To be presented at the 25th National Vacuum Symposium, San Francisco, CA
11/27 - 12/1/78.

HEAT OF VAPORIZATION SPECTROMETER*

D. Edwards, Jr.
Brookhaven National Laboratory
Upton, New York

Abstract

Multilayer desorption measurements of various substances adsorbed on a stainless steel substrate are found to exhibit desorption profiles consistent with a zeroth order desorption model. The singleness of the desorption transients together with their narrow peak widths makes the technique ideally suited for a heat of vaporization spectrometer for either substance analysis or identification.

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

*Work performed under the auspices of the U.S. Department of Energy.

61A

CONFIDENTIAL

MASTER

I. Introduction

Recently multilayer desorption results have been reported¹ for a small number of layers adsorbed on a single crystal substrate. It is the purpose of this study to examine the desorption properties of a larger number (20-100) of adsorbed layers of various substances (ammonia, acetone, water, methanol, carbon dioxide) adsorbed onto a stainless steel substrate. The present results have indicated that the desorption process occurs in a single transient (as opposed to the submonolayer desorption spectra), the profile of which is consistent with a simple zeroth order desorption model.

II. Instrument

The instrument which has been used to measure the multilayer desorption processes is shown schematically in Fig. 1. Briefly it consists of a coolable stainless steel sample attached onto a small (0.3 L volume) all metal vacuum chamber with a thermocouple type gauge for pressure measurements. The system is connected through two all-metal valves to a gas input manifold and a LN_2 trapped mechanical pump respectively. The chamber is operated at 50-70 C to reduce wall adsorption effects during the desorption cycle. In addition a small (0.3 L/s) orifice has been inserted in the pump circuit reducing the vacuum time constant to 1.0 s when the valve is fully opened. The sample itself is in thermal contact with a rather large block of Al to minimize temperature gradients over the 9.4 cm^2 of geometric sample area. A thermocouple attached to the Al block is used for temperature measurements and a heater attached

to the tube slightly above the sample insures that the sample is, in fact, the coldest part of the system.

All temperatures are derived from the thermocouple reference table without adjustment. As a partial check of the temperature measurement system the sample was immersed in LN_2 with a temperature reading of 76.7 K and in an ice bath with a temperature reading of 274 K. It should be noted that before the cooldown is started the sample temperature is 90 C.

III. Measurement Technique

With the sample warm the gas to be adsorbed is introduced into the system to a pressure typically of 0.4 Torr which consists of 3.9×10^{18} molecules. Assuming a surface roughness factor of ~ 4 , there will be $\sim 10^{17}$ molecules per cm^2 of real area after cooldown or ~ 100 monolayers of adsorbed molecules. After introducing the gas into the system the sample is cooled down to 77 K by immersing a portion of the Al block in LN_2 . When cold (~ 10 min.) the LN_2 is removed and the sample temperature increases at a rate of ~ 0.1 K/s.

Two modes of desorption measurements are used. The first consists of desorbing the gas into a pumpless system and monitoring dp/dt . The pressure during the desorption cycle should increase until the adsorbed layer is depleted after which the pressure should be constant. dp/dt will exhibit the peak nature of the desorption transient in this mode.

The second mode used consists of having the pump valve open during the desorption and allows the peak of the desorption process to be observed by monitoring $p(t)$ alone.

Knowledge of the peak temperature, T_p , and peak width, ΔW , will enable the heat of vaporization of the desorption process to be determined from a single transient measurement. Details of the analysis will be presented elsewhere with only the results listed below.

$$E/KT_p = \frac{\ln 2}{w} \{1 + \varphi(w)\} , \text{ dp/dt mode} \quad (1)$$

$$\frac{\ln 2}{w} \{1 + \varphi(w)\} , \text{ p(t) mode}$$

where $w = \Delta W/T_p$. It is noted that the equations are independent of either the temperature sweep rates or adsorbed layer thicknesses and have been derived allowing the possibility of large sample pumping during the desorption process.

IV. Experimental Results

Figure 2 shows water vapor measured using the two modes described above. Both transients are seen to have i) the very rapid fall after the peak maximum characteristic of a zeroth order desorption process, and ii) a single peak structure; i.e. no evidence that the stainless steel substrate is causing any multiple peak structures. That the peaks occur at different temperatures is explicit evidence that readsorption is occurring during the desorption process. Said slightly differently if there were no sample readsorption during desorption both peaks would occur at the same temperature for these two measurement modes although the transients would have slightly different widths. It is noted that for the dp/dt mode three or more trials are in general made with the same charge of gas.

Figure 3 shows the acetone desorption transient again exhibiting the very sharp cutoff following the peak maximum and the very small peak width ($\Delta W/T_p \approx 0.036$) as compared with a normal first order desorption process² ($\Delta W/T_p \approx 0.080$).

In Fig. 4 the desorption of pure methanol is shown together with that obtained with the addition of 50% water vapor. Although the dynamics of the peak distortion seen in this figure is likely quite complicated it is clear that water vapor is able to significantly distort the pure methanol desorption spectrum.

The ammonia transient shown in Fig. 5 again exhibits the normal type of transient profile while lastly in Fig. 6 the CO_2 spectrum is reported for a 25 layer film.

Heats of vaporization are obtained for the substances studied via Eq. (1), and the results are listed in Table I. Seen is that the desorption energy values obtained here are within ~ 1 K cal/mole of the reference values. For closer comparisons more precision is necessary for the measurement of the desorption transient width which at present has an uncertainty of $\sim 10\%$.

In summary, the desorption transients studied exhibit single structures the profiles of which are consistent with a zeroth order desorption process. Thus, the instrument should be able either to determine the heat of vaporization of known substances or to identify unknown substances by a heat of vaporization determination.

References

1. T.E. Madey and J.T. Yates, Jr., Surf. Sci. (in press).
2. E.V. Kornelsen (private communication).
3. Handbook of Chemistry and Physics (Chemical Rubber Co., Cleveland, Ohio 1977 ed.)

Table I.

Substance	Mode	T_p (K)	E (kcal/mole)	$E^{(3)}$
Acetone	$\Delta p/\Delta t$	200	8.3	7.6
Methanol	$\Delta p/\Delta t$	218	9.0	9.4
H ₂ O	$\Delta p/\Delta t$	241	11.4	10.9
H ₂ O	p	212.5	11.4	
NH ₃	$\Delta p/\Delta t$	153	6.7	7.5
CO	$\Delta p/\Delta t$	125	5.5	5.5
CO	p	115	4.6	

Figure Captions

- Fig. 1. A schematic of the desorption instruments showing the sample cell, pressure gauge, etc.
- Fig. 2. Water vapor desorption (~ 90 layers) measured using the two different modes. The open circles correspond to the dp/dt mode whereas the dots indicate the $p(t)$ mode.
- Fig. 3. The average of ~ 5 trials of the desorption of ~ 100 layers of acetone. Note that some desorption seems to be occurring after the multilayer transient is completed.
- Fig. 4. The desorption of methanol and methanol plus water vapor. Note that the composite spectra is not the simple superposition of the methanol and water vapor spectra.
- Fig. 5. The desorption of NH_3 (3 trials) measured in the dp/dt mode.
- Fig. 6. The desorption of 25 layers of carbon dioxide measured in the $p(t)$ mode.

Table Captions

Table I. The heat of vaporization, E , evaluated by means of the present desorption data is compared with the values found in Ref. 3. (See text for discussion.)

- Fig. 1 9-857-78
2 9-854-78
3 9-853-78
4 9-852-78
5 9-848-78
6 9-849-78

9-76-1

ACETONE, 400μ

$T_p \approx 200\text{ K}$, $\Delta W \approx 7.3\text{ K}$

30

22.5

15

7.5

0

$\Delta P/\Delta t$
($\mu/10\text{s}$)

100

120

140

160

180

200

220

240

T (K)

NH_3 , 280μ $\Delta W = 4.5 \text{ K}$ $T_p = 155.4 \text{ K}$

50

40

 $\Delta P / \Delta t \text{ (}\mu\text{/11s)}$

30

20

10

0

-10

100

110

120

130

140

150

160

170

180

T (K)