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THE INFLUENCE OF SURFACE OXYGEN ON RELEASE OF DEUTERIUM FROM TANTALUM

W. R. Wampler
Sandia National Laboratories, Albuquerque, NM 87185-5800

ABSTRACT

Here we examine the influence of surface oxygen on both the absorbtion of deuterium (D) from gas into solution in tantalum (Ta) and the release from solution back to the gas. The D uptake rate was proportional to gas pressure with a sticking coefficient of 0.0085±.00025 for clean Ta surfaces. Exposure to 10 Langmuirs (L) of O_2, giving about one monolayer of chemisorbed oxygen, decreased the D uptake rate by about two orders of magnitude. D release was studied using the $D(^3He,P)\alpha$ nuclear reaction to measure the concentration of D in the Ta versus time during release at constant temperature. D release was surface-limited and obeyed second order kinetics for both clean and oxygen covered Ta surfaces which shows that molecular recombination must be occuring from sites which have much smaller binding energies for D than the low-coverage chemisorption sites. Exposure to 10^6 L of O_2 resulted in an additional energy barrier to D recombination of 0.25±.04 eV/D which greatly reduces the D release rate. This activation barrier should also reduce D dissociation and uptake rates as observed.

I. INTRODUCTION

Kinetics of hydrogen transfer between gas phase and solution in metals is often controlled by recombination and dissociation of hydrogen molecules at metal surfaces. These processes are strongly affected by surface impurities, as shown by previous studies [1-4]. However, few systematic investigations of the influence of impurities on H uptake and release in metals have been made. In a previous study [5] the kinetics of surface-limited release of D from solution in tantalum with a clean surface were studied. Here we examine the influence of chemisorbed oxygen on the kinetics of uptake and release of deuterium in Ta using experimental methods similar to those used in the previous study.

II. EXPERIMENTAL METHOD AND RESULTS

Deuterium uptake was studied by recording the change in gas pressure as D was absorbed by a Ta foil sample after injecting a known quantity of D_2 gas into a vacuum chamber containing the Ta sample. The release of D from solution was studied by measuring the concentration of D in solution in the Ta sample during release at constant temperature. Nuclear reaction analysis using the $d(^3He,p)\alpha$ reaction was used to measure the concentration of D in the Ta. Experiments were conducted in an ultra-high vacuum chamber with a residual gas pressure below 10^{-10} Torr.

The samples were polycrystaline Ta foil 99.999% pure and 0.7 cm x 0.7 cm x 51 μm thick [6]. Surface impurities were removed from the Ta by sputtering with 2 keV Ar. The surface composition was determined by Auger electron spectroscopy (AES). The only impurities detectable after cleaning were carbon and oxygen at levels of ~0.08 ML and ~0.04 ML respectively.

Here a monolayer (ML) is defined as the Ta atomic density to the two-thirds power or 1.45×10^{15} cm^{-2}. The peak-to-peak amplitudes in the dN(E)/dE spectra were used to calculate the areal density of impurities as described by Seah [7] assuming a thin overlayer of impurities on a Ta substrate. The Auger peaks used were those at 271 eV for carbon, 503 eV for oxygen and 342 eV for Ta.

After cleaning, the Ta was loaded with D by isolating the vacuum chamber and injecting a known quantity of D_2 gas. A palladium diffusion cell was used to filter impurities from the gas. The gas pressure was monitored versus time during the uptake using a capacitance manometer. Typically about 0.1 Torr-liter of gas was injected giving an initial gas pressure of about 2×10^{-3} Torr and a concentration of about 0.05 D/Ta when absorbed. The D_2 pressure only decreased when the Ta sample had been sputter cleaned which shows that the D was absorbed by the Ta and not by other sinks, such as adsorption on the chamber wall.

The rate of D uptake is shown in Fig. 1 for several gas pressures. These measurements were made on a clean Ta foil at a temperature of 30° C. A fit to the data in Fig. 1 shows that the uptake rate is proportional to gas pressure and that the ratio of the uptake rate to the flux impinging on the surface (also referred to as the sticking coefficient) is 0.0085 ± 0.0025. Because of the rapid diffusion of D in Ta [8] the D uptake in these experiments is not limited by bulk diffusion.

Sticking coefficients much less than one for absorption of H into solution in Ta have been observed previously [4,9,10]. Small sticking coefficients are expected when the D must pass through a strongly bound chemisorbed surface state to go into solution since the chemisorption sites can become saturated and cause a bottleneck to D uptake [11,12].

Chemisorbed oxygen strongly decreased the D uptake rate as shown in Fig. 2. Exposure to 10 L of O_2, resulting in about one monolayer of oxygen, decreased the D uptake rate by two orders of magnitude. In these experiments the Ta was exposed to various doses of O_2 prior to the D uptake measurement. The resulting oxygen coverage was determined by AES as described above. The oxygen dosing and D uptake were done at a temperature of 30°C. The D uptake rate was measured at a D_2 pressure of 2 millitorr. Fig. 3 shows the oxygen coverage versus dose measured during these experiments. The oxygen coverage did not change significantly during the D uptake.

After loading, the concentration of D in the Ta was measured using nuclear reaction analysis (NRA). An analysis beam of 700 keV ^{3}He was directed onto the sample and the energetic protons from the $D(^3He,p)\alpha$ nuclear reaction were counted with a silicon surface barrier detector. The stopping power [13] of the ^{3}He and the reaction cross section [14] are such that D within about 0.5μm of the surface (~1% of the sample thickness) contributes to the measured yield. The detector was calibrated using a thin target standard sample with a known areal density of D. This calibration allowed the D concentration in the Ta samples to be determined from the proton yield. The initial D concentrations determined by NRA agreed within about 6% with the concentrations determined from the D_2 pressure change during loading. This excellent agreement confirms that both the NRA calibration and the loading procedure are behaving as expected.

The kinetics of D release were studied by measuring the concentration of D in solution versus time with the sample held at constant temperature. The D concentration was measured by NRA as described above. Fig. 4 shows typical results from such measurements for Ta with 0.1 ML and 0.5 ML of oxygen. The linear time dependence of the reciprocal concentration shows that the release kinetics are second order. The release rate obeys

$$dn/dt = N_o d\, dc/dt = -K_r(N_o c)^2 \qquad (1)$$

and

$$1/c(t) = 1/c(0) + K_r N_o/d\ t \qquad (2)$$

where c is the concentration of D in units of D/Ta, $N_o = 0.55\times10^{23}/cm^3$ is the atomic density of Ta and d =0.0051 cm is the sample thickness. The recombination coefficient K_r, relating the release rate to the concentration of D in solution, is the main parameter used to characterize the D release rate throughout this paper. Values for K_r are obtained from the slope of 1/c versus t as shown in Fig. 4.

Increasing the oxygen coverage decreases the D release rate and the value of K_r. Fig. 5 shows values of K_r versus oxygen coverage measured at a temperature of 275°C. A monolayer of oxygen decreases the release rate by about 2 orders of magnitude. This is similar to the reduction in the D uptake rate shown in Fig. 2.

The temperature dependence of D release from oxygen covered Ta was also examined. In these experiments the Ta was loaded with D and then exposed at 30°C to 10^6 Langmuirs of O_2. The sample was then heated to various temperatures between 250°C and 425°C and held constant during the release measurement. AES analysis showed that this procedure results in about one monolayer of oxygen on the Ta during the D release. Values of K_r, obtained from plots similar to those in Fig. 4, are plotted versus 1/T in Fig. 6. For comparison Fig. 6 also shows K_r measured on a clean Ta surface [5]. The lines in Fig. 6 are least squares fits of

$$K_r = K_{ro} \exp(Q_K/kT) \tag{3}$$

to the data. Values and standard deviations for the parameters obtained from the fits are $K_{ro} = 36\pm(\text{factor of } 3) \times 10^{-18}$ (cm^4/s) and $Q_K = -1.19\pm0.06$ (eV/D) for oxygen dosed Ta and $K_{ro} = 2\pm1 \times 10^{-18}$ (cm^4/s) and $Q_K = -0.74\pm.02$ (eV/D) for clean Ta.

III. DISCUSSION

Recombination-limited release can be described by a model based on two main assumptions. First, the release rate is equal to the rate of molecular recombination at the surface given by

$$dn/dt = -k_r\theta_r^2. \tag{4}$$

where θ_r is the occupied fraction of sites from which recombination occurs. The rate constant is

$$k_r = k_{ro} \exp[-2(Q_b-Q_r)/kT] \tag{5}$$

where Q_b-Q_r is the energy barrier per atom for molecular recombination. Q_r is the energy of a D atom in a recombination site. The possibility of an additional barrier Q_b to recomination as illustrated in Fig. 7 is included in this analysis. Here we use the convention that energy levels below the 1/2 H_2 level are negative.

The second assumption is that the recombination sites and the solution sites are in quasi-equilibrium, ie.

$$\theta_r/(1-\theta_r) \exp(G_r/kT) = \theta_s/(1-\theta_s) \exp(G_s/kT) \tag{6}$$

where $G_s = Q_s - TS_s$ and $G_r = Q_r - TS_r$ are the free energies of D in solution sites and recombination sites respectively. Q_s, S_s, Q_r and S_r are the energies and entropies per atom relative to the gas for solution and recombination sites. $\theta_s = c/z$ is the fraction of solution sites occupied by D and z=6 is the number of solution sites per Ta atom. Equations (4)-(6) can be solved analytically to give the D concentration versus time [12,15]. Here we consider two limiting cases. When the recombination sites are highly saturated, ie. $\theta_r \simeq 1$, then from eq. (4) $dn/dt \simeq -k_r$ and the D release rate is nearly independent of the concentration of D in solution. When the recombination sites are far from saturation, ie. $\theta_r \ll 1$, then the release rate is proportional to the square of the D concentration (second order kinetics) since

$$\theta_r \simeq \theta_s \exp[(G_s - G_r)/kT] \tag{7}$$

and

$$dn/dt = -k_r \, \theta_s^2 \exp[2(G_s - G_r)/kT)], \tag{8}$$

or

$$dn/dt = -(c/z)^2 \, k_{ro} \exp[-2(Q_b - Q_r)/kT] \exp[2(Q_s - TS_s - Q_r + TS_r)/kT]. \tag{9}$$

From eqs. 1,3 and 9 we obtain

$$K_{ro} = k_{ro}/(N_o \, z)^2 \exp[2(S_r - S_s)/k)] \tag{10}$$

and

$$Q_K = 2(Q_s - Q_b). \tag{11}$$

The energy barrier Q_b can be determined from the values of Q_K obtained from the fit to the data (fig. 6) using eq. 11 and the value $Q_s = -0.35 \pm .01$ eV/D reported by Veleckis and Edwards [16] for the energy of solution. We find that $Q_b = 0.02 \pm .02$ eV/D for clean Ta and $Q_b = 0.25 \pm .04$ eV/D after exposure to 10^6 Langmuirs of oxygen. This situation is illustrated in Fig. 7. The small value of Q_b for clean Ta surfaces is consistent with the observation that the sticking coefficient for adsorption of H at low coverages onto clean Ta surfaces is large [4], since a barrier to desorption should also act as a barrier to adsorption. The increase in Q_b due to surface oxygen leads one to also expect a reduction in the D uptake rate as observed (Fig. 2). The continuous decrease in uptake and release rates with increasing oxygen coverage shown in Figs. 2 and 5 may result from the gradual coverage of the surface by islands of chemisorbed oxygen where the rates for release or uptake of D are smaller on the covered fraction of the surface due to the larger activation barrier as indicated in fig. 7.

The prefactor K_{ro} can be estimated by assuming that $S_r = S_s$ and that $k_{ro} = n_r \nu$ with the areal density of recombination sites $n_r = N_o^{2/3}$ and the attempt frequency $\nu = 10^{13}$ s^{-1}. This gives $K_{ro} = 0.13 \times 10^{-18}$ cm^4/s which is close to the experimentally determined value for clean Ta considering the uncertainties involved in the estimate. Values of K_r measured for Pd and Fe are also in excellent agreement with the model, using the same value of ν as was used for Ta [5]. These three metals span a broad range in hydrogen solubilities from strongly endothermic (Fe) to strongly exothermic (Ta) and a broad range (~18 orders of magnitude) in the recombination coefficient. The good agreement between the model and experiment for these three metals suggests that the model may be generally applicable for predicting D release rates for many metals.

It is important to note that the binding energy Q_r of D to the recombination sites has cancelled out of the expression for K_r as can be seen by examining eq. 9. Physically this is because sites which bind D more strongly have a smaller release rate coefficient k_r (eq. 5) but are more highly populated (eq. 7) so that the net release rate for a given D concentration is the same. This holds as long as the sites remain unsaturated. This cancelation of Q_r from the rate coefficient for release of D from solution in metals has important consequences. It means that at low concentrations weakly bound states contribute as effectively as strongly bound states to the release. At higher concentrations the strongly bound states saturate first and the release will then be dominated by the weakly bound states.

In the experiments reported here the chemisorption sites were highly saturated as shown by eq.6 using a value of Q_c=-0.95 eV/D for the energy of chemisorption [17] and assuming equal entropy terms for solution and chemisorption. The chemisorption sites are saturated for D concentrations above 2×10^{-5} D/Ta at 275°C, whereas the actual D concentrations during the release measurement at 275°C ranged from 0.06 to 0.001 D/Ta. The fact that second order release kinetics are observed shows that recombination must be occuring from sites which are not saturated and which therefore must have much smaller binding energies for D than the low-coverage chemisorption sites.

IV. CONCLUSIONS

The measurements of D uptake into Ta showed that the uptake rate is proportional to gas pressure and that the sticking coefficient is 0.0085±.00025 on Ta with a clean surface. Chemisorbed oxygen from exposure to O_2 gas strongly decreased the D uptake rate. A monolayer of oxygen decreased the D uptake rate by two orders of magnitude.

D release obeyed second order kinetics for both clean and oxygen covered Ta surfaces. The second order kinetics show that recombination must be occuring from sites which are not saturated and which therefore must have much smaller binding energies for D than the low-coverage chemisorption sites. Chemisorbed oxygen strongly decreased the D release rate.

A model for surface-limited release based on surface recombination from sites in quasi-equilibrium with the solution sites gives good agreement with the observed D release. The energy barrier to recombination, denoted by Q_b in Fig. 7, was small for clean Ta but increased to 0.25 eV/D after exposure to 10^6 Langmuirs of O_2. This is consistent with the large low-coverage sticking coefficient for adsorption of H on clean Ta surfaces, and the large decrease in the sticking coefficient due to chemisorbed oxygen.

In summary, the effect of chemisorbed oxygen on uptake and release of D in Ta appears to be due to a barrier to recombination and dissociation of 0.25 eV/D induced by the oxygen.

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REFERENCES

1. W. R. Wampler, Appl. Phys. Lett. **48**, 405 (1986).

2 W. R. Wampler, J. Appl. Phys. **65**, 4040 (1989).

3. E. Pörschke, D. Shaltiel, K. H. Klatt and H Wenzl, J. Phys. Chem. Solids 47, 1003 (1986).

4. E. Fromm and H. Uchida, J. of the Less Common Metals **66**, 77 (1979).

5. W. R. Wampler, J. Appl. Phys. in press.

6. Ta foil purchased from Comprehensive Research Chemical Corporation, P. O. Box 4039, Orange CA, 92667.

7. Practical Surface Analysis, pg. 211, Edited by D Briggs and M. P. Seah, John Wiley & Sons, Ltd., 1983.

8. Zh. Qi, J. Völkl, R. Lässer and H. Wenzl, J. Phys. F **13**, 2053 (1983).

9. M. A. Pick, M. C. Green and M. Strongin, J. of the Less Common Metals 73, 89 (1980).

10. S. M. Ko and L. D. Schmidt, Surface Science 42, 508 (1974).

11. M. A. Pick, J. W. Davenport, M. Strongin and G. J. Dienes, Phys. Rev. Lett. 43, 286 (1979).

12. J. W. Davenport, G. J. Dienes and R. A. Johnson, Phys. Rev. B 25, 2165 (1982).

13. The Stopping and Ranges of Ions in Matter, Vol. 4, J. F. Ziegler, Pergamon Press, New York, (1977).

14. W. Möller and F. Besenbacher, Nucl. Instr.and Meth. **168**, 111 (1980).

15. P. M. Richards, S. M. Myers, W. R. Wampler and D. M. Follstaedt, J. Appl. Phys. **65**, 180 (1989).

16. E. Veleckis and R. K. Edwards, J. Phys. Chem. **73**, 683 (1969).

17. S. R. Lee, S. M. Myers and R. G. Spulak, J. Appl. Phys. **66**, 1137 (1989).

FIGURE CAPTIONS

1. Measured D uptake rate into clean Ta at 30° C versus D_2 pressure (dots). The slope of the linear least-squares fit (line) is 1.00±.03 which shows the uptake rate is proportional to pressure.

2. D uptake versus oxygen coverage at 30°C and a D_2 pressure of 2 millitorr.

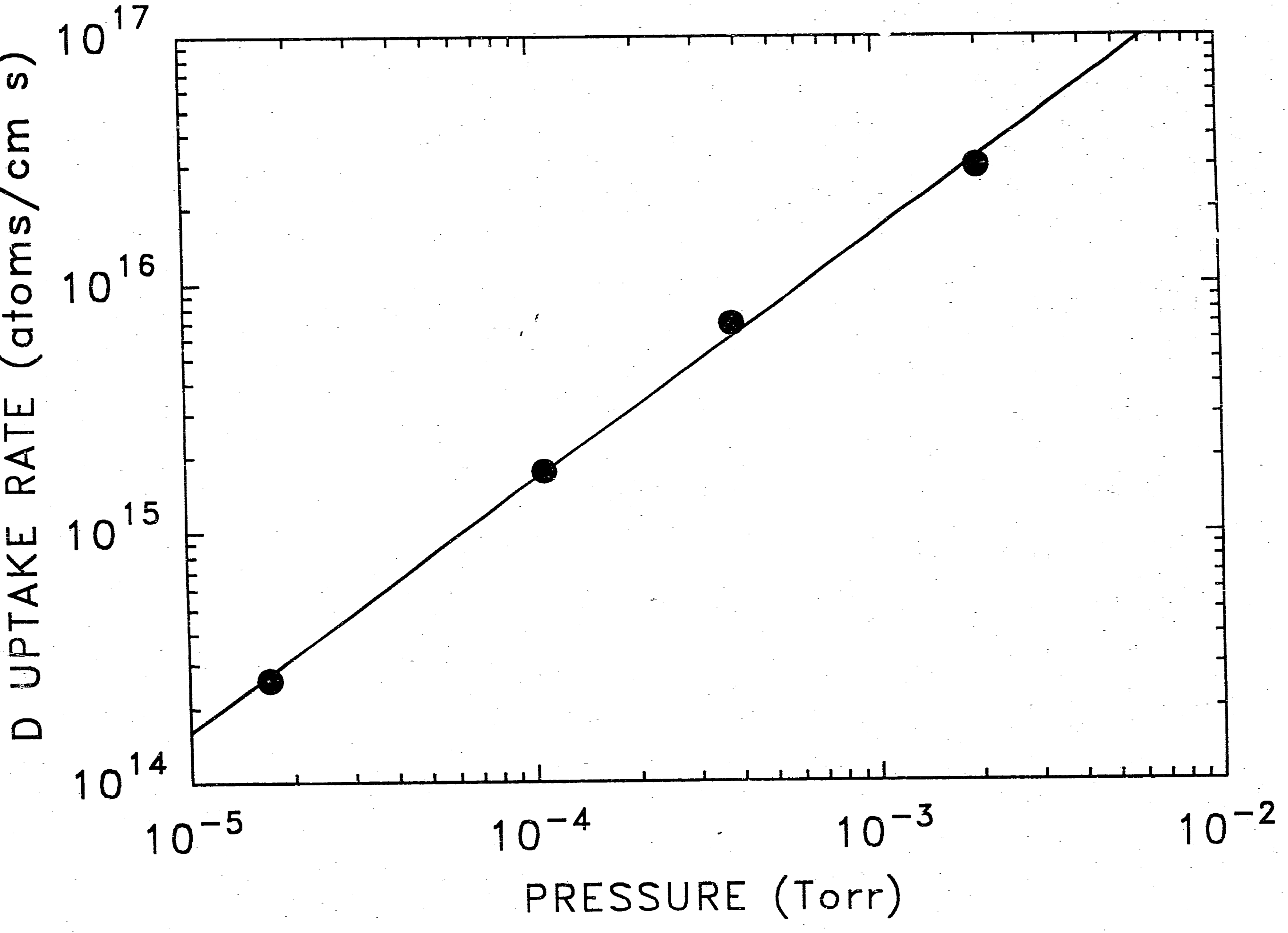
3. Coverage of oxygen and ratio of intensities of oxygen and Ta Auger peaks versus exposure to O_2.

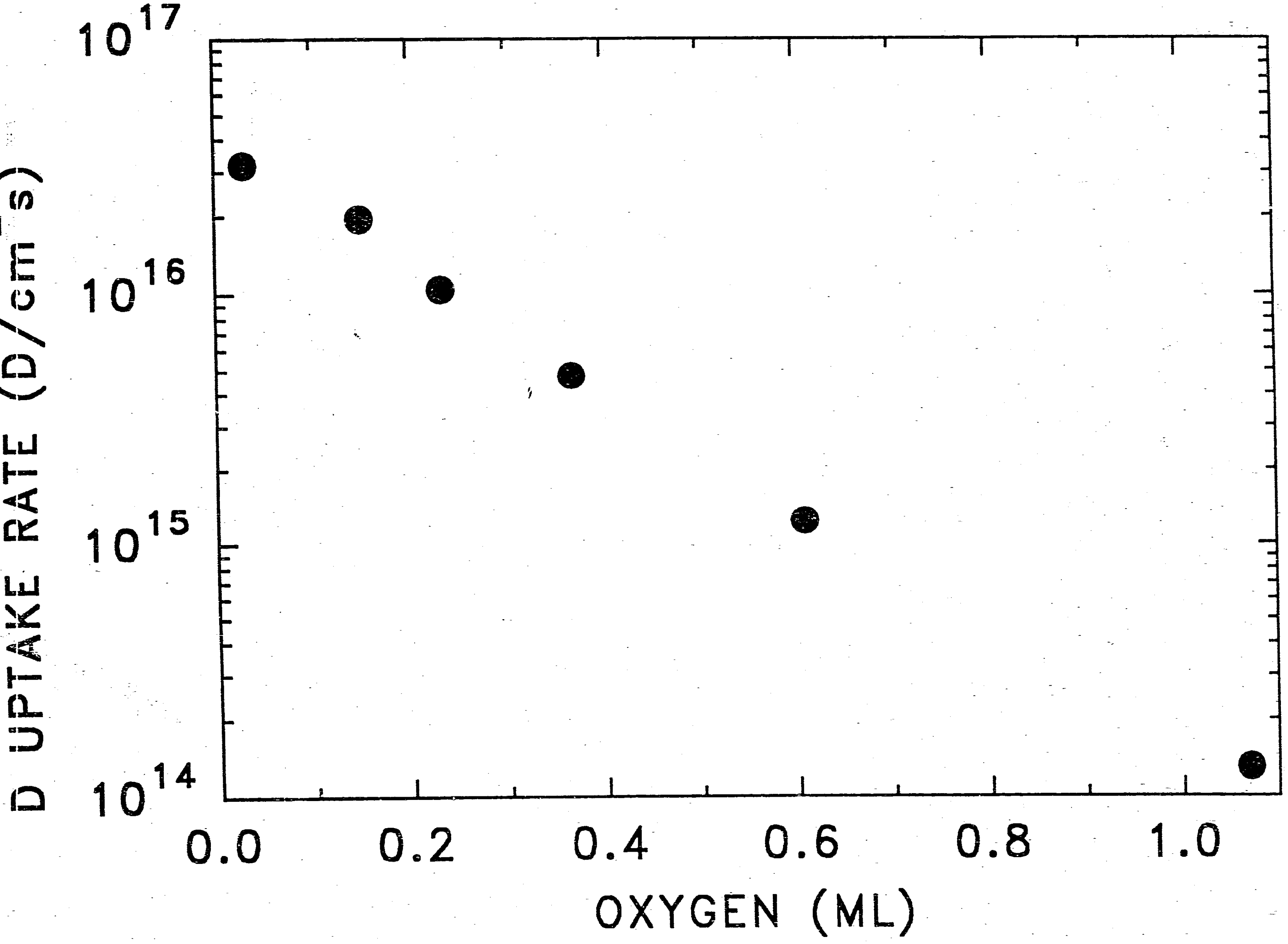
4. Reciprocal of D concentration versus time during isothermal release at 275°C for low and medium oxygen coverages. The linear time dependence implies second order release kinetics.

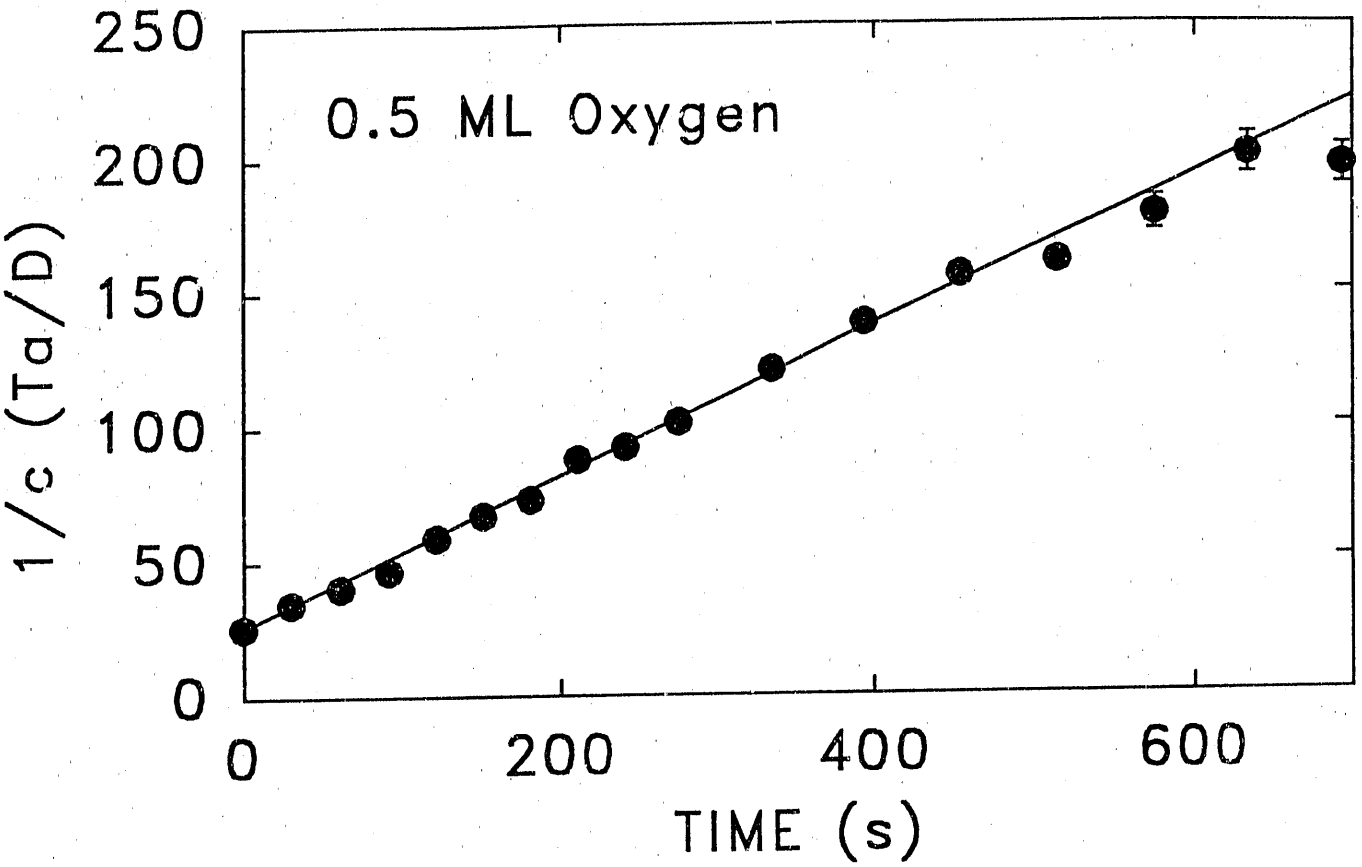
5. Recombination coefficient K_r versus oxygen coverage measured at 275°C.

6. Measured values of K_r for clean (squares) and oxygen dosed (dots) Ta. The lines are least-squares fits of eq. 3 to the data.

7. Energy of D in solution, recombination and chemisorption sites in Ta relative to D_2 gas. Chemisorbed oxygen induces a barrier Q_b=0.25eV/D to recombination. The horizontal scale is intended only for illustrative purposes.


D UPTAKE RATE (atoms/cm^{2}s)
10^{17}
10^{16}
10^{15}
10^{14}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
PRESSURE (Torr)


D UPTAKE RATE (D/cm^{2}s)
10^{17}
10^{16}
10^{15}
10^{14}
0.0
0.2
0.4
0.6
0.8
1.0
OXYGEN (ML)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1/c (Ta/D)
TIME (s)
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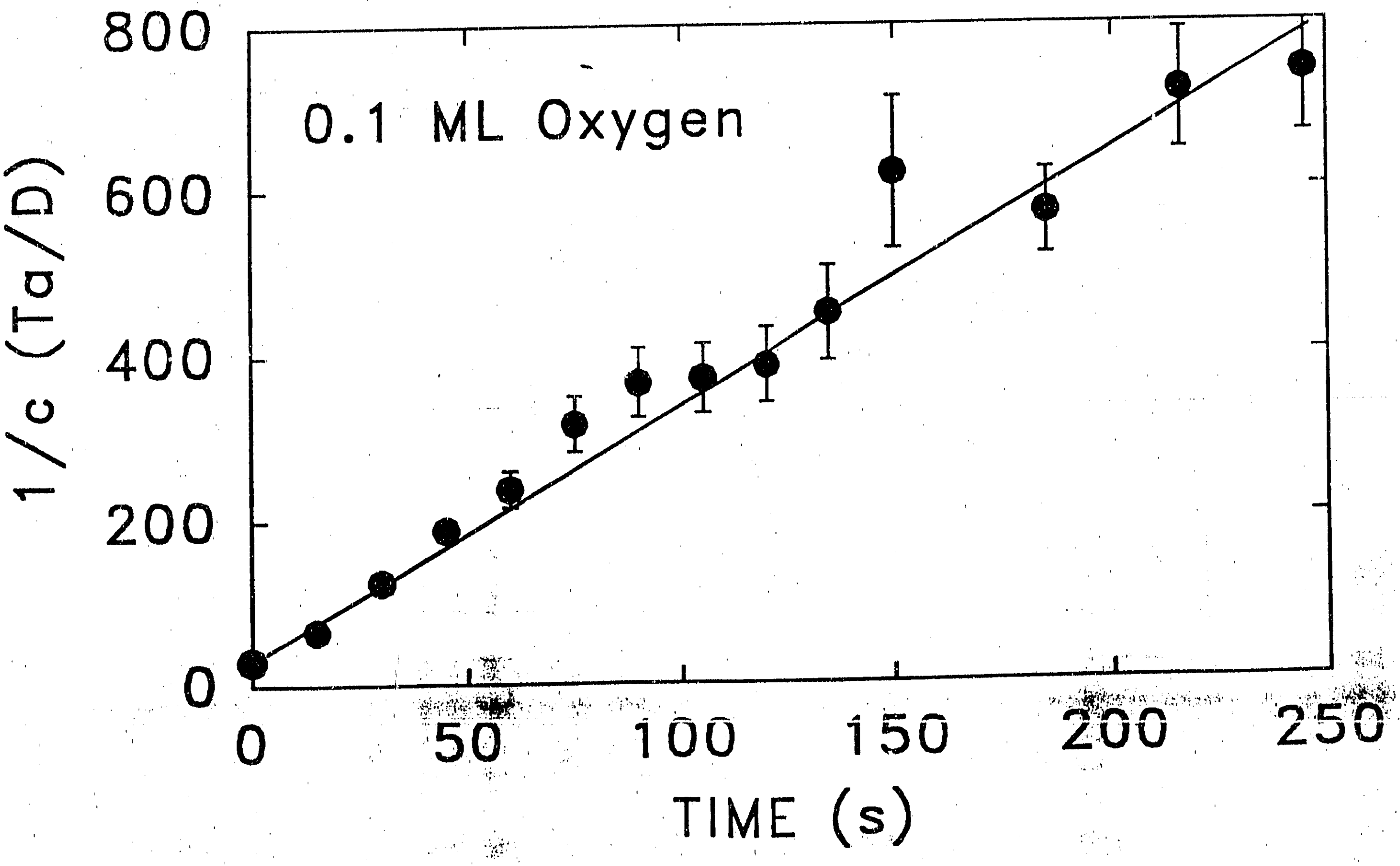
100
150
200
250
0
200
400
600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1/c (Ta/D)
TIME (s)
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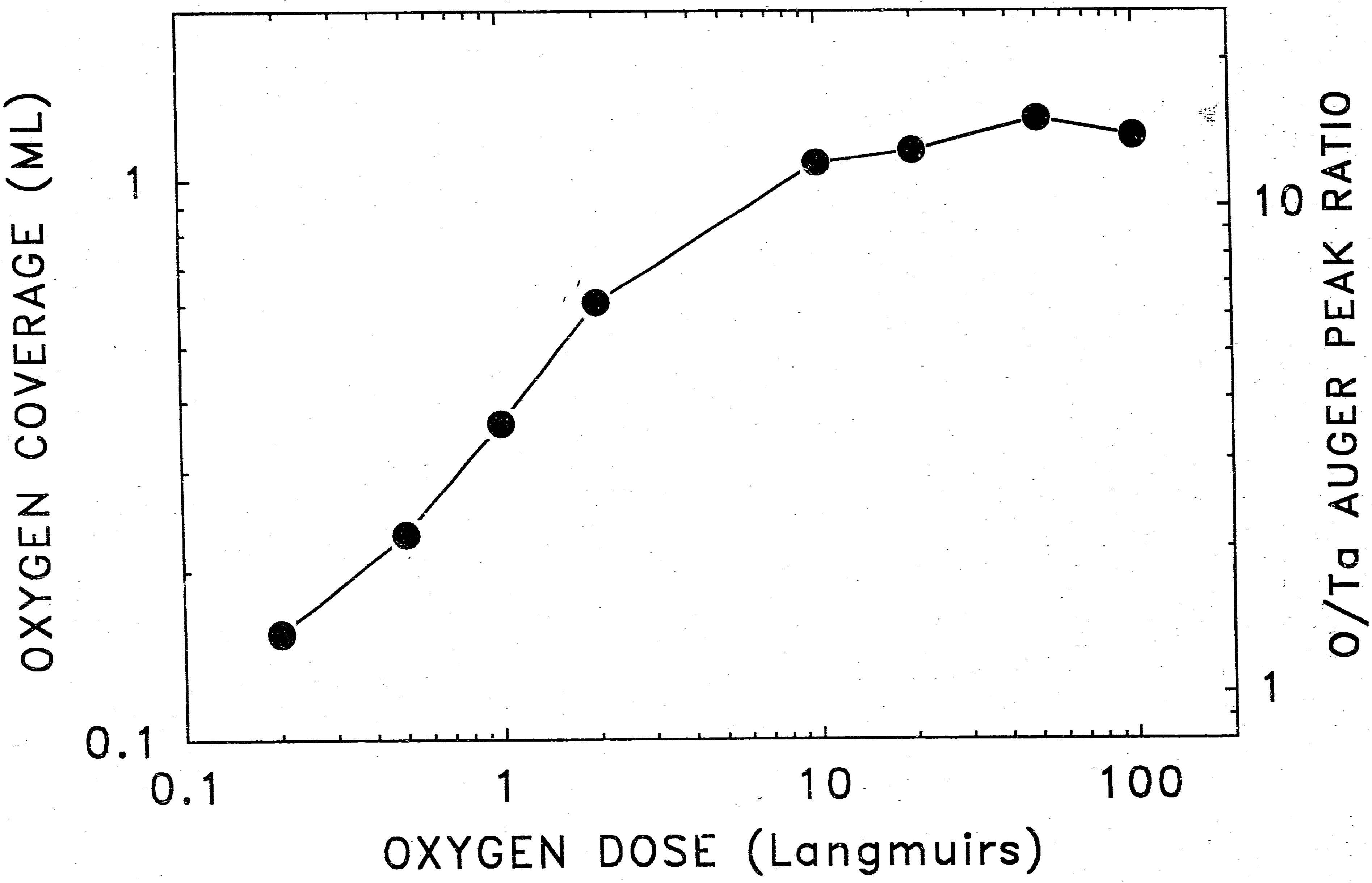
200
400
600
800
0
50
100
150
200
250

3


OXYGEN COVERAGE (ML)
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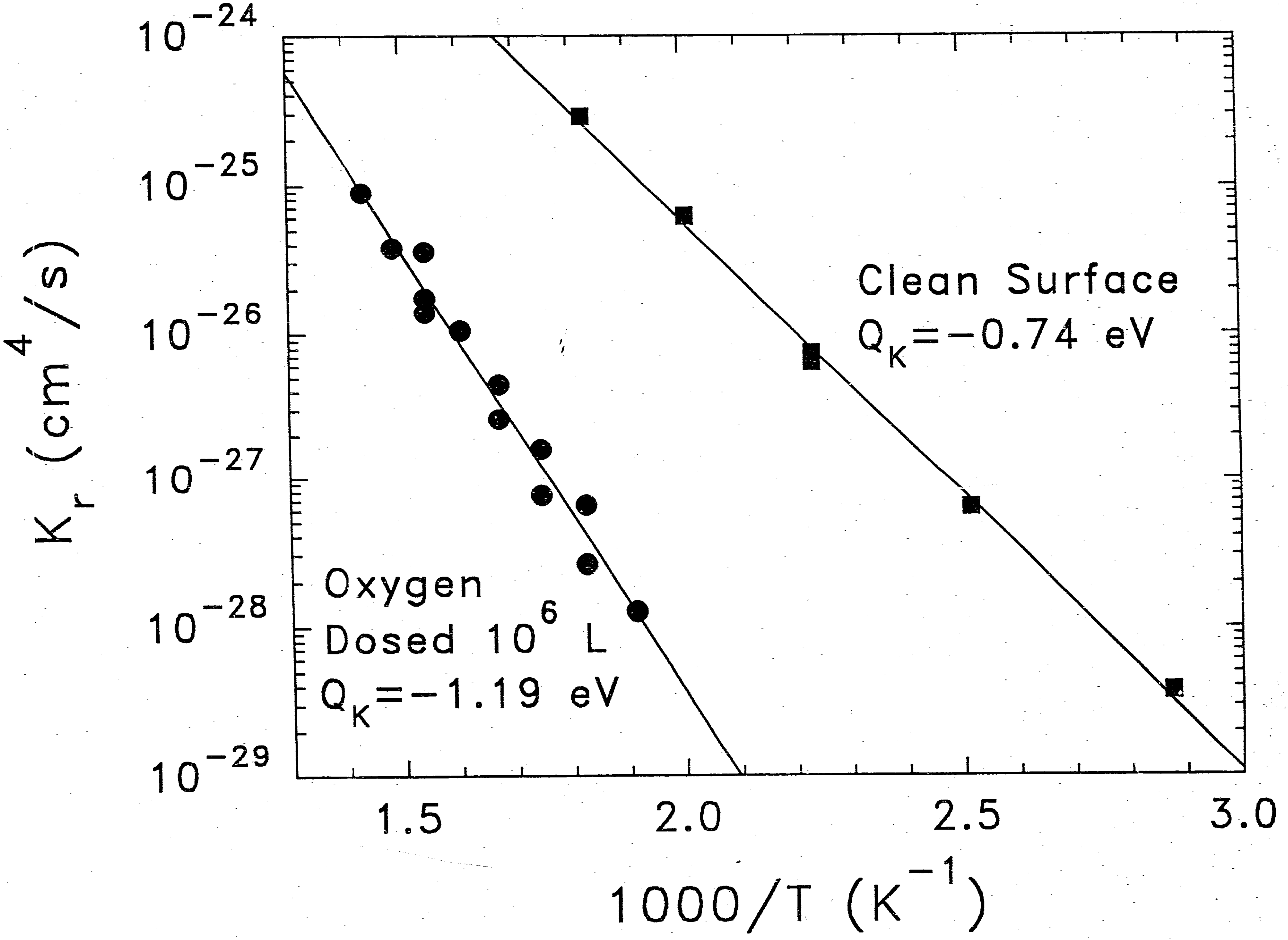
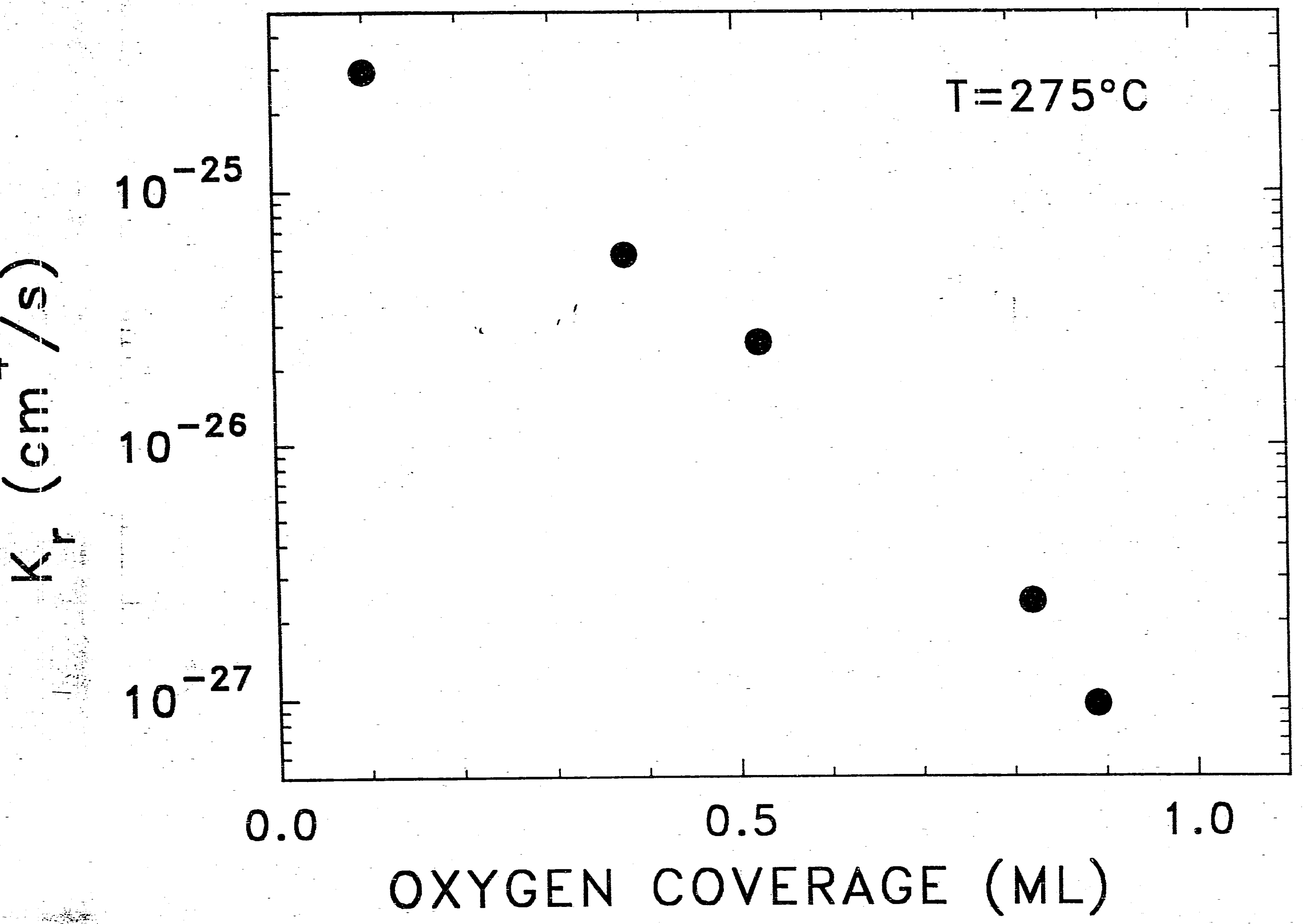
0.1
1
10
100
OXYGEN DOSE (Langmuirs)
O/Ta AUGER PEAK RATIO
10
1


K_r (cm^4/s)
10^{-24}
10^{-25}
10^{-26}
10^{-27}
10^{-28}
10^{-29}
1.5
2.0
2.5
3.0
1000/T (K^{-1})
Clean Surface
Q_K=−0.74 eV
Oxygen
Dosed 10^6 L
Q_K=−1.19 eV


T=275°C
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10^{-27}
K_r (cm^4/s)
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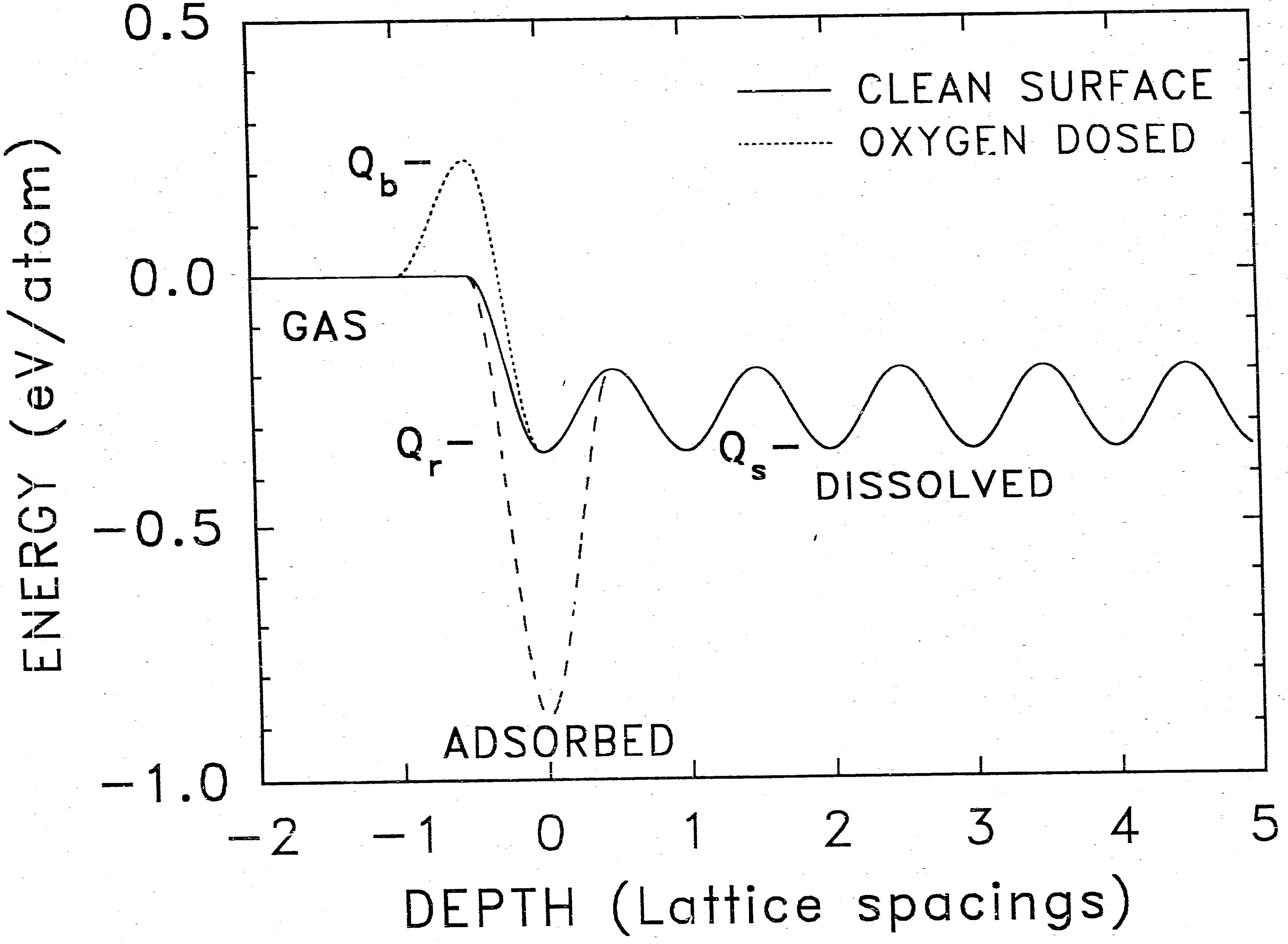
0.5
1.0
OXYGEN COVERAGE (ML)


CLEAN SURFACE
OXYGEN DOSED
Q_b
GAS
Q_r
Q_s
DISSOLVED
ADSORBED
0.5
0.0
−0.5
−1.0
−2
−1
0
1
2
3
4
5
ENERGY (eV/atom)
DEPTH (Lattice spacings)

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