Conf-8904215--3

# DESORPTION ACTIVATION ENERGIES FOR TRITIUM RELEASE FROM CERAMIC BREEDERS

J. P. Kopasz, A. K. Fischer, and C. E. Johnson
Argonne National Laboratory, Argonne IL 60439 --

CONF-8904215--3

DE89 014667

## Abstract

Desorption has been identified as an important process in determining the kinetics of tritium release from ceramic tritium breeder materials considered for use in fusion reactors. However, details of the desorption of tritium from ceramic materials are mostly unknown. Models of tritium release have treated desorption as a simple process with desorption occurring from one type of site with one activation energy. Recent measurements of the rates of water uptake by $LiAlO_2$, and evolution of water from $LiAlO_2$ exposed to water, indicate the presence of multiple types of desorption sites. Estimates of desorption activation energies were obtained from these data and from data in the literature suggesting multiple types of desorption sites for desorption from $Li_2O$ and $Li_4SiO_4$.

## Introduction

The kinetics of tritium release is an important issue to consider in choosing a breeder material for use in a fusion reactor. Slow tritium release will result in a large inventory of tritium in the reactor, which is unacceptable from both economic and safety viewpoints. Tritium release is determined primarily by two processes: bulk diffusion within the grains and adsorption-desorption on the surfaces. Desorption has been determined to be the rate-limiting process in some cases.[1-3] Despite the importance of tritium desorption in determining the merits of candidate breeder materials, little is known about the tritium desorption process. Tritium

---

This work supported by the U.S. Department of Energy, Office of Fusion Energy under contract no. W-31-109-ENG-38.

desorption has been treated as occurring from one site with one desorption activation energy in most cases. Recent experiments suggest that there are several sites for desorption, each with a corresponding activation energy.[4-6]

In this paper, we will review the evidence for the presence of multiple desorption sites, including our own recent evidence for multiple desorption sites in $LiAlO_2$. Estimates of desorption activation energies will be calculated based on this data and the data in the literature.

## Evidence for Multiple Desorption Sites

### $LiAlO_2$

In some of the experiments on the adsorption-solubility relationships for $LiAlO_2$,[7] after uptake of $H_2O(g)$ was complete, the sample was heated to a higher temperature in a helium stream, and the evolution of water vapor was recorded. During the temperature ramp, the rate of evolution of $H_2O(g)$ was observed to go through several maxima. This was interpreted as showing that evolution proceeded from several types of sites. An example is shown in Fig. 1 for a heating ramp from 586 to 888 K. Two major peaks are clearly visible and several minor ones are suggested. These particular measurements were only crude examples of temperature programmed desorption (TPD), since the experiments were designed for adsorption measurements. As such, the samples were too large to assure freedom from error due to readsorption effects, and the only inference drawn is that more than one type of adsorption site was present.

Isotherms and isobars derived from the adsorption data revealed two adsorption processes with different activation energies for adsorption.[7] Furthermore, the heats of adsorption were found to depend on the degree of surface coverage. Thus, in the 773-873 K range, for fractional surface coverages ranging from 10% to 0.1%, the minimum estimated heats of adsorption ranged from approximately 80 to 360 kJ/mol (19 to 86 kcal/mol).

Though not designed as kinetic experiments, the adsorption measurements were examined further to extract information on the rates of adsorption. Figure 2 shows the rate of adsorption as a function of temperature. In the regions where this rate increases with temperature, the slopes allow an estimate of the activation energy of adsorption to be made. In confirmation of the deduction from the adsorption isotherms and isobars that two different adsorption processes with different activation energies were involved in different temperature ranges, these curves suggest a 3 kJ/mol (0.7 kcal/mol) adsorption activation energy in the 573 to 623 K range and a 15 kJ/mol (3.7 kcal/mol) adsorption activation energy in the 673 to 773 K range. The distinction was made that the high temperature adsorption process was probably dissociative chemisorption, and that the low temperature process was perhaps a low activation energy chemisorption or unimolecular physisorption. This figure also illustrates the possibility that observed net rates of adsorption decrease with increasing temperature when different processes with different activation energies and different dependencies on coverage coexist.

Due to the fact that the activation energy for desorption is equal to the sum of the heat of adsorption and the activation energy of adsorption, the desorption activation energy will exhibit the same trend as observed for the heat of adsorption. The observed range of values for the heat of adsorption indicates a range of activation energies for desorption. The physical basis for such a range is the existence of multiple types of sites for adsorption and, hence, multiple types of sites from which desorption occurs. Earlier work on other materials revealed the same complexity. For example, a theoretical analysis of the types of $OH^-$ sites possible on the surface of alumina, characterized in terms of the number of $O^{2-}$ nearest neighbors, showed five types to be present. These were related to experimentally measured infrared spectra.[8]

Supporting evidence for multiple desorption sites on $LiAlO_2$ was obtained in the tritium release from the LILA-1 experiment. For several runs an increase in temperature resulted in a small decrease in tritium release followed by an increase to a maximum then a decay to steady state.[9] Similar tritium release curves were observed for release from $Li_2O$ in the CRITIC experiment.[10] This type of tritium release behavior could not be explained using a diffusion-desorption release model with one desorption activation energy, but could be modeled with a desorption activation energy which varies with surface coverage.[11]

## $Li_2O$

A constant-rate heating experiment was performed by Tanifuji et al. on irradiated $Li_2O$.[4] This experiment is, in essence, a TPD study. In TPD, a sample with adsorbed material on it is heated at a specified rate, and the quantity of desorbed species is measured as a function of temperature. For a constant heating rate, a peak will be observed in a plot of the amount desorbed versus temperature. The position of the peak is indicative of the desorption activation energy. The presence of more than one peak indicates multiple desorption processes. Tanifuji et al. interpreted their results based on the presence of one broad desorption peak for each sample;[4] however, if the data are examined more closely, one can recognize several overlapping peaks. This is seen clearly in Fig. 3. An analysis of these peaks indicates five types of sites for desorption of tritium from $Li_2O$.

Supporting evidence for the presence of multiple desorption sites in $Li_2O$ was also observed in the CRITIC in-pile tritium release experiment. In this experiment, an increase in sample temperature resulted in a sharp decrease in tritium release followed first by an increase to maximum release and then decay to steady state.[10] This behavior was successfully modeled using a desorption activation energy which varied with surface coverage; it could not be modeled by a diffusion-desorption model with a single desorption activation energy.[11]

### $Li_4SiO_4$

Evidence for multiple types of desorption sites in $Li_4SiO_4$ has been observed in several out-of-pile tritium release experiments.[3,5,6] The first suggestion of multiple desorption site types in this material came from attempts to fit tritium release data from out-of-pile annealing studies. Breitung et al. found that the best fit to their data was obtained for a desorption model with two types of desorption sites.[3] More conclusive data have recently been reported. Two separate studies describing tritium release and water release from TPD experiments indicate multiple desorption activation energies.[5,6] In the first of these experiments, pre-irradiated samples of doped and undoped $Li_4SiO_4$ were heated at a rate of 4.8°C/min, and the amount of tritium released was measured as a function of temperature.[5] Multiple desorption peaks were observed in the TPD curve for all the samples, with six desorption peaks present for the pure silicate. The second study investigated the desorption of water from $Li_4SiO_4$.[6] The TPD curve for water desorbed from $Li_4SiO_4$ powder stored in air showed what appear to be six overlapping peaks, indicating six types of desorption sites. Both of these studies on $Li_4SiO_4$ are consistent with the presence of up to six different desorption activation energies. Since the details of the experimental set-up and procedure were not reported in these papers, it is possible that one of the peaks is due to diffusion in the bulk; however, that still leaves five peaks to be accounted for. Grain boundary diffusion may be rate controlling under some circumstances, but this is considered unlikely. The evidence from these papers suggests that there are five to six different desorption activation energies for desorption of HTO from $Li_4SiO_4$.

## CALCULATIONS

The mathematics governing desorption in TPD or constant-rate heating experiments have been covered in detail elsewhere[12,13] and are beyond the scope of this paper. A brief description of the relevant equations follows.

For first-order desorption into a vacuum (or into a rapidly flowing purge stream), the pressure of the desorbing species in the purge stream from one site with desorption activation energy $E_a$ can be calculated as follows[12]:

$$P = (\nu/C)\exp\{-\nu\beta\ (E_a/R)I - E_a/RT\} \tag{1}$$

where

$$I = \exp(-\epsilon)\ [1 - (2!/\epsilon) + (3!/\epsilon^2) - (4!/\epsilon^3) + \ldots]/\epsilon^2 \tag{2}$$

and $\nu$ = desorption preexponential term

$\beta$ = heating rate

$E_a$ = desorption activation energy

C = the initial concentration

T = the temperature

R = the gas constant

$\epsilon = E_a/RT$

Second-order desorption gives the pressure as[12]

$$p = \frac{\nu \exp(-E_a/RT)}{C(E_a/R)\ (1 + \nu\beta\ I\ E_a/R)^2} \tag{3}$$

The total release at any time would be the sum of the release over all the active desorption sites. Using these equations, one can calculate the tritium release profile as a function of time or temperature given the desorption activation energies, preexponential terms, and the heating rate.

Using the data from constant-rate heating experiments, one can estimate the desorption activation energies from the temperatures at which the maxima in plots of tritium release versus temperature occur. For experiments where the flow rate and heating rate are such that readsorption does not interfere, if the desorption is first order, then an estimate of the activation energy can be obtained by the following:[13]

$$E_a = RT[\ln(\nu\ T/\beta) - 3.46] \tag{4}$$

Using an estimate of $1 \times 10^8$ for the desorption preexponential, (a value in agreement with tritium release measurements from $Li_2O$ and kinetic studies of the decomposition of LiOT + LiOH[14]), we obtained estimates for the activation energies of desorption of tritium from $Li_2O$ from the Tanifuji et al. data[4] and for desorption from $Li_4SiO_4$ using $\nu = 1 \times 10^8$ and the Skokan et al.[5] and Schauer and Schumacher data.[6] These estimates were then used as input to a program calculating the tritium release as a function of temperature using equation (1) or (3). The initial concentrations and activation energies for each site were then varied to optimize the fit to the data.

## Estimates of Activation Energies of Desorption

### $LiAlO_2$

We estimated the desorption activation energies for $LiAlO_2$ using heats of adsorption of 80 to 360 kJ/mol,[7] (depending on the surface coverage), at temperatures from 773-873 K, and an estimate of the activation energy of adsorption of 15 kJ/mol. The estimated desorption activation energies were approximately 95 to 375 kJ/mol in this temperature range. At the low temperature (573 K), where the heat of adsorption may have been about 42 kJ/mol, we estimated the desorption activation energy to be 46 kJ/mol for a high degree of coverage.

## $Li_2O$

Our analysis of the data obtained by Tanifuji et al. for their constant heating rate experiment suggests that there are six different sites for desorption of tritium from $Li_2O$. The estimates of the activation energies from the first-order desorption equation are 140.6±0.4, 149.4±1.7, 162.8±1.7, 178.2±3.8 and 186.2±1.7 kJ/mol (33.6±0.1, 35.7±0.4, 38.9±0.4, 42.6±0.9 and 44.5±0.4 kcal/mol). The desorption peak corresponding to the highest activation energy, 186.2 kJ/mol (44.5 kcal/mol), was of low intensity and was not always seen. Examples of the calculated tritium release curves are illustrated in Fig. 4. The relative populations of the sites responsible for the different desorption peaks were dependent on the history of the sample and the heating rate. For experiments with a heating rate of 1 K/min the major desorption peak was due to the process with an activation energy of 149.4 kJ/mol (35.7 kcal/mol), while the peak corresponding to an activation energy of 140.6 kJ/mol (33.6 kcal/mol) was dominant when the heating rate was 10 K/min. This suggests that there is a redistribution in the population of the sites as the sample is heated. In part, a low heating rate allows the most active sites to remain filled longer.

The tritium released from $Li_2O$ and collected as HT was also determined as a function of temperature by Tanifuji et al.[4] These curves were analyzed using our model with multiple desorption activation energies. Estimates of desorption activation energies of 139.7, 148.5, 159.4, 175.7, and 187 kJ/mol (33.4, 35.5, 38.1, 42.0, and 44.7 kcal/mol) were obtained. These energies are in good agreement with those determined from the curves of total tritium released. The amount of released tritium detected as HT was found to be of the order of 1% of the total tritium released.[4] The agreement between the desorption activation energies for the tritium detected as HT and the total tritium released (detected as mostly HTO) suggests that tritium collected as HT and that collected as HTO are released by the same mechanisms. Thus, the form of tritium detected downstream is probably not determined by the form in which it is released from the solid, but by the gas phase chemistry.

It is of interest to compare our estimates of desorption activation energies with some reported in the literature. The first in the sequence of desorption processes, with an estimated activation energy of 140.6 kJ/mol (33.6 kcal/mol), is expected to be for desorption from a surface with a relatively high surface coverage. This value is in good agreement with the desorption activation energy reported by Kudo and Okuno of 129.7 kJ/mol (31 kcal/mol)[14] and the activation energies reported by Quanci, (for tritium release into a helium purge stream containing 0.1 to 1.0% added hydrogen), of 130.6 kJ/mol (31.2 kcal/mol).[15] The second energy (149.4 kJ/mol, 35.7 kcal/mol) is expected to correspond to desorption from a slightly more energetic type of sight. Desorption from this site would begin to dominate when the population of a previously active site is diminishing. This activation energy is in excellent agreement with that reported by Quanci (for desorption into a pure helium purge) of 152.2 kJ/mol (36.4 kcal/mol).[15] Bertone has reported lower activation energies than our estimates,(118.8 kj/mol, 28.4 kcal/mol)[2] as has Quanci (102.0 kJ/mol, 24.4 kcal/mol, for a purge gas of He +4.82% $H_2$).[15] There may be sites for desorption from $Li_2O$ with even lower activation energies than those we estimated, but these are expected to correspond to samples with a higher surface coverage than the samples studied by Tanifuji et al. As a possible limiting case for high surface coverage, we note that Kudo and Okuno reported the activation energy for thermal decomposition of LiOH as 123.4 kJ/mol (29.5 kcal/mol).[14] However, additional depression of the activation energy might result from radiation effects or reaction of the surface with $H_2$ in the purge.

The degree of surface coverage present at any particular time determines which activation energy will control the desorption process at that time. Unfortunately, we could not obtain estimates of surface coverage from the Tanifuji et al. data so we can not determine what surface coverages our estimated activation energies relate to. However, because these experiments were performed with pure helium purge gas, the results should be comparable with and relevant to tritium release experiments that were also performed with pure helium purge streams. A detailed experimental study is needed to quantitatively relate the hydrogen/tritium surface coverage to the desorption activation energies.

## $Li_4SiO_4$

We derived approximations for desorption activation energies for $Li_4SiO_4$ obtained from the data of Skokan et al.[5] and Schauer and Schumacher[6] using equation 4 and an estimated value of the desorption preexponential term of 1 x $10^8$. Activation energies of 73.6, 96.7, 110.9, 143.1, 178.2, and 215.9 kJ/mol (17.6, 23.1, 26.5, 34.2, 42.6, and 51.6 kcal/mol) were obtained from Skokan et al. Values of 83.3, 97.9, 112.1, 146.9, 171.1, 193.3 and 218.8 kJ/mol (19.9, 23.4, 26.8, 35.1, 40.9, 46.2 and 52.3 kcal/mol) were obtained from Schauer and Schumacher. The expected first-order release was calculated and compared to the observed release of $H_2O$ in the Schauer and Schumacher experiment.[6] The positions of the calculated peaks were found to agree well with the experimental data; however, the peak widths for the calculated curves were narrower than the observed peak widths. Calculations based on second-order desorption using activation energies of 83.3, 97.9, 112.1, 144.3, 171.5, and 194.1 kJ/mol (19.9,23.4,26.8,34.5 ,41.0, and 46.4 Kcal/mol) provided a much better fit to the observed data. The agreement between the activation energies calculated from the Skokan et al.[5] and Schauer and Schumacher[6] data is quite good, with a maximum deviation of less than 10 kJ/mol. One additional peak was observed in the tritium release curve from the Schauer paper. This peak may be masked by other more intense peaks in the curves of Skokan et al.

Our estimates of these desorption activation energies can be compared with values calculated by Breitung et al. from a fit of LISA data to a two-site desorption model of 53.6 and 90.9 kJ/mol (12.8 and 21.7 kcal/mol).[3] The energy we calculated of 97.9 kJ/mol is in good agreement with the second of their energies, suggesting that we have made a reasonable choice for the preexponential term. Again, it is not possible to determine the surface coverage from the data given in the Schauer and Schumacher paper; thus, the surface coverages which correspond to our estimates of desorption activation energies are unknown.

## Conclusions

Evidence from a number of studies on breeder materials and analogy with related materials indicates that several types of sites, with their associated activation energies for desorption, are involved in the desorption of $H_2O(g)$, $HTO(g)$, or $T_2O(g)$ from oxidic ceramic tritium breeders. The degree of surface coverage at a given time, the result of adsorption of $H_2O$ or $H_2$ and diffusion of T to the surface, will determine which type of site is dominant in the release process and what the desorption activation energy will be at that time. Theoretical predictions of release curves by a model based on this desorption behavior have been successful in matching observed data.

## References

1) M. Briec, F. Botter, J. J. Abassin, R. Benoit, P. Chenebault, M. Masson, B. Rausner, P Sciers, H. Werle, and E. Roth, "In and Out-of-Pile Tritium Extraction From Samples of Lithium Aluminates" J. Nucl. Mater. 141-143 (1986) 357-363.

2) P. C. Bertone, "The Kinetics that Govern The Releaseof Tritium from Neutron-Irradiated Lithium Oxide," J. Nucl. Mater. 151 (1988)281-292.

3) W. Breitung, H. Elbel, J. Lebkucher, G. Schumacher, and H. Werle, "Out-of-pile Tritium Extraction From Lithium Silicate," J. Nucl. Mater. 155-157 (1988) 507-512.

4) T. Tanifuji, K. Noda, S. Nasu, and K. Uchida, "Tritium Release from Neutron-Irradiated $Li_2O$; Constant Rate Heating Measurements," J. Nucl. Mater. 95 (1980) 108-118.

5) A. Skokan, D. Vollath, H. Wedemeyer, E. Gunther, and H. Werle "Preparation, Phase Relationships and First Irradiation Results of Lithium Orthosilicate Doped with $Al^{3+}$ and $P^{5+}$ Ions," 15th Symp. on Fusion Technology, Utrecht, The Netherlands, Sept. 1988.

6) V. Schauer and G. Schumacher, "Study of Adsorption and Desorption of Water on $Li_4SiO_4$," presented at STNM-7, Chicago, IL, Sept. 1988 (to be published in J. of Nucl. Mater.).

7) A. K. Fischer and C. E. Johnson, "Measurements of Adsorption in the $LiAlO_2$-$H_2O$(g) System," Fusion Technology 15 (1989) 1212-1216.

8) J. B. Peri,"A Model for the Surface of $\gamma$-Alumina," J. Phys. Chem. 69 (1965) 220.

9) M. Briec and E. Roth, "Tritium Extraction Mchanisms from Lithium Aluminates During In-Pile Irradiation Experiments," Proc. of Specialists' Workshop on Modelling Tritium Behavior in Fusion Blanket Ceramics, Chalk River, Canada, pp 28-57 (1987).

10) J. M. Miller, R. A. Verrall, D. S. MacDonald, and S. R. Bokwa, "The CRITIC Irradiation of $Li_2O$-Tritium Release and Measurement," presented at the Third Topical Meeting on Tritium Technology in Fission, Fusion and Isotopic Applications, Toronto, Canada, May 1988.

11) J. P. Kopasz, S. W. Tam, and R. A. Verrall, "Modeling Unusual Tritium Release Behavior from $Li_2O$," Fusion Technology 15 (1989) 1217-1222.

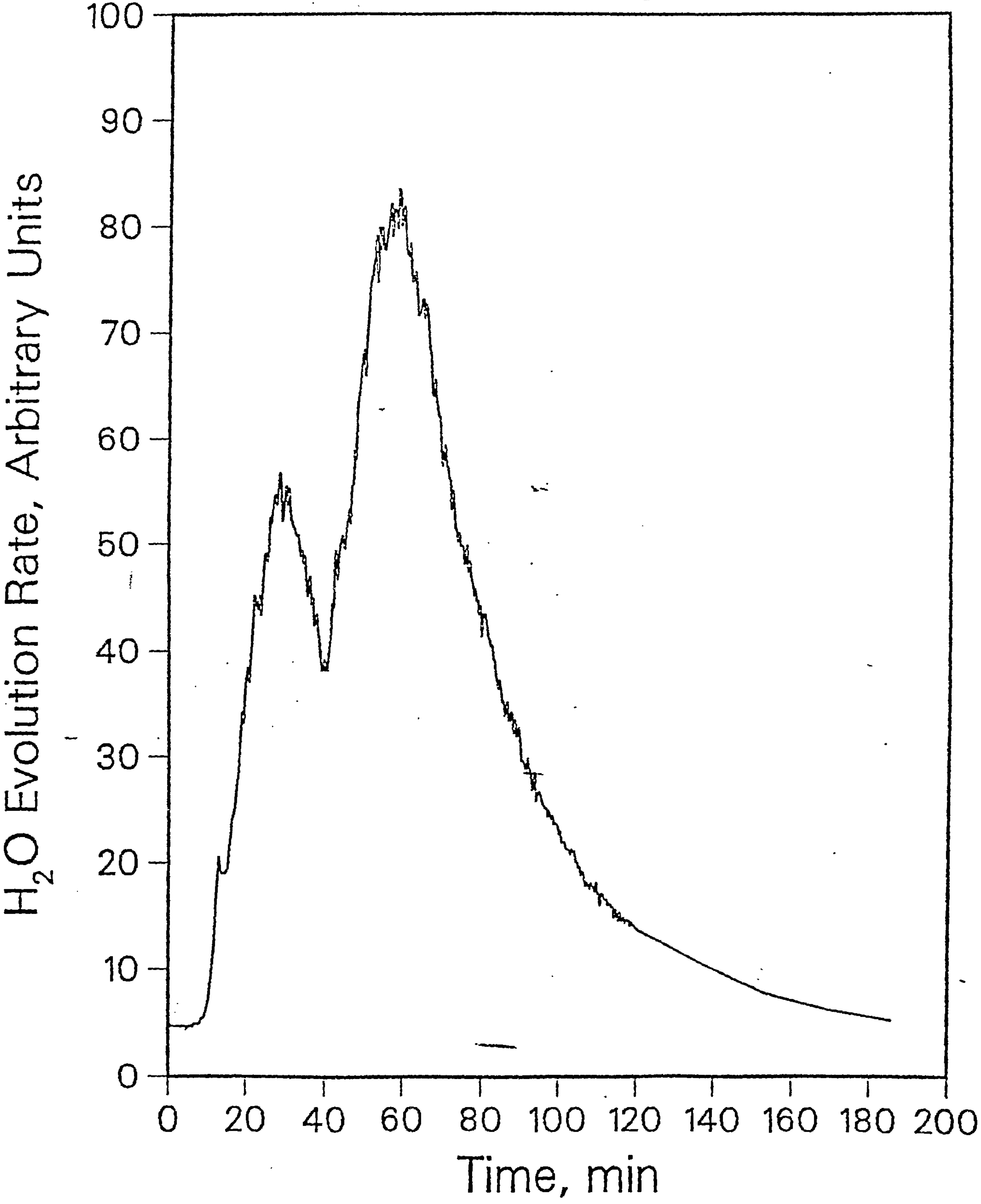
12) A. W. Smith and S. Aranoff, "Thermodesorption of Gases from Solids," J. Phys. Chem. 62 (1958) 684-686.

13) D. A. King, "Thermal Desorption From Metal Surfaces: a Review," Surf. Sci. 47 (1975) 384-402.

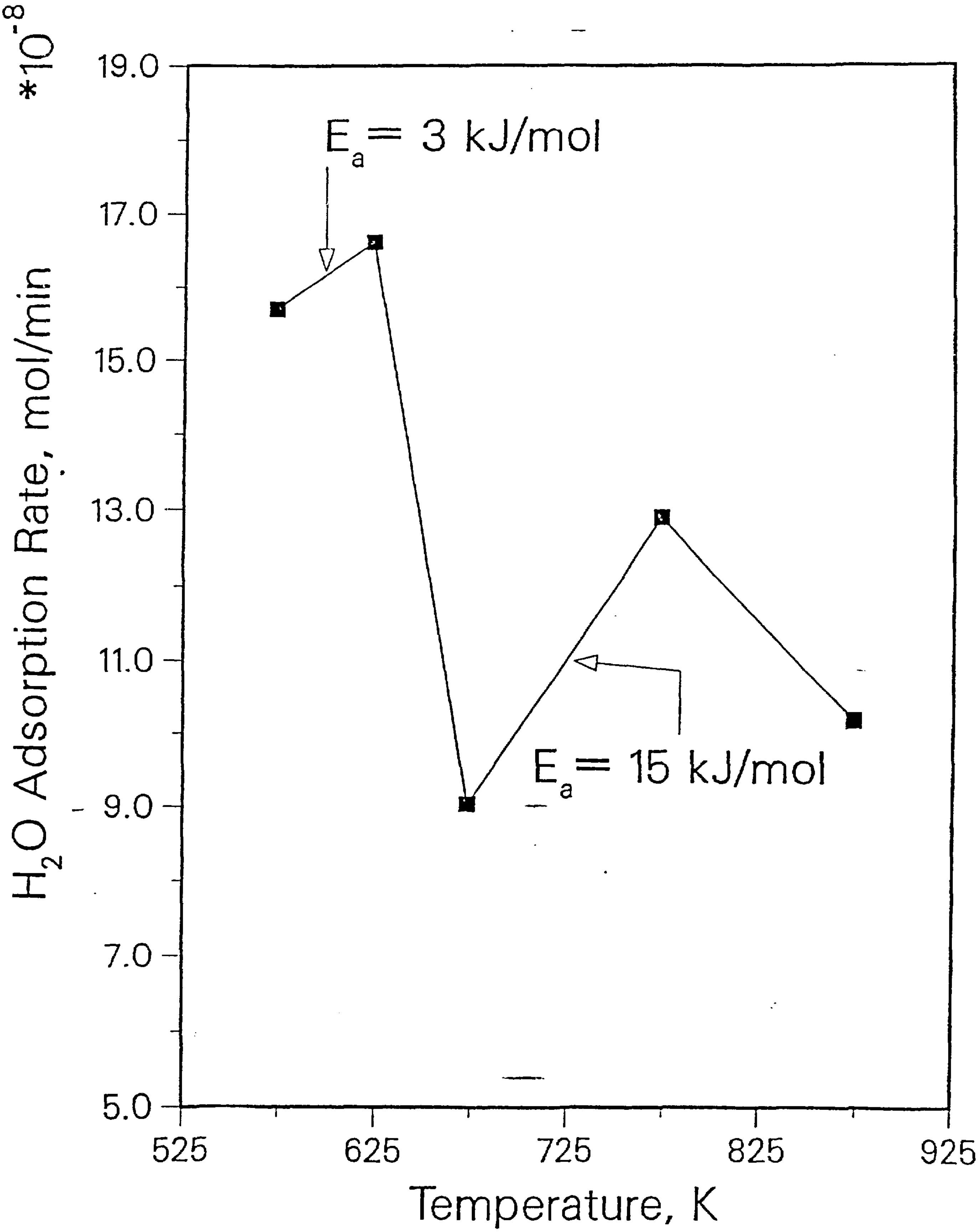
14) H. Kudo and K. Okuno, "Kinetic Studies of the Tritium Release Process in Neutron-Irradiated $Li_2O$ and LiOH," J. Nucl. Mater. 101 (1981) 38-43.

15) J. Quanci, "Tritium Breeding and Release-Rate Kinetics from Neutron-Irradiated Lithium Oxide," Phd. Thesis, Dept. of Chemical Engineering, Princeton University, January 1989.

# $H_2O$ Evolution Rate
# 586 to 888 K Temperature Ramp



## Adsorption Rate at 15 Pa



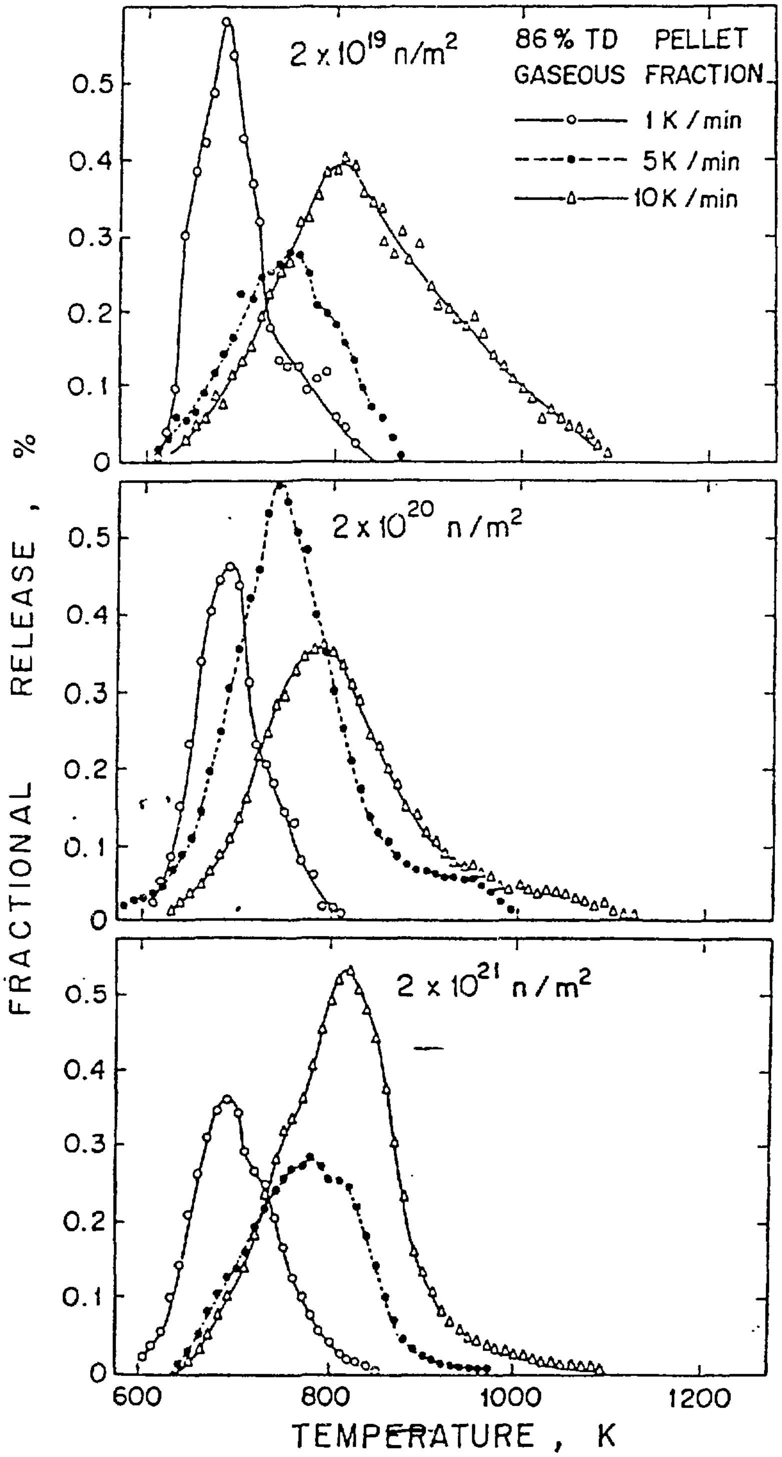

2 x 10^19 n/m^2
86 % TD PELLET
GASEOUS FRACTION
1 K/min
5 K/min
10 K/min
2 x 10^20 n/m^2
2 x 10^21 n/m^2
0
0.1
0.2
0.3
0.4
0.5
FRACTIONAL RELEASE, %
600
800
1000
1200
TEMPERATURE, K

Fig 4A

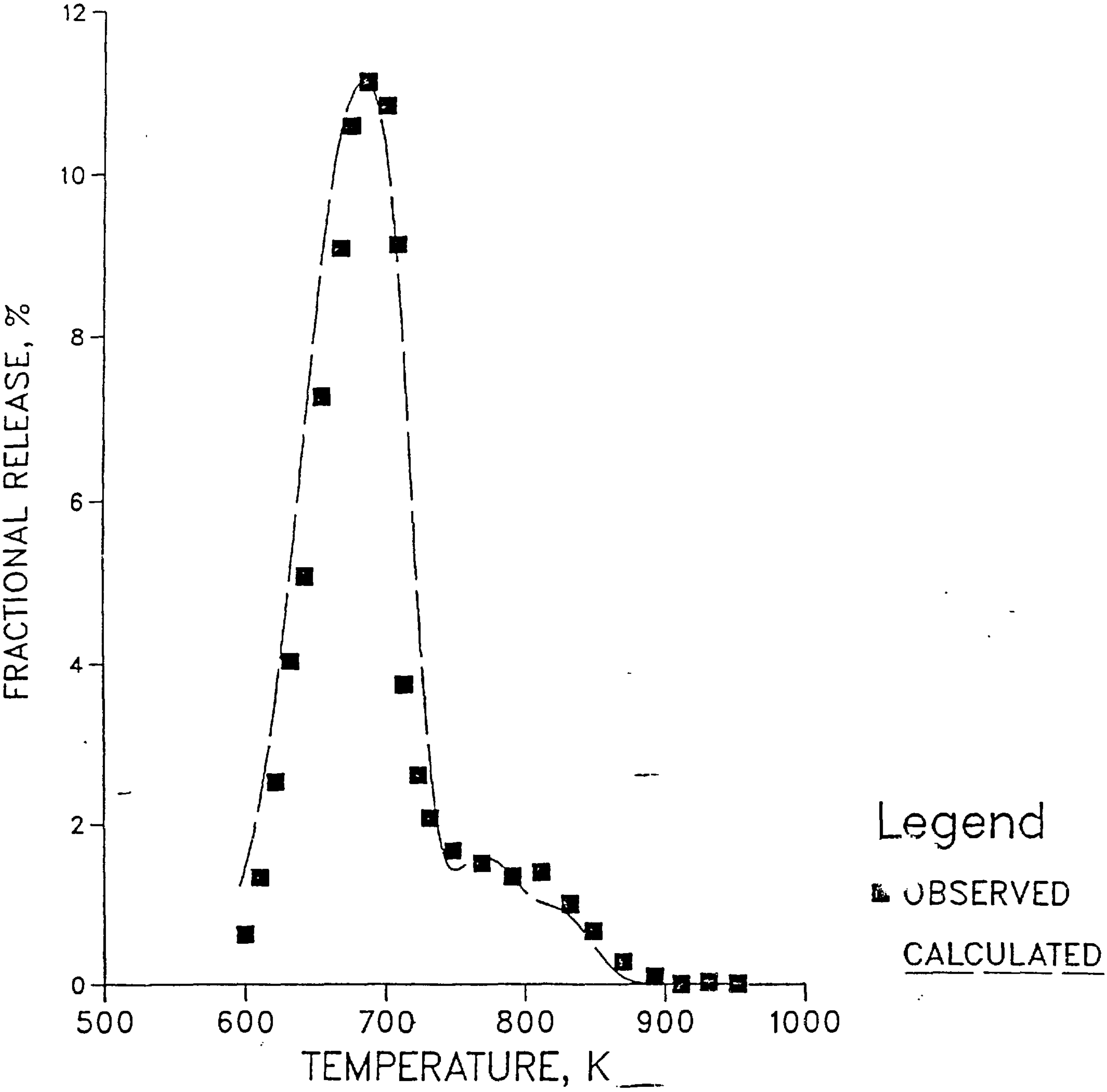
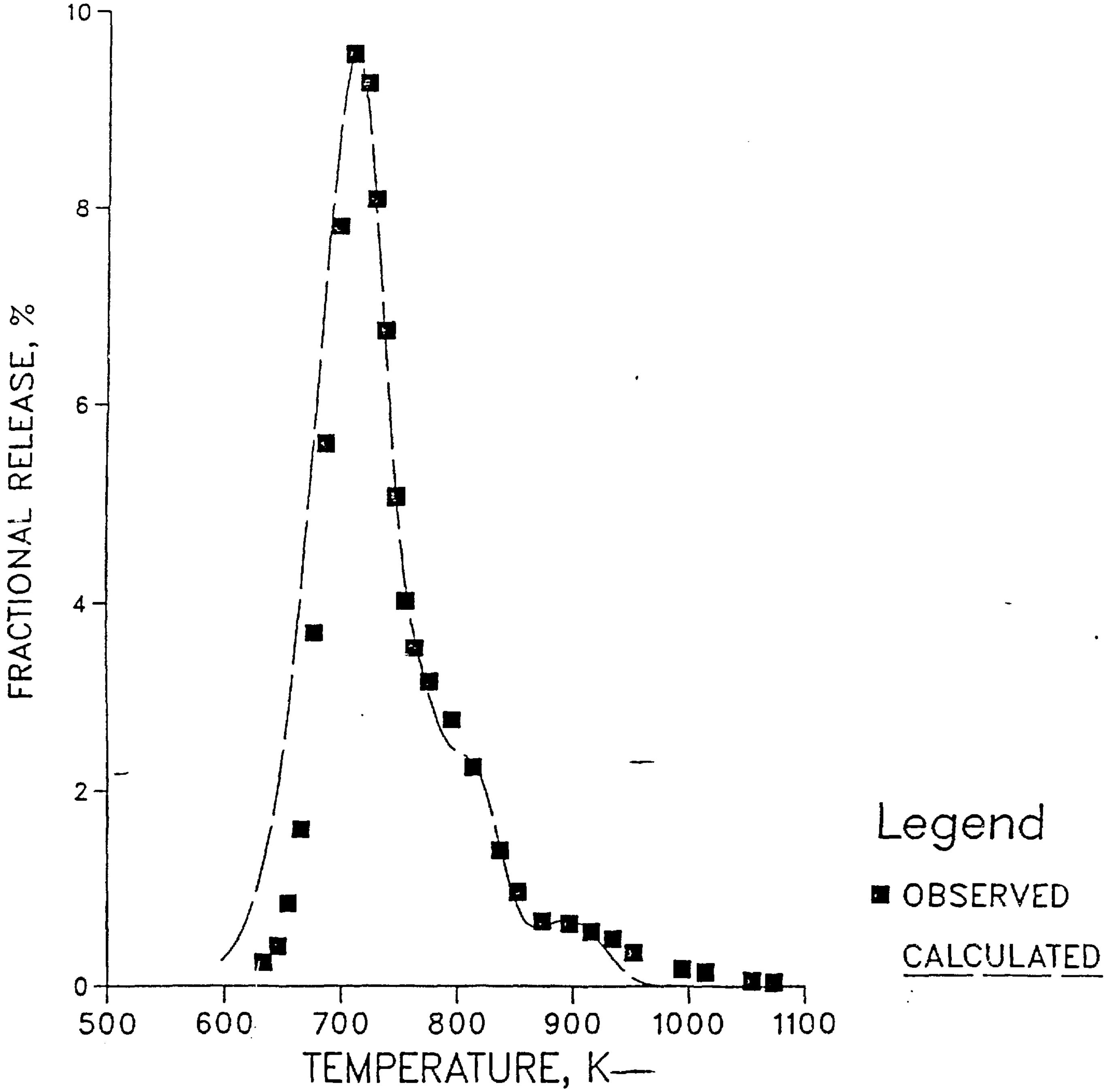
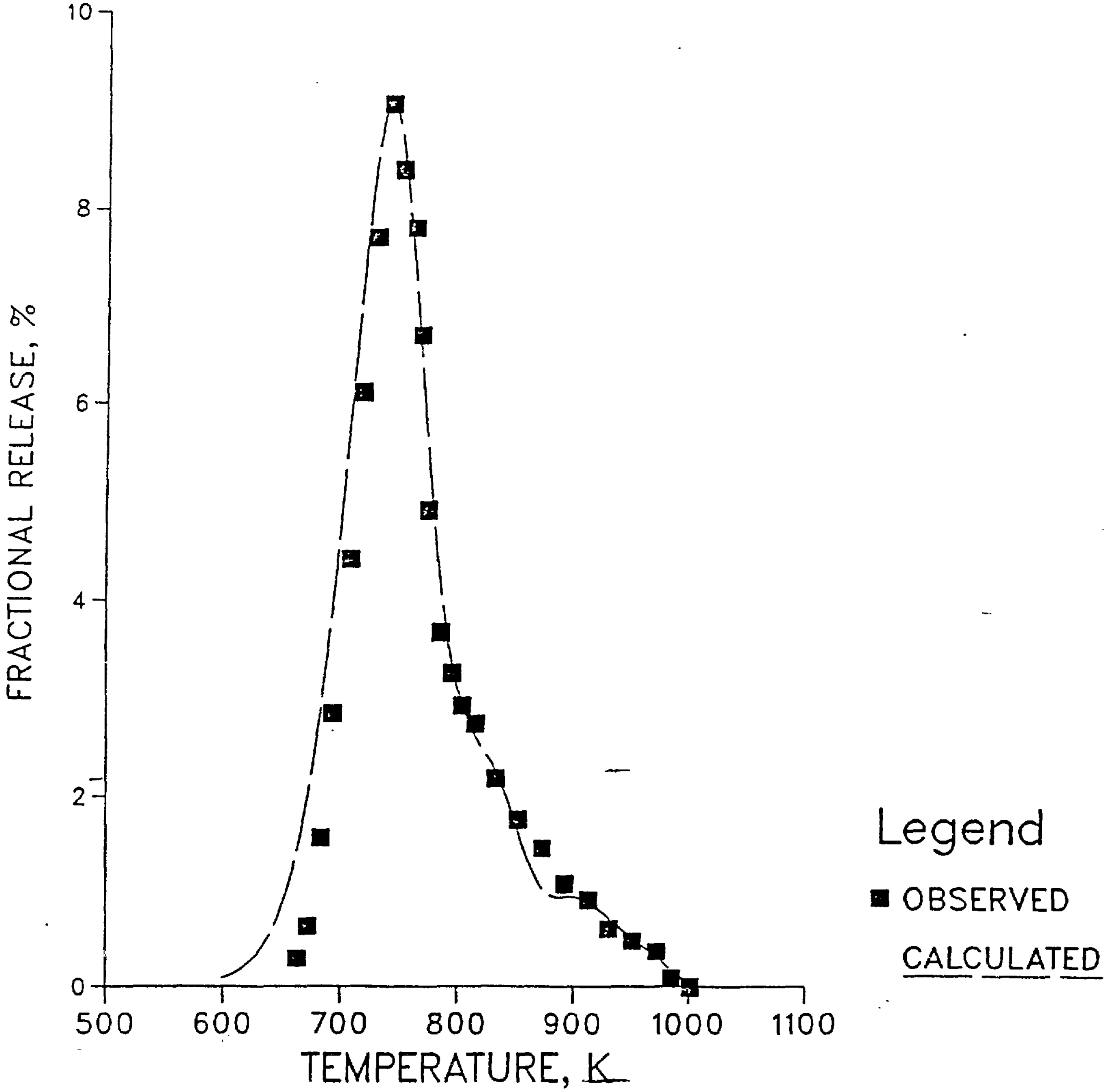

FRACTIONAL RELEASE, %
12
10
8
6
4
2
0
500
600
700
800
900
1000
TEMPERATURE, K
Legend
■ OBSERVED
CALCULATED

Fig 7D



FRACTIONAL RELEASE, %
10
8
6
4
2
0
500
600
700
800
900
1000
1100
TEMPERATURE, K—
Legend
■ OBSERVED
CALCULATED

4c


10
8
6
4
2
0
FRACTIONAL RELEASE, %
500
600
700
800
900
1000
1100
TEMPERATURE, K
Legend
■ OBSERVED
CALCULATED