UNCLASSIFIED

[redacted]

[redacted]

AAEC/X2

AAEC/X2

COPY NO

AUSTRALIAN ATOMIC ENERGY COMMISSION

RESEARCH ESTABLISHMENT

LUCAS HEIGHTS

ESCAPE OF FISSION PRODUCTS FROM SLURRY PARTICLES

by

B. S. HICKMAN

February, 1956.

CONFIDENTIAL

AAEC/X.2

AUSTRALIAN ATOMIC ENERGY COMMISSION

RESEARCH ESTABLISHMENT

LUCAS HEIGHTS

ESCAPE OF FISSION PRODUCTS FROM SLURRY PARTICLES

by

B. S. Hickman

Summary

The escape of fission products from fissile particles by recoil and by diffusion are discussed in general terms and equations governing these processes are derived. Experimental determinations of the mean free paths of the fission fragments and of the diffusion coefficients are reviewed. This data is then applied to a slurry of the composition under consideration viz. 1 or 2 atomic percent uranium, as metal or oxide in sodium. Tentative conclusions are drawn as to the optimum size for the slurry particles.

TABLE OF CONTENTS

		Page
1.	Introduction	1
2.1	Escape by Recoil	1
2.2	Numerical Evaluation of Escape by Recoil	2
2.3	Recoil into Neighbouring Particles	3
3.	Escape by Diffusion	3
3.1	Effect of Recoil	4
3.2	Escape from Surface of Particles	4
3.3	Numerical Evaluation of Diffusion Effect	5
3.4	Diffusion Coefficients for Fission Products	5
3.5	Other Factors Affecting Diffusion	6
4.	Disintegration of Particles	6
5.	Conclusion	7

1. INTRODUCTION

The optimum size for the fissile particles in a slurry for use as a reactor fuel depends on a number of factors. Preliminary work has shown that it is possible to produce uranium metal powder of particle size $1 - 5\ \mu$ by repeated formation and decomposition of uranium hydride. Production uranium dioxide from Springfields has a particle size in the range $0.1-1\ \mu$ and this may be altered by sintering. Perhaps the most important factor governing the selection of a suitable particle size from these ranges is the effect of this size on the escape of fission products. If conditions can be found under which a large proportion of the fission products escape into the liquid medium then chemical processing methods will be profoundly influenced. For instance it may be possible to continuously remove some of the elements (in particular the rare gases) and hence delay considerably poisoning of the reactor. Radiation damage due to fission product accumulation will also, of course, be influenced by escape of these fission products. This radiation damage may simply cause swelling and hence density changes or may cause disintegration of the particles. Thus massive uranium metal undergoes a 30–40% decrease in density after 0.3–0.4% burn up at 800 °C and uranium foil has been found to disintegrate completely after 0.5–1.0% burn up. This will of course, influence the settling and circulating properties of the slurry.

The escape of fission products may occur by two means, viz:–

(i) Recoil at the moment of fission.

(ii) Diffusion to the surface followed by escape into the liquid medium.

In the following sections general equations governing these processes are derived and the results applied to particle sizes in the range of interest, viz., $1-100\ \mu$. Consideration is also given to the possibility of recoil occurring from one particle into another and of reabsorption of the fission products into the particles.

2.1 ESCAPE BY RECOIL

The fission fragments are projected away from the site of fission with an energy of about 80 MEV and they will have a definite range in any given medium. The proportion of fission products escaping from a particle by this mechanism can be derived as follows. (1) The assumption is made that the particles are spherical in shape and this should be fairly valid for uranium and uranium dioxide powder. Suppose the average range of a fission fragment in the fissile matrix is R and that the radius of the particle is r_o. The probability of a fragment, at distance r from the centre of the particle, escaping is given by the ratio of that part of the surface of a sphere centre at r and radius R which lies outside the particle to the total surface area of the sphere. Simple geometrical considerations show this to be

$$P = \frac{2Rr - r_o^2 + R^2 + r^2}{4r R}$$

Hence the number of fragments escaping in unit time will be

$$N = 2F \int_{r_o-R}^{r_o} P.\, 4\pi r^2\, .dr$$

where F = number of fissions/unit volume/second

Integrating and dividing by the total number of fission fragments one obtains

$$f = \frac{3}{4}\left(\frac{R}{r_o}\right) - \frac{1}{16}\left(\frac{R}{r_o}\right)^3 \qquad \text{——————} \quad 1$$

where f = fraction escaping

for the case when $r_o > \frac{R}{2}$ When $r_o < \frac{R}{2}$ all the fragments will escape by recoil

2.2 NUMERICAL EVALUATION OF ESCAPE BY RECOIL

Estimates of the range of the fission fragments vary. As the fission fragments will be ejected with approximately the same energy, their range will not vary over very wide limits. Ozeroff (2) has calculated a "typical" range of 4.3μ for uranium metal. Siegre and Wiegand (3) measured experimentally the stopping power of aluminium, copper, silver and gold for the fission fragments. Using the approximation that the atomic stopping power is proportional to the square root of the atomic number, they calculated mass stopping powers of 12.6 mgm/m^2 and 10.0 mgm/cm^2 for uranium metal and U_3O_8 respectively. This is equivalent to maximum ranges of 6.5μ and 12μ respectively. Finkle et alia (4) measured the stopping power of aluminium for individual fission fragments and found values ranging from 3.74 mg/cm^2 for the lighter elements to 2.54 mg/cm^2 for the heavier elements. This corresponds to a range variation of 4.5–6.5 μ in uranium metal.

Stubbs and Walton are carrying out an investigation of recoil by passing a stream of helium over thin foils of fissile material suspended in the neutron flux of BEPO. The activities of the resulting gases are then measured and figures obtained for the quantity of Xe^{133}, Xe^{135} and Kr^{87} which has been evolved.

Preliminary results (5) using uranium foil, 0.005 ins. thick, showed much smaller quantities (10–50%) of the fission product gases that would be expected. However this can probably be explained by losses due to the geometry of the system and diffusion effects. Subsequent work using a layer of U_3O_8 0.3 μ thick on platinum foil has shown excellent agreement between theoretical and observed values. The yields in this experiment were quite independent of temperature in the range 100–400°C indicating that diffusion effects were absent. The work is to be continued using graduated thicknesses of U_3O_8 until a temperature dependent yield is found. This should enable a fairly accurate estimate of the recoil distance in U_3O_8 and hence in uranium to be made.

Hence although no really reliable data is available it would appear that 5μ and 10 μ should be a fairly close approximation to the mean free paths of the fission fragments in uranium metal and uranium dioxide respectively. Substitution of these figures in equation (1) gives the results quoted in Table I.

TABLE I

Percentage of fission products escaping from fissile particles of various sizes.

Particle Size	1μ	5μ	10μ	20μ	50μ	100μ
Uranium Metal	100	100	69	37	15	7.5
Uranium Dioxide	100	100	100	69	30	15

2.3 RECOIL INTO NEIGHBOURING PARTICLES

The above discussion takes no account of the possibility of the fission fragments recoiling from one particle into a neighbouring particle. This will of course, depend on the mean free path in the liquid medium and on the distance apart of the particles. By analogy with the figures obtained by Siegre and Wiegand one would expect a maximum mean free path of about 20 μ in sodium. Assuming a regular distribution, the distance apart of the particles in a sodium slurry are given in the table for the compositions of interest.

TABLE II

Distance apart of particles (diameter = d) in a sodium slurry.

SLURRY COMPOSITION	1 at %	2 at %
Uranium Metal	5d	3.75d
Uranium dioxide	3.75d	3d

It is obvious from this table that for particle sizes greater than about 5 μ recoil from one particle to another will be negligible. For particle sizes less than this value this effect will depend on the solid angle subtended at the original particle by all particles within the range of 20 μ. Consideration will show that for a slurry of this composition the effect will be small even for very small particle sizes.

3. ESCAPE BY DIFFUSION

Fission products which do not escape by recoil will be free to diffuse to the particle Surface from where they may escape into the liquid media. Lomer (6) has treated this diffusion process quantitatively. His discussion neglects any effects due to recoil and he assumes that the slurry particles are spherical in shape.

The radial flow at a distance r from the centre of the particle is given by

$$Q_r = D. 4\pi r^2 . \frac{dC}{dr}$$

D = diffusion coefficient of the fission product under consideration. If a steady state is reached in which the fission products are diffusing away as rapidly as they are formed then

$$D. 4\pi r^2 \frac{dC}{dr} = -\frac{4\pi r^3}{3}.F$$

F = rate of fission

Integrating one obtains

$$C = C_o - \frac{r^2 F}{6D}$$ where Co = concentration at centre of particle.

Assuming that the liquid removes the fission products as rapidly as they arrive at the surface (i.e. C = o when $r = r_o$) one obtains

$$C_o = \frac{r_o^2 F}{6D} \qquad \text{——— 2}$$

A similar result has been obtained by Le Claire (7).

3.1 EFFECT OF RECOIL

The foregoing assumes that production of fission products is uniform throughout the particle and hence neglects any effects due to loss by recoil. As a first approximation this can be allowed for by introducing a factor into equation 2 as follows:-

$$C_o = (1 - f) \frac{r_o^2 F}{6D} \qquad \text{——— 3}$$

where f = fraction of fission products which escape by recoil.

3.2 ESCAPE FROM SURFACE OF PARTICLES

Formula (2) was derived assuming zero concentration of fission products at the particle surface. Lomer (6) considers the case of a settled slurry when escape from the surface will depend on diffusion rates in the liquid. However for a circulating slurry this factor will not be important and the removal of the fission products from the surface will depend to a large extent on their chemical and physical properties. The majority of the fission products can be divided into five different classes whose behaviour on reaching the particle surface will differ as follows:-

I. Rare Gases

These elements will probably nucleate to form gas bubbles and escape into the liquid.

II. Rare Earths

Little information is available on the solubility of the rare earths in liquid sodium but it would appear that they are slightly miscible (8). Hence these elements would dissolve from the particle surface, at least until the limit of solubility was reached.

III. Alkali Metals and Alkaline Earth Metals

All these elements are at least partially miscible with sodium and hence would dissolve from the surface of the particles.

IV. Heavy Metals

The metals such as zirconium, niobium and molybdenum which in liquid sodium would probably not pass the particle surface.

V. Electronegative Elements

The electronegative elements such as iodine would react with the strongly electro-positive sodium.

Hence it would appear that for a circulating slurry the assumption, that the fission produce concentration at the particle surface is zero, is valid for all the elements except the heavy metals such as zirconium, niobium, etc.

3.3 NUMERICAL EVALUATION OF DIFFUSION EFFECT

Using formula 2 a family of curves (figure 1) have been drawn of concentration against particle size for various values of the diffusion coefficient and neutron flux. Pure fissile material has been assumed and the concentration is given in units of burn up. By interpolation it is a simple matter to make allowance at least roughly for escape by recoil.

3.4 DIFFUSION COEFFICIENTS FOR FISSION PRODUCTS

In order to interpret the above curves, it is, of course, necessary to know the values for the diffusion coefficients of the fission products in uranium metal and oxide.

(a) Uranium Metal

Experimental determinations of diffusion coefficients in uranium have been mostly limited to the rare gases. Several workers (9–12) have determined these coefficients by heating irradiated uranium metal in a vacuum or a stream of inert gas. The accompanying graph (fig.2) shows the wide spread of results obtained. These variations can probably be explained by the fact that in all the measurements escape by diffusion took place in only a thin surface layer ($> 10^{-3}$cms) and hence any surface oxidation would profoundly influence the results. This suggestion has been confirmed by Bates and Clark (10) and by Stubbs, who found large increases in the diffusion coefficients on allowing oxygen into their apparatus. For this reason the lower values of the coefficient such as those obtained by Bates and Clark by a vacuum heating method are thought to be more reliable.

The only determination of the diffusion coefficients of the other fission products was a very crude series of experiments by Spedding (9). A programme on this subject is in progress at Windscale (15) but no results are available, apart from those mentioned above for the rare gases. Hence in the absence of more reliable data, the following table gives estimates of the diffusion coefficients of the various classes of fission products. The results due to Bates and Clark (10) have been used for the rare gases and the other figures have been estimated from the results of Spedding.

TABLE III

Fission product diffusion coefficients at various temperatures.

		600° C	800°C	1000°C
Class I	Rare Gases	10^{-15}cm^2/sec	10^{-14}cm^2/sec	10^{-12}cm^2/sec
Class II	Rare earths	10^{-16}	10^{-14}	10^{-10}
Class III	Alkali metals, etc.	10^{-17}	10^{-15}	10^{-12}
Class IV	Heavy metals	10^{-16}	10^{-15}	10^{-13}
Class V	Electronegative elements	10^{-16}	10^{-14}	10^{-11}

(b) Uranium Dioxide

No determinations of the diffusion coefficients in uranium dioxide have been made. However due to the open crystal lattice of this compound one would expect higher values than for uranium metal. This has been confirmed, qualitatively, by some measurements at Chalk River (13). Irradiated uranium dioxide powder was heated in a stream of helium and it was found that all the gaseous fission products were released after half an hour at 1000°C and 50% after a similar period at 800°C. However, as no indication was given of particle size or length of irradiation, no calculations can be made from these figures.

(c) Application to Graph

Examination of Table III in conjunction with the curves of figure 1 indicate that at 600°C escape by diffusion will only be appreciable for particle sizes of the order of 1 μ when the majority of the fission products escape by recoil anyway. At 800°C escape by diffusion will only be appreciable for particle sizes of the order of 10 μ and only at 1000°C will appreciable diffusion take place from 50-100 μ particles. Any further and more definite conclusions must await more accurate determination of the diffusion coefficients.

3.5 OTHER FACTORS AFFECTING DIFFUSION

(a) Irradiation

All the measurements mentioned above were carried out after a very short period of irradiation. It may well be that the diffusion coefficients are considerably altered by a neutron flux and by lattice damage occurring at high burn up. It has been shown (16) that the diffusion coefficients in non fissile materials are substantially unaltered by irradiation but this will not necessarily follow for fissile material. Measurement of the quantity of fission product gases released on decanning an irradiated, sintered uranium powder specimen (14) and on a Windscale bar (10) gave values for the diffusion coefficient under irradiation of the same order as those mentioned earlier. However the measurements were not sufficiently accurate to warrant drawing any conclusions.

(b) Thermal Cycling

Reports from the U.S. indicate that cycling of irradiated uranium metal through a phase change causes a large evolution of fission product gases. During circulation of a slurry through the reactor and heat exchangers it is quite possible that uranium will pass through either the $\alpha - \beta$ transformation temperature (670°C) or the $\beta - \gamma$ transformation (770°C) and hence escape of fission products may be influenced considerably.

(c) Effect of Crystal Imperfections

It has been suggested that the rare gas fission products diffuse in uranium metal until they reach an imperfection in the crystal, where they collect and form gas pockets which cause swelling. Hence if the slurry particles contain imperfections of any description the rare gases may collect at these rather than diffusing the longer distances to the surface and escaping into the sodium.

4. DISINTEGRATION OF PARTICLES

If all or a large proportion of the fission products escape from a slurry particle then disintegration of the particle would not be expected to occur, as has been found with massive uranium at high burn up. However there is another factor which may come into play for small particle sizes. Ozeroff (2) has calculated that due to recoils from collisions with the fission fragments there is an atom current in uranium metal under irradiation of 6.5×10^{-3} n atoms/cm^2/sec. where n is the number of fissions/cm3/sec. If this atom current is uniform throughout the particle then there will be a continual escape of fissile material from the surface. This phenomena may explain the disintegration of thin uranium foils after comparatively short burn up. Neglecting escape of fission fragments from the particle this effect can be treated roughly quantitatively as follows:-

If f is the fraction of atoms escaping then

$$f = 6.5 \times 10^{-3} \times \frac{A}{V} \times F$$

where F = fractional burn up

$$= 6.5 \times 10^{-3} \times \frac{3}{r} \times F$$

For r = 10 μ and F = 0.05 f = 1 i.e. complete disintegration has occurred. This does not take into account that, with small particles, a large proportion of the path of the fission fragments will lie outside the particle. This will be an important factor particularly when it is remembered that a fragment undergoes the majority of its collissions towards the end of its path and for the majority of its path slows down by electron excitation only.

However it is suggested that this factor should be given some consideration. It may well mean that the particle size will be reduced by fission to a level at which a large proportion of the fission fragments escape by recoil, and then remain substantially constant. Readsorption of ejected atoms back onto the particle surface may, of course, occur to a large extent.

5. CONCLUSION

The foregoing discussion has indicated that:-

(i) For uranium metal virtually all the fission fragments escape by recoil if the particle size is below 5μ and an appreciable proportion escapes up to 10 or 15μ.

(ii) For uranium dioxide total escape by recoil occurs for a particle size of about 10μ or less and is still appreciable at 20 μ.

(iii) For a slurry of the composition proposed (1 or 2 at % uranium) recoil from one particle into another is not very significant.

(iv) At temperatures less than 1000°C escape by diffusion from uranium metal is only appreciable for particle sizes at which the majority of the fission products have already escaped by recoil. The data on diffusion, is however, very unreliable.

(v) From the very limited data available it would appear that escape by diffusion from uranium oxide would occur more readily than from uranium metal.

(vi) Other effects such as irradiation, thermal cycling may influence the above conclusions.

(vii) Complete disintegration of particles may possibly occur at high burn up.

On the data available at present, therefore, it would appear that for fission product escape from a uranium metal slurry to be appreciable the particle size should be kept down to the level (< 10μ) at which escape by recoil is appreciable. Larger particles may be permissible in the case of a uranium dioxide slurry.

However it must be emphasised that definite conclusions must await more accurate experimental data. The work of Stubbs (5) at Harwell and Bates and Clark (10) at Windscale may shortly provide more reliable figures for the recoil length and diffusion coefficients.

REFERENCES

1. S. Flugge and K. Zimens – Z. Physiln Chem. B42 179 (1939).

2. J. Ozeroff – KAPL 205 (AECD 2973), (1949) (Unclassified).

3. E. Siegre and C. Wiegand – Phys. Rev. 70, 808, (1946).

4. B. Findle et alia – Radiochemical Studies – The Fission Products Book I, P471 (Wiley).

5. F. Stubbs and G. Walton – Geneva Conference P/435 (1955).

6. W. Lomer – A.E.R.E. T/M 116 (1954) (Unclass.)

7. A. Le Claire – A.E.R.E. M/R 1417, (1954) (Unclass.)

8. Liquid Metals Handbook.

9. F. Spedding et alia – MUC–NS–3067 (1944).

10. J. Bates and A. Clarke – R & D.B. (W) TN 200 (1955).

11. F. Zimen and P. Schmeling – Zeit. fur Electrochemie 85 599 (1954).

12. M. B. Reynolds – KAPL 894.

13. A. H. Booth et alia – CRDC 721 (1955) (Unclass.)

14. O. S. Plail (AERE) – Private Communication

15. D. S. Oliver et alia – R & D.B. (C) TN 98 (1954).

16. F. E. Faris – Geneva Conference P/747 (1955).

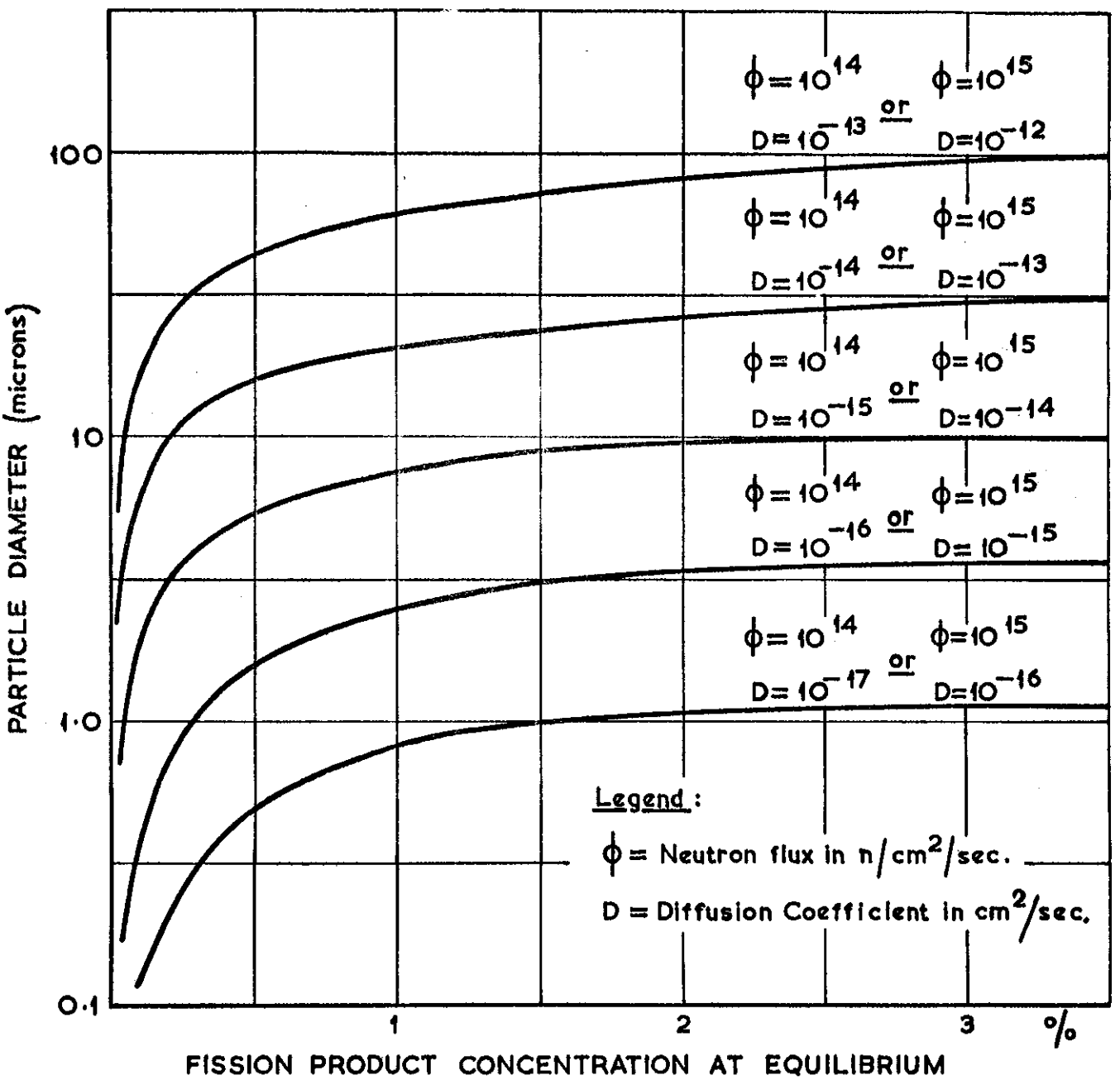

FIG. 1 FISSION PRODUCT CONCENTRATION AT CENTRE OF PARTICLES

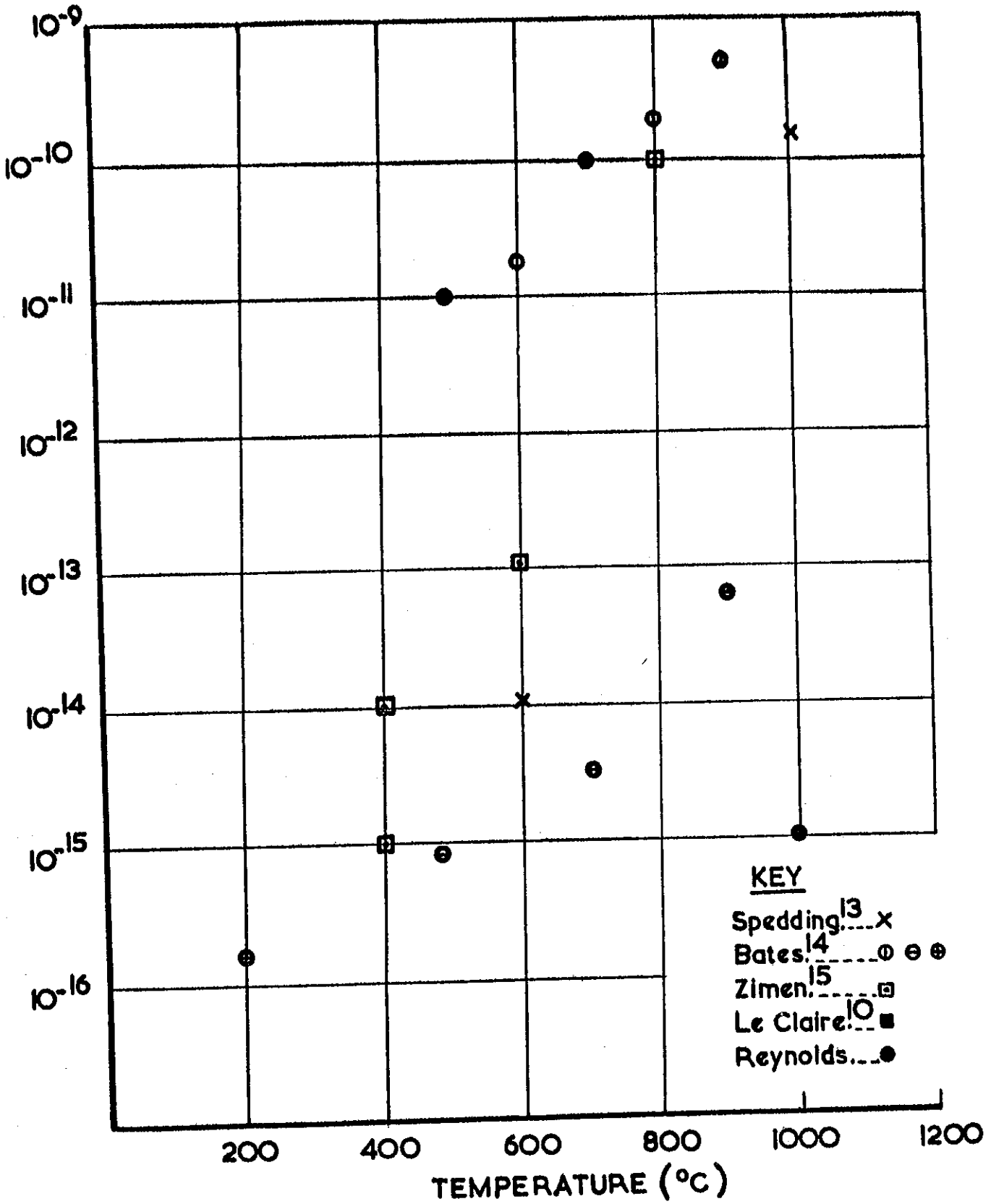

Fig. 2. Diffusion coefficients for rare gas fission products.