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Measurements of Helium Release
from Materials Containing $^{238}\text{PuO}_2$

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MEASUREMENTS OF HELIUM RELEASE FROM MATERIALS CONTAINING $^{238}\text{PuO}_2$

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ABSTRACT

Measurements of the isothermal helium release rates as a function of time for five materials containing 80% ^{238}Pu are described. The materials were plasma-torch microspheres, and cylindrical 1/4- by 1/4-in. pellets of PuO_2 , PuO_2 -56 wt% ThO_2 , PuO_2 -7 wt% ZrO_2 , and PuO_2 -35 wt% ZrO_2 . Attempts to fit the data with a classical diffusion model, and the deviations therefrom, are discussed.

I. INTRODUCTION

The experiments described here involved potential fuels for radioisotopic heat sources whose active component is ^{238}Pu in the form of oxide. The buildup, storage, and release of helium due to the trapping and subsequent release of alpha particles from the radioactive decay process in such solid fuels, either at operating temperatures or when the power source experiences temperature excursions, must be considered in the heat-source design. The experiments had a twofold purpose. One purpose was to characterize the helium release in terms that would be directly applicable in making engineering evaluations. To this end, we tried to fit the data to a diffusion model, although it became evident that such a model does not completely describe the phenomenon. The second purpose was to accumulate a body of experimental data

against which proposed release models may be tested.

The materials examined were $^{238}\text{PuO}_2$ plasma-torch microspheres, and cylindrical 1/4- by 1/4-in. pellets of $^{238}\text{PuO}_2$, $^{238}\text{PuO}_2$ -56 wt% ThO_2 , $^{238}\text{PuO}_2$ -35 wt% ZrO_2 , and $^{238}\text{PuO}_2$ -7 wt% ZrO_2 .

II. EXPERIMENTAL

A. The Samples

The production-grade $^{238}\text{PuO}_2$ microspheres were obtained from Mound Laboratory as part of lot 93, made in March 1967. Thus, they were about 2 yr old at the time of the experiments. They apparently had been stored in small enough batches at ambient temperature so that their temperature probably had not exceeded 50°C before the experiments. Examination showed that the microspheres varied considerably in degree of fusion and presence of porosity (or central voids) and impurity phases. Thus a sample consisted of a number of dissimilar individual spheres.

*Throughout this report, ^{238}Pu means plutonium consisting of about 80% of the ^{238}Pu isotope, the balance being mainly ^{239}Pu . (See Appendix A.)

We measured the particle size of the microspheres by optical microscopy. The average calculated diameter, counting broken bits as well as complete spheres, was 0.0086 cm. The standard deviation from 144 measurements was 0.0022 cm, and the extreme range observed was 0.0025 to 0.0122 cm.

The 1/4- by 1/4-in. pellets were prepared at this Laboratory as part of a ^{238}Pu fuel-development program. The dry oxide components were blended, cold pressed into pellets, and fired for 6 h at 1650°C in a CO_2 atmosphere.¹ Densities determined from the dimensions and weights are listed in Table I. Theoretical densities in Table I are from Ref. 1.

We examined the microstructures of only a few pellets before making the helium-release measurements, but examined fragments of all the pellets by optical metallography after completion of the experiments. The dimensions of all pellets were determined to within 0.001 in. before and after helium release to detect swelling. At most, 100 days elapsed between the pellet sintering during manufacture and the release measurements. Therefore, the helium content of the pellets was not so great as that of the microspheres. Also, we found that some of the pellets, particularly the PuO_2 composition, contained more helium than could have been generated since they had been fired, which suggests that the sintering did not remove all the helium. Unless all of the gas is evolved from a batch of pellets during sintering, the pellets start their existence with various amounts of helium. This makes application of diffusion theory somewhat unsatisfactory, as one cannot take accurate account of an unknown initial helium concentration.

B. The Apparatus

Figure 1 shows the experimental apparatus. Samples were contained in an open tantalum crucible lined with tungsten foil to prevent reaction between the samples and the tantalum. Temperature

TABLE I
PELLET DESCRIPTION^a

Expt No.	Length (cm)	Diameter (cm)	Weight (g)	Density (% theo.)
100% PuO_2 ($\rho_{\text{theo.}} = 11.46 \text{ g/cm}^3$)				
12582	0.785	0.610	2.294	87
12583	0.706	0.610	2.056	87
12584	0.699	----	1.833	--
12585	0.686	0.610	2.011	88
PuO_2 -56 wt% ThO_2 ($\rho_{\text{theo.}} = 10.65 \text{ g/cm}^3$)				
12571	0.635	0.635	1.975	92
12572	0.632	0.635	1.973	93
12573	0.643	0.632	1.947	91
PuO_2 -7 wt% ZrO_2 ($\rho_{\text{theo.}} = 10.75 \text{ g/cm}^3$)				
12579	0.348	0.668	0.990	76
12580	0.345	0.668	0.989	76
12581	0.348	0.668	0.980	75
PuO_2 -35 wt% ZrO_2 ($\rho_{\text{theo.}} = 8.60 \text{ g/cm}^3$)				
12574	0.643	0.648	1.486	81
12575	0.645	0.643	1.485	82
12576	0.612	0.645	1.438	84

^aTheoretical densities are from Ref. 1; calculated densities are probably slightly low because of chipping at pellet edges.

was measured by sighting an optical pyrometer into a blackbody hole in the crucible base. A suitable correction was made for the quartz window in the vacuum chamber. Estimated accuracy of temperature measurement was $\pm 2^\circ\text{C}$.

We used a Perkin-Elmer Corp. Ultek, EAI quadrupole residual-gas analyzer (RGA), model 200, to monitor the intensity of the mass-4 peak while the sample was being heated. Under constant pumping speed, the helium pressure, and hence the mass-4 intensity, is proportional to the release rate. The RGA was calibrated with a standard glass helium leak at a single rate (1.5×10^{-7} std $\text{cm}^3 \text{ sec}^{-1}$), and the response was assumed to be linear over the range of experimental measurements. We measured the multiplier gain on mass 28 after each experiment and corrected the data for slight gain changes. Vacuums were of the order of 5×10^{-7} Torr during helium-release measurements.

RGA Apparatus

Fig. 1. Experimental apparatus for helium-release measurements.

C. Procedure

Samples were heated to the desired temperature as rapidly as possible, then held at temperature, usually for about 24 h, while the helium-release rate was monitored continuously. The crucible reached a steady temperature about 2 min after the power had been turned on. Fluctuations in temperature during the isothermal period were always less than 10°C and usually less than 5°C. Since we wanted fractional release data, we heated the samples further, after the isothermal period, until substantially all the helium had been released. However, because the release rate from the pellets was relatively slow, even at 1600°C, and because higher temperatures vaporized the sample, we had to pulverize the pellet after the isothermal run had been completed and then heat the powder until the rate of helium evolution approached the helium generation rate. (For the microspheres, pulverizing was unnecessary.) The area under the release rate-vs-time plot is proportional to the quantity of helium released. The fraction released at any time, then, is the area up to that time divided by the total area. Thus the fractional release data are independent of equipment calibration and demand only that the RGA be stable over 1 or 2 days. The total measured helium inventory data, of course, depend on calibration of the RGA against a standard leak. We took a small piece of each pellet for metallographic examination when the pellet was pulverized after the isothermal heating.

III. RESULTS

The data are presented as fraction released-vs-square root of time in Figs. 2-6. Zero time is the time that the furnace was turned on, and the curves show that about 100 sec elapsed before the helium release became significant, which is about the time required for the sample to reach a steady temperature from a cold start.

To apply chemical-diffusion theory, a single diffusion coefficient D is assumed. If the geometry is spherical, the sphere radius is a , and, in the

fractional-release equations, D/a^2 appears as the single parameter that characterizes the system at constant temperature.

In Figs. 2-6, calculated curves for fractional release are shown for comparison with the experimental data. We selected the values of D/a^2 (see below) for the calculated curves to give reasonable fits to the observed data, and adjusted the calculated curves for nonzero starting times. Figure 2 shows that for the microspheres the fit of the data to a simple diffusion model is relatively good, so D/a^2 values can be found which will provide a reasonably useful description of their fractional helium release, at least under the conditions of these experiments. For the pellet samples (Figs. 3-6), however, the fit is less satisfactory. One feature common to all the samples, including the microspheres, is that the observed release rates drop off faster than the diffusion model permits. That is, as the released fraction increases, the release rate decreases to less than that theoretically predicted from the initial rate. For some of the samples, notably the $\text{PuO}_2\text{-ZrO}_2$ solid-solution pellets, the rate drops nearly to zero at less than 100% release, suggesting that, although the first helium is released by diffusion, an appreciable part of it is released very slowly by some other process, or perhaps not at all.

Fig. 2. Fractional release vs square root of time for microspheres. Calculated lines are for $D/a^2 = 2.3 \times 10^{-7} \text{ sec}^{-1}$ at 935°C and $D/a^2 = 1.7 \times 10^{-5} \text{ sec}^{-1}$ at 1129°C .

Fig. 3. Fractional release vs square root of time for 100 wt% PuO_2 . Calculated line for $D/a^2 = 4.5 \times 10^{-5} \text{ sec}^{-1}$.

Fig. 4. Fractional release vs square root of time for $\text{PuO}_2\text{-56 wt% ThO}_2$. Calculated lines are for $D/a^2 = 7.0 \times 10^{-7} \text{ sec}^{-1}$ at 1423°C and $D/a^2 = 7.0 \times 10^{-6} \text{ sec}^{-1}$ at 1616°C .

Fig. 5. Fractional release vs square root of time for $\text{PuO}_2\text{-7 wt% ZrO}_2$. Calculated line is for $D/a^2 = 7.4 \times 10^{-4} \text{ sec}^{-1}$.

Fig. 6. Fractional release vs square root of time for PuO_2 -35 wt% ZrO_2 . Calculated line is for $D/a^2 = 2.6 \times 10^{-4} \text{ sec}^{-1}$.

Table II contains additional helium-release data. The times for release of 50 and 90% of the helium content, respectively, are given in columns 3 and 4; the measured helium contents as calculated from calibration of the RGA against the standard leak are given in column 5; the D/a^2 's calculated from the 50% release time, as based on spherical geometry (i.e., for 50% release $Dt/a^2 = 0.0310$), are shown in column 6; and the times between pellet sintering and the release measurements are given in column 7.

For the classical diffusion model, the diffusion coefficient D is expected to obey the Arrhenius law: $D = D_0 \exp(-Q/RT)$. So the data for a particular type of sample should fall on a straight line whose slope is proportional to the activation energy Q when plotted on $\log D/a^2$ vs $1/T$ coordinates. Figure 7 is a plot of $\log D/a^2$ vs $10^4/T$. The D/a^2 values are slightly different from those of Table II, because they were obtained from the tau calculations (see Appendix B) and represent "instantaneous" values at 50% release. Of the materials for which we obtained more than two data points, only the microspheres yielded data that fell along a reasonably straight line.

Another test to show how well the data fit the diffusion model is afforded by assuming a time-dependent diffusion coefficient.² If $D(t)$ represents the function describing the variation of D with time,

TABLE II HELIUM RELEASE DATA						
Expt. No.	Temp (°C)	t(50%) (sec)	t(90%) (sec)	He Content (cm^3/g)	$D/a^2 \times 10^{5a}$	Age (days)
100% PuO_2						
12582	1476	3652	----	0.29	0.85	178
12583	1613	1127	4800	0.26	2.75	182
12584	1412	4662	----	----	0.66	220
12585	1364	52926	----	0.22	0.059	193
PuO_2-56 wt% ThO_2						
12571	1087	----	----	0.056	----	92
12572	1423	84780	----	0.046	0.037	102
12573	1616	5100	75480	0.063	0.608	108
PuO_2-7 wt% ZrO_2						
12579	1412	239	29190	0.23	13.0	155
12580	1609	102	706	0.26	39.4	161
12581	1240	----	----	----	----	167
PuO_2-35 wt% ZrO_2						
12574	1215	----	----	0.15	----	167
12575	1082	----	----	0.12	----	176
12576	1403	119	5835	0.14	26.1	193
Microspheres						
11637	935	----	----	----	----	599
11638	1056	5160	57600	0.73	0.601	611
11639	1240	393	2312	0.71	7.89	619
11640	1129	1922	17200	0.79	1.61	635

^aDerived from 50% release time.

Fig. 7. "Effective" diffusion coefficients vs $10^4/T$.

it can be shown that the solution of the differential equation for spherical geometry is the same as that given in Appendix B, except that the characteristic parameter Dt/a^2 is replaced by τ where $\tau = (1/a^2) \int_0^t D(t) dt$. Thus $D/a^2 = d\tau/dt$, and, from a set of data comprising fraction released as a function of time, one can obtain a value for D/a^2 for each data point. This is called the "tau calculation." The values of D/a^2 from all the experiments are plotted against fraction released in Fig. 8. The derivation of the sensitivity of the tau calculation to measurement errors is described in Appendix C. Figure 8 shows that D/a^2 can vary by $\pm 40\%$ for $\pm 5\%$ variation in the fraction released. Since we believe that the measured fractions are accurate only to within 5%, the variations in D/a^2 shown in Fig. 8 seem truly characteristic of the helium-release phenomenon and are probably not due to experimental error.

The release characteristics of the various kinds of samples are compared in Fig. 9, where isochronal fractional release is plotted against temperature. We chose the time period, 1600 sec, to take advantage of the best-behaved parts of the fractional release curves in Figs. 2-6 and thus avoid, as far as possible, the anomalous parts.

A. Characteristics of the Helium Release

The release rates as recorded by the RGA were not smooth, but appeared as extremely "noisy" signals. Two general features can be resolved. In one the helium appears to have been released in intense bursts, each lasting only a fraction of a second, causing many spikes on the curve. Figure 10 shows this type of release. The second type of release, which appears as slower bursts, some persisting for 2 or 3 min and decaying exponentially, is shown in Fig. 11. For some samples, both types of rate irregularity appeared simultaneously, for others only the spikes were observed. As the helium content of a sample decreased, the bursts decreased in both

Fig. 8. Time-dependent diffusion coefficient vs fraction released.

intensity and frequency. Particularly noteworthy is Fig. 12 in which both types of bursts appear simultaneously along with some abrupt decreases in rate.

We ran some tests to provide assurance that the irregularities were not due to instrumental artifacts. A crucible containing no sample was heated in the system and, with helium provided by the standard leak, a quiet steady signal was observed. Also, the normal electrical-noise background

Fig. 9. Fraction released in 1600 sec vs temperature.

Fig. 10. Recorder trace of the signal from the RGA showing helium bursts of very short duration.

observed for other mass peaks such as $^{18}(\text{H}_2\text{O}^+)$ or $^{28}(\text{N}_2^+ \text{ and } \text{CO}^+)$, which are always present in the vacuum system, was many orders of magnitude below the fluctuations observed at mass 4 when helium was being evolved from a sample.

B. Optical Microscopy

Metallography of polished samples after the helium-release experiments were finished revealed that the samples contained large irregular voids. Specimen 12584 was the only one examined both before and after the release experiment. Before the experiment, the ceramic was fairly porous and the pores tended to be small and equiaxed except near the edge of the specimen where they were more irregular. After the experiment, the pores had increased in both number and size and had become more irregular. The void volume, determined from photomicrographs, was 10% before the experiment (in reasonable agreement with the geometrically determined density, Table I) and 16% afterwards.

Fig. 11. Recorder trace of the signal from the RGA showing large helium bursts with exponential decay.

Fig. 12. Recorder trace of RGA signal showing bursts of helium and abrupt decreases in the release rate.

We found that helium was released comparatively rapidly from the ZrO_2 solid solutions. A possible explanation was found when metallography revealed that these samples consisted of three phases: a matrix and two inclusion phases. One of the inclusion phases had boundary cracks, probably caused by differential thermal expansion. There was enough of this phase to have provided a continuous path for helium release through cracks to the surface, and thus to have accounted for the unusually rapid release. We observed no other microscopic features that could be related to helium behavior in these specimens.

C. Specimen Dimensional Changes

We measured all the pellets to ± 0.001 in. before and after helium release. In only one pellet out of 13 was swelling detected. Two of the PuO_2 pellets developed a few large cracks, whose planes were perpendicular to the cylinder axis, and the pellet lengths had increased by the width of these cracks, but the diameters were unchanged.

IV. DISCUSSION

In a study such as this on helium release, the most desirable situation would be to have available some theoretical model that describes the release mechanism. Experimental data could then be fitted into the theoretical framework. At present, however, there is no proven model for the release of helium from oxides.

Consequently, it is evident from comparing diffusion curves and the data in Figs. 2-6 and 8 that simple diffusion, assuming a constant D/a^2 , is not adequate to describe the results. In Fig. 8 the deviation from constancy of D/a^2 is seen to vary for the different kinds of materials, although all show the same general behavior: D/a^2 rises to a maximum, then decreases. Although some regularity of behavior was observed, use of this model must be considered only as an empirical fit to the data, in the sense that the model cannot be used to predict behavior for conditions other than those studied. For example, although

it is possible to plot D/a^2 as a function of fraction released and to obtain some correlations, there is no guarantee that such information would be applicable for longer times at lower temperatures. Also, since the pellets behaved differently from the microspheres, extension of the results of other geometries, such as larger pieces, is problematical.

The similarity between helium release from PuO_2 and fission-gas release from UO_2 is evident. For xenon release from UO_2 , it has also been found that simple diffusion theory is inadequate. Fission-gas-release results are presently explained by a trapping model in which several kinds of traps exist in the solid. Some of the traps, such as closed pores, retain the gas atoms permanently, others can anneal out and release the trapped atoms. In addition, a trapping site can serve as a nucleus for collection of gas atoms, eventually producing a bubble. The bubbles can migrate in the presence of a temperature gradient. Such a model might well apply to the release of helium from PuO_2 . Although it is not within the scope of this report to attempt an application, Hurst³ has developed a theory for gas release from a solid having closed pores that act as permanent traps. The general shape of Hurst's fractional-release curves is similar to that of the curves for the helium-release data.

The PuO_2 lattice can store damage from alpha particles and recoil nuclei at room temperature. Studies of the annealing of this damage show that, for temperatures and times comparable to those we used, much or all of the accumulated damage can anneal out, as judged by lattice-parameter measurements. Inasmuch as lattice imperfections can trap helium atoms, it is possible that the helium release may thus be largely controlled by the annealing rate, or perhaps by a combination of annealing and diffusion. In some of our data, it appears that the release rate becomes slower with time (D/a^2 decreases). Thus a qualitative parallel between amount of annealing and release rate can be discerned.

APPENDIX A HELIUM GENERATION RATE

The half-life of the ^{238}Pu isotope is 86.4 yr. The plutonium used in this work contains about 80% of the 238 isotope, the rest being largely ^{239}Pu . The decay rate of a given specimen changes less than 2% in 2 yr, and was taken as constant for our purposes. For 1 g of pure oxide containing 88.1 wt% of plutonium, 80 wt% of which is ^{238}Pu , $1.69 \times 10^{-8} \text{ cm}^3 \text{ (STP)/sec}$ (or $1.46 \times 10^{-3} \text{ cm}^3 \text{ (STP)/day}$) is the rate of helium generation if every alpha particle produces a helium

atom. In 1 yr, the total generation of helium is $0.53 \text{ cm}^3 \text{ (STP)/g}$ of 80% enriched PuO_2 . Surface losses are negligible for large pellets but must be considered for microspheres whose degree of packing determines the extent of surface loss of alpha particles. The range of a 5-MeV alpha particle in PuO_2 is estimated to be about $10 \text{ }\mu\text{m}$ so that the outer $10\text{-}\mu\text{m}$ -thick shell of a piece will lose part of its helium as alpha particles unless a contiguous piece of oxide is present to absorb them.

APPENDIX B CLASSICAL DIFFUSION THEORY

The theory based on Fick's laws for a constant diffusion coefficient is well developed and discussed in many places.^{2,4} Only a summary of pertinent results is given here.

For our experiments, two geometries, the sphere and the finite cylinder, were of interest. Generation is not included, because the experimental data are for times so short that helium generation in the sample can be neglected.

The differential equation for a sphere where only radial flow is considered, is

$$\frac{\partial c}{\partial t} = D \left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} \right),$$

where c is the helium concentration,

t is time,

D is the diffusion coefficient, and

r is the radial coordinate.

For a finite cylinder with both endwise and radial flow,

$$\frac{\partial c}{\partial t} = D \left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial x^2} \right),$$

where x is distance along the cylinder axis.

Because helium is generated uniformly throughout the sample, and the rate of diffusion at the storage temperature for small pellets is very low, the initial condition is taken to be uniform concentration at the start of the release measurement. At the surface of the sample, a vaporization condition (corresponding to radiation at the surface for the analogous heat-flow problem) can be applied. If solutions are obtained for this boundary condition and the rate of helium vaporization at the surface is estimated, it can be shown that vaporization is so rapid compared to the rate of arrival of helium at the surface that the solutions reduce to those for zero surface concentration. Consequently, a boundary condition of zero surface concentration can be used.

The solution desired is the fraction of the initial helium content released as a function of time, with D and the geometric parameters as constants. Since the differential equation is in terms of concentration, time, and distance, the first solution will be concentration within the specimen as a function of time, distance, and initial concentration. This can be integrated over

the dimensions of the specimen to give the total helium content at any time. The total content divided by the initial content is the fraction retained in the specimen. The ultimate result for the sphere is

$$F = 1 - (6/\pi^2) \sum_{k=1}^{\infty} (1/k^2) \exp(-k^2 \pi^2 Dt/a^2),$$

and that for the cylinder is

$$F = 1 - \left[\frac{6}{\pi^2} \sum_{k=1}^{\infty} \frac{1}{(2k-1)^2} \exp\left(-\frac{(2k-1)^2 \pi^2}{l^2} \frac{Dt}{4}\right) \right] \times \left[\sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-n^2 \pi^2 \frac{Dt}{b^2}\right) \right].$$

where a is the sphere radius

l is the length of the cylinder

b is the cylinder radius

F is the fraction released.

The π_n 's are roots of the zeroth-order Bessel function $J_0(x)$. Note that the first series may be made less cumbersome by replacing $2k-1$ by m and taking only terms with m odd.

For the spherical case, Dt/a^2 is a dimensionless number, and one can compute a table of F as a function of Dt/a^2 that will serve for all cases.

For the cylinder, although the expression can be evaluated for various combinations of Dt , l and b , it is easier to use the sphere solution which coincides within a few percent with that for an equiax-

ed cylinder.⁷ The "equivalent sphere" for a 1/4-in. by 1/4-in. cylinder has a radius of 0.250 in. Note, however, that for cylinders that are not equiaxed one must use the proper solution, and to predict long-term behavior one should include a generation term in the differential equations, which will, of course, modify the solutions.

Approximate Solutions

For the sphere, Darken and Gurry⁸ give, for fractions of less than 0.1 released, $F = (6/\pi^2) \sqrt{Dt/a^2}$. MacLennan and Stevens⁶ give a more general approximation: for $F < 0.1$, $F = 2/\sqrt{\pi} \sqrt{S/V}$, where S/V is the surface-to-volume ratio of the specimen. In either case, a plot of F vs. $\sqrt{t}$ will be a straight line passing through the origin for F less than 0.1.

Time-Dependent Diffusion Coefficient--"Tau Calculations"

Crack² has shown that the situation in which D varies with time can be analyzed to yield the same form of solution as given above, except that Dt/a^2 is replaced by τ where $\tau = \int_0^t D'(t) dt$. Here, $D'(t)$ represents the function describing the variation of D/a^2 with time. The fractional-release data can thus be analyzed to give a value of τ at each point. The instantaneous value of D/a^2 is $d\tau/dt$. At present, this seems to be the most sensitive method for testing the data against the diffusion model.

⁷Given the same D , one can find a value for a which yields a fractional-release curve corresponding very closely to the curve for the given l and b .

APPENDIX C ERROR ANALYSIS

We want to derive the relation between fractional error in the fraction released, f_F , and the fractional error in D' , $f_{D'}$. For the fraction released, we have

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-n^2 \pi^2 D't}$$

$$\frac{\partial F}{\partial D'} = 6\pi \sum_{n=1}^{\infty} e^{-n^2 \pi^2 D't}$$

Limits may be found by replacing the infinite sum by the appropriate integrals

$$\frac{\partial F}{\partial D'} < 6\pi \int_0^{\infty} e^{-\pi^2 x^2} dx,$$

and

$$\frac{\partial F}{\partial D'} > 6\pi \int_1^{\infty} e^{-\pi^2 x^2} dx,$$

where $\pi^2 x^2 = n^2 \pi^2 D't$.

Evaluating the integrals gives

$$\frac{3}{\sqrt{\pi}} \frac{1}{\sqrt{D't}} > \frac{\partial F}{\partial D'} > \frac{3}{\sqrt{\pi}} \frac{1}{\sqrt{D't}} \operatorname{erfc}(\pi/\sqrt{D't}).$$

The fractional error in F is dF/F , and that in D' is dD'/D' .

$$\text{Also, } dF = \frac{\partial F}{\partial D'} dD'.$$

$$\text{Thus, } f_F = \frac{D'}{F} \frac{\partial F}{\partial D'} f_{D'}.$$

Substituting the limits on $\frac{\partial F}{\partial D'}$ gives

$$f_F < \frac{3}{\sqrt{\pi}} \frac{\sqrt{D't}}{F} \cdot f_{D'}$$

and

$$f_F > \frac{3}{\sqrt{\pi}} \frac{\sqrt{D't}}{F} \operatorname{erfc}(\pi/\sqrt{D't}) \cdot f_{D'}.$$

Since for every fraction released, F , there is a corresponding $D't$, the expressions may be evaluated for each F . The results are:

Fraction Released, F	$D't$	Upper Bound on f_D	Lower Bound on f_D
0.10	0.93×10^{-3}	$2.2 f_F$	$1.9 f_F$
0.50	0.031	$3.8 f_F$	$1.7 f_F$
0.75	0.092	$8.1 f_F$	$1.5 f_F$
0.90	0.19	$26 f_F$	$1.2 f_F$

Restricting consideration to values of F between 0.1 and 0.75, we see that for $f_F = 0.05$ (5 rel% accuracy in fraction released), $f_{D'}$ must be less than 0.40. Although the derived restriction on $f_{D'}$ is somewhat more complicated, this will suffice as a test for the present data, almost all of which show a variation of more than 40% in D' .

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