Journal of Thermal Analysis, Vol. 41 (1994) 767-788

PARAMETER DETERMINATION OF A THERMAL DESORPTION MODEL

S. Zhou, G. Schulz-Ekloff and D. Popovic[1]

Institut für Angewandte und Physikalische Chemie
[1]Institut für Automatisierungstechnik, Universität Bremen, 28334 Bremen, Germany

(Received April, 1993)

Abstract

A new method for the analysis of thermal desorption spectra is presented, based on the experimental peak maximum functions for temperature $\mathbf{T}_m(\beta)$ and pressure $\mathbf{P}_m(\beta)$ and a rigorous mathematical treatment. The resonant heating rate β_r is determined, satisfying $T_m(\beta_r)=T_r$, where T_r is the resonant temperature defined by $A\ \exp(-E_d/(RT_r))=1$. Desorption energy E_d and frequency factor A can be determined simultaneously with relatively high robustness towards statistical experimental errors as demonstrated by computer-simulated thermal desorption spectra.

Keywords: kinetics, thermal desorption, thermal desorption spectroscopy

Introduction

The thermal desorption spectroscopy (TDS) method is widely used to characterize the chemical reactivity of surfaces by analysis of the desorption kinetics of an adsorbate and has been desribed in various review papers [1–8]. For the majority of real systems the values of the most important kinetic parameters, such as the frequency factor A and the activation energy of desorption E_d, depend on the method of their determination and suffer from limited accuracies in the experimental data and the assumed model and are, thus, ambiguous [9, 10]. Generally, the influences of surface heterogeneity, lateral interactions between adsorbed species or surface migration on the desorption kinetics are not considered due to a lack of corresponding detailed information and due to the complexity of resulting determination methods.

It this case, it might be useful to restrict the analysis to the simplest possible model, in order to focus on the determination of the most important parameters, i.e. the activation energy of desorption E_d and the frequency factor A, and to define an adsorption system by these characteristic coefficients regardless of any physical meaning. For this strategy well-defined and easily reproducible experimental parameters and unambiguous determination procedures are described. Most experimental designs apply high pumping speeds and make use of the resulting correlations between the recorded pressure and the rate of desorption with respect to time or to temperature. The determination of the kinetic parameters from peak shape analysis procedure suffers from the sensitivities of peak shapes on systematic errors and from statistical fluctuations, mathematical complexity, and limited computational precision.

A more straightforward determination method makes use of peak maximum variations with altered heating rates and constant initial coverage [11–14]. The evaluation accuracy of the method suffers, however, from the assumption, that the surface coverage at peak maximum is independent of the heating rate and constant [13, 14], and from sensitivity to statistical fluctuations of the measured values of the peak maximum temperature. It is required, that the heating rate β has to be varied by about two orders of magnitude for reasonable accuracy [15]. In many experimental arrangements this would also result in sensitivity problems at low rates β and in peak shape distortions by readsorption or diffusion limitation at high rate β.

In the following, a new method is described, enabling simultaneously a precise determination of E_d and A for a restricted range of heating rates β and being robust both to statistical fluctuations of measured data and to constrained model errors.

TDS procedure of analysis

Definition of the resonant parameters

Thermal desorption experiments employ continuous variation of temperature

$$T = T_o + \beta t \tag{1}$$

starting at T_o and the surface coverage $\theta(T_o)=\theta_o$, and using a linear heating rate β to obtain a variety of kinetic parameters. θ is normally applied as fractional coverage, i.e. dimensionless, which means that a maximum value of adsorbed species per surface unit has to be defined for each experiment. Usually, the partial pressure P or, more correctly, the density of a gaseous desorbate is measured. In an experiment with the high pumping speed and negligible readsorption, in which $P \propto -\mathrm{d}\theta/\mathrm{d}t$, the maximum $\mathbf{P}_m(\beta)$ occurs, for a given β, at

$$(\mathrm{d}P/\mathrm{d}T)\big|_{T_m(\beta)} = 0, \tag{2}$$

where $\mathbf{T}_m(\beta)$ is the peak maximum temperature for the same β. For a series of β values $\mathbf{P}_m(\beta)$ and $\mathbf{T}_m(\beta)$ can be recorded. Defining $r_\beta(T) = -\mathrm{d}\theta/\mathrm{d}T$ as the derivative function of coverage with respect to temperature, the relationship between this derivative function and pressure *vs.* temperature for a given heating rate can be expressed as

$$r_\beta(T) = (K_{pr}/\beta)P_\beta(T) \tag{3}$$

where the factor K_{pr} is given by the temperature, the size of the recipient and the pumping rate [4, 11]. Hence, $\mathbf{P}_m(\beta)$ can be transformed to $\mathbf{r}_m(\beta)$, i.e. to the peak maximum value of $r_\beta(T)$. The shapes of $\mathbf{r}_m(\beta)$ and $\mathbf{T}_m(\beta)$ depend on the kinetics of desorption. The experimentally available quantities, based on which the desorption parameters should quantitatively be determined, are related to the functions $\mathbf{T}_m(\beta)$ and $\mathbf{r}_m(\beta)$ defined on a rationally limited range of β values with the same constant θ_o. Up to now, there is no rigorous mathematical method for simultaneous determination of E_d and A based on the above information about desorption processes.

Many approaches to a modelling of the temperature dependence of the rate of desorption are based on a simple Arrhenius expression, called Polanyi-Wigner equation, which can be described as

$$-\mathrm{d}\theta/\mathrm{d}t = \theta^n A \exp(-E_d/(RT)), \tag{4}$$

where n is the reaction order and R the gas constant. In the following, two important parameters will be introduced.

Definition 1

The temperature T_r, at which the desorption velocity constant

$$K_d = A \exp(-E_d/(RT_r)) = 1, \tag{5}$$

is called resonant temperature of desorption.

Hence, the desorption velocity constant K_d, having the same dimension as A, can be represented by

$$K_d = \exp(\alpha(T-T_r)/T), \tag{6}$$

where $\alpha = \ln A$ is the logarithmic frequency factor and $T_r = E_d/(R\alpha)$ the resonant temperature of desorption [16]. The question arises, how the kinetic parameters T_r and α, corresponding to E_d and A with a certain n value, can be determined simultaneously by the analysis of the information included in the experimentally observed $\mathbf{T}_\mathbf{m}(\beta)$ and $\mathbf{r}_\mathbf{m}(\beta)$.

Definition 2

The linear heating rate β_r, satisfying

$$\mathbf{T}_\mathbf{m}(\beta_r) = T_r, \tag{7}$$

is called resonant heating rate.

Kinetic model of a n-order desorption process

In the following, we will consider $\mathbf{r}_\mathbf{m}(\beta)$ and $\mathbf{T}_\mathbf{m}(\beta)$ as the observed outputs of a desorption process, for which a linear heating rate β is treated as the input both of the process and of the assumed process model.

Due to the applied linear heating program, the Eq. (4) can now be expressed by the use of T as the only variable. Furthermore, from Eq. (1) we have

$$\mathrm{d}\theta/\mathrm{d}T = (1/\beta)(\mathrm{d}\theta/\mathrm{d}t), \tag{8}$$

thus Eq. (4), in combination with Eq. (6), becomes

$$r_\beta(T) = -\mathrm{d}\theta/\mathrm{d}T = (1/\beta)\theta^n \exp(\alpha(T-T_r)/T), \tag{9}$$

that describes the used process model.

The general solution of Eq. (9) can be written as

$$\theta(T) = \theta_o \exp(-I(T_o, T)/\beta, \text{ for } n=1; \tag{10}$$

$$\theta(T) = \theta_o / \sqrt[n-1]{1 + (n-1)\theta_o^{n-1} I(T_o, T)/\beta} \quad \text{for } n \geq 2 \tag{11}$$

where

$$I(T_o, T) = \int_{T_o}^{T} \exp(\alpha(T - T_r)/T)\mathrm{d}T \tag{12}$$

can be calculated by numerical methods, e.g. the Runge-Kutta method.

Using the input signal, $\{\beta_i,\ i=\overline{1,N}\}$, and the output signals, $\{\mathbf{T}_m(\beta_i), \mathbf{r}_m(\beta_i), i=\overline{1,N}\}$, where N is the sampling number, the proposed method for parameter determination can be considered as the procedure of finding the kinetic parameters n, α, T_r of the model expressed by the Eq. (9), which gives the model output signals $\{r_m(\beta_i), T_m(\beta_i), i=\overline{1,N}\}$ in such a way that the performance index

$$V=\sum_{i=1}^{N}\left[\,|\mathbf{r}_m(\beta_i)-r_m(\beta_i)|+h\,|\mathbf{T}_m(\beta_i)-T_m(\beta_i)|\,\right]$$

is minimized with h as a scaling factor. Assuming now that n is known and that $V=0$, we have $\mathbf{r}_m(\beta_i)=r_m(\beta_i)$ and $\mathbf{T}_m(\beta_i)=T_m(\beta_i)$, so that only α and T_r of the proposed model represented by Eq. (9) have to be estimated.

The suggested method

The suggested method is characterized as rigorous, since it considers, for the first time, that the fractional coverage at the peak maximum is dependent on the heating rate. It will be shown in the following sections, that the simplification $\theta_m^{n-1}=\theta_o^{n-1}/n(n\geq 2)$ or $\theta_m=\theta_o/e(n=1)$ underlying the methods used, up to now, affects the accuracy for the simultaneous determination of E_d and A and the robustness towards statistical errors.

In this paper three procedures have been developed to treat different cases.

Procedure 1

For known n and α the condition-function (cf. Appendix Eqs (27)–(36))

$$\overline{T_m}(\beta)=\frac{\alpha}{n}\cdot\frac{\sqrt[n]{\beta\mathbf{r}_m(\beta)}}{\mathbf{r}_m(\beta)} \tag{13}$$

and the experimentally observed functions $\mathbf{T}_m(\beta)$ are plotted on the T_m–β plane. The crosspoint from $\overline{T_m}(\beta)$ and $\mathbf{T}_m(\beta)$ is (β_r, T_r).

Generally, α and T_r are unknown, so that an additional condition which does not contain α for the determination of β_r has to be found. Procedure 2 and Procedure 3 are developed for this issue.

The data set applied is $\{\mathbf{T}_m(\beta_i), \mathbf{r}_m(\beta_i)\ i=\overline{1,N}\}$. Considering that the surface coverage at the peak maximum is a function of heating rate for known n, the resonant heating rate β_r defined by Eq. (7) should be estimated from the information included in the function $\mathbf{r}_m(\beta)$. The resonant temperature T_r defined by Eq. (5) can be obtained on the curve $\mathbf{T}_m(\beta)$ by Definition 2, and, then, the logarithmic frequency factor α introduced by Eq. (6) is determined by Eq. (13), i.e. $\alpha = nT_r r_m(\beta_r)/\sqrt[n]{\beta_r r_m(\beta_r)}$. From Eq. (6) the activation energy $E_d = R\alpha T_r$ and the frequency factor A=exp(α) are obtained. The conditions for the determination of β_r on the curve $\mathbf{r}_m(\beta)$ is given by (cf. Appendix Eqs (37)–(42))

$$\ln\frac{\theta_o}{\beta_r r_m(\beta_r)} = 1 + \beta_r r_m^{-1}(\beta_r)\left.\frac{dr_m(\beta)}{d\beta}\right|_{\beta_r}, \quad \text{for } n=1 \tag{14}$$

and

$$n\frac{r_m(\beta_r)}{\sqrt[n]{\beta_r r_m(\beta_r)}} = \theta_o^{n-1}\left[\beta_r^{-1} - (n-1)r_m^{-1}(\beta_r)\left.\frac{dr_m(\beta)}{d\beta}\right|_{\beta_r}\right], \quad \text{for } n \geq 2. \tag{15}$$

Procedure 2

If n=1 or n=2, the two experimentally observed data sets $\{\beta_i, \mathbf{r}_m(\beta_i)\ i=\overline{1,N}\}$ and $\{\beta_i, \mathbf{T}_m(\beta_i)\ i=\overline{1,N}\}$ are best-fitted by

$$r_m(\beta) = \gamma_{ro}\beta^{-\gamma_r} \text{ and } T_m(\beta) = \gamma_{to}\beta^{\gamma_t}. \tag{16}$$

The parameters α and T_r can be simultaneously estimated with the help of the following equations, (cf. Appendix Eqs (43)–(48)):

$$\hat{\beta}_r = \frac{1}{e}\left(\frac{\theta_o}{\gamma_{ro}}\right)^{\frac{1}{1-\gamma_r}}, \ n=1; \quad \hat{\beta}_r = \left[\frac{\theta_o^2(1+\gamma_r)^2}{4\gamma_{ro}}\right]^{\frac{1}{1-\gamma_r}}, \ n=2. \tag{17}$$

$$\hat{T}_r = T_m(\hat{\beta}_r) = \gamma_{to}\hat{\beta}_r^{\gamma_t}. \tag{18}$$

$$\hat{\alpha} = \frac{\hat{T}_r}{\hat{\beta}_r}, \ n=1; \quad \hat{\alpha} = 2\hat{T}_r\sqrt{\gamma_{ro}}\hat{\beta}_r^{-\frac{1+\gamma_r}{2}}, \ n=2. \tag{19}$$

As an alternative to Procedure 2, the resonant isocline of the observed function $\mathbf{r}_m(\beta)$ for the graphic determination of the point (β_m, $\mathbf{r}_m(\beta_r)$) is introduced in the following (cf. Appendix Eqs (49)–(53)).

Definition 3

The curve described by the equation for $n = 1$

$$\overline{r_m}(\beta) = \frac{\theta_o}{\beta} e^{-\frac{c}{\beta}}, \quad c > 0 \tag{20}$$

or by the equation for $n \geq 2$

$$\overline{r_m}(\beta) = \frac{\theta_o^n}{(c+\beta)} \sqrt[n-1]{\frac{\beta}{c+\beta}}, \quad c > 0 \tag{21}$$

where c is a constant factor, is called resonant isocline of the observed function $\mathbf{r}_m(\beta)$, if it is a tangent to $\mathbf{r}_m(\beta)$ at the point (β_r, $\mathbf{r}_m(\beta_r)$).

Procedure 3

Assuming n is known, we have two experimentally observed functions $\mathbf{T}_m(\beta)$ and $\mathbf{r}_m(\beta)$. The point (β_r, $\mathbf{r}_m(\beta_r)$) can be graphically determined by plotting the resonant isocline of $\mathbf{r}_m(\beta)$. Then, on the T_m–β plane, T_r is read out at β_r on the function $\mathbf{T}_m(\beta)$, i.e. $T_r=\mathbf{T}_m(\beta_r)$. Finally, α is obtained in the way represented by Eq. (13), i.e.

$$\alpha = n\mathbf{T}_m(\beta_r)\frac{\mathbf{r}_m(\beta_r)}{\sqrt[n]{\beta_r \mathbf{r}_m(\beta_r)}}, \tag{22}$$

Hence, α and T_r are determined simultaneously.

Experimental design

Prior to a TDS experiment, the possible β_r existence range should be estimated, because the core information about the desorption kinetics lies in the neighborhood of the resonant point $\{\mathbf{r}_m(\beta_r), \mathbf{T}_m(\beta_r), \beta_r\}$ because of Definition 1–2 and the condition described by Eq. (13). If the boundary values for α and T_r are known, i.e.

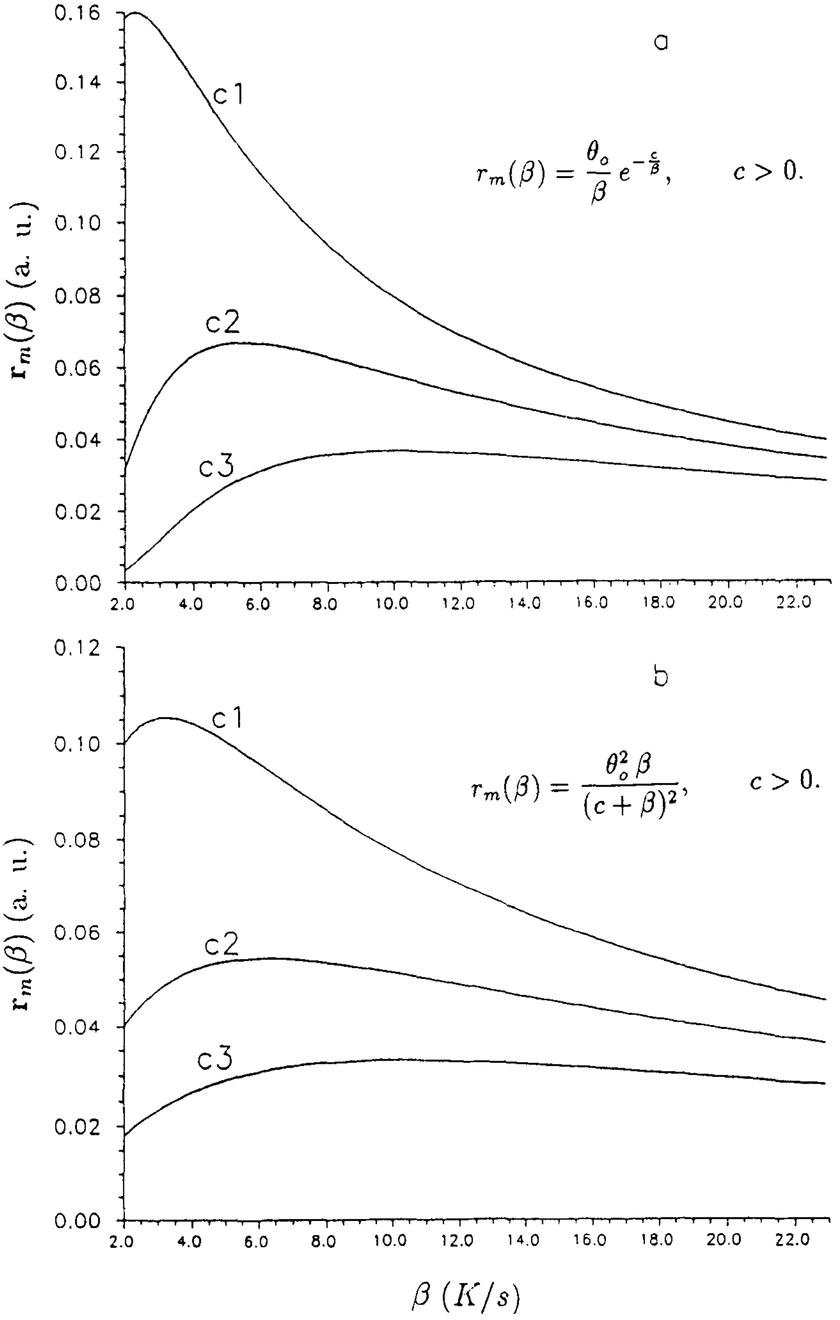

Fig. 1 Isoclines in the $r_m(\beta)$–β plane for varied values of c($c1 < c2 < c3$) a: n=1 (Eq. (20)). b: n=2 (Eq. (21))

$$T_{r1} \leq T_r \leq T_{r2} \text{ and } \alpha_1 \leq \alpha \leq \alpha_2.$$

for given values of n and θ_o, the adequate value $\beta_{r,\min}$ from (T_{r1}, α_2) and $\beta_{r,\max}$ from (T_{r2}, α_1) can be determined, and the β_r existence range is

$$\beta_{r\,\min} \leq \beta_r \leq \beta_{r\,\max}.$$

If the above estimated range is experimentally available, data sets $\{\mathbf{r}_m(\beta_i), \mathbf{T}_m(\beta_i), i = \overline{1, N}\}$ and Procedure 2 or Procedure 3 can then be used to determine simultaneously the parameters α and T_r. If the range is beyond the accessibility of experiments, Procedure 2, enabling an extrapolation to the β_r range, can be used.

The constant factor c of the resonant isocline can be determined systematically by trials, since the isocline function described by Eq. (20) or Eq. (21) is monotonously changing with respect to c for a given β_r (Fig. 1). The tangential point denoted by (β_r, $\mathbf{r}_m(\beta_r)$) will be readily matched by trials.

It is shown from simulations, that the resonant heating rate exists in the range

$$0.576 \leq \beta_r \leq 49.177 \tag{23}$$

for a second-order desorption process in the intervals for $\theta_o \in [0.1, 1.0]$, for $\alpha \in [23.0, 33.0]$ and $T_r \in [180.0, 1050.0]$ corresponding to $A \in [0.97 \cdot 10^{10}, 2.1 \cdot 10^{14}]$ and $E_d \in [21.0, 287.0]$. For example, if θ_o=0.5, $\alpha \in [27.0, 30.0]$ and $T_r \in [615.0, 832.5]$, the estimated β_r exists in the range $10.875 \leq \beta_r \leq 16.448$ (Table 1).

Evaluation accuracies

To check the evaluation accuracy of the above procedures, simulated desorption curves

$$r_\beta(T) = -\mathrm{d}\theta/\mathrm{d}T = (1/\beta)\theta^n \exp(\alpha(T - T_r)/T)$$

have been calculated with the constant values of n, T_o, θ_o, α, T_r. Using the input signal $\{\beta_i, i = \overline{1, N}\}$, the peak maximum points ($T_m(\beta_i)$, $r_m(\beta_i)$) are determined.

Taking θ_o = 0.025, T_o = 293.0, α = 29.93 (equal to $A = 9.964 \cdot 10^{12}$[1/s]), T_r = 523.71 (equal to E_d = 130.256[kJ/mol]), the functions $r_m(\beta)$ (Curve 1) and $T_m(\beta)$ (Curve 2) are plotted in Fig. 2 for n = 1 with β_i ranging from 15.0 to 20.0

in steps of 0.5, and in Fig. 3 for $n = 2$ with β_i in the interval [0.1, 2.1] in steps of 0.1.

In order to re-evaluate α and T_r by Procedure 1, the condition-function described by Eq. (13) is plotted as Curve 3 in Fig. 2 for $n = 1$ and in Fig. 3 for $n = 2$. The crosspoint from Curve 2 and Curve 3 is $(\beta_r, \hat{T}_r)=(17.5, 523.7)$ for $n = 1$ and $(\beta_r, \hat{T}_r)=(0.475, 524.0)$ for $n = 2$. The standard deviation $|(T_r-\hat{T}_r)/T_r|$ of the resonant temperature is calculated as 0.002% for $n = 1$ and 0.055% for $n = 2$.

Table 1 Values of β_r in deg·s^{-1} for a selected range of frequency factors $A \in [0.97\cdot10^{10}, 2.1\cdot10^{14}]$ in s^{-1}, activation energies $E_d \in [21.0, 287.0]$ in kJ·mol^{-1}, and $\theta_o = 0.5$

α	T_r				
	180.0	397.5	615.0	832.5	1050.0
	β_r				
23	4.215	9.309	14.401	19.495	24.589
24	4.029	8.896	13.766	18.633	23.502
25	3.858	8.519	13.182	17.845	22.504
26	3.700	8.175	12.645	17.116	21.589
27	3.555	7.853	12.152	16.448	20.745
28	3.421	7.557	11.693	15.827	19.963
29	3.298	7.283	11.268	15.253	19.238
30	3.182	7.026	10.872	14.718	18.562
31	3.075	6.789	10.504	14.221	17.933
32	2.973	6.568	10.159	13.754	17.346
33	2.879	6.356	9.836	13.316	16.795

Now, making the best fit of Curve 1 and Curve 2 in Fig. 2 for $n=1$ and in Fig. 3 for $n=2$ for the application of Procedure 2, we get

$$r_m(\beta) = 664.931\cdot10^{-6}\beta^{-0.0608796},\ T_m(\beta) = 478.88\cdot\beta^{0.0312685} \text{ in Fig. 2,}$$

$$r_m(\beta) = 361.304\cdot10^{-6}\beta^{-0.0613017},\ T_m(\beta) = 536.688\cdot\beta^{0.0314806} \text{ in Fig. 3.}$$

For $n=1$, we obtain from Eq. (17)

$$\hat{\beta}_r = e^{-1}(0.025/(664.931\cdot10^{-6}))^{1.064826} = 17.50$$

and from Eqs (18)–(19)

$$\hat{T}_r = 478.88 \cdot 17.50^{0.0312685} = 523.71,\ \hat{\alpha} = 523.71/17.50 = 29.926.$$

The standard deviation of the resonant temperature is nearly 0% and that of the logarithmic frequency factor 0.013%.

For n=2 we have

$$\hat{\beta}_r = \left[\theta_o^2(1+\gamma_r)^2/(4\gamma_{ro})\right]^{\frac{1}{1-\gamma_r}} = 0.48711^{1.065305} = 0.465,$$

$$\hat{T}_r = 536.68 \cdot 0.465^{0.0314806} = 523.90,$$

$$\hat{\alpha} = 2 \cdot 523.9 \cdot \sqrt{361.304\, 10^{-6}} \cdot 0.465^{-\frac{1.0613017}{2}} = 29.90.$$

Table 2 Accuracy and robustness comparisons

Case	n	Applied method	$\hat{A}$ / s^{-1}	$\hat{E}_d$ / kJ·mol^{-1}
	1	NM	$9.924 \cdot 10^{12}$	130.236
Evaluation	1	OM	$4.522 \cdot 10^{12}$	126.926
accuracy	2	NM	$9.994 \cdot 10^{12}$	130.341
	2	OM	$7.460 \cdot 10^{9}$	130.774
	1	NM	$2.230 \cdot 10^{13}$	133.490
Robustness	1	OM	$1.141 \cdot 10^{3}$	36.981
	2	NM	$9.115 \cdot 10^{12}$	129.738
	2	OM	$1.663 \cdot 10^{9}$	124.172
Robustness of	2	NM	$5.692 \cdot 10^{12}$	127.089
extended model	2	O M	$1.890 \cdot 10^{10}$	131.800

The parameters to be determined A =$9.964 \cdot 10^{12}$ s^{-1} ; E_d = 130.256 kJ·mol^{-1}

The standard deviation of T_r is 0.036% and that of α 0.10%. The transformation of these re-evaluated parameters into A and E_d for n = 1 and n = 2 is given in Table 2 (line 1 and line 3).

For Procedure 3, the corresponding resonant isocline of $r_m(\beta)$ (Curve 1) is plotted as Curve 4 in Fig. 2 for n = 1 and in Fig. 3 for n = 2. The tangential point (β_r, $r_m(\beta_r)$) can be read out for n = 1 in Fig. 2 as (17.5, 558.0) and for n = 2 in Fig. 3 as (0.475, 377.2). At β_r for n = 1 in Fig. 2, $\hat{T}_r = T_m(\beta_r)$ = 523.70; at β_r

for $n = 2$ in Fig. 3, $\hat{T}_r = T_m(\beta_r) = 524.0$ and $r_m)(\beta_r) = 377.2 \cdot 10^{-6}$. Hence, from Eq. (22), i.e.

$$\hat{\alpha}_o = \hat{T}_r/\beta_r,\ n = 1;\quad \hat{\alpha}_o = 2\hat{T}_r\sqrt{r_m(\beta_r)/\beta_r},\ n = 2,$$

we can get sequentially the value of $\hat{\alpha}_o$ for $n = 1$ and $n = 2$, i.e. 29.926 and 29.933. The standard deviation of the resonant temperature is 0.002% for $n = 1$ and 0.055% for $n = 2$; that of the logarithmic frequency factor is 0.013% for $n = 1$ and 0.01% for $n = 2$.

The above results show that the errors generated by the proposed procedures can be neglected as compared to the normal experimental uncertainties.

For a comparison between the ordinary heating rate variation method (OM) and the proposed new method (NM), the same data set as used above is applied to determine E_d and A by OM.

The most frequently used equation of the heating rate variation methods can be written as [13, 14]

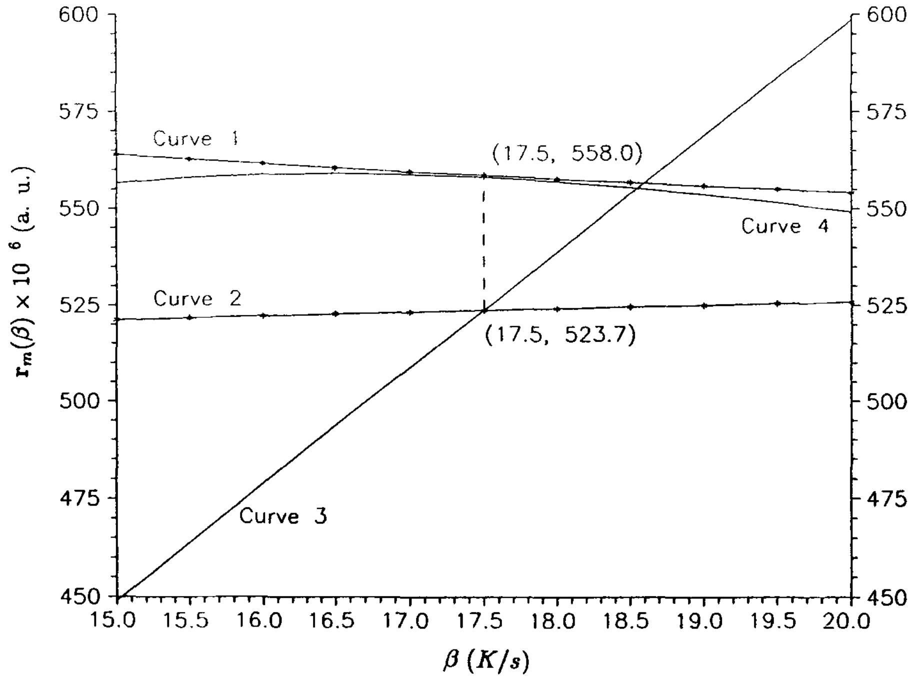

Fig. 2 Computer-simulated $r_m(\beta)$ (a. u.) labelled with Curve 1 and $T_m(\beta)$ (in K) labelled with Curve 2 for the reaction order $n = 1$, the condition-function (Curve 3) from Eq. (13) related with the Procedure 1 and the resonant isocline (Curve 4) from Eq. (20) related with the Procedure 3. β is the heating rate in deg·s^{-1}

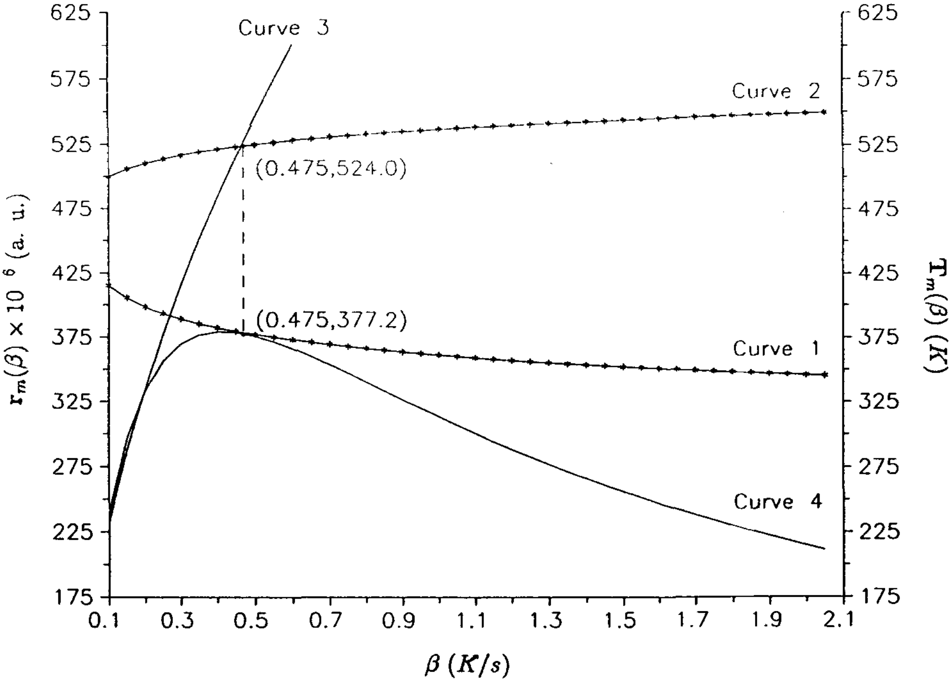

Fig. 3 Computer-simulated $r_m(\beta)$ (a. u.) labelled with Curve 1 and $T_m(\beta)$ (in K) labelled with Curve 2 for the reaction order $n = 2$, the condition-function (Curve 3) from Eq. (13) related with the Procedure 1 and the resonant isocline (Curve 4) from Eq. (21) related with the Procedure 3. β is the heating rate in deg·s^{-1}

$$\ln(T_m^2/\beta) = (E_d/(1000R))(1000/T_m) + \ln(E_d/(RA\theta_o^{n-1})). \qquad (24)$$

For $n = 1$ we have

$$\ln(T_m^2/\beta) = 15.2739(1000/T_m) - 19.5054$$

and for $n = 2$

$$\ln(T_m^2/\beta) = 15.7369(1000/T_m) - 16.7579,$$

from which the two parameters E_d and A are calculated and given in Table 2 (line 2 and line 4). The larger errors resulting from OM have to be referred to the neglect of the heating rate dependence of θ_m.

Robustness comparisons

The OM is considered to be very sensitive to minor experimental errors, so that it may be difficult to obtain reliable kinetic parameters [6]. To compare the sensitivity of different methods, i.e. NM and OM, towards statistical errors, two types of robustness studies are described in the following.

First, the same data set as used in the previous section, i.e. $\{\mathbf{T}_m(\beta_i), \mathbf{r}_m(\beta_i)\ i=\overline{1,N}\}$, is disturbed by addition of a random small error, namely $\{\mathbf{T}_m(\beta_i)+\sigma_T(\beta_i),\ \mathbf{r}_m(\beta_i)+\sigma_r(\beta_i), i=\overline{1,N}\}$, where $\sigma_T(\beta_i)\leq 1\%\ \max\{\mathbf{T}_m(\beta_i)\}$, $\sigma_r(\beta_i)\leq 1\%\ \max\{\mathbf{r}_m(\beta_i)\}$. Both NM and OM are applied to re-evaluate A and E_d. The results presented in Table 2 (line 5–8) demonstrate the different robustness towards statistical errors.

Secondly, an extended model for the desorption with coverage dependent activation energy

$$E(\theta) = E_d + \gamma\theta,$$

i.e. with coverage dependent resonant temperature

$$T_r(\theta) = T_{ro} + W_t\theta,$$

where $T_{ro}=E_d/(R\alpha)$ and $W_t=\gamma/(R\alpha)$, is considered. A condition-equation similar to Eq. (13) can be described in the following (cf. Appendix Eqs (27)–(33))

$$T_m(\beta) = \frac{\alpha}{n}\frac{\sqrt[n]{\beta \mathbf{r}_m(\beta)}}{\mathbf{r}_m(\beta)}(1 + W_t\mathbf{r}_m(\beta)). \tag{25}$$

If $|W_t\mathbf{r}_m(\beta)|<<1$, Procedure 1–3 can be applied for a desorption with coverage dependent activation energy (cf. Appendix Eqs. (34)–(35).

Taking $W_t=-10$ for $n=2$ and the same values of the other parameters used in the previous section, the data set $\{\mathbf{T}_m(\beta_i), \mathbf{r}_m(\beta_i), i=\overline{1,N}\}$ is obtained by the Runge-Kutta method from the equation

$$r_\beta(T) = -\,\mathrm{d}\theta/\mathrm{d}T = 1/\beta\theta^n \exp(\alpha(T-T_r(\theta))/T). \tag{26}$$

Making the best fit of $\mathbf{r}_m(\beta_i)$ and $\mathbf{T}_m(\beta_i)$ for the application of Procedure 2 of NM, gives

$$r_m(\beta) = 357.401\cdot 10^{-6}\beta^{-0.0624292},\quad T_m(\beta) = 532.964\,\beta^{0.0308685}.$$

The same data set is fitted using OM as

$$\ln(T_m^2/\beta) = 15.8603\,(1000/T_m) - 17.2098.$$

The results are shown in Table 2 (line 9–10). The better robustness of NM can be attributed to the complete mathematical treatment, again.

Conclusions

Although the TD experiment with linear heating rate seems to be very straightforward and simple, some experimental precautions must be taken into account with regard to the range in which the heating rate is varied. The core information about the kinetics of desorption processes described by the Polányi-Wigner equation lies at the defined resonant point $\{\mathbf{r}_m(\beta_r), \mathbf{T}_m(\beta_r), \beta_r\}$. Hence, the alteration of β in close vicinty to the resonant heating rate $[(\beta_r-\Delta\beta_r), (\beta_r+\Delta\beta_r)]$ is sufficient for a parameter determination with resonable accuracy. If a constant initial coverage θ_o can be realized, and the boundary values for the expected kinetic parameters are known, the optimal range of β values for an experimental design can be predicted. Thus, the proposed method for parameter determination of a thermal desorption model is related to those determination Procedures 1–3 making use of peak maximum variations with constant initial coverage and altered heating rates in or close to the resonant heating rate. The values of the kinetic parameters E_d and A can be determined simultaneously and with improved accuracy and robustness, since Procedures 2–3 consider the dependence of θ_m on β. Additionally, the definition $K_d = A\exp(-E_d/(RT_r)) = 1$ could be considered as a normalization procedure for a better comparison of results from thermal analysis data obtained at identic systems in different laboratories.

Notations

A frequency factor
E_d energy of desorption
R gas constant
n kinetic order
t time
t_o initial time
$\mathbf{P}_m(\beta)$ observed peak maximum pressure as a function of β
$r_\beta(T)$ derivative function of coverage to temperature *vs.* T for a given β

$r_\mathrm{m}(\beta)$ model peak maximum value of $r_\beta(T)$ as a function of β
$\mathbf{r}_\mathbf{m}(\beta)$ observed peak maximum value of $r_\beta(T)$ as a function of β
T temperature at t
T_o temperature at t_o
T_r resonant temperature of desorption
$T_\mathrm{m}(\beta)$ model peak maximum temperature as a function of β
$\mathbf{T}_\mathbf{m}(\beta)$ observed peak maximum temperature as a function of β
α logarithmic frequency factor
β linear heating rate
β_r resonant heating rate
θ fractional surface coverage at t
θ_o fractional coverage at t_o
$\theta_\mathrm{m}(\beta)$ peak maximum fractional coverage as a function of β

References

1 G. Ehrlich, Adv. Catal., 14 (1963) 256.
2 R. J. Cvetanovic and Y. Amenomiya, Adv. Catal., 17 (1967) 103.
3 L. A. Petermann, Progr. Surf. Sci., 3 (1972) 2.
4 M. Smutek, S. Cerny and F. Buzek, Adv. Catal., 24 (1975) 343.
5 D. A. King, Surf. Sci., 47 (1975) 384.
6 J. L. Falconer and J. A. Schwarz, Catal. Rev.-Sci. Eng., 25 (1983) 141.
7 M. A. Morris, M. Bowker and D. A. King, Comprehensive Chemical Kinetics, Eds. C. H. Bamford, C. H. F. Tipper and R. G. Compton, Elsevier, Amsterdam 1984, Vol. 19, p. 1.
8 A. M. de Jong and J. W. Niemantsverdriet, Surf. Sci., 233 (1990) 355.
9 S. Ceckiewicz and M. Kozik, Surf. Sci., 110 (1981) 491.
10 N. I. Jaeger, A. L. Jourdan and G. Schulz-Ekloff, J. Chem. Soc., Faraday Trans., 87 (1991) 1251.
11 P. A. Redhead, Vacuum, 12 (1962) 203.
12 G. Carter, Vacuum, 12 (1962) 245.
13 F. M. Lord and J. S. Kittelberger, Surf. Sci., 43 (1974) 173.
14 J. L. Falconer and R. J. Madix, Surf. Sci., 48 (1975) 393.
15 R. P. H. Gasser, An introduction to chemisorption and catalysis by metals, Clarendon Press, Oxford, 1985.
16 S. Zhou, G. Schulz-Ekloff and D. Popovic, Chem. Eng. Sci., 46 (1991) 2961.

Zusammenfassung — Es wird eine neue Methode für die Analyse von Thermodesorptionsspektren vorgestellt, die auf den experimentellen Peakmaximumfunktionen für die Temperatur $\mathbf{T}_\mathbf{m}$(ß) und den Druck $\mathbf{P}_\mathbf{m}$(ß) sowie auf einer strikten mathematischen Verarbeitung *bsiert. Es wurde die resonante Aufheizgeschwindigkeit ß$_\mathrm{r}$ ermittelt, die die Bedingung T_m(ß$_\mathrm{r}$)=T_r erfüllt, wobei T_r die Resonanztemperatur mit der Definition $A\ \exp(-E_\mathrm{d}/(RT_\mathrm{r}))=1$ ist. Wie an computersimulierten Desorptionsspektren gezeigt wurde, können Desorptionsenergie E_d und Frequenzfaktor A mit relativ geringer Anfälligkeit gegen statistische experimentelle Fehler gleichzeitig bestimmt werden.

Appendix: Principle of the suggested method

The gas evolution function will have its maximum at T_m for which $(dP/dT)|_{T_m}=0$ holds. Taking into account Eq. (3), and supposing the differential of Eq. (26) with respect to T is zero

$$\left.\frac{dr_\beta(T)}{dT}\right|_{T_m}=\frac{1}{\beta}\cdot e^{\alpha\frac{T_m-T_r(\theta_m)}{T_m}}\left[n\theta_m^{n-1}(\beta)\left.\frac{d\theta}{dT}\right|_{T_m}+\theta_m^n(\beta)\left(\frac{\alpha T_r(\theta_m)}{T_m^2}-\frac{\alpha W_t}{T_m}\cdot\left.\frac{d\theta}{dT}\right|_{T_m}\right)\right]=0. \quad (27)$$

where $T_r(\theta)=T_{ro}+W_t\theta$, we have

$$\left(n-\theta_m\frac{\alpha W_t}{T_m}\right)\cdot\left.\left(-\frac{d\theta}{dT}\right)\right|_{T_m}=\theta_m(\beta)\frac{\alpha T_r(\theta_m)}{T_m^2}.$$

Substitution of $-d\theta/dT$ from Eq. (26) finally results in

$$\left(n-\theta_m\frac{\alpha W_t}{T_m}\right)\theta_m^{n-1}(\beta)e^{\alpha\frac{T_m-T_r(\theta_m)}{T_m}}=(\beta)\frac{\alpha T_r(\theta_m)}{T_m^2}. \quad (28)$$

For the resonant heating rate β_r is $T_m(\beta_r)=T_r(\theta_m(\beta_r))$, so that the last equation becomes

$$\left(n-\theta_m(\beta_r)\frac{\alpha W_t}{T_m}\right)\theta_m^{n-1}(\beta_r)=(\beta_r)\frac{\alpha}{T_m(\beta_r)}. \quad (29)$$

On the other hand, rearranging Eq. (26) at $T=T_m$ gives

$$\beta r_m(\beta)=\theta_m^n(\beta)e^{\alpha\frac{T_m-T_r(\theta_m(\beta))}{T_m}}, \quad (30)$$

which, for β_r, is reduced to

$$\beta_r r_m(\beta_r)=\theta_m^n(\beta_r), \quad (31)$$

so that

$$\theta_m(\beta_r)=\sqrt[n]{\beta_r r_m(\beta_r)}. \quad (32)$$

Substituting this value of $\theta_m(\beta_r)$ in Eq. (29) finally gives

$$T_r(\theta_m(\beta_r)) = \bar{T}_m(\beta_r) = \frac{\alpha}{n}\,\frac{\sqrt[n]{\beta_r r_m(\beta_r)}}{r_m(\beta_r)}(1 + W_t r_m(\beta_r)), \tag{33}$$

or

$$\bar{T}_m(\beta_r) = \frac{\alpha}{n}\cdot\frac{\sqrt[n]{\beta_r r_m(\beta_r)}}{r_m(\beta_r)}\left(1 + \left(1 - \frac{n}{\alpha}\right)W_t r_m(\beta_r)\right) + W_t\theta_m(\beta_r). \tag{34}$$

For a desorption with coverage dependent resonant temperature under the condition $|W_t r_m(\beta)| << 1$, it is rational

$$T_{ro} = T_m(\beta_r) = \frac{\alpha}{n}\cdot\frac{\sqrt[n]{\beta_r r_m(\beta_r)}}{r_m(\beta_r)}. \tag{35}$$

For a desorption without coverage dependent resonant temperature, i.e. $W_t = 0$, we have the condition-function

$$T_r = T_m(\beta_r) = \frac{\alpha}{n}\cdot\frac{\sqrt[n]{\beta_r r_m(\beta_r)}}{r_m(\beta_r)}. \tag{36}$$

So the Procedure 1 is derived.

For simplicity only a desorption without coverage dependent resonant temperature is considered to derive Procedures 2–3. An obvious difference between NM and OM is that, NM considers θ_m as function of β. Differentiating Eq. (30) with respect to β at $\beta = \beta_r$ gives

$$r_m(\beta_r) + \beta_r\left.\frac{\mathrm{d}r_m(\beta)}{\mathrm{d}\beta}\right|_{\beta_r} = n\,\theta_m^{n-1}(\beta_r)\left.\frac{\mathrm{d}\theta_m}{\mathrm{d}\beta}\right|_{\beta_r} + \theta_m^{n}(\beta_r)\left.\frac{\alpha}{T_m(\beta_r)}\cdot\frac{\mathrm{d}T_m}{\mathrm{d}\beta}\right|_{\beta_r}. \tag{37}$$

The $(n-1)$th power of Eq. (11) at $T=T_m$ results in

$$\beta + (n-1)\theta_o^{n-1} I(T_o, T_m) = \beta\left[\frac{\theta_o}{\theta_m(\beta)}\right]^{n-1}, \tag{38}$$

and the derivative of Eq. (12) for $T=T_m$ results in

$$\left.\frac{\mathrm{d}I(T_o, T_m)}{\mathrm{d}\beta}\right|_{\beta_r} = \left.\frac{\mathrm{d}T_m}{\mathrm{d}\beta}\right|_{\beta_r}, \tag{39}$$

so that Eq. (38), differentiated with respect to β at β_r, becomes

$$1+(n-1)\theta_o^{n-1}\frac{dT_m}{d\beta}\bigg|_{\beta_r} = \left[\frac{\theta_o}{\theta_m(\beta_r)}\right]^{n-1} + \beta_r(n-1)\left[\frac{\theta_o}{\theta_m(\beta_r)}\right]^{n-2}\cdot\left[\frac{\theta_o}{-\theta_m^2(\beta_r)}\right]\cdot\frac{d\theta_m}{d\beta}\bigg|_{\beta_r},$$

or, after rearrangement,

$$n\theta_m^{n-1}(\beta_r)\frac{d\theta_m}{d\beta}\bigg|_{\beta_r} = \frac{n}{n-1}\cdot\frac{\theta_m^n(\beta_r)}{\beta_r}\left\{1-\left[\frac{\theta_m(\beta_r)}{\theta_o}\right]^{n-1} - (n-1)\theta_m^{n-1}(\beta_r)\frac{dT_m}{d\beta}\bigg|_{\beta_r}\right\}.$$

Taking into account Eq. (31), the last equation results in

$$n\theta_m^{n-1}(\beta_r)\frac{d\theta_m}{d\beta}\bigg|_{\beta_r} = \frac{r_m(\beta_r)}{n-1}\left[n-\frac{n\theta_m^{n-1}(\beta_r)}{\theta_o^{n-1}} - (n-1)n\theta_m^{n-1}(\beta_r)\frac{dT_m}{d\beta}\bigg|_{\beta_r}\right].$$

On the other side, dividing Eq. (37) by $r_m(\beta_r)$ and substituting from the above equation $n\theta_m^{n-1}(\beta_r)\ (d\theta_m/d\beta)|_{\beta_r}$ gives

$$1+\beta_r\frac{\left.\frac{dr_m(\beta)}{d\beta}\right|_{\beta_r}}{r_m(\beta_r)} = \beta_r\frac{\alpha}{T_m(\beta_r)}\cdot\frac{dT_m}{d\beta}\bigg|_{\beta_r} + \frac{n}{n-1} - \frac{n}{n-1}\,\frac{\theta_m^{n-1}(\beta_r)}{\theta_o^{n-1}} - n\theta_m^{n-1}(\beta_r)\frac{dT_m}{d\beta}\bigg|_{\beta_r}.$$

Subsequently substituting $n\theta_m^{n-1}(\beta_r)$ from Eq. (29) into the above equation gives

$$1+\beta_r\frac{\left.\frac{dr_m(\beta)}{d\beta}\right|_{\beta_r}}{r_m(\beta_r)} = \frac{n}{n-1} - \frac{1}{n-1}\cdot\frac{\beta_r}{\theta_o^{n-1}}\frac{\alpha}{T_m(\beta_r)},$$

or

$$\frac{\alpha}{T_m(\beta_r)} = \theta_o^{n-1}\left[\beta_r^{-1} - (n-1)r_m^{-1}(\beta_r)\frac{dr_m(\beta)}{d\beta}\bigg|_{\beta_r}\right].$$

This, compared with Eq. (36), gives the following condition equation from which the resonant heating rate β_r for the case $n \geq 2$ can be obtained

$$n\frac{r_m(\beta_r)}{\sqrt[n]{\beta_r r_m(\beta_r)}} = \theta_o^{n-1}\left[\beta_r^{-1} - (n-1)r_m^{-1}(\beta_r)\left.\frac{dr_m(\beta)}{d\beta}\right|_{\beta_r}\right]. \tag{40}$$

For the case $n=1$ the condition equation, derived in the same way as above, is given by

$$\ln\frac{\theta_o}{\beta_r r_m(\beta_r)} = 1 + \beta_r r_m^{-1}(\beta_r)\left.\frac{dr_m(\beta)}{d\beta}\right|_{\beta_r}. \tag{41}$$

As the important special case of condition Eq. (40) for $n=2$ we have

$$2\sqrt{\frac{r_m(\beta_r)}{\beta_r}} = \theta_o\left[\beta_r^{-1} - r_m^{-1}(\beta_r)\left.\frac{dr_m(\beta)}{d\beta}\right|_{\beta_r}\right]. \tag{42}$$

If $r_m(\beta)$ can be represented as

$$r_m(\beta) = \gamma_{ro}\beta^{-\gamma_r} \tag{43}$$

and $T_m(\beta)$ as

$$T_m(\beta) = \gamma_{to}\beta^{\gamma_t} \tag{44}$$

for a best fit of the trends of the available data sets $\{\beta_i, \mathbf{r}_m(\beta_i), i = \overline{1,N}\}$ and $\{\beta_i, \mathbf{T}_m(\beta_i), i = \overline{1,N}\}$, we can estimate the resonant heating rate by substituting Eq. (43) in Eq. (41) for $n=1$

$$\hat{\beta}_r = \frac{1}{e}\left(\frac{\theta_o}{\gamma_{ro}}\right)^{\frac{1}{1-\gamma_r}} \tag{45}$$

and in Eq. (42) for $n=2$

$$\hat{\beta}_r = \left[\frac{\theta_o^2(1+\gamma_r)^2}{4\gamma_{ro}}\right]^{\frac{1}{1-\gamma_r}}. \tag{46}$$

Furthermore, since it holds

$$\hat{T}_r = T_m(\hat{\beta}_r) = \gamma_{to}\hat{\beta}^{\gamma_t} \tag{47}$$

we get finally from Eq. (36)

$$\hat{\alpha} = \hat{T}_r / \hat{\beta}_r, \ n = 1; \quad \hat{\alpha} = 2\hat{T}_r\sqrt{\gamma_{ro}}\,\hat{\beta}_r - \frac{1+\gamma_r}{2}, \ n = 2. \tag{48}$$

Procedure 2 is now developed.

Procedure 3 is developed to graphically determine the resonant point $(\beta_r, r_m(\beta_r))$. Introducing the coordinate $W(\beta) = \ln(\beta r_m(\beta)/\theta_o)$ for n = 1 in Eq. (41), the equation becomes

$$\left.\frac{\mathrm{d}W(\beta)}{\mathrm{d}\beta}\right|_{\beta_r} = -\frac{W(\beta_r)}{\beta_r}, \tag{49}$$

the solution of which gives the corresponding isocline

$$W(\beta_r) = -\frac{c}{\beta_r} \text{ or } \ln\left(\frac{\beta_r r_m(\beta_r)}{\theta_o}\right) = -\frac{c}{\beta_r}.$$

The isocline for n=1 is

$$r_m(\beta_r) = \frac{\theta_o}{\beta_r} e^{-\frac{c}{\beta_r}}, \quad c > 0. \tag{50}$$

For $n \geq 2$, transforming Eq. (40) by coordinate change $W(\beta) = r_m^{n-1}(\beta)/\beta$ to

$$\left.\frac{\mathrm{d}W(\beta)}{\mathrm{d}\beta}\right|_{\beta_r} = -\frac{n}{\theta_o^{n-1}} W^{\frac{n+1}{n}}(\beta_r), \tag{51}$$

and solving it, the corresponding isocline is

$$\frac{\theta_o^{n-1}}{\sqrt[n]{W(\beta_r)}} = c + \beta_r \text{ or } r_m(\beta_r) = \frac{\theta_o^n}{c+\beta_r} \sqrt[n-1]{\frac{\beta_r}{c+\beta_r}} \tag{52}$$

where $c > 0$, that, for n = 2, results in the isocline

$$r_{\mathrm{m}}(\beta_{\mathrm{r}}) = \frac{\theta_{\mathrm{o}}^2 B_{\mathrm{r}}}{(c+\beta_{\mathrm{r}})^2}, \quad c > 0. \tag{53}$$

A special isocline, which is a tangent to $\mathbf{r}_{\mathbf{m}}(\beta)$ at the point $(\beta_{\mathrm{r}}, \mathbf{r}_{\mathbf{m}}(\beta_{\mathrm{r}}))$, is noted in Definition 3 as resonant isocline of the observed function $\mathbf{r}_{\mathbf{m}}(\beta)$. Using the concept of the resonant isocline, Procedure 3 is naturally constructed.