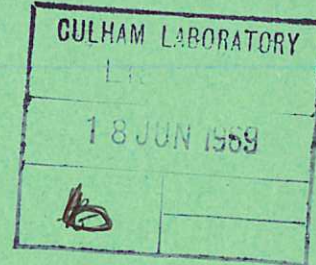
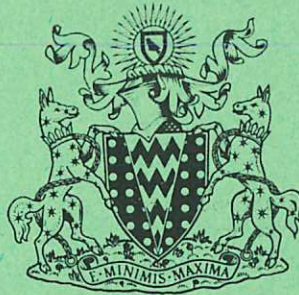


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# TRAPPING AND RE-EMISSION OF FAST DEUTERIUM IONS FROM NICKEL

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A B S T R A C T

A simple diffusion model is proposed for the re-emission of fast ions during bombardment of a metal surface. Experiments using a nickel target have been conducted in order to make a comparison with this model. Although the experimental results agree qualitatively with the predicted behaviour, the rate of re-emission is much lower than expected on the basis of known diffusion coefficients of deuterium in nickel. Thermal desorption of gas initially trapped in the nickel by bombardment at low temperatures indicates a number of specific activation energies for release, in addition to that associated with diffusion, and these are attributed to radiation damage sites produced during the ion bombardment.

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## 1. Introduction

Recent experimental investigations into the trapping of fast hydrogen and deuterium ions incident on metal surfaces has indicated that the re-emission process may be controlled primarily by diffusion of the gas from within the metal (Borovik et al, 1965 ; Lewin and Martin, 1966; McCracken and Maple, 1967. Measurements using metals which react exothermically with hydrogen indicated that in these cases their heats of solution also play an important role (McCracken, Jefferies and Goldsmith 1968). However, no experiments have been performed with sufficiently well defined initial conditions that a direct comparison could be made between experimental results and the predictions of diffusion theory, and we have therefore attempted in the present investigation to set up conditions where such a comparison may be made.

## 2. Theory

Hydrogen or deuterium ions entering a metal lattice with energies greater than  $\sim 1$  keV lose energy primarily by interaction with electrons. They undergo some scattering, but only a small proportion are backscattered out of the surface (McCracken and Freeman 1968). The remainder slow down in the lattice and have an approximately Gaussian range distribution with a mean range of the order of  $1500 \text{ \AA}$  at 20 keV (Schjøtt 1966). However, at temperatures above  $300^\circ\text{K}$  the diffusion rate of hydrogen in most metals is appreciable so that after slowing to thermal energies the trapped ions will be expected to diffuse throughout the metal lattice. Whether they escape from the metal surface when they diffuse back to it depends on the potential distribution at the surface. The situation can be

readily analysed if it is assumed that every ion reaching the surface from the bulk immediately desorbs. Under the conditions of the present experiment where there is continuous bombardment of the surface by further incident ions this assumption should be reasonable.

Let us consider an incident ion beam of infinite cross section striking a target, thickness  $d$ , and assume initially that the ion range is a constant,  $R$ . We now assume that the gas source at  $x = R$  diffuses into the two regions I and II (Fig.1) divided by the plane  $x = R$  with a constant diffusion coefficient,  $D$ . If the gas concentrations in the regions I and II are  $C_1(x,t)$  and  $C_2(x,t)$  and the fluxes in the two regions are  $J_1(x,t)$  and  $J_2(x,t)$ , then following the assumptions just made we have the boundary conditions:

$$\begin{aligned} C_1(x,0) &= C_2(x,0) = 0 \\ C_1(0,t) &= C_2(d,t) = 0 \\ C_1(R,t) &= C_2(R,t) \end{aligned} \quad \dots (1)$$

and

$$\frac{dN}{dt} = J_0 - \left[ -J_1(0,t) - J_2(d,t) \right]$$

where

$$N(t) = \int_0^d C(x',t) dx'$$

integrated over regions I and II and  $J_0$  is a constant input flux at  $x = R$ .

In most practical cases the ion range will be much smaller than the beam dimension or the target thickness. Since we have the boundary condition  $C(0,t) = 0$  the flow will be mostly towards the bombarded surface. A one-dimensional analysis will therefore be sufficient and we may write the diffusion equation in the two regions:

$$\frac{\partial C_1}{\partial t} = D \frac{\partial^2 C_1}{\partial x^2} \quad \dots (2)$$

$$\frac{\partial C_2}{\partial t} = D \frac{\partial^2 C_2}{\partial x^2} .$$

A solution is required for  $J_1(o,t)$  and  $J_2(d,t)$ . This may be done by taking Laplace transforms and finally obtaining the Laplace

transforms of the fluxes  $\tilde{J}_1$  and  $\tilde{J}_2$  viz :

$$\tilde{J}_1(o,p) = - \frac{J_0 \exp(R \sqrt{\frac{p}{d}})}{2p} \left\{ \exp\left(-R \sqrt{\frac{p}{d}}\right) + \frac{\exp(R \sqrt{\frac{p}{d}}) - \exp(-R \sqrt{\frac{p}{d}})}{1 - \exp(2d \sqrt{\frac{p}{d}})} \right\} \quad \dots (3)$$

$$\tilde{J}_2(d,p) = - \frac{J_0}{p} \frac{\exp(d+R) \sqrt{\frac{p}{d}} \left\{ 1 - \exp\left(-2R \sqrt{\frac{p}{d}}\right) \right\}}{\left\{ 1 - \exp\left(2d \sqrt{\frac{p}{d}}\right) \right\}} \quad \dots (4)$$

In most practical cases  $R \ll d$  and hence (3) and (4) reduce to

$$\tilde{J}_1(o,p) = - \frac{J_0}{p} \exp\left(-R \sqrt{\frac{p}{d}}\right) \quad \dots (5)$$

$$\tilde{J}_2(d,p) = 0 \quad \dots (6)$$

from which we obtain

$$J_1(o,t) = - J_0 \operatorname{erfc} \left[ \frac{R}{\sqrt{4Dt}} \right] \quad \dots (7)$$

$$J_2(d,t) = 0 \quad \dots (8)$$

It can be shown that this result is also true for a distribution of ranges if the mean range is substituted for  $R$ .

The fact that  $J_2(d,t) = 0$  is readily envisaged when considering the equilibrium state as  $t \rightarrow \infty$ , where  $\frac{\partial c(x,\infty)}{\partial x} = \text{const.}$  and

$\frac{J_1}{J_2} = \frac{(d-R)}{R}$ . Curves of  $J_1(o,t)$  as a function of time are shown in Fig.2 for various values of  $\frac{R}{\sqrt{D}}$ .

### 3. Experiment

The important experimental requirements necessary to obtain results which may be compared with the theoretical analysis are, firstly, that the sample may be thoroughly outgassed so that the initial condition  $C(x,0) = 0$  can be achieved. A thin target with a high diffusion coefficient for hydrogen at moderate temperature is therefore necessary. Secondly, the target should be capable of being held at constant temperature during bombardment, over a wide range of temperatures. A thin-walled nickel tube bombarded on the outside and either cooled by fluid flow on the inside, or heated by the passage of current, was chosen to meet these requirements.

The ion beam apparatus used for these experiments has been described fully previously (McCracken et al. 1966). Ions from an r.f. source are accelerated to an energy in the range 5 - 30 keV, mass analysed and focused onto the target in a target chamber which can be maintained at a pressure of  $\sim 10^{-9}$  torr. In order that the fraction of incident beam re-emitted from the nickel surface can be recorded during bombardment, the beam is focused through a small slit into an inner target chamber, the pumping speed of which is defined by an orifice of  $220 \text{ l s}^{-1}$  for hydrogen, (Fig.3). The partial pressure rise of hydrogen or deuterium in this chamber is recorded by a quadrupole mass filter, and is used as a measure of the fraction of re-emitted beams during bombardment as described previously (McCracken and Maple 1967). The pumping speed of the outer chamber is typically  $10^4 \text{ l s}^{-1}$  for hydrogen.

The polycrystalline nickel target tube 3 mm dia.  $\times$  0.01 mm wall



is formed into a 25 mm dia. semicircle and supported on thick-walled copper tubes. It can be cooled to 77°K by liquid nitrogen, or held at any temperature between 77°K and 900°K during bombardment by a combination of liquid nitrogen flow and/or resistive heating. A thermocouple, located near to the point of impact of the beam, records the target temperature and holds it constant to within  $\pm 3^{\circ}\text{C}$  during the bombardment by feedback using an electronic servo system.

A deuterium ion beam, rather than hydrogen, was used for most investigations in order to eliminate background effects due to hydrogen already in the system. In all the present work, a constant ion energy of 18 keV was used. The beam was focused to hit the target at essentially normal incidence over an area of  $3 \text{ mm}^2$ . Under these conditions a maximum ion dose rate of  $4 \times 10^{15} \text{ ions cm}^{-2} \text{ s}^{-1}$  could be obtained. In addition to the nickel tube a molybdenum target, which can be heated to 800°K by resistive heating, may be lowered into the beam. At this temperature, molybdenum is believed to re-emit all incident ions (McCracken and Maple 1967). The total number of ions striking the target is obtained by measurement of the ion current, and hence a direct calibration of the mass filter can be obtained. A molybdenum plate situated behind the nickel target, is used to check that all incident ions strike the tube. Both targets are biased positively to suppress secondary electron emission.

#### 4. Results and Discussion

Measurements have been made of the percentage of incident 18 keV deuterium ions which are subsequently re-emitted from the nickel target, as a function of time during bombardment, for different target temperatures in the range 77 - 570°K (Fig.4). Measurements

at temperatures higher than 600°K were not possible because the vacuum time constant of 0.03 s became comparable with the signal rise rate. All curves resulting from bombardments at temperatures > 240°K have a similar form to those obtained from the diffusion theory outlined though they do not appear to increase to 100% re-emission. Even at 900°K,  $\frac{J}{J_0}$  has not been observed to rise to a value greater than ~0.8. The curve shape varies with incident ion current density  $J_0$  as shown in Figs.5 and 6. From Fig.5, at 373°K there is a consistent increase of the percentage re-emission rate  $\frac{J}{J_0}$  as the ion current density  $J_0$  is increased; whereas at 243°K (Fig.6) there is no definite trend. Also shown in Figs.5 and 6 are the theoretical curves obtained from Equation 7 using the value for the diffusion coefficient obtained in a direct measurement of the diffusion of hydrogen in nickel (Edwards 1957), corrected for deuterium by the normally observed square root of mass dependence, (e.g. Eichenauer 1965).

A large number of theoretical curves were plotted ( $\frac{J}{J_0}$  as a function of time) for different values of diffusion coefficient,  $D$ . Best matches between these curves and the experimental curves shown in Fig.4 were made, and values of  $D$  so obtained are shown in Fig.7, plotted on a logarithmic scale as a function of  $\frac{1}{T^{\circ}K}$ . Also shown in this figure are results from investigations by Edwards (1957) and Hill and Johnson (1955), for diffusion of hydrogen in unbombarded nickel. (Here  $D_0$  has again been corrected for deuterium.) The results of Fig.7 do not show a completely linear dependence between  $\ln D$  and  $\frac{1}{T}$ , which would indicate a unique activation energy for the diffusion process. However, an almost linear region does exist for bombardments made between 300°K and ~ 400°K, from which an average activation energy of  $11.5 \pm 2.0$  kcal mole<sup>-1</sup> may be deduced. The corresponding

value of  $D_0$  in this region is  $\sim 10^{-3} \text{ cm}^2 \text{ s}^{-1}$ .

The important conclusion which may be drawn from Fig.7 is that our diffusion coefficient is always much lower than that obtained by other investigators using undamaged nickel. The apparent retardation of diffusion could be due, either to the release from the surface being the controlling step, or to the disordered state of the lattice under bombardment. However, measurements of diffusion by outgassing from a nickel surface have led Edwards (1957) to conclude that the surface barrier effects are not significant; while a rough estimate of the number of displaced atoms per incident ion (c.f. Kinchin and Pease 1955) has led us to think that the latter process should be considered. Even if one recognises the possibility of annealing of damage, it is quite probable that some tens of point defects are produced per incident 18 keV deuterium ion during the initial stages of bombardment. The deuterium diffusing through the metal lattice could become trapped at these defects. If the trapped atoms then had a higher activation energy for release than that for normal diffusion via interstitial sites then the apparent rate of diffusion would be reduced. Moreover, if the activation energy for release from the trapped sites was appreciably higher than for diffusion then the release would behave like a single step process.

Another approach to measuring activation energies for gas release is that described by Carter (1962) and Redhead (1962) in which the gas remaining in a target after bombardment is released by application of a linear heating schedule. Maxima in the gas release rate are obtained at specific temperatures,  $T_M$ , which may be correlated to the activation energies for release,  $Q$ , by the expressions:

$$\frac{Q}{RT_M^2} = \frac{1}{\tau_0 b} \exp \cdot \left\{ \frac{-Q}{RT_M} \right\} \quad \dots (10)$$

for a single step release process, and

$$T_M^2 \exp \cdot \left\{ \frac{-Q}{RT_M} \right\} \approx \frac{p^2 b Q \tau_0}{R} \quad \dots (11)$$

for a diffusion process, (Farrell and Carter 1967). In these expressions,  $b^0K s^{-1}$  is the target heating rate,  $\tau_0$  is the frequency factor,  $R$  the gas constant and  $p$  the number of lattice spacings through which the diffusing entity must travel prior to release at the surface.

Although it must be noted that conditions for release are not exactly the same as when the sample is under continuous bombardment, some measurements have been made using this technique, and results are shown in Fig.8. The nickel tube was bombarded at  $77^0K$ , after which the temperature was increased linearly at a rate of  $1.6^0K s^{-1}$ , up to a maximum temperature of  $900^0K$ . Distinct peaks in the gas release spectra are clearly visible, and their number increases with total incident ion dose. Assuming a diffusion process, and the value of activation energy  $8.6 kcal mole^{-1}$  obtained by Hill and Johnson (1955) the calculated maximum gas release rate should occur at a temperature of  $220^0K$  - in good agreement with the lowest experimentally observed peak. Assuming a single step process for the other peaks, and following the usual practice of assuming that  $\tau_0 = 10^{-13} s$  (Kornelsen 1964) their activation energies deduced from the values of  $T_M$  at  $263^0K$ ,  $304^0K$ ,  $335^0K$  and  $383^0K$  are  $16.7 kcal$ ,  $19.5 kcal$ ,  $21.4 kcal$  and  $24.8 kcal mole^{-1}$  respectively. No further re-emission of gas in the temperature range  $500 - 900^0K$  has been detected. It has also been observed by Chleck et al. (1963)

that krypton release from nickel occurs at temperatures up to 500°K and only very little further release in the temperature range 500 - 900°K.

It is interesting to note that the change in gas release spectra with increasing ion dose which we observe follows a completely different pattern to that observed by Kornelsen (1964) and Erents and Carter (1966) after  $\text{Ne}^+$  and  $\text{He}^+$  ion bombardment of polycrystalline tungsten. In these cases the peak of highest activation energy was correlated with diffusion via a vacancy mechanism, and this was the dominant form of release after high dose bombardments.

The thermal desorption spectra seem to confirm the hypothesis that defect sites are produced by the ion bombardment, and that the incident ions are trapped at these defects. The temperature required either to anneal the damage or to release a trapped atom from a defect is probably higher than that required for normal interstitial diffusion through the nickel lattice. Each peak might then correspond to gas release from a different type of damage configuration, except for the lowest one which appears when the damage in the lattice is saturated after ion doses of  $> 5 \times 10^{17}$  ions  $\text{cm}^{-2}$  and is consistent with a diffusion release. Such a saturation of damage sites with gas atoms can only occur after the damage itself has reached a maximum concentration. One can envisage this situation when collision cascades overlap previously damaged regions, and further bombardment only causes a re-orientation of the damage. Once saturation is complete, no further incident ions can occupy sites of high activation energy, and gas atoms are forced to reside in interstitial positions from which they can then diffuse interstitially with an activation energy which is similar to that for an undamaged lattice. That such a build

up to a saturation in available damage sites does take place has been demonstrated by Erents and Carter (1966) for inert gas ions incident on a tungsten surface.

#### 5. Conclusions

The experimental results show that both during and after energetic ion bombardment of a polycrystalline nickel surface, deuterium ions are not re-emitted with a single activation energy characteristic of a diffusion process. The rate of re-emission is much lower than that predicted from existing experimental data for the diffusion of deuterium in undamaged nickel.

Thermal desorption spectra indicate that in fact a number of discrete activation energies for deuterium release exist, and we have attributed these activation energies and the retarded re-emission to trapping of the incident ions in a variety of damage configurations. At the largest dose used ( $\sim 5 \times 10^{18}$  ions  $\text{cm}^{-2}$ ) a peak at 2200K is dominant. Release at this temperature is consistent with a known activation energy for interstitial diffusion in undamaged nickel (i.e. 8.6 kcal  $\text{mole}^{-1}$ ). The appearance of the peak is thought to occur only after the maximum possible density of gas atoms trapped in damage configurations has been achieved, ( $\sim 1 \times 10^{18}$  ions  $\text{cm}^{-2}$ , distributed over the ion range). With total doses of this order, one would certainly expect bubble formation and perhaps migration - but the reproducibility of the gas release spectra would seem to indicate that we do not observe gas release in bubbles.

## 6. Acknowledgements

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## 7. References

- BOROVIK, E.S., KATRICH, N.F. and NIKOLAEV, G.T. 1965, *Atomn. Energ.* 18, 91 - 96.
- CARTER, G. 1962, *Vacuum*, 12, 245 - 254.
- CHLECK, D., MACHL, R. and CUCCHIARA, O., 1963, USAEC report no. NYO 2757-3.
- EDWARDS, A.G. 1957, *Brit. J. Appl. Phys.*, 8, 406 - 409.
- EICHENAUER, W. 1965, *Z. fur Metallkunde*, 56, 287 - 293.
- ERENTS, K. and CARTER, G. 1966, *Vacuum*, 16, 523 - 527.
- ERENTS, K. and CARTER, G. 1967, *Vacuum*, 17, 215 - 218.
- EURINGER, G. 1935, *Z. Physik*, 96, 37 - 52.
- FARRELL, G. and CARTER, G. 1967, *Vacuum*, 17, 15 - 19.
- HILL, M.L. and JOHNSON, E.W. 1955, *Acta, Met.* 3, 566 - 571.
- KINCHIN, G.H. and PEASE, R.S. 1955, *Rep. Prog. Phys.*, 18, 1 - 51.
- KORNELSEN, E.V., 1964, *Can. J. Phys.*, 42, 364 - 381
- LEWIN, G. and MARTIN, G. 1966, *J. Vac. Sci. and Tech.*, 3, 6 - 10.
- MCCRACKEN, G.M., JEFFERIES, D.K. and GOLDSMITH, P. 1968, *Proc. 4th International Vacuum Congress*, 1968, 149 - 154.
- MCCRACKEN, G.M., MAPLE, J.H.C. and WATSON, H.H.H. 1966, *Rev. Sci. Instrum.*, 37, 860 - 866.
- MCCRACKEN, G.M. and MAPLE, J.H.C., 1967, *Brit. J. Appl. Phys.* 18, 919 - 930.
- REDHEAD, P.A. 1962, *Vacuum*, 12, 203 - 211.
- SANDERS, J.B. and SIGMUND, P. 1967, *Int. Conf. on Applications of Ion Beams to Semiconductor Technology*, Grenoble, 24-26 May, 1967.
- SCHIØTT, H.E. 1966, *Mat. Fys. Medd. Dan. Vid. Selsk*, 35, no.9.





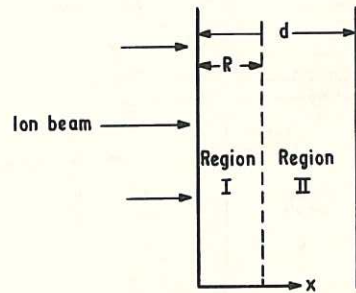


Fig. 1 Theoretical model (CLM-P 205)

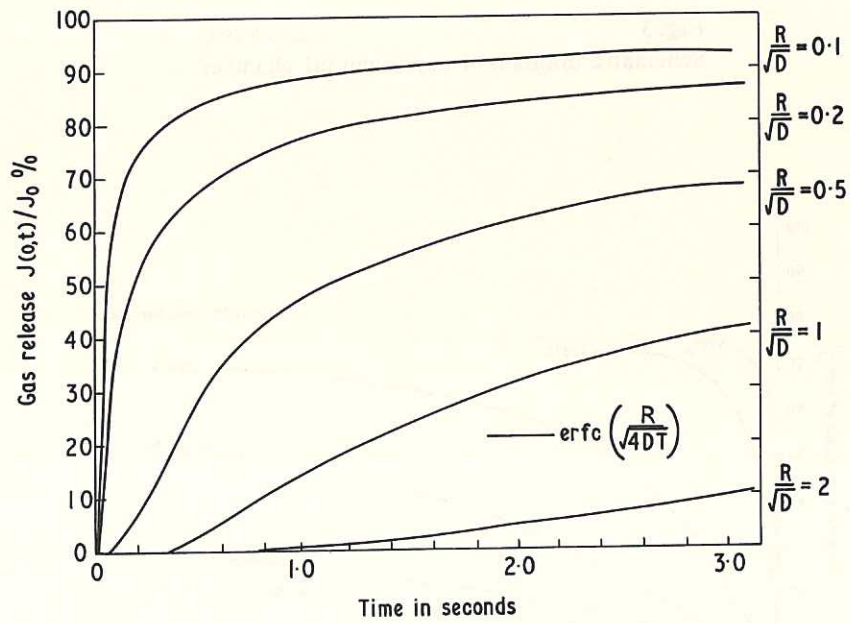


Fig. 2 (CLM-P 205)  
Theoretical gas re-emission calculated from diffusion model

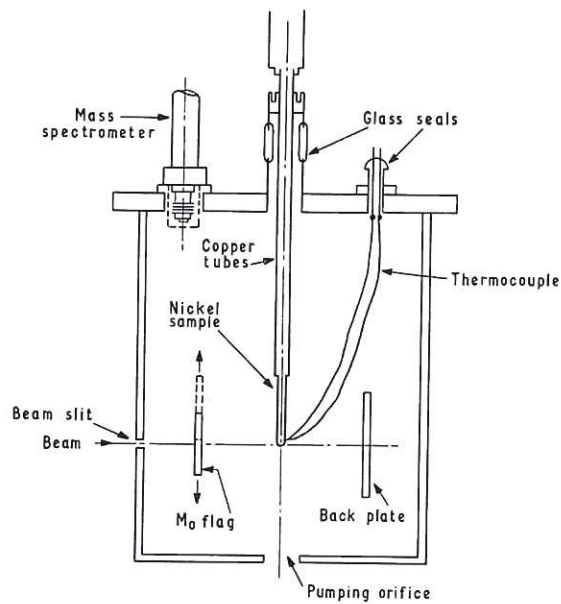


Fig. 3 (CLM-P 205)  
Schematic diagram of experimental chamber

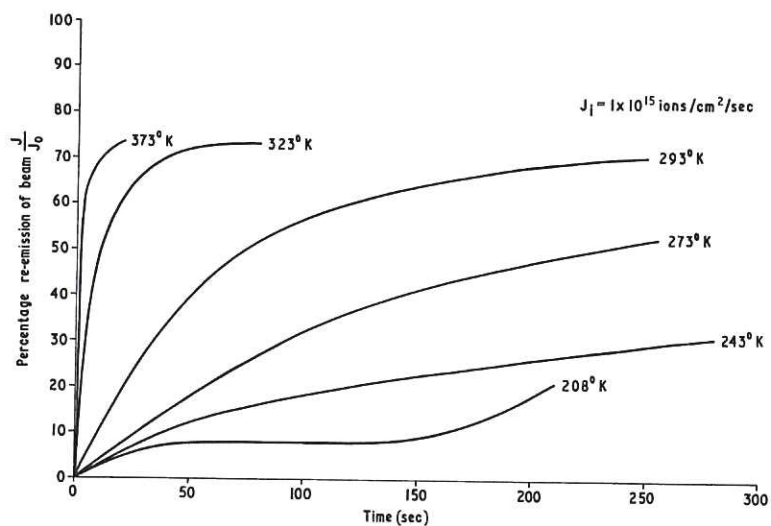


Fig. 4 (CLM-P 205)  
Percentage of beam re-emitted from nickel as a function of bombardment time, at different target temperatures

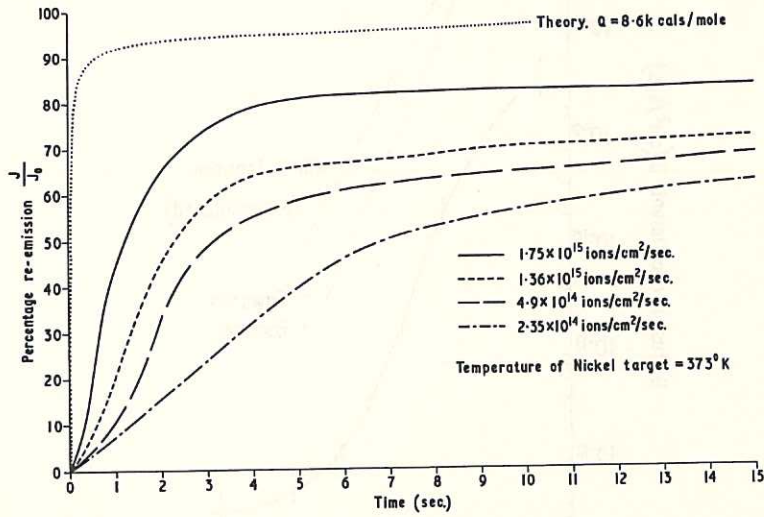


Fig. 5 (CLM - P 205)  
 Percentage of beam re-emitted from nickel as a function of bombardment time, for different D+ dose rates at 373°K

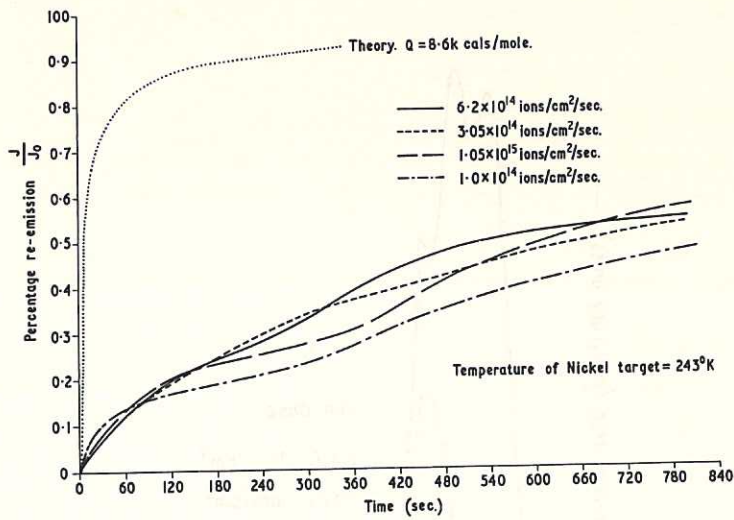


Fig. 6 (CLM - P 205)  
 Percentage of beam re-emitted from nickel as a function of bombardment time, for different D+ dose rates at 243°K

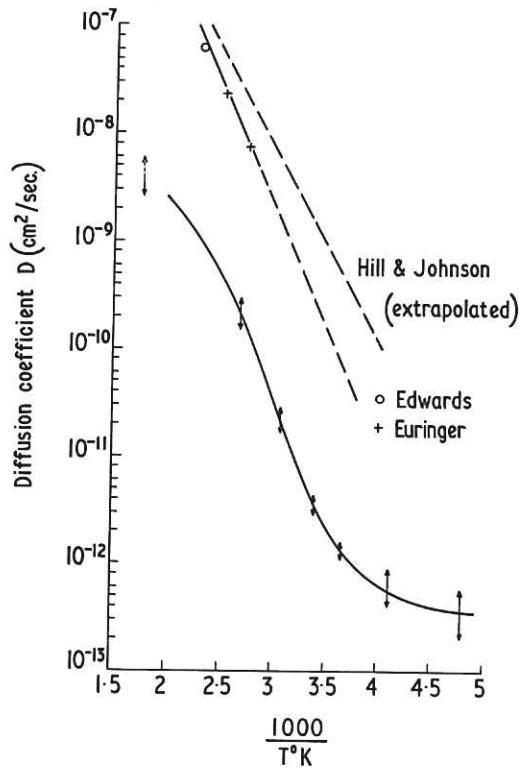


Fig. 7 (CLM-P 205)  
 Diffusion coefficient estimated by matching to theoretical curves assuming ion range  $R = 1500 \text{ \AA}$

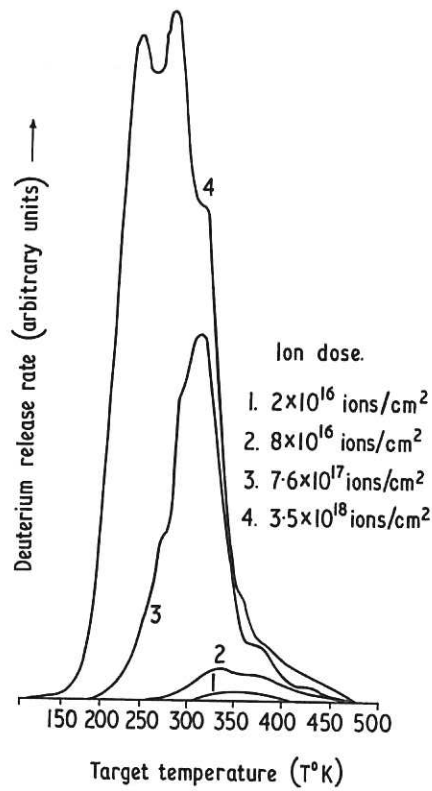


Fig. 8 (CLM-P 205)  
 Gas release spectra of deuterium from nickel for various ion doses

