ diffusion are smaller than earlier radiotracer results (*2*), but the influence of the transmutation effect depends strongly upon the duration of the diffusion annealing and the initial specific activity of the radioisotope. As our two sets of experiments differed only in the nature of the tracer that was used and the technique used to measure its concentration, we attribute the different transport rates to the Pb^{2+} daughter product created during the diffusion of the radiotracer (6).

Figure 2 compares the data for stable and radioactive Tl diffusion in a different way. The least-squares fit to the temperature dependence of the diffusion coefficient for stable Tl was taken to represent the "true" tracer diffusion coefficient (that is, proportional to the native vacancy concentration). Against this value we plot the apparent radiotracer diffusion coefficient, D^*_{app}, obtained in each radioisotope experiment. All data points lie well above the line $D^*_{\text{app}} = D^*$. To test the ability of our model (1) to qualitatively account for the discrepancy we then calculated the expected magnitude of D^*_{app}, using the true D^* and the actual experimental conditions (time, specific activity, and native cation vacancy concentration as inferred from the "knee" temperature or the enthalpy for Schottky defect formation) of each experiment. The model contains a disposable defect generation parameter, g, to account for the effectiveness of internal vacancy sources in maintaining electroneutrality; $g = 1$ corresponds to complete neutralization of the aliovalent daughter, whereas $g = 0$ represents a situation in which no vacancies are created and every daughter creates space charge. The vertical line drawn through each data point in Fig. 2 represents the range of apparent diffusion coefficients computed for $0 < g < 1$. (The maximum and minimum values for D^*_{app} do not obtain for the extreme limits of g.) In each case the range of computed values includes the observed value for D^*_{app}. Given an appropriate value of g, the model is thus capable of satisfactorily predicting the magnitude of the transmutation effect. The best agreement between theory and experiment was obtained for $g = 1$ for the high-temperature data. That is, internal sources and sinks are fully effective in producing vacancies to maintain electroneutrality and no space charge is developed. At the lowest temperatures that were examined, the best fit obtained for $g = 0.8 \pm 0.1$. This result suggests, not unreasonably, that the reduced rates of vacancy formation or migration have resulted in the accumulation of a slight space charge.

G. C. T. WEI*
B. J. WUENSCH
Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge 02139

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6. A disparity in diffusion rates could conceivably result from different impurity concentrations (including Pb^{2+} produced by transmutation prior to the experiment) carried in the tracer. This possibility seems unlikely since the tracer was supplied to the host crystal by two distinct procedures: exchange with a vapor and direct deposition of a film upon the crystal. Data obtained from the two types of specimens are in complete agreement.
7. This report is based on a thesis (G.C.T.W.), Massachusetts Institute of Technology (1976). Work was supported by the U.S. Atomic Energy Commission under contract AT(11-1)-2390.

* Present address: Oak Ridge National Laboratory, Oak Ridge, Tenn. 37830.

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Ammonia in the Human Airways: Neutralization of Inspired Acid Sulfate Aerosols

Abstract. *In the human being, expired ammonia concentrations from 7 to 520 micrograms per cubic meter are controlled by the last airway segment traversed by the air, and such concentrations are higher in the mouth than nose. Inspired submicrometric sulfuric acid aerosol at a mass concentration of 600 ± 100 micrograms per cubic meter was found to be an ammonium salt with an average ammonium to sulfate molar ratio of ≥1, when sampled within 0.5 second after exhalation.*

We hypothesize that gaseous ammonia which is released into the respiratory system of the human being can neutralize inhaled acidic aerosols and may potentially alter or mitigate their toxicity. To support this hypothesis we present (i) measurements of NH_3 in expired air following several breathing procedures designed to identify the sources and sinks of NH_3, and (ii) evidence that inhaled acid sulfate particles which remain airborne and are subsequently exhaled undergo a change in molecular form during passage.

A persistent sulfate aerosol, submicrometric in diameter, has been observed in the lower troposphere over the eastern and midwestern United States and northern Europe (1). The aerosol consists of sulfuric acid (H_2SO_4) plus its products of neutralization with ammonia, that is, NH_4HSO_4, $(NH_4)_3H(SO_4)_2$, and $(NH_4)_2SO_4$ (2, 3). Surface measurements near St. Louis (2) have shown concentrations ranging from 10 to 20 $\mu g/m^3$.

The recent CHESS report (4) of the Environmental Protection Agency concluded that ambient levels of "sulfate aerosol" in the concentration range found near St. Louis may affect health adversely. The report did not specify the molecular composition nor size-distribution of the aerosol, ambiguities that limit the value of the conclusions, particularly with respect to policy on air quality standards.

Evidence has also been adduced that sulfate aerosols with comparable mass concentrations and size-distributions may differ in toxicity depending on their molecular form. For example, H_2SO_4 is reported to cause greater impairment of pulmonary function in guinea pigs than does $ZnSO_4$ which, in turn, is reported to be more irritating than $(NH_4)_2SO_4$ (5). The relative irritancy of these compounds in human subjects has not been reported.

To the extent that the acidity of sulfate aerosol may contribute to toxicity, any chemical change that reduces this acidity following inhalation should be mitigating. We hypothesize that acidity may be reduced in two ways: (i) by dilution resulting from the hydration of the aerosol following inhalation and (ii) by neutralization with NH_3 (6). Neutralization with NH_3 is the potentially more significant way in which acidity may be changed. Just as NH_3 may regulate the molecular form of acid aerosols in ambient air (7), we propose that NH_3, normally present in the respiratory system, reacts with these aerosols in the gas phase to reduce their acidity before they become deposited on tissue surfaces.

Ammonium ion (NH_4^+) is a normal constituent of a variety of body fluids including those lining the respiratory tract (8). Ammonia, a highly soluble and diffusable gas, is likely to be present in air passing over these fluids. Concentrations ranging from 37 to 102 $\mu g/m^3$ have been reported in expired air collected from tracheostomized dogs [see (9); we report here concentrations at 25°C and 1 atm]; a concentration of about 120 $\mu g/m^3$ has been reported in the expired air of dogs breathing by mouth (10). In human subjects, concentrations ranging from 210 (11) to about 700 $\mu g/m^3$ (10) have been found in expired air collected during quiet mouth breathing.

We measured gas phase NH_3 with a chemiluminescent nitric oxide (NO) analyzer that was equipped with a stain-