Int. J. Heat Mass Transfer. Vol. 13, pp. 1559-1570. Pergamon Press 1970. Printed in Great Britain

DIFFUSION AND CHEMI-DESORPTION RATE COEFFICIENTS FROM DESORPTION TRANSIENT MEASUREMENTS

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(*Received* 21 *April* 1969 *and in revised form* 6 *March* 1970)

Abstract—The rates of gas release from a solid which is subjected to a linear temperature increase, i.e. desorption transients, have been computed assuming bulk diffusion to be the rate controlling process. The sample shapes considered are those of a sphere, a cylinder of infinite length, and a plane sheet of infinite extension. The assumed activation energies of diffusion range from 5 to 60 kcal/mole while $D_0/a^2\beta$ lies between 10^{-4} and 10^{+11} (time^{-1}), *a* being the radius of the sphere, or the cylinder, or the half-thickness of the plane sheet. The results are presented in a form suitable for simplified curve fitting of experimental data. Based on this procedure, one can normally distinguish single or uncomplicated diffusion processes from simple surface desorptions; the rate controlling steps in composite processes, however, can usually be identified only if additional experimental criteria are used.

NOMENCLATURE

a,	radius of sphere or cylinder, or half thickness of plane sheet considered as sample;
b,	constant, only used in equation (8);
c,	concentration of sorbate, equation (1) only;
D,	diffusion coefficient;
D_0,	preexponential factor in Arrhenius equation (3);
E,	activation energy for diffusion, equation (3);
M_t,	amount of sorbate desorbed at time t;
M_∞,	total amount of sorbate desorbed after infinite time;
n,	summation index, equations (5)–(7) only;
t,	time;
t',	time as integration variable, equation (2) only;
T,	absolute temperature;
T_0,	initial temperature in a given experiment;
$T(m)$,	temperature at which desorption rates reach maximum;
$T(\frac{1}{2}, l)$,	temperature at which rates are one half the maximum rate, on left branch of desorption transient;
$T(\frac{1}{4}, l)$ $T(\frac{1}{2}, r)$, $T(\frac{1}{4}, r)$,	defined analogous to $T(\frac{1}{2}, l)$;
α_n,	zeros of zeroth order Bessel functions divided by "a" equation (5) only;
β,	constant, equation (4) only;
τ,	modified time, defined by equation (2).

INTRODUCTION

DIFFUSION and chemi-desorption rate coefficients are normally calculated from data obtained under isothermal conditions [1–3]. The experimental measurements and the data evaluation are often relatively simple, in this case, but very lengthly experiments may be required to obtain useful results, especially for the activation energies. By contrast, the rates of gas desorption from samples which are heated at a suitable rate, often termed desorption transients, can normally be measured within a much shorter time, hours or minutes. Many chemisorption studies have been carried out by this method [4–6], but only few workers have used this approach to obtain bulk diffusion coefficients and corresponding activation energies, presumably because the evaluation of the experimental data is cumbersome. In some of these previous studies, the initial distribution of the diffusate in the bulk of the solid is non-uniform [7–9], and the desorption transients therefore depend on the nature and the range of this sorbate distribution, or concentration profile. Also, there are many instances where several different diffusion mechanisms are known to compete with each other, in certain temperature ranges [7, 8].

To cope with some of these complications, many desorption transients were computed and are presented in this report. The computations refer to one of the simplest cases of diffusion rate control, i.e. where the concentration of diffusate is initially uniform throughout the material, where only a single diffusion process is important, and where the sample temperature increases linearly with time. Hanbaba and his co-workers [11] have computed some typical desorption transients for this particular case, but their results are not detailed enough to be of general utility.

As will be clear later, the computed results will probably be useful in discerning the dominant mechanisms in many desorption experiments, especially if used in conjunction with other approaches. The work is thus somewhat analogous to the studies of Redhead [4], and of Madey and Yates [6], who discussed the evaluation of desorption transients for experiments where one or several surface processes were rate controlling.

COMPUTATIONS

The programs used in this work are based on the usual transformation of Fick's second law [12] for the case where the diffusion coefficient, D, can be assumed to be a function of time [13]:

$$\frac{\partial c}{\partial \tau} = \frac{\partial^2 c}{\partial x^2} \tag{1}$$

with

$$\tau \equiv \int_0^t D(t')\,\mathrm{d}t' \tag{2}$$

where c is the concentration of diffusing substance at point x and at the modified time τ. Next, the Arrhenius equation

$$D = D_0 \exp(-E/RT) \tag{3}$$

is used to relate D and T, all symbols having their standard meaning. For the present, the temperature is assumed to increase linearly with time, t, that is

$$T = T_0 + \beta t \tag{4}$$

and in the bulk of this work:

$$T_0 = 0 \qquad \beta = 1{\cdot}0\,(^\circ/\text{min}) = \text{constant}.$$

[The cases $T_0 \neq 0$ and $\beta \neq 1{\cdot}0$ (°/min) will be discussed briefly, at a later time.]

The first step of the computation consists of substituting equations (4) and (3) into equation (2) to obtain τ at various t, using a 16 point Gaussian quadrature formula.

Next, the τ values so obtained are used in the appropriate solutions to the diffusion equation [14]. One obtains for a cylinder of infinite length and radius a.

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} (4/a^2\alpha_n^2)\exp(-\alpha_n^2\tau) \tag{5}$$

for a plane sheet of infinite extension and thickness $2l$:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty} [1/(2n+1)^2] \times \exp(-(2n+1)^2\pi^2\tau/l^2) \tag{6}$$

and for a sphere of radius a:

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} (1/n^2) \exp(-n^2\pi^2\tau/a^2). \qquad (7)$$

In all equations, M_t/M_∞ is the fractional amount of diffusate desorbed at time t, and the quantities $a\alpha_n$ in equation (5) are the roots of the Bessel functions of zeroth order [15].

The M_t/M_∞ ratios were computed from above equations, using 40 terms in the sum of equation (5), while the series in equations (6) and (7) were cut off when the terms became smaller than 10^{-5} or 10^{-7}. From the ratios M_t/M_∞ finally, the rates of desorption were computed as difference quotients, $(1/M_\infty)(\Delta M_t/\Delta t)$.

The programs are flexible enough to compute selected portions of desorption rate curves for intervals Δt adjustable from 1 (s or min) on up, and the first and last term of each sum are given in the print-out to facilitate the verification of the computations.

RESULTS

Table 1 contains the principal results from this work, that is: $T(m)$, the temperatures at which the desorption transient maxima occur, $T(\frac{1}{2}, l)$ and $T(\frac{1}{2}, r)$, the temperatures at which the rates become equal to one-half of $T(m)$, at the left or ascending branch of each curve $[T < T(m)]$, and the right or descending branch $[T > T(m)]$, respectively. Figure 1 illustrates some typical results on a semi-logarithmic scale for the three different geometries discussed here, corresponding to equations (5)–(7).

The information contained in Table 1 defines the desorption transient curve shapes within narrow limits: If one defines $T(\frac{1}{4}, l)$ and $T(\frac{1}{4}, r)$ as the temperatures at which the desorption rates are one quarter of the rate at $T(m)$, on the left and right branches, respectively, one can calculate and compare the ratios

$$\frac{T(m) - T(\frac{1}{2}, l)}{T(m) - T(\frac{1}{4}, l)} \quad \text{and} \quad \frac{T(\frac{1}{2}, r) - T(m)}{T(\frac{1}{4}, r) - T(m)}.$$

It turns out that these ratios vary only little

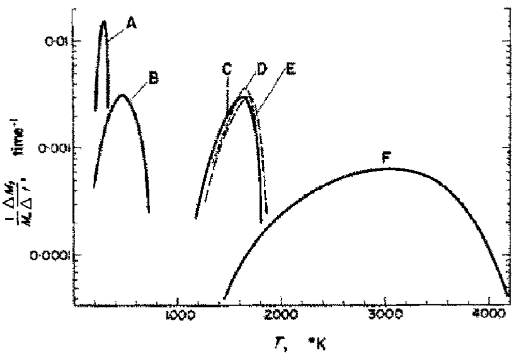

FIG. 1. Rates of desorption $(1/M_\infty)\ \Delta M/\Delta t$ (min^{-1}) as a function of temperature. All curves computed for bulk diffusion rate control, assuming the temperature to increase linearly with time. Curves (A), (B), (C) and (F) pertain to a spherical sample, Curve (D) to a plane sheet and Curve (E) to a cylinder. The activation energies, E(kcal/mole) and the parameters $D_0/a^2\beta$ (deg^{-1}) assumed are: Curve (A), 10 and 10^5, respectively; (B) 5 and 10^{-1}; (C), (D) and (E), 60 and 10^5; (F) 40 and 10^{-1}. D_0 is the pre-exponential factor in the Arrhenius equation 3, β is the rate of heating, a the radius of the spherical sample. $T_0 = 0$ in these computations.

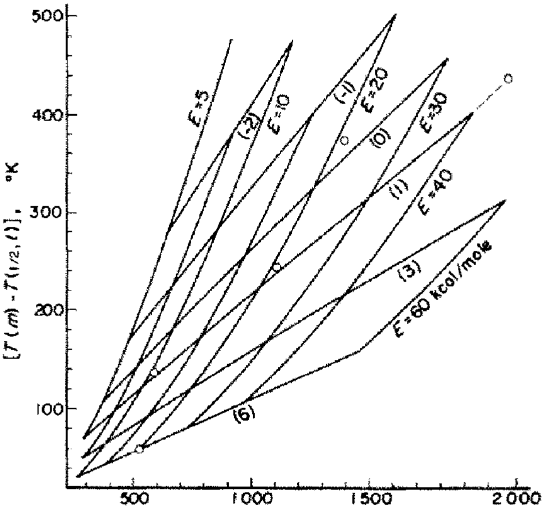

FIG. 2. Differences $[T(m) - T(\frac{1}{2}, l)]$ against $T(m)$ for computed desorption transients. $T(m)$ is the temperature at which the maximum rate occurs, $T(\frac{1}{2}, l)$ is the temperature at which the rates first become one-half of the maximum rates, on the ascending part of each curve (see Fig. 1). E is the activation energy (kcal/mole) Numbers in parentheses are the logarithms of $(D_0/a^2\beta)$, defined as in the legend to Fig. 1. Encircled points are computed for samples of (infinite) cylindrical shape; the E and $(D_0/a^2\beta)$ parameters for these points are the same as those for the closest intersection points to the lower left, in each case.

Table 1. Characteristic parameters of desorption transients

E(kcal/mole) \ Log $(D_0/a^2\beta)$		−4			−3			−2			−1		
		$T(\frac{1}{2}, 1)$	$T(m)$	$T(\frac{1}{2}, r)$	$T(\frac{1}{2}, l)$	$T(m)$	$T(\frac{1}{2}, r)$	$T(\frac{1}{2}, l)$	$T(m)$	$T(\frac{1}{2}, r)$	$T(\frac{1}{2}, l)$	$T(m)$	$T(\frac{1}{2}, r)$
5000	C	537·9	1351·4	4695·6	460·5	1062·9		401·3	759·2	1135·2	337·7	541·9	698·9
	P	522·1	1613·2	(4675)	510·9	1259·1	1932·1	443·9	780·0	1018·1	363·3	531·3	641·0
	S	478·8	1207·2	(3490)	430·1	906·8	1736·5	368·6	651·2	970·4	309·5	477·7	626·4
7500	P												
	S		1736·9	4615·1	629·6	1284·2	2327·2	537·0	922·7	1339·9	450·0	681·7	879·3
10000	C	1017·1	2550·5	(7460)	(880)	1931·9	(3507)	763·7	1367·9	1932·4	634·4	987·1	1238·5
	P	1044·0	3223·3	(7010)	991·2	2162·2	3111·4	838·0	1376·1	1745·0	682·7	962·8	1142·5
	S	932·8	(2235)	(5620)	824·4	1642·9	2872·6	700·0	1181·8	1684·0	587·1	877·7	1120·6
15000	P												
	S				(1210)	(2310)		1018·2	1677·1	2332·2	853·7	1255·0	1580·6
20000	C							1449·9	2469·0	3334·8	1211·7	1806·2	2215·1
	P							1577·2	(2452)	3031·9		(1740)	
	S							1328·0	2151·8	2944·8	1113·9	1618·8	2020·6
30000	P												
	S										1621·6	2319·8	(2850)
40000	C												
	P												
	S										(2217)	(2997)	
60000	C												
	P												
	S												

Table 1 —*continued*

Log ($D_0/a^2\beta$) / *E*(kcal/mole)		0			1			2			3		
		$T(\frac{1}{2}, l)$	$T(m)$	$T(\frac{1}{2}, r)$	$T(\frac{1}{2}, l)$	$T(m)$	$T(\frac{1}{2}, r)$	$T(\frac{1}{2}, l)$	$T(m)$	$T(\frac{1}{2}, r)$	$T(\frac{1}{2}, l)$	$T(m)$	$T(\frac{1}{2}, r)$
5000	C	282·5	404·1	483·8	237·9	315·8	362·2	203·6	256·2	286·1			
	P	296·6	392·1	451·6	246·6	306·1	342·3	208·9	248·9	273·0			
	S	260·2	365·9	445·3	221·3	291·2	339·2	190·8	239·8	271·2			
7500	P	430·3	560·8	642·5									
	S	379·0	525·3	634·0	323·0	421·2	487·6	279·2	348·8	392·5	244·8	295·8	326·6
10000	C	535·3	747·1	(883)	453·4	589·9	671·3	389·7	484·2	537·3	339·7	408·2	445·2
	P	560·3	723·9	827·5	468·2	537·0	636·7	399·0	470·9	513·9	346·0	397·8	428·5
	S	494·8	680·8	815·5	422·6	547·9	631·3	366·0	454·8	510·6	321·3	386·8	426·4
15000	P	813·0	1038·8	1178·2				(583)	(684)	(745)			
	S	721·3	979·8	1164·8	617·5	793·8	909·8	536·2	661·9	740·3	471·7	565·1	621·2
20000	C	1017·2	1386·2	1613·1	864·9	1109·7	1250·2	746·7	917·9	1012·1	653·7	779·1	846·0
	P	1059·6	1343·2	1518·2	890·7	1076·6	1189·0	763·2	892·9	970·1	664·8	759·2	815·5
	S	942·5	1270·0	1501·8	808·2	1032·9	1179·9	703·0	864·3	964·3	619·4	739·9	811·7
30000	P	1538·9	1932·1	2173·5				(1216)	(1300)	(1409)			
	S	1374·5	1832·8	2151·4	1181·9	1498·7	1703·8	1030·3	1259·8	1400·6	909·8	1081·9	1184·1
40000	C	1934·2	2582·7	2971·5	1652·3	2089·8	2337·1	1432·7	1743·1	1912·3	1259·2	1488·9	1611·1
	P	2006·8	2502·9	2806·5	1697·2	2028·9	2228·4	1461·9	1696·1	1836·3	1279·1	1452·8	1555·4
	S	1797·3	2378·9	2779·3	1547·6	1952·7	2212·6	1350·9	1646·1	1825·9	1195·3	1417·1	1548·3
60000	C	2818·9	3722·5	4257·9	(2420)	(3010)	(3365)	2098·7	2539·2	2778·0	1848·7	2176·8	2350·5
	P	2918·3	3608·2	4029·1	(2490)	(2920)	(3220)	2140·0	2472·7	2670·8	1872·8	2124·7	2271·0
	S	2623·0	3438·5	3992·2	2264·8	2837·1	3201·2	1982·4	2401·5	2656·2	1756·6	2074·5	2261·3

Table 1—*continued*

E(kcal/mole) \ Log $(D_0/a^2\beta)$		4			5			6			7		
		$T(\frac{1}{2}, l)$	$T(m)$	$T(\frac{1}{2}, r)$	$T(\frac{1}{2}, l)$	$T(m)$	$T(\frac{1}{2}, r)$	$T(\frac{1}{2}, l)$	$T(m)$	$T(\frac{1}{2}, r)$	$T(\frac{1}{2}, l)$	$T(m)$	$T(\frac{1}{2}, r)$
5000	C												
	P	157·8	179·1	202·2									
	S												
7500	P	231·8	261·9	279·8									
	S	217·1	255·9	278·6	195·1	225·0	242·1						
10000	C	300·1	351·5	378·7	268·3	307·9	328·6	241·8	273·4	289·7			
	P	304·0	343·1	366·2	271·2	301·2	319·0	244·1	268·1	282·1			
	S	285·4	335·4	364·7	256·2	295·5	317·9	232·1	263·8	281·2	211·9	237·8	251·9
15000	P	447·0	502·8	534·5				(360)	(393)	(415)			
	S	419·8	491·8	532·3	377·5	433·9	466·2	342·0	387·9	413·5	312·9	250·2	371·0
20000	C	579·4	674·3	724·3	519·3	593·3	632·2	470·1	529·5	559·3			
	P	587·3	659·1	701·5	524·9	581·1	613·9	473·9	518·8	546·1			
	S	552·1	644·9	698·6	497·0	570·1	611·9	451·5	510·9	543·6	412·8	461·9	488·4
30000	P	862·8	965·8	1026·4				(699)	(763)	(800)			
	S	812·4	945·8	1022·6	732·5	838·1	898·1	665·9	751·5	799·5	609·8	680·9	719·7
40000	C	1120·0	1259·9	1387·7	1006·7	1145·1	1216·3	912·9	1024·2	1081·0			
	P	1134·2	1267·1	1345·3	1017·1	1121·9	1182·9	920·7	1005·1	1052·4			
	S	1068·7	1241·1	1340·3	965·7	1102·0	1179·4	878·5	990·2	1051·5	804·8	897·1	947·7
60000	C	1647·9	1900·2	2031·4	1483·3	1682·9	1785·3	1347·0	1508·2	1590·2			
	P	1667·7	1858·5	1970·8	1498·0	1649·0	1737·5	1358·1	1480·2	1551·7			
	S	1573·3	1821·5	1963·8	1422·4	1620·9	1732·5	1296·2	1458·2	1547·6	1189·7	1323·9	1397·2

Table 1—*continued*

Log $(D_0/a^2\beta)$ / E(kcal/mole)		8			9			10			11		
		$T(\frac{1}{2}, l)$	$T(m)$	$T(\frac{1}{2}, r)$	$T(\frac{1}{2}, l)$	$T(m)$	$T(\frac{1}{2}, r)$	$T(\frac{1}{2}, l)$	$T(m)$	$T(\frac{1}{2}, r)$	$T(\frac{1}{2}, l)$	$T(m)$	$T(\frac{1}{2}, r)$
5000	C												
	P												
	S												
7500	P												
	S												
10000	C												
	P												
	S	194·8	216·2	227·9	180·1	198·1	207·0	167·2	182·8	191·1			
15000	P												
	S	287·9	319·1	336·2	266·4	293·0	307·2	247·8	270·4	282·6			
20000	C												
	P												
	S	380·0	420·9	443·1	351·9	386·6	405·2	327·7	357·2	372·6	306·2	331·9	345·5
30000	P												
	S	562·3	621·7	653·9	521·1	571·9	598·7	485·4	528·5	551·8			
40000	C												
	P												
	S	742·4	819·9	861·9	688·5	754·7	789·9	641·7	698·4	728·6			
60000	C												
	P												
	S	1098·5	1211·5	1272·5	1019·7	1116·2	1167·6						

E is the assumed activation energy of diffusion, see equation (3). $(D_0/a^2\beta)$ contains the pre-exponential factor of that equation, D_0, divided by the square of the typical length parameter, a, see equations (5)–(7), and by β, the rate of heating. $(D_0/a^2\beta)$ has the dimensions of (deg^{-1}): consequently the dimensions of β must be observed in calculating D_0.

$T(m)$, $T(\frac{1}{2}, l)$, and $T(\frac{1}{2}, r)$ are defined in the text. All temperatures are given in °K. Values in parentheses are approximate. C, P and S designate data obtained for cylindrical, planar and spherical sample shape, respectively.

with E and $(D_0/a^2\beta)$ where $(D_0/a^2\beta)$ stands for $(D_0/a^2\beta)$ or $(D_0/l^2\beta)$, the principal parameters in these computations. The ratios range from about 0·66 to 0·79.

Figure 2 shows $[T(m) - T(\frac{1}{2}, l)]$ plotted against $T(m)$ for the spherical sample shape, corresponding to equation (7), with a few points indicating the corresponding results for a cylindrical sample, according to equation (5). A family of curves of similar appearance can be drawn from the data in Table 1 for the quantity $[T(\frac{1}{2}, r) - T(m)]$, as a function of $T(m)$. There is very good agreement of these data with those reported by Hanbaba and his co-workers [11], considering the appreciable reading errors in using Fig. 2 of that study.

The $T(m)$, $T(\frac{1}{2}, l)$ and $T(\frac{1}{2}, r)$ values listed in Table 1 are considered accurate to a few tenths of a degree, except in a few cases as indicated. The data are thus quite suitable for precise non-linear interpolations*.

From the practical point of view, one can use working drawings of the type shown in Fig. 2, to obtain a first estimate of E and $(D_0/a^2\beta)$ as soon as the quantities $T(m)$ and $[T(m) - T(\frac{1}{2}, l)]$ have become available, in the course of a given experiment. Later on, when $[T(\frac{1}{2}, r) - T(m)]$ is known, this may serve to refine the earlier estimates of E and $(D_0/a^2\beta)$ or to test the agreement of experimental and computed curve shapes.

The ratios involving $T(\frac{1}{4}, l)$ and $T(\frac{1}{4}, r)$ defined above, or the entire computed desorption transient curves may be of value in this phase of the work, provided the experimental data are very precise.

DISCUSSION

As stated earlier, the computed desorption transients presented in this study are to furnish a simple basis for estimating the parameters E and D_0 in the Arrhenius equation (3), wherever one can be sure that the desorption rates are controlled by bulk diffusion. Conversely, when the rate controlling process is not identified with certainty, it would be interesting to have useful and unambiguous criteria to make this identification.

From Fig. 1, above, it is clear that diffusion rate controlled desorption transients have simple and similar curve shapes, even though the half-widths differ greatly. Curves of such general shape of course can always come about accidentally, that is by a superposition of desorption processes, whether bulk diffusion or surface rate controlled.

Assuming for the moment that this complicacation does not exist, one may consider two methods, (A) and (B) for discerning bulk diffusion rate control from certain other possibilities.

(A) In principle, and if the experimental data are of high precision, one can carry out a detailed computer-based fit of all data, using for example the computer programs described in this work to test for diffusion rate control, or the formal developments of Redhead [4] or of Grant and Carter [10] to test for the presence of first or second order surface desorption processes, or the calculations of Carter *et al.* [16, 17] to determine whether desorption may have occured by a single-jump mechanism from a sorbate layer below the surface.

(B) A second fairly direct method of distinguishing diffusion rate control from other processes, which might be successful in many cases, is based on order of magnitude estimates of the (apparent) Arrhenius parameters, E and D_0, as obtained from the comparison of the experimental data with Table 1 or Fig. 2. For example, the surface desorption transients or the subsurface layer desorption transients computed by Grant and Carter [18] have $T(m)$ and $\Delta T = T(\frac{1}{2}, r) - T(\frac{1}{2}, l)$ values which would lead to very high $(D_0/a^2\beta)$ parameters, perhaps 10^{15} or 10^{17} (deg^{-1}) and activation energies, E, between 30 and 40 (Kcal/mole) based on a rough extrapolation of the data of Table 1. Using $\beta = 1$ (deg/s) and assuming that the desorption transients in

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* Representative runs and copies of the computer programs, together with explanatory notes are available from the American Society for Information Sciences, NAPS-00939.

question were measured on a thin glass sheet of half-thickness 10^{-2} (cm), one estimates $D_0 \geqslant 10^9$ (cm^2/s). This value in turn is outside the range of known values, for approximately the same activation energies [19]. The estimate must thus be distrusted or discarded and a process other than diffusion rate control becomes more likely, as was indeed assumed in the model calculations [18].

It is interesting to note that the activation energy determined on the wrong assumption, as described in this example, is quite close to the one assumed in the original model calculation. Similar agreement is obtained if the procedure is applied to the desorption transients computed by Redhead [20]. As a consequence, comparisons of activation energies are not as useful as those of the parameters $(D_0/a^2\beta)$ in trying to determine the dominant mechanism.

Parenthetically, one may note that in desorption studies on catalysts Amenomiya and Cvetanovič [5] used plots of 2 log $T(m)$ vs. $1/T(m)$ for $T(m)$ values obtained at different heating rates, β, to determine the activation energies of the desorption processes. If one uses the data of Table 1 to produce an analogous plot, one again obtains fairly straight lines with slopes very similar to those of [5] for the same activation energies. Clearly this type of plot, and the activation energies determined from it do not permit one to identify the mechanism involved in the process.

Returning now to the problem of analyzing desorption rate data if several mechanisms are present, one recognizes at once that any such superposition would normally lead to desorption transients of increased half-widths. To identify the component mechanisms one probably must use additional experimental criteria. A curve fit based on the present computed results alone seems insufficient.

A very interesting illustration of this situation arises in the work of Hanbaba *et al.* [11]. On the one hand, these authors found excellent agreement between experimental and computed transients and yet one can see from the grain size dependence of the apparent diffusion coefficients that the materials they studied were heterogeneous, as far as bulk diffusion is concerned, or that a superposition of surface or bulk mechanisms controlled the rate. As a consequence, the agreement of experimental and computed transients may be considered fortuitous, in this case.

A second case in point arises in the desorption studies of Grant and Carter [21]. These workers introduced noble gases into glasses by ion bombardment, and they found broad desorption transients which could not be ascribed to surface desorption by a single mechanism. It is known that ion bombardment leads to a very non-uniform initial concentration of sorbate, high near the surface and decreasing toward the interior [7, 8]. Furthermore, experimental evidence and theory indicate that the concentration profile approaches a typical form as the desorption experiment progresses [22, 23] and it is therefore plausible that the right or descending branches, $T > T(m)$, of the desorption transients agree with the curves computed for a uniform initial distribution of sorbate, as presented in this study.

On the other hand, the left or ascending branches of the transients measured by Grant and Carter [21] also fit the computed results rather well, in spite of the very non-uniform initial distribution of sorbate. Carter interpreted this by assuming that the atoms located near the surface can desorb via a single jump, but are held at their respective sites by a wide range of binding energies. As an alternative, one may consider damage diffusion to be dominant in these experiments. Typically this process involves many different diffusion paths, and a variety of "mechanism". As a consequence, the desorption transients would tend to be broader than otherwise expected. As an argument in support of this interpretation, one may note that the activation energy of diffusion of Ne is larger than that for Xe, but both values are very low compared to other known data [19] (see Table 2).

Table 2. Summary of computed and experimental desorption transient characteristics for various mechanisms and initial concentration profiles.

Type of process	Initial sorbate concentration profile	$T(m)$	$T(m) - T(\frac{1}{2}, l)$	$T(\frac{1}{2}, r) - T(m)$	E from Fig. (2)	$(D_0/a^2\beta)$ from Fig (2)	Ref.
Surface desorption First order	Surface only involved	1470 (C)	70 (C)	46 (C)	not applicable	not applicable	[20]
Surface desorption Second order	Surface only involved	1470 (C, E)	84 (C, E)	80 (C, E)	not applicable	not applicable	[20]
Diffusion	Non-uniform; assumed delta function	505 (C)	9 (C)	23 (C)	not applicable	not applicable	[18]
Surface desorption	Surface only involved	505 (C)	17 (C)	8 (C)	not applicable	not applicable	[18]
Diffusion, probably composite	Uniform	362 (C, E)	50 (C, E)	60 (C, E)	12	$10^{4\cdot 5}$	[22]
Diffusion, possibly composite	Non-uniform	393 (E)	57 (E)	71 (E)	12	$10^{4\cdot 0}$	[21]
Diffusion, possibly composite	Non-uniform	519 (E)	120 (E)	165 (E)	9	$10^{0\cdot 9}$	[21]

E or C in parentheses indicates that the entry is experimental information, or derived by model computations, respectively.

As stated earlier, one needs additional experimental criteria to discern the dominant mechanisms whenever composite processes are found. A simple curve fit using for example the data of Table 1 will not suffice.

In the present computations, $\beta = 1$ (deg/unit time). Obviously, one can use data obtained at very different β, by noting the proper value of $(D_0/a^2\beta)$ and its dimensions. One must recognize, however, that the present computed desorption transients are obtained on the assumption that the sample temperature is uniform throughout, i.e. heat conduction is assumed to be relatively fast. Clearly, whenever this assumption is not justified, much more complicated desorption transients are to be expected. If one decides to follow the temperature schedule

$$1/T = 1/T_0 - bt \tag{8}$$

with b = constant [16], one may encounter more tractable solutions of the diffusion equations, but the temperature, or time, at which heat conduction becomes the rate controlling process must be established.

As a final comment, T_0 need not be set equal to zero in the computation as long as it lies about 50° below $T(\frac{1}{2}, l)$, the resulting parameters $T(\frac{1}{2}, l)$, $T(m)$ and $T(\frac{1}{2}, r)$ will be correct. The same approximate condition holds for the experimental work [11].

ACKNOWLEDGEMENTS

The present work was supported by the U.S. Atomic Energy Commission under Grant AT (11-1)-1550, and by a contribution of computer funds from NSF Grant GU-2608. The author is indebted to Mr. T. Kehrwald for his excellent help in the computer work.

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MESURE DES COEFFICIENTS DE DIFFUSION ET DE VITESSE DE CHIMIDÉSORPTION PAR THERMODÉSORPTION

Résumé—La vitesse de dégazage d'un solide qui est soumis à un accroissement linéaire de température, c'est-à-dire la vitesse de thermodésorption, a été calculée dans le cas où la diffusion dans le solide contrôle le processus global. Les éprouvettes considérées ont la forme d'une sphère, d'un cylindre de longueur infinie ou d'une plaque plane infinie. Les énergies d'activation envisagées pour la diffusion s'étalent de 5 à 60 Kcal/mole et D_0/a^2 est compris entre 10^{-4} et 10^{+11} (temps^{-1}), a est le rayon de la sphère ou du cylindre ou encore de la demi-épaisseur de la plaque plane. Les résultats sont présentés sous une forme permettant de reporter les résultats expérimentaux sur une courbe simple. Cette procédure permet de distinguer les processus de diffusion lorsqu'ils sont isolés ou simples uniquement par désorption de surface; cependant lorsque les processus sont complexes, les paliers de vitesse ne peuvent généralement être identifiés qu'en faisant usage de critères expérimentaux supplémentaires.

BESTIMMUNG DER DIFFUSIONS- UND CHEMI-DESORPTIONSKOEFFIZIENTEN DURCH INSTATIONÄRE DESORPTIONS-MESSUNGEN

Zusammenfassung—Die Entgasungsrate eines festen Körpers, der einer linearen Temperaturzunahme unterworfen ist, d.h. instationäre Desorption, wurde unter der Annahme, dass die Haupt-Diffusion der beherrschende Parameter dieses Prozesses ist, berechnet. Die dabei betrachteten Körperkonfigurationen waren eine Kugel, ein Zylinder unendlicher Länge und eine ebene Platte unendlicher Ausdehnung. Die angenommene Aktivierungsenergie für die Diffusion lag im Bereich von 5 bis 60 kcal/mol während D_0/a^2 zwischen 10^{-4} und 10^{+11} (Ziet^{+1}) lag; D_0 ist dabei der Kugelradius, der Zylinderradius oder die Halbschichtdicke der ebenen Platte. Die Ergebnisse sind so dargestellt, dass die experimentellen Daten durch geeignete einfache Kurven wiedergegeben werden. Auf der Grundlage dieses Verfahrens kann man einzelne oder unkomplizierte Diffusions-Prozesse unterscheiden von einer einfachen Oberflächen-Desorption; die Grösse des Kontrollschritts bei überlagerten Prozessen jedoch kann gewöhnlich nur dann festgelegt werden, wenn weitere experimentelle Daten zur Verfügung stehen.

КОЭФФИЦИЕНТЫ ДИФФУЗИИ И СКОРОСТИ ХЕМОДЕСОРБЦИИ ПРИ НЕСТАЦИОНАРНЫХ ИЗМЕРЕНИЯХ ДЕСОРБЦИИ

Аннотация—При допущении о том, что основным фактором, влияющии на процесс, является объемная диффузия, рассчитаны скорости выделения газа из твердого тела при линейном увеличении его температуры, т.е. характеристики нестационарной десорбции. Рассматривались следующие конфигурации рабочих тел: шар, цилиндр бесконечной длины и тонкая пластина бесконечной протяженности. Энергии активации диффузии принимались в пределах от 5 до 60 ккал / моль, aD_0/a^2 от 10^{-4} до 10^{+11} (время$^{-1}$), где D_0 — радиус сферы или цилиндра, или половина толщины тонкой пластины. Результаты представлены в виде, соответствующем упрощенной кривой, описывающей экспериментальные данные. С помощью описанного метода можно легко отличить изолированный или неусложненный процессы диффузии от простой поверхностной десорбции. Однако, в общем случае скорости различных стадий сложного процесса можно определять, только используя дополнительные экспериментальные критерии.