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K. ERENTS
G. M. McCRACKEN

Culham Laboratory
Abingdon Berkshire

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by

K. Erents
G.M. McCracken

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ABSTRACT

Measurements have been made of the release rate of hydrogen and deuterium from a cold surface during uniform heating from 2.5-6.5 K. A simple theory has been formulated to account for the experimental results, which show good agreement with vapour pressure measurements by Lee[2]. Our results indicate binding energies higher than the thick layer sublimation energy for coverages $\leq 10^{16}$ molecules/cm^2. Extrapolation of hydrogen and deuterium data has provided thermal release data for tritium.

UKAEA Research Group
Culham Laboratory
Abingdon
Berks

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Introduction

The increasing use of cryopumps, and also of superconducting magnet assemblies for plasma physics and associated experiments, has demanded a knowledge of sorption and desorption of hydrogen and its isotopes on these cold surfaces. Until recently, however, there has been very little experimental data on the vapour pressure of solid hydrogen, and even less on deuterium and tritium. Measurements of vapour pressure by Chubb[1], and Lee[2], for hydrogen and deuterium down to 2 K have been made, allowing an estimate of the surface temperature required for a given base pressure. Chubb[1] has shown that the temperature differential across quite thick layers is small, and so large quantities of gas may be pumped before desorption.

For subsequent cleaning of a cryogenic surface, which will be required for both gas retrieval and pump re-activation, it is useful to know the desorption rate as the surface is heated up, and also the temperature required for complete desorption of the gas. In this paper we present experimental results for the desorption rate of both hydrogen and deuterium and show that there is good agreement with a simple calculation of the temperature required to desorb all the gas.

Theoretical Considerations

Let us consider a layer of condensed hydrogen on a surface in a region with negligible heat loading, so that there is no temperature gradient across the hydrogen. We will also assume that desorbing gas is pumped away immediately without re-adsorption. For a thick hydrogen layer the desorption rate will be determined by vapour pressure and depend only on temperature, T, i.e.

$$\frac{dn}{dt} = - C.\exp\left(\frac{-Q}{RT}\right) \qquad \ldots (1)$$

where Q is the sublimation energy, and R the gas constant. The pre-exponential constant C may be deduced from vapour pressure

measurements. Then the initial concentration of gas atoms/cm^2

$$N_o = -\int_{N_o}^{o} dn = C \cdot \int_{o}^{t_m} \exp(-\frac{Q}{RT})\, dt \,. \qquad \ldots (2)$$

If in order to desorb the gas rapidly we increase the temperature linearly with time, i.e. $T = T_o + bt$, then (2) may be integrated approximately to obtain

$$N_o b \simeq \frac{CR}{Q}\left\{T_m^2 \exp\left(\frac{-Q}{RT_m}\right) - T_o^2 \exp\left(\frac{-Q}{RT_o}\right)\right\} \qquad \ldots (3)$$

where T_o is the starting temperature and T_m the temperature at which all condensed gas is desorbed, i.e. the maximum temperature to which it is necessary to heat the surface.

This model does not take into account two factors. Firstly, at low concentrations the desorption rate will be proportio nal to the to the amount of gas remaining, and secondly, the gas adsorbed on the metal surface may have a higher activation energy for desorption than gas condensed on itself. This situation can be analysed if we assume first order kinetics with a constant activation energy Q', i.e.

$$\frac{dn}{dt} = -n \cdot \nu_o \exp\left(\frac{-Q'}{RT}\right) \qquad \ldots (4)$$

where ν_o is the attempt frequency for desorption. This equation may be integrated for the linear temperature-time function in a similar manner to equation (1), when

$$n \simeq N'_o \exp\left\{\frac{\nu_o R}{bQ'}\left(T_o^2 \exp\left(\frac{-Q'}{RT_o}\right) - T^2 \exp\left(\frac{-Q'}{RT}\right)\right)\right\} \qquad \ldots (5)$$

which leads to the solution

$$\frac{dn}{dt} \simeq -\nu_o N'_o \exp\left\{\frac{v_o R}{bQ'}\left(T_o^2 \exp\left(\frac{-Q'}{RT_o}\right) - T^2 \exp\left(\frac{-Q'}{RT}\right)\right)\frac{-Q'}{RT}\right\} \qquad \ldots (6)$$

A difficulty with this analysis is that in practice the value of Q' is likely to change with coverage, and a criterion has to be found for the value of surface coverage N'_o where we change from zero order (equation 1) to first order (equation 4) kinetics.

It has been found experimentally that if the coverage is greater than 10^{16} molecules/cm^2, then equation (1) fits the experimental results with suitable choice of Q.

Experiment

The experimental arrangement used for thermal desorption studies is shown in Figure 1. It consists of a copper cryostat, a small area of which protrudes into a liquid nitrogen shielded chamber. Background gas pressures (mainly carbon monoxide) total $\sim 5 \times 10^{-10}$ torr. Hydrogen or deuterium gas may be admitted to this chamber via a palladium leak, and partial pressure measurements are made on a quadrupole mass spectrometer connected to the chamber. A germanium resistance thermometer is used to record the temperature of the 3 cm^2 of copper suface onto which gas is condensed. By pumping or pressurising the cryostat, a controllable temperature range of 2.5-5 K can be achieved. A linear temperature rise above 5 K is possible by boiling off the liquid helium.

For mass spectrometer calibration purposes a proton beam was focussed through a small hole in the chamber and allowed to strike a palladium target. This target quickly saturates and re-emits all incident beam, providing a calibration in terms of hydrogen molecules/sec. desorbing, (McCracken, Jefferies and Goldsmith[3]). The calibration is determined by the pumping speed which in turn is determined by the size of the ports in the chamber and the sticking coefficient at the cold surface. However, the area of the ports is larger than the cold surface and the vapour pressure of the solid hydrogen is higher than the chamber pressure throughout most of the desorption stage. The calibration is therefore expected to be

constant, except at the very initial stage of desorption where some desorbed gas may readsorb leading to a lower pressure rise than expected.

Measurements of release rate of desorbing hydrogen or deuterium as a function of cryostat temperature were made, for different thickness layers of condensed gas. The initial condensation of hydrogen was made at a starting temperature (T_o) of 2.5 K, (4.2 K for deuterium), where thermal desorption is too low to be detectable. Hydrogen partial pressures of $\sim 10^{-7}$ torr were used for condensation.

Discussion of Results

Typical thermal desorption curves for various thickness layers of hydrogen and deuterium are shown in Figure 2. The curves have been normalised to a fixed maximum desorption rate. It is seen that the initial desorption rate increases exponentially with temperature, as expected from equation (1).

Equation (3) indicates that as the initial surface concentration N_o is increased, the temperature (T_m) required to deplete the surface of gas molecules increases also. Our experimental data may be compared with the prediction of equation (3), if we plot $N_o b$ as a function of T_m. The product $N_o b$ was chosen for the variable rather than N_o, the coverage, as radiation heating of the cryostat resulted in slightly different values of b from one run to the next. Experimental values for the constants C and Q for both hydrogen and deuterium from the work of Lee[(2) and (4)], were used to plot the solid curves in Figure 3. Our experimental points are seen to be in good agreement with the predictions from this vapour pressure data.

Returning to the desorption curves of Figure 2, it is clear that the release rate does not fall to zero immediately after the peak. This is almost certainly due to a change to a first order desorption process, as described above. The effect of the last

few monolayers is of course proportionally greater as the initial concentration N_o is lowered and for the case of the first deuterium peak in Figure 2, (10^{17} moles/cm^2 initial coverage), a quite broad tail is seen to exist. The number of molecules undergoing the first order desorption process (N_o') may be estimated from the area under the peak at temperatures above T_m. This is $\sim 1.5 \times 10^{16}$ molecules/cm^2 for both hydrogen and deuterium. In order to compare the shape of our experimental curves with the theory, initially a value of Q of 190 cals/mole (Lee[2]) was chosen for both the zero and first order desorption processes. The starting temperature T_o for the first order desorption (equation 6) was made equal to the final temperature in the zero order case (i.e. T_m). The value of C was obtained from the vapour pressure date, and ν_o was calculated by equating the rate of desorption by zero order (equation 1) and first order (equation 6) processes, at $T = T_m$. The value thus obtained for ν_o was 10^{13}/sec. Thus all constants were absolutely determined. The computed curves showed good quantitative agreement with the experimental results for increasing gas release rates, but the computed fall-off after T_m was practically immediate even at the lowest values of T_m. However by varying Q′ only a reasonable fit was obtained to the decreasing part of the curves using Q′ = 250 cals/mole for hydrogen and Q′ = 350 cals/mole for deuterium. An example of the comparison of the experimental and theoretical desorption curves is shown in Figure 4 for deuterium.

No experimental measurements have been made of the vapour pressure of tritium, as far as we are aware. It is, however, of interest to obtain information for cryopumping of tritium, comparable to that for hydrogen and deuterium. An attempt has therefore been made to estimate the vapour pressure of tritium, by extrapolation from the hydrogen and deuterium data. On the basis of quantum mechanical arguments, Lunbeck[5] has obtained values for the sublimation energy Q for hydrogen, deuterium and tritium

at 0 K. The value of Q for solid hydrogen increases with temperature above 0 K (cf. Mullins, Ziegler and Kirk[6]), but this theoretical data shows reasonable agreement with the experimental value of 190 cals/mole obtained by Lee[2, 4] in the region 3-4 K. The theoretical values of Q obtained by Lunbeck at 0 K have been used together with Lee's experimental values for hydrogen and deuterium to obtain a value of the sublimation energy for tritium, which will correspond to the temperature range ~ 5-6 K. Experimental errors estimated by Lee have been included, and a value of $Q = 350 \pm 5$ cals/mole obtained for tritium. Possible error in the measured value of the pre-exponential constant C results in wide limits on extrapolation of this parameter, but the value should lie between 3×10^{26} moles/cm^2/sec and 2.5×10^{27} moles/cm^2/sec. Using these figures, a band for tritium has been plotted in Figure 3.

Conclusion

Our results illustrate clearly the temperatures to which surfaces have to be raised to desorb condensed layers of hydrogen isotopes, for any given thickness of layer.

Values of activation energy (Q) of 190 cals/mole and 285 cals mole for desorption of thick layers of hydrogen and deuterium, respectively, obtained by Lee[2], [4] are in close agreement to our experimental results.

The thermal desorption curves further indicate that condensed gas close to the copper substrate (of up to approximately 10 monolayers thickness), is bound with a higher activation energy than that required for desorption of the thicker layers. Indeed, it is suggested that the energy required for desorption increases as the surface is depleted. Average values of Q for the higher binding energy states of 250 cals/mole, for hydrogen, and 350 cals/mole, for deuterium, provide the best fit to our experimental data.

Finally, by extrapolation of experimental data from hydrogen and deuterium vapour pressure measurements, a theoretical curve has been obtained for the desorption of solid tritium. This extrapolation should provide useful information on tritium hold-up problems in fusion reactor design, for example.

REFERENCES

1. CHUBB, J.N., GOWLAND, L. and POLLARD, I.E., Brit. J. Appl. Phys. (J. Phys. D) 1, 1968, 361.
2. LEE T.J., 1971, to be published
3. McCRACKEN, G.M., JEFFERIES, D.K. and GOLDSMITH, P., Proc. 4th Int. Vacuum Cong., Manchester, April, 1968.
4. LEE, T.J., GOWLAND, L., and REDDISH, V.C., Nature, 1971, (to be published).
5. LUNBECK, R.J., Thesis University of Amsterdam, 1951, p. 80.
6. MULLINS, J.C., ZIEGLER, W.T., and KIRK, B.S. Advances in Cryogenic Engineering, 8 1963, 116.

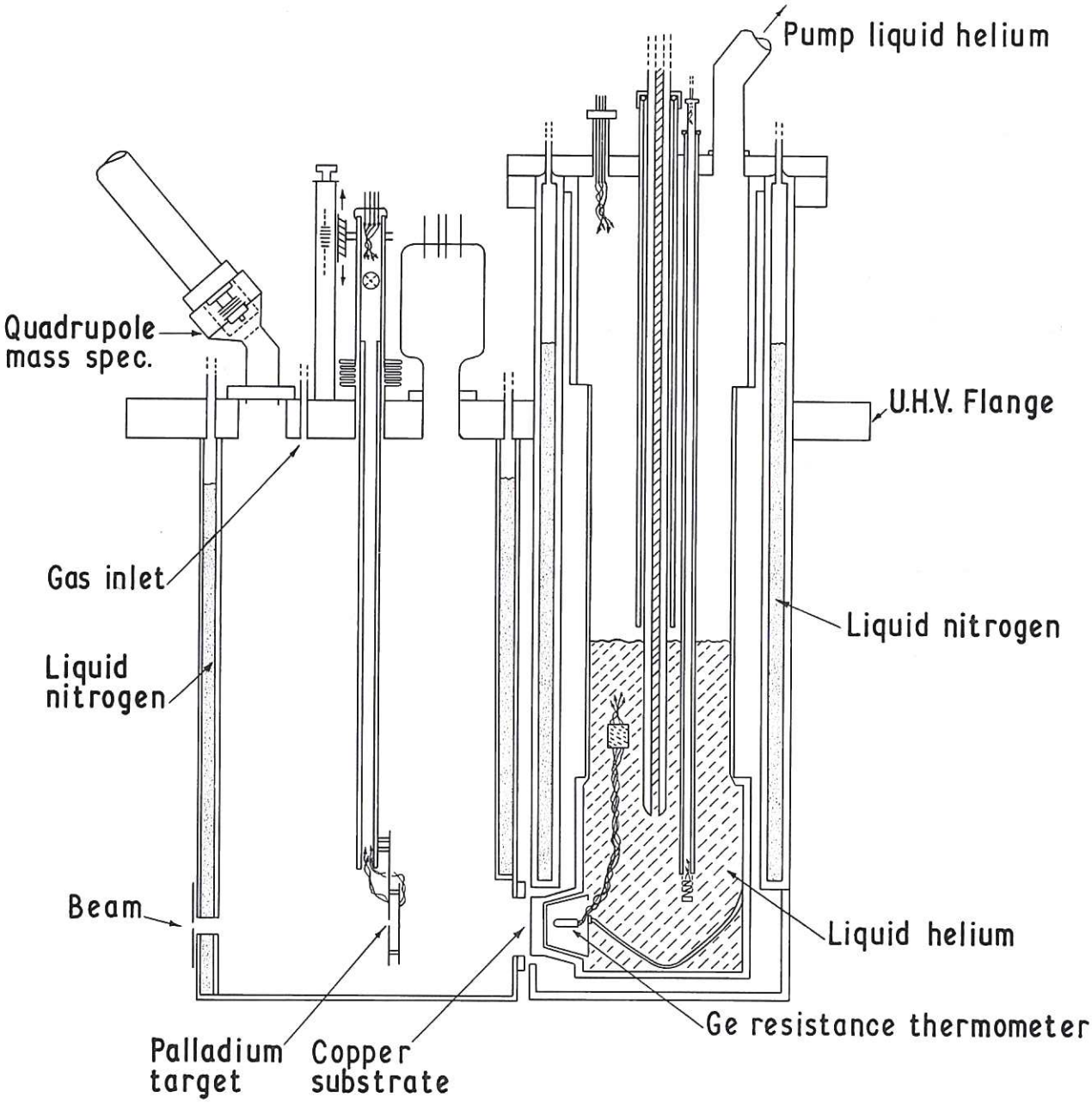

Fig. 1 Schematic diagram of experimental chamber

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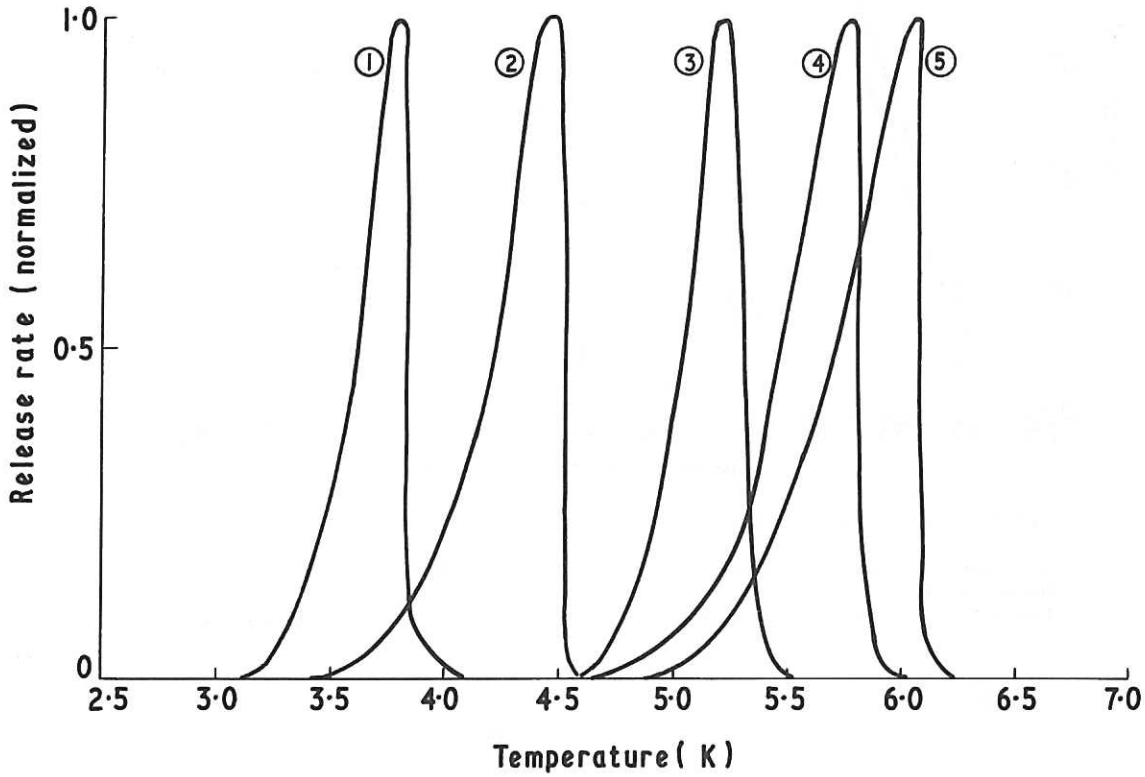

Fig. 2 Thermal release spectra for H_2 and D_2 from copper

Hydrogen: (1) b = 0.0017 K/s; $N_o = 1.1 \times 10^{17}$ mols/cm^2
(2) b = 0.0013 K/s; $N_o = 1.1 \times 10^{18}$ mols/cm^2
Deuterium: (3) b = 0.0017 K/s; $N_o = 1.1 \times 10^{17}$ mols/cm^2
(4) b = 0.0045 K/s; $N_o = 5.5 \times 10^{17}$ mols/cm^2
(5) b = 0.013 K/s; $N_o = 8.0 \times 10^{17}$ mols/cm^2

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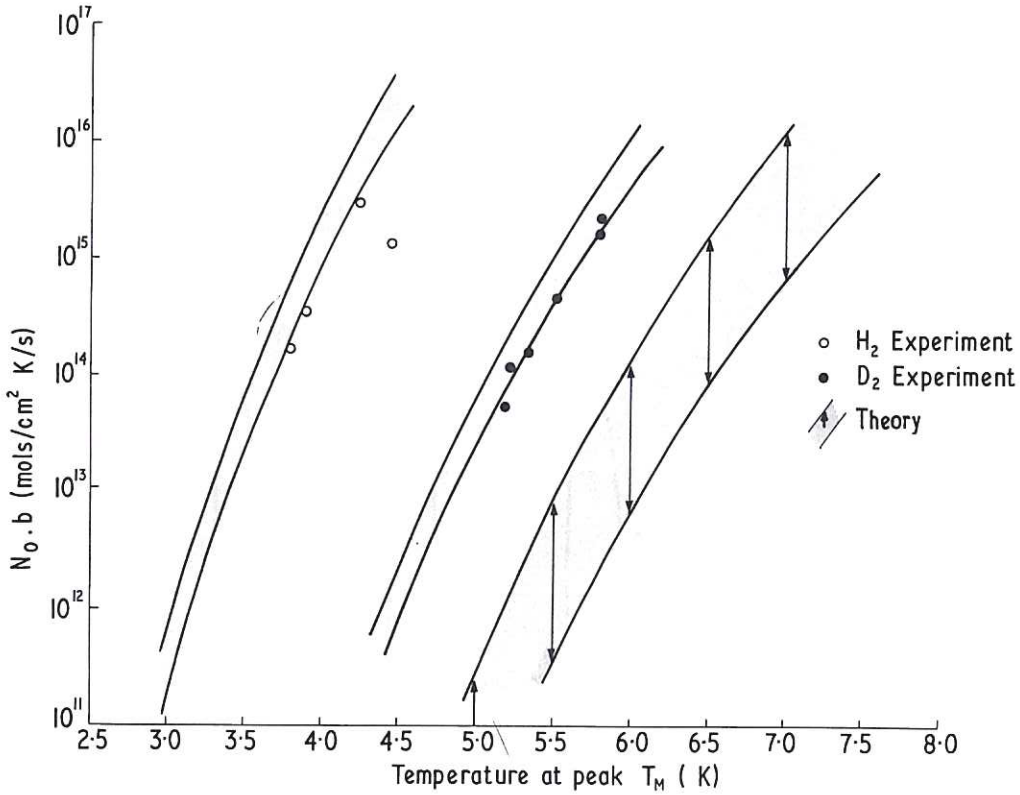

Fig. 3 N_o. b versus temperature for maximum desorption rate

Hydrogen: Q = 190 ± 2 cals/mole., C = 1.75-3.25 x 10^{26} moles/cm^2/s
Deuterium: Q = 286 ± 3 cals/mole., C = 0.5-1.0 x 10^{27} moles/cm^2/s
Tritium: Q = 350 ± 5 cals/mole., C = 3.0 x 10^{26} - 3.0 x 10^{27} moles/cm^2/s

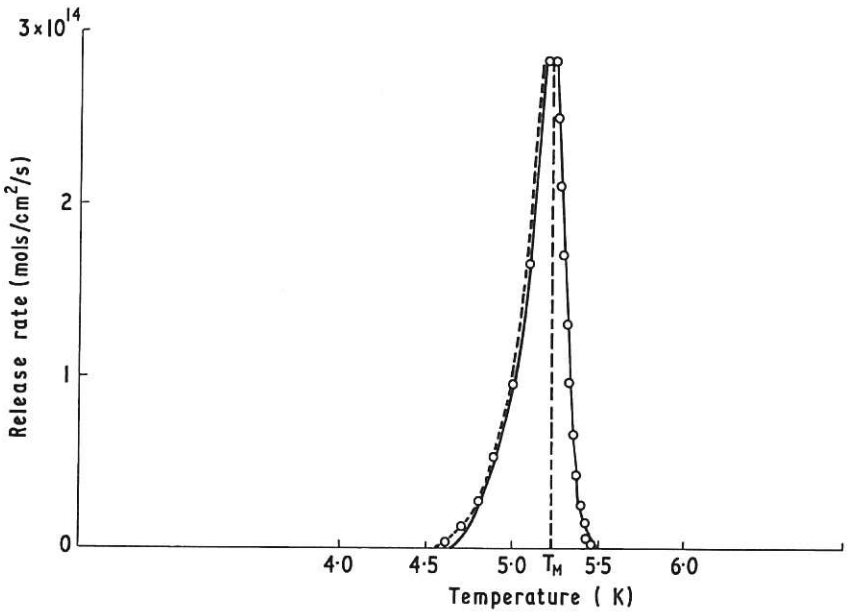

Fig. 4 Fitting of theoretical desorption data to a typical experimental curve

____ Experimental desorption curve for deuterium N_o = 7.5 x 10^{16} moles/cm
b = 0.0017 K/s

----- Computed curve using Q = Q^1 = 285 cals/mole

ooooo Computed curve using Q = 285 cals/mole, Q^1 = 350 cals/mole