EVALUATION OF THE TEMPERATURE RESPONSES IN CALORIMETRIC MEASUREMENTS OF CHEMISORPTION ENTHALPIES ON METAL FILMS

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Received May 17th, 1979

Dedicated to Professor E. Hála on the occasion of his 60th birthday.

An analysis was performed of various estimates of the adiabatic temperature T_{tot} that corresponds to the total heat liberated by a gas dose adsorbed on a metal film in the calorimeter for measurement of chemisorption enthalpies. Besides the two common procedures consisting either in the construction of the adiabatic temperature–time curve or in the extrapolation of the single-exponential cooling part of the actual temperature–time curve to zero time, we have examined estimates of T_{tot} by extrapolating the cooling exponential to the mid-point between zero time and the temperature maximum ($t = t_{max}/2$). Model calculations have shown the merit of the latter extrapolation, particularly in the cases of slow heat evolution. This has been verified on the data measured in the chemisorption of methane and ethane on molybdenum films. Extrapolation to $t_{max}/2$ has turned out to be a simple and reasonably reliable procedure for handling the data obtained in film calorimeters.

Enthalpic effects called forth by irreversible dissociative chemisorption of organic gases on reasonably clean metal surfaces have been measured mainly in calorimeters designed for experiments with vacuum-evaporated metal films. The film calorimeters belong to the class of diathermic calorimeters[1-3] characterized by a defined heat exchange between the calorimeter cell and the surrounding thermostat. The heat evolution inside the cell causes an increase of its wall temperature, opposed by the heat flow to the thermostat. Thus, for a finite heat signal the cell temperature reaches a maximum and then returns gradually to its initial value. In the film calorimeter virtually all the cooling of the cell occurs by radiation across the outer evacuated jacket[4] and it is governed to a good approximation by a single linear process. Then, the time dependence of the temperature difference T between the wall of the cell and the surrounding thermostat due to the heat liberated in the cell at the rate $\mathrm{d}Q/\mathrm{d}t$, is described with sufficient accuracy by the Tian equation

$$\mathrm{d}Q/\mathrm{d}t = C\,\mathrm{d}T/\mathrm{d}t + kT\,. \qquad (1)$$

Here, C is the heat capacity of the calorimeter and k is the Newton's cooling coefficient. After the termination of the heat supply, the calorimeter temperature returns to its initial value according to Newton's law, *i.e.* exponentially, as

$$T(t) = T(t_i) \exp\left[-(t - t_i)/\tau\right]; \quad t > t_i, \tag{2}$$

where t_i is any time after the heat signal termination, $T(t_i)$ is the temperature difference between the cell and the thermostat at t_i, and $\tau = C/k$ is the time constant of the calorimeter. Practically, no appreciable distortion on the cooling exponential (*2*) is detected when the heat supply rate $\mathrm{d}Q/\mathrm{d}t$ becomes sufficiently small, as it occurs at long times after a gas dose admission.

The total heat evolved in the given process is obtained by integration of Eq. (*1*)

$$Q(t) = CT(t) + k\int_0^t T\,\mathrm{d}t \tag{3}$$

provided C and k are known. At sufficiently long cooling times, T comes back practically to zero[4], making the first term in Eq. (*3*) zero, and Q then equals to the product of k and the integral of the total $T(t)$ curve. With film calorimeters, an adequately reliable base line is not always met on account of their simple construction and high sensitivity (typically about $5 \,.\, 10^{-5}$ K or $5 \,.\, 10^{-4}$ Joule per 1 cm of recorder deflection). Therefore, both terms in Eq. (*3*) have to be determined. Two ways of obtaining Q are then available. In the first one, Q is found by means of an explicit expression for $T(t)$ requiring an independent determination of both the heat supply and dissipation rate[5,6]. Such a determination, however, is not always possible[7]. In the second way it is necessary to estimate the maximum cell temperature T_{tot} that would be reached under adiabatic conditions after the heat Q has been evolved. The product of T_{tot} and the constant C established in calibration experiments gives the required value of Q. T_{tot} can be found by correcting the experimental $T(t)$ curve for the escaped heat according to Eq. (*3*), *i.e.* by constructing the adiabatic curve[8,9]. Recently, such a construction was described for the case when two time constants of the film calorimeter were considered[10]. The integration procedure involved in the construction of an adiabatic curve is rather time consuming. Therefore, a simplified estimation of T_{tot} by extrapolating the single-exponential cooling part of the $T(t)$ curve (Eq. (*2*)) back to the start of the heat input[5,11] is attractive. Essentially, it should be sufficient to insert into Eq. (*2*) a few readings of $T(t)$ for $t > t_i$ together with τ established in calibration experiments to obtain

$$T_0^e = T(t) \exp \Theta\,, \tag{4}$$

where $\Theta = t/\tau$ stands for the dimensionless reduced time. Statistical evaluation provides then the arithmetic mean and the standard deviation of the estimate of T_0^e. In practice, however, it is worthwhile to establish the actual value of τ for each particular $T(t)$ curve by linearizing its cooling part for $t > t_i$ when $\ln T(t)$ is plotted against t[8,11]. The slope $1/\tau$ can be found either graphically or by linear regression. The latter procedure provides us with the uncertainty of the slope estimate. Differences encountered sometimes between the value of τ obtained in this way and in the calibration experiment indicate that some effective changes in C and/or k may take place.

The estimate of T_0^e by the extrapolation of the cooling back to zero time in fact neglects the kinetics of the heat evolution and implies that the energy input occurred by a Dirac pulse. Therefore, it may be applied as a reasonable approximation only when the heat liberation time is short in comparison with τ.

When a film calorimeter equipped with thermocouples was calibrated by Joule heat, the obtained cooling curve was linear and was extrapolated back to the mid-point of the heating period instead of to its beginning[12]. Such an extrapolation was also discussed for calibration of other types of calorimeters[13].

The heat of chemisorption of unsaturated hydrocarbons on transition metal films is liberated rapidly[14], so that T_{tot} is reasonably well approximated by T_0^c. With saturated hydrocarbons, however, the kinetics of the heat liberation slows down at higher surface coverages[15] and T_0^c becomes much higher than T_{tot}. In an attempt to find a more suitable way of extrapolation, we compare in the present paper the values of T_{tot} obtained from adiabatic curves with the values $T_{1/2}^c$ determined by the extrapolation of the cooling exponential back to the mid-point $t_{\max}/2$ between the zero time and the maximum on the $T(t)$ curve.

Model calculations

Let us consider exothermic processes and the heat transfer from the calorimeter cell to the thermostat. The total heat evolved in the process is $Q = CT_{\text{tot}}$. The extrapolation (*4*) of the cooling exponential to $t = 0$ gives for the ratio T_0^c/T_{tot} and hence for the ratio of the estimated to the true (adiabatic) Q the expression

$$P_0 = T_0^c/T_{\text{tot}} = T(t)\exp(\Theta)/T_{\text{tot}}\,; \quad t > t_i \tag{5}$$

P_0 expresses the relative goodness of the approximate use of T_0^c instead of T_{tot} and should be independent of t for times, when the heat evolution in the cell becomes negligible. Practically, P_0 will fluctuate around the true value due to inaccuracies in the readings of $T(t)$. Further, it can be shown that always $P_0 > 1$, representing thus the upper limit estimate of T_{tot} and hence of Q.

Similarly, the extrapolation of the cooling exponential to $t_{\max}/2$ gives the approximate estimate

$$P_{1/2} = T_{1/2}/T_{\text{tot}} = P_0\exp(-\Theta_{\max}/2)\,. \tag{6}$$

The relative merits of the two estimates of T_{tot} have been examined for the following two types of models of the heat evolution kinetics.

Type 1. Let the rate of the heat evolution $\mathrm{d}Q(t)/\mathrm{d}t = q(t)$ be

$$q(t) = a_0 + a_1 t = -a_1\tau(x - \Theta) \tag{7}$$

with $x = -a_0/a_1\tau$. The heat supply to the calorimeter cell up to the time t is

$$Q(t) = CT^a(t) = a_0 t + (a_1/2)\,t^2 = -a_1\tau^2\,\Theta(x - \Theta/2)\,, \tag{8}$$

where $T^{a}(t)$ is the theoretical adiabatic temperature at time t. The substitution of Eq. (*7*) into Eq. (*1*) gives its solution

$$CT(t) = -a_1\tau^2\{(x + 1)\left[1 - \exp(-\Theta)\right] - \Theta\}\,. \tag{9}$$

For a non-negative a_1, *i.e.* for a constant or increasing rate of the heat supply, $T_{\max}$ is reached simultaneously with the end of the heat supply at $t = t_1$. By definition, $Q(t_1) = Q$, and $T^{a}(t_1) = T_{\mathrm{tot}}$. Then, Eq. (*5*) gives

$$P_0 = \frac{(1 + x)\left[\exp(\Theta_1) - 1\right] - T(t_1)\exp(\Theta_1)}{\Theta_1(x - \Theta_1/2)} \approx 1 + \frac{(\Theta_1/2)(x - 2\Theta_1/3)}{x - \Theta_1/2} + \dots\,. \tag{10}$$

It follows from Eq. (*6*) that

$$P_{1/2} = P_0 \exp(-\Theta_1/2)\,. \tag{11}$$

The same value of $P_{1/2}$ applies to the linearly decreasing rate of the heat supply ($a_1 < 0$) provided that the heat evolution is terminated before the maximum on the $T(t)$ curve is reached given by $\Theta_{\max} = \ln(1 + x)$. For $\Theta_1 > \ln(1 + x)$, a maximum on the $T(t)$ curve appears before the heat input is terminated, and

$$P_{1/2} = P_0(1 + x)^{-1/2} \tag{12}$$

applies instead of Eq. (*11*).

The practically most important case is $q(t) = a_0$, *i.e.* the heat is supplied into the calorimeter cell at a constant rate up to the time t_1. This occurs in the electric calibration of C and k. Then, Eqs (*10*) and (*11*), respectively, read

$$P_0 = \left[\exp(\Theta_1) - 1\right]/\Theta_1 \approx 1 + \frac{1}{2}\Theta_1 + \frac{1}{6}\Theta_1^2 + \frac{1}{24}\Theta_1^3 + \dots \tag{10.1}$$

and

$$P_{1/2} = 2\sinh(\Theta_1/2)/\Theta_1 \approx 1 + \frac{1}{24}\Theta_1^2\left(1 + \frac{1}{80}\Theta_1^2 + \dots\right). \tag{11.1}$$

Thus the difference between T_0^{c} and T_{tot} does not exceed 1 per cent only for short heat signals of $\Theta_1 < 0{\cdot}02$; however, $T_{1/2}^{e}$ does not differ from T_{tot} by more than 1 per cent even for the heat signals up to $\Theta_1 = 0{\cdot}5$. The superiority of the extrapolation to $t_{\max}/2$ instead of to $t = 0$ in this case is evident.

The cases with $a_1 \neq 0$ lack practical significance and will not be treated in detail. Also here $P_{1/2}$ is closer to unity than P_0. For $a_1 < 0$, however, $P_{1/2}$ exhibits a minimum which can reach down to 0·970.

Type 2. Let the rate of the heat evolution $q(t)$ be

$$q(t) = At^n \exp(-at)\,. \qquad (13)$$

Theoretically, the heat evolution is completed at infinity. Practically, however, it becomes negligible in comparison with the heat transfer to the thermostat at rather short times. The total supplied heat is given by

$$Q = CT_{\text{tot}} = A\int_0^\infty t^n \exp(-at)\,\mathrm{d}t = An!/a^{n+1}\,. \qquad (14)$$

With the notation $x = (a\tau - 1)\,\Theta$, the solution of Eq. (*1*) with Eq. (*13*) and $a \neq 1$ is

$$CT(t) = An!\left(\frac{\tau}{a\tau - 1}\right)^{n+1}\left[\exp(-\Theta) - \left(1 + \frac{x}{1!} + \frac{x^2}{2!} + \ldots + \frac{x^n}{n!}\right)\exp(-at)\right]. \qquad (15)$$

The maximum value of $CT(t)$ from Eq. (*15*) is given generally by the solution of the transcendent equation

$$\exp(x) = 1 + x + \frac{x^2}{2!} + \ldots. + \frac{x^{n-1}}{(n-1)!} + a\tau\frac{x^n}{n!}\,. \qquad (16)$$

Provided the heat signal decays more quickly than the thermal non-equilibrium (a condition assumed throughout the present paper), $a\tau > 1$ and consequently $x > 0$. One can always find then such a value of t that the second term in Eq. (*15*) becomes negligible as compared to the first one, and the $T(t)$ curve becomes a single-exponential function of time. Its extrapolation according to Eq. (*4*) gives

$$CT_0^c = An!\left(\frac{\tau}{a\tau - 1}\right)^{n+1}. \qquad (17)$$

Hence,

$$P_0 = \left(\frac{a\tau}{a\tau - 1}\right)^{n+1} > 1 \qquad (18)$$

and

$$1/P_0 \approx 1 - \frac{n+1}{a\tau} + \frac{n(n+1)}{2(a\tau)^2} - \ldots \tag{18a}$$

$P_{1/2}$ is given by the relationship (*6*).

In the present paper we shall deal only with the simplest case of $n = 0$ representing a reasonable approximation to the actual kinetics of heat liberation in the chemisorption of a gas dose on a metal surface. Then, $q(t) = A \exp(-at)$, giving

$$P_0 = a\tau/(a\tau - 1)\,. \tag{10.2}$$

The condition (*16*) for the maximum reduces to $\exp(x) = 1 + a$, and

$$\Theta_{\max} = \frac{\ln a\tau}{a\tau - 1}\,. \tag{19}$$

Then, Eq. (6) gives

$$P_{1/2} = \frac{a\tau}{a\tau - 1} \exp(-\Theta_{\max}/2)\,. \tag{11.2}$$

Fig. 1 shows a $T(t)$ curve calculated for $a\tau = 4{\cdot}7$ and $\Theta_{\max} = 0{\cdot}418$, together with the extrapolation of its exponential cooling part to $t = 0$ and $t = t_{\max}/2$ and with the corresponding adiabatic curve $T^a(t)$. As can be seen, $P_{1/2} = 1{\cdot}03$, while P_0 is as high as $1{\cdot}27$. The values of $\Theta_{\max}$, P_0 and $P_{1/2}$ as functions of $a\tau$ are given in figure 2. With $\Theta_{\max} = 0{\cdot}4$, for example, $P_{1/2}$ and P_0 are $1{\cdot}02$ and $1{\cdot}25$, respectively.

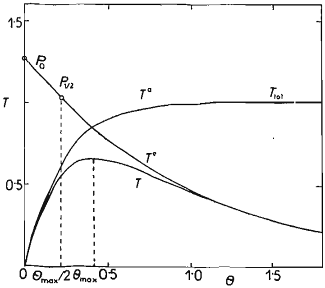

FIG. 1

The Model Temperature–Time Curve with $a\tau = 4{\cdot}7$ and $\Theta_{\max} = 0{\cdot}418$, Its Extrapolation T^e to Obtain P_0 and $P_{1/2}$, and the Corresponding Adiabatic Curve T^a

The model calculations can be summarized as follows: *1*) The extrapolation P_0 to $t = 0$ is a fair approximation to T_{tot} for rapidly decaying heat signals only and deteriorates with the increase of n in Eq. (*13*) (see expansion in Eq. (*18a*)). *2*) The extrapolation $P_{1/2}$ to $t = {}_{\max}/2$ holds well over a large range of $a\tau$ values. With a slow heat evolution it gives estimates higher than 1: $P_{1/2} = 1$ for $a\tau = 6{\cdot}23$; 11·7; and 19·8, with $n = 0$; 1; and 2, and $\Theta_{\max} = 0{\cdot}350$; 0·357; and 0·311, respectively. With a fast heat evolution (high $a\tau$ values), $P_{1/2}$ drops below unity and attains a minimum of 0·972; 0·981; and 0·988, for $a\tau = 16{\cdot}8$; 31·5; and 52·5, with $n = 0$; 1; and 2, and $\Theta_{\max} = 0{\cdot}179$; 0·167; and 0·140, respectively. *3*) In our chemisorption experiments[14,15], $\Theta_{\max}$ between 0·10 and 0·15 were typical. The model calculations gave in this range $P_{1/2} = 0{\cdot}97$, while P_0 varied from 1·03 to 1·05 for $n = 0$, and up to 1·07 for $n = 2$. Thus, in view of other uncertainties involved in actual experiments, both the extrapolation P_0 and $P_{1/2}$ can be expected as applicable to the evaluation of the experimental $T(t)$ curves with about the same, reasonable accuracy. The same kind of extrapolation should be used throughout the whole set of the evaluated curves, indeed.

Verification of the Model Calculations

The outcome of the model calculations of P_0 and $P_{1/2}$ has been proved using the data measured in the calorimetric experiments with ethane and methane on molybdenum films (Expt 50 and 54, respectively, in the paper[15]).

With ethane, 27 approximately equal doses were successively admitted to the molybdenum film to saturate its adsorption capacity. The first 19 doses were adsorbed readily to a very low residual pressure. The maximum on the $T(t)$ curve was always reached within 7·5—9 s after the dose admission. From the 20th dose on, the rate of the heat evolution was gradually decreasing (Table 1).

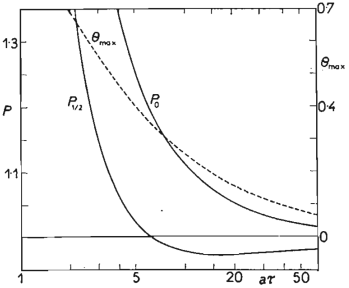

FIG. 2

$\Theta_{\max}$, P_0 and $P_{1/2}$ as Functions of $a\tau$

Methane exhibited on the molybdenum film an exceptionally low chemisorption reactivity which was manifested among others by a very low rate of the heat evolution, decreasing with the increasing coverage of the surface (Table I). The chemisorption capacity of the film was saturated after 17 doses.

Twenty measured $T(t)$ curves given in Table 1 were treated by the following three methods to obtain estimates of T_{tot}: *a*) the single-exponential cooling part of the recorded trace was extrapolated back to zero time; *b*) the mentioned extrapolation was performed to $t = t_{max}/2$; *c*) an adiabatic curve was constructed using the time constant obtained sub *a*) and *b*). The procedures were as follows: the temperature base line was extrapolated by hand from its course before the dose admission, and readings of the time t_{max} and of deflections on the $T(t)$ curve were noted. Six readings on the cooling part of the $T(t)$ curve well away from its maximum (with fast, slow, and extremely slow heat evolution about 120; 160—260; and 400 s, respectively, after the gas admission in a pulse-like way[16]) in steps of 10 s from each other, were fed into a desktop calculator which found the best values of τ by the least squares method. Thereafter, additional readings in 10 s steps in the direction towards shorter times were put into the calculator, until the mean deviation of the fit began to deteriorate significantly, signalling thus the end of the single-exponential cooling part of the $T(t)$ curve. The calculator extrapolated this exponential back to $t = 0$ and to $t = t_{max}/2$. Further, the calculator performed construction of the adiabatic curve from the obtained τ and from the readings on the $T(t)$ curve made in 5 s steps starting at $t = 0$, by means of the trapezoidal integration. In this way, the role of the human factor in establishing the value of τ and of T_{tot}, T_0^e, and $T_{1/2}^e$ was reduced. Results of the outlined treatments are given in Table I.

Table I shows clearly that the extrapolation to $t_{max}/2$ in all the examined doses is superior to the extrapolation to $t = 0$. This confirms the expectations based on the model calculations. With a fast heat evolution, the extrapolations to $t = 0$ and to $t = t_{max}/2$ give T_{tot} by 3—5 per cent higher and by 0—2 per cent lower, respectively, in comparison with T_{tot} from the adiabatic

TABLE I

Comparison of the P_0 and $P_{1/2}$ Values Obtained from the Experimental $T(t)$ Curves of Ethane and Methane on Molybdenum Films

	Ethane									
Dose No	3	17	20	21	22	23	24	25	26	27
t_{max}, s	8	8·5	9·5	11	11·5	14	24	34	55	64
$100P_0$	104·7	103·1	103·4	103·0	103·9	104·6	107·4	111·7	117·6	111·0
$100P_{1/2}$	100·0	99·1	99·0	98·1	98·9	98·3	97·5	97·8	98·9	97·9
	Methane									
Dose No	1	3	4	5	8	9	12	13	15	16
t_{max}, s	23	37	40·5	40·5	62	64	83	86	94·5	109·5
$100P_0$	108·4	118·1	119·2	126·7	122·5	134·2	126·7	131·1	129·7	120·2
$100P_{1/2}$	96·8	99·9	99·3	101·9	98·5	106·3	103·9	99·5	104·0	100·0

curve. When the duration of the heat liberation increases, the superiority of the extrapolation to $t_{max}/2$ becomes more and more obvious. Some uncertainty in localizing the exact position of t_{max} in the cases of a very slow heat evolution has no serious effect.

CONCLUSIONS

The estimate of T_{tot} by the extrapolation of the cooling part of the $T(t)$ curve to $t = 0$ is reasonably applicable in film calorimeters with processes that evolve the heat of chemisorption rapidly so that t_{max} does not exceed approximately $\tau/10$. This is in a good accord with the finding of the Calvet type calorimetry, where it was observed that the heat amount/peak height ratio for a constant power heat supply was constant if the duration of the heat input did not exceed $\tau/10$ (ref.[17]).

The estimate of T_{tot} by the extrapolation of the cooling exponential back to $t = t_{max}/2$ has been found to be equivalent over the whole range of the heat evolution rates examined to the T_{tot} obtained by construction of the adiabatic curve. Promptness and simplicity are strong arguments in favour of the extrapolation method. Results of both procedures depend on the reliability of determining the time constant τ from the single-exponential cooling part of the particular $T(t)$ curves in question. An analysis of this determination and of the effect of τ on the evaluation of the experiments in film calorimeters deserve a detailed study which would be beyond the scope of the present paper.

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