

## ON THE ANALYSIS OF THERMAL DESORPTION CURVES

Received 7 January 1974

The phenomenon of thermal desorption was investigated by several groups<sup>1-4</sup>). Hickmott and Ehrlich<sup>1</sup>) who studied the desorption of gases from tungsten gave an equation for the rate at which the number of molecules per unit area,  $n$ , is depleted by desorption

$$- dn/dt = n^l s \exp(- E/kT), \quad (1)$$

where  $t$  is the time (sec),  $l$  the order of reaction resulting in desorption,  $s$  the pre-exponential factor ( $\text{sec}^{-1}$ ),  $E$  the activation energy (joule/mole),  $R$  the gas constant (joule/mole K) and  $T$  the absolute temperature (K). The order of kinetics was usually assumed to be either first ( $l=1$ ) or second ( $l=2$ ). Hickmott and Ehrlich also mentioned that eq. (1) is mathematically similar to the equations governing the process of thermoluminescence (TL) glow curves where  $I = -dn/dt$  gives the TL intensity and where  $n$  is the concentration of trapped carriers in a trap having an activation energy  $E^*$ . Here too, one can consider first order kinetics<sup>10</sup>) as well as second order<sup>11</sup>).

The solution of eq. (1) both for first and second order kinetics, includes the integral

$$\int_{t_0}^t \exp(- E/RT) dt.$$

When the "usual" linear heating rate,  $T = T_0 + \beta t$ , is applied, the solution of this integral is not immediate, and an asymptotic series is usually used for its evaluation<sup>12</sup>). In order to overcome this mathematical complication, a hyperbolic heating rate, in which  $dT = \beta_0 T^2 dt$  is sometimes used where  $\beta_0$  is a constant. This was suggested by Halperin et al.<sup>13</sup>) and Arnold and Sherwood<sup>14</sup>) for TL glow curves, and for thermal desorption curves by Ehrlich<sup>2</sup>), who gave some experimental curves measured with hyperbolic heating rate.

\* In TL theory, Boltzmann's constant  $k$  (eV/K) replaces  $R$ , and  $E$  is given in eV. The ratios  $E/kT$  and  $E/RT$  are, however, the same. This can be seen by multiplying both the numerator and denominator of  $E/kT$  by Avogadro's number.

The solution of eq. (1) for the first order case and linear heating rate is<sup>10)</sup>

$$I = sn_0 \exp[-E/RT] \exp\left[(-s/\beta) \int_{T_0}^T \exp(-E/RT') dT'\right], \quad (2)$$

and by equating its derivative to zero, one gets the condition for the maximum

$$\beta E/(RT_m^2) = s \exp(-E/RT_m), \quad (3)$$

where  $T_m$  is the temperature at the maximum. Redhead<sup>3)</sup> and McCarroll<sup>7)</sup> assumed that  $s = 10^{13} \text{ sec}^{-1}$  for the thermal desorption curves, and thus used eq. (3) as a transcendental equation for evaluating the activation energy. Hickmott and Ehrlich<sup>1)</sup> and Redhead<sup>4)</sup> showed that  $T_m$ , the maximum temperature peak, slightly depends, in the second order case, on the initial coverage  $n_0$ . McCarroll<sup>6)</sup> showed that the mass-spectrometer signal intensity is given by

$$I(t) = -g\dot{n}(t) T(t)^{-\frac{1}{2}} \quad (4)$$

where  $g$  is a constant. In a later paper, McCarroll<sup>6)</sup> added to eq. (1) the assumption that the activation energy may be slightly dependent on the coverage, as  $E = E_0 - xn(t)/n(0)$  where both  $E_0$  and  $x$  are constants, and  $x \geq 0$ . This is an empirical assumption with no theoretical justification, enabling better fitting between experimental and theoretical curves. In a recent paper, Hill et al.<sup>9)</sup> discuss the thermal desorption of Na and K from  $\alpha$  iron. Here too, it is assumed that  $s = 10^{13} \text{ sec}^{-1}$  and the activation energy is calculated under this assumption.

The methods mentioned above for evaluating the activation energies of thermal desorption have the disadvantage that either we have to assume a certain pre-exponential factor and solve a transcendental equation, or follow the rather tedious procedure of curve fitting. On the other hand, relatively simple methods for extracting information – e.g. activation energies and frequency factors – from TL glow curves were developed<sup>15-18)</sup> in recent years, which can easily be applied to thermal desorption curves.

A typical formula for calculating the activation energy from a first order curve is<sup>16)</sup>

$$E = 2.52 kTm^2/\omega - 2kT_m, \quad (5)$$

where  $\omega = T_2 - T_1$ ,  $T_1$  and  $T_2$  being the lower and higher temperatures of half intensity, respectively. For the present purposes,  $k$  can be replaced by  $R$  and  $E$  will thus be found in Joule/mole. Insertion of the calculated activation energy into eq. (3) enables the evaluation of the frequency factor  $s$ . Other equations of this class, both of first and second order, use the high

temperature half intensity  $\delta = T_2 - T_m$  and the low temperature one  $\tau = T_m - T_1$ . All these equations can be summed up as follows

$$E = c_\alpha (kT_m^2/\alpha) - b_\alpha (2kT_m), \quad (6)$$

where  $\alpha$  stands for  $\tau$ ,  $\delta$  or  $\omega$ . Again,  $k$  should be replaced by  $R$  in the thermal desorption case. The values of the coefficients  $b_\alpha$  and  $c_\alpha$  for the various cases are given in table 1. A slight correction to these methods can be made by taking into account the  $T^{-\frac{1}{2}}$  factors in eq. (4). In TL theory, a  $T^a$  dependence of the frequency factor has been assumed with  $-2 \leq a \leq 2$ , the correction was that  $akT_m$  should be subtracted from the expression in eq. (6). In the

TABLE I

Coefficients appearing in eq. (6) for the various methods of calculating activation energies

	First order			Second order		
	$\tau$	$\delta$	$\omega$	$\tau$	$\delta$	$\omega$
$c_\alpha$	1.51	0.98	2.52	1.81	1.71	3.54
$b_\alpha$	1.58	0.00	1.00	2.00	0.00	1.00

present case where  $a = -\frac{1}{2}$  this would mean addition of  $\frac{1}{2}RT_m$ . The form of the TL peak has also been studied<sup>15,16</sup>) and the results can be used in the present case. The form factor  $\mu_g = \delta/\omega$  was shown there to be about 0.42 for a first order peak and about 0.52 (nearly symmetric peak) for the second order one.

The case of a general order kinetics has been investigated<sup>17</sup>), namely, the case where TL intensity is governed by eq. (1) where  $l$  is neither 1 nor 2. This is an empirical approach which permits the investigation of peaks which are neither of first nor of second order kinetics. The measured value of  $\mu_g$  was shown to be related to the kinetics order Empirical formulas for the evaluation of activation energies while using the measured values of  $\mu_g$  in these cases of general order were given<sup>17</sup>). This approach can be pursued for the thermal desorption curves as well. As mentioned by McCarroll<sup>8</sup>), when the activation energy behaves as  $E = E_0 - xn(t)/n(0)$ , the high temperature half of the peak tends to broaden. In this way, with the appropriate values of  $x$ , a first order peak can look like a second or general order one. We now suggest to preserve the assumption of a constant activation energy and adopt the notion of possibly non integer values of  $l$  in the thermal desorption case. Both of these approaches are merely empirical. In both, parameters can be adjusted to give good agreement with the experiment, but the general order approach is much easier to work with when using the methods developed for TL. Thus the value of  $l$  can be evaluated from the measured  $\mu_g$  and the activation energy can be calculated by measuring  $T_m$ ,  $\mu_g$  and  $\tau$ ,  $\delta$  or  $\omega$ .

The variation of the peak intensity and the maximum temperature at various heating rates (linear and non-linear) and with various initial concentrations ( $n_0$ ) were studied by Chen and Winer<sup>18</sup>) for first, second and intermediate orders of kinetics. These variations can be used for the evaluation of activation energies,  $\ln(I_m)$  or  $\ln(\beta_m/T_m^2)$ , where  $I_m$  is the maximum intensity and  $\beta_m$  the instantaneous heating rate at maximum intensity, plotted as a function of  $1/T_m$ , should result in a straight line with a slope of  $-E/R$ ; the activation energy is thus evaluated. For a non-first-order kinetics case, the peak shifts while changing the initial concentration  $n_0$ <sup>11</sup>). Plotting  $\ln[I_m^{l-1} T_m^{2l}]$  versus  $1/T_m$  should yield a straight line, the slope of which is  $E/R$ . These methods can be applied without alteration to the thermal desorption curves.

Finally, the hyperbolic heating rate ( $1/T = 1/T_0 + \beta_0 t$ ) which was used rather extensively for thermal desorption<sup>2,4,5</sup>) will now be considered. Kelly and Laubitz<sup>19</sup>) gave two equations for calculating the activation energy of TL first order curves measured with hyperbolic heating rate

$$E = 1.461 kT_1 T_m / \tau = 0.985 kT_m T_2 / \delta. \quad (7)$$

For second order kinetics they found

$$E = 1.763 kT_m T_1 / \tau = 1.763 kT_m T_2 / \delta. \quad (8)$$

These equations can conveniently be used for the thermal desorption case. In many cases, it is of advantage to use methods based on the full half width  $\omega$  (for comparison between the various methods see discussion in ref. 16). From the two equations (7) one can rather easily derive for first order kinetics<sup>20</sup>)

$$E = 2.446 kT_1 T_2 / \omega, \quad (9)$$

and for second order, one gets from eq. (8)

$$E = 3.525 kT_1 T_2 / \omega. \quad (10)$$

For the present case of thermal desorption curves,  $R$  should again replace  $k$  in eqs. (7)–(10).

This work was supported by the National Research Council of Canada.

REUVEN CHEN\*

*Department of Physics, Queen's University,  
Kingston, Ontario, Canada*

\* On leave of absence from the Department of Physics and Astronomy, Tel-Aviv University, Tel-Aviv, Israel.

### References

- 1) T. W. Hickmott and G. Ehrlich, *J. Phys. Chem. Solids* **5** (1958) 47.
- 2) G. Ehrlich, *J. Appl. Phys.* **32** (1961) 4.  
G. Ehrlich, *Advan. Catalysis and Related Subjects* **14** (1963) 255.
- 3) P. A. Redhead, *Trans. Faraday Soc.* **57** (1961) 641.
- 4) P. A. Redhead, *Vacuum* **12** (1962) 245.
- 5) G. Carter, *Vacuum* **12** (1962) 245.
- 6) B. McCarroll, *J. Chem. Phys.* **46** (1967) 863.
- 7) B. McCarroll, *J. Chem. Phys.* **47** (1967) 5077.
- 8) B. McCarroll, *J. Appl. Phys.* **40** (1969) 1.
- 9) R. V. Hill, E. K. Stefanakos and R. F. Tinder, *J. Appl. Phys.* **43** (1972) 1976.
- 10) J. J. Randall and M. H. F. Wilkins, *Proc. Roy. Soc. (London) A* **184** (1945) 366, 390.
- 11) G. F. J. Garlick and A. F. Gibson, *Proc. Phys. Soc. (London)* **60** (1948) 574.
- 12) R. Chen, *J. Comtemp. Phys.* **6** (1970) 314.
- 13) A. Halperin, M. Leibovitz and M. Schlesinger, *Rev. Sci. Instr.* **33** (1962) 1168.
- 14) W. Arnold and H. J. Sherwood, *J. Phys. Chem.* **63** (1959) 2.
- 15) A. Halperin and A. A. Braner, *Phys. Rev.* **117** (1960) 408.
- 16) R. Chen, *J. Appl.* **40** (1969) 570.
- 17) R. Chen, *J. Electrochem. Soc.* **116** (1969) 1254.
- 18) R. Chen and S. A. Winer, *J. Appl. Phys.* **41** (1970) 5227.
- 19) P. J. Kelly and M. J. Laubitz, *Can. J. Phys.* **45** (1967) 311.
- 20) See also: P. Müller and J. Teltow, *Phys. Status Solidi (a)* **12** (1972) 471.