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Note

# CVETANOVIC—AMENOMIYA MASTER CURVES FOR KINETIC ANALYSIS OF TPD CURVES: A GENERALIZATION OF THE METHOD

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Temperature Programmed Desorption (TPD) and its homologous "flash desorption" (FD) techniques have attained a paramount interest in the study of interaction of gases with solid surfaces in the last few years [1—4].

In spite of their analogies the theoretical analysis of line-shape of TPD curves is less well developed than in the flash desorption technique from a theoretical point of view, probably due to the higher complexity of the TPD technique itself.

Early works of Cvetanovic and Amenomiya [5] developing "master curves" to analyse line-shape of simple TPD peaks corresponding to processes occurring according to a first-order desorption mechanism, with or without free readsorption of the desorbed phase on an homogeneous surface, have been followed by the analysis of the effect of heterogeneity on the TPD trace by the same authors [6] and, more recently, by the development of "master curves" for second-order desorption accompanied by readsorption carried out by Scholten and Konvalinka [7].

Although these analyses follow a similar procedure, no attempts have been made, to our knowledge, to make a general statement of the method in order to extend it to any other kinetics of desorption.

The scope of this work was to make such a generalization of the Cvetanovic and Amenomiya method (hereafter CA method) and, as an example, to extend it to a new case not yet studied in the literature.

In a general way, assuming the Arrhenius law to be valid to describe the desorption process of a gas previously adsorbed on a solid surface, the desorption rate from the surface can be expressed as

$$-\frac{d\theta}{dt} = A^* \exp(-\Delta H/RT)f(\theta) \qquad (1)$$

where $\theta$ is the surface coverage, $A^*$ the pre-exponential factor, $\Delta H$ the adsorption enthalpy, and $f(\theta)$ a function giving the rate dependence with $\theta$, which depends on the actual mechanism of the process.

If the diffusional process in the carrier gas can be neglected, eqn. (1) may be written as a material balance, by equating the amount of gas detected in the carrier gas stream per unit time to the amount of gas desorbed per unit time

$$FC = -V_s V_m(d\theta/dt) = -V_s V_m \beta(d\theta/dT) \qquad (2)$$

for linear heating schedule ($T = T_0 + \beta t$). $V_s$ is the volume of the solid phase in the catalytic bed, $V_m$ is the amount of gas adsorbed per unit volume of the solid phase at $\theta = 1$, $F$ is the carrier gas flow rate, and $C$ is the concentration of the desorbing gas in the carrier gas stream expressed as partial pressure.

From eqn. (2) the value of $C$ results

$$C = -\frac{V_s V_m \beta}{F}\frac{\mathrm{d}\theta}{\mathrm{d}T} \tag{3}$$

At the peak maximum, $(\mathrm{d}C/\mathrm{d}T)_{T=T_M} = 0$ and therefore

$$A^* \exp(-\Delta H/RT_M) = \frac{\Delta H}{RT_M^2}\,\frac{1}{f'(\theta_M)}\,\beta \tag{4}$$

where $T_M$ is the temperature at the peak maximum and $\theta_M$ is the coverage when $T = T_M$.

Equation (4) may be written in the logarithmic form

$$\ln\beta - 2\ln T_M = \ln\frac{RA^* f'(\theta_M)}{\Delta H} - \frac{\Delta H}{RT_M} \tag{5}$$

This expression can be used to experimentally obtain $\Delta H$ and $A^*$ from the values of $T_M$ at different heating rates and at constant $\theta_i$ and $F$.

To obtain the coverage at the peak maximum ($\theta_M$), a normalized form of eqn. (2) may be used, where the value of $C$ and $T$ are expressed with respect to their maximum values ($C_n = C/C_M$, $T_n = T/T_M$). From this variable change, it follows

$$-\frac{\mathrm{d}\theta}{\mathrm{d}T_n} = \frac{A^*}{\beta}\exp(-\Delta H/RT_n T_M) f(\theta) T_M$$

and using the value of $A/\beta$ from eqn. (4)

$$-\frac{\mathrm{d}\theta}{\mathrm{d}T_n} = \epsilon_M \exp(-\epsilon_M/T_n)\,\frac{f(\theta)}{f'(\theta_M)}\,\exp(\epsilon_M) \tag{6}$$

where $\epsilon_M = \Delta H/RT_M$. As has been assumed by Scholten et al. [7], this substitution implies the independence of entropy with temperature, so the following expressions are entropy independent.

Integration of eqn. (6) between initial and maximum gives

$$-f'(\theta_M)\int_{\theta_i}^{\theta_M}\frac{\mathrm{d}\theta}{f(\theta)} = \epsilon_M \exp(\epsilon_M)\int_0^1 \exp(-\epsilon_M/T_n)\mathrm{d}T_n$$

If

$$I_1 = \int_0^1 \exp(-\epsilon_M/T_n)\mathrm{d}T_n \qquad \text{and} \qquad g(\theta) = -\int_{\theta_i}^{\theta}\frac{\mathrm{d}\theta}{f(\theta)}$$

it follows that the condition

$$f'(\theta_M)\,g(\theta_M) = \epsilon_M \exp(\epsilon_M) I_1 \tag{7}$$

TABLE 1

$f(\theta)$, $f'(\theta)$ and $g(\theta)$ functions for different desorption mechanisms

| Mechanism | Symbol | $f(\theta)$ | $f'(\theta)$ | $g(\theta)$ |
|---|---|---|---|---|
| First order without readsorption | 1W | $\theta$ | $1$ | $-\ln(\theta/\theta_i)$ |
| First order with first-order readsorption | 1R1 | $\frac{F}{V_sV_m}\cdot\frac{\theta}{1-\theta}$ | $\frac{F}{V_sV_m}\cdot\frac{1}{(1-\theta)^2}$ | $\frac{V_sV_m}{F}\{-\ln(\theta/\theta_i)+\theta-\theta_i\}$ |
| Second order without readsorption | 2W | $\theta^2$ | $2\theta$ | $\frac{1}{\theta}-\frac{1}{\theta_i}$ |
| Second order with first-order readsorption | 2R1 | $\frac{F}{V_sV_m}\cdot\frac{\theta^2}{1-\theta}$ | $\frac{F}{V_sV_m}\cdot\frac{2\theta-\theta^2}{(1-\theta)^2}$ | $\frac{V_sV_m}{F}\left[\frac{1}{\theta}-\frac{1}{\theta_i}+\ln(\theta/\theta_i)\right]$ |
| Second order with second-order readsorption | 2R2 | $\frac{F}{V_sV_m}\cdot\frac{\theta^2}{(1-\theta)^2}$ | $\frac{F}{V_sV_m}\cdot\frac{2\theta}{(1-\theta)^3}$ | $\frac{V_sV_m}{F}\left[\frac{1}{\theta}-\theta+2\ln(\theta/\theta_i)-\frac{1}{\theta_i}+\theta_i\right]$ |

must be fulfilled at peak maximum.

With the value of $\theta_M$ evaluated from eqn. (7) integration of eqn. (6) gives theoretical line-shape. However, it is convenient, first of all, to do the variable change

$$x = \epsilon_M(1 - 1/T_n)$$

which transforms expression (6) to

$$-\frac{d\theta}{dx} = \frac{\exp(x)}{(1 - x/\epsilon_M)^2}\,\frac{f(\theta)}{f'(\theta_M)}$$

Integration between $\theta_M$ and $\theta$

$$-f'(\theta_M)\int_{\theta_M}^{\theta}\frac{d\theta}{f(\theta)} = \int_0^x \frac{\exp(x)}{(1 - x/\epsilon_M)^2}\,dx$$

If

$$I_2 = \int_0^x \frac{\exp(x)}{(1 - x/\epsilon_M)^2}\,dx$$

using $g(\theta)$ it follows

$$f'(\theta_M)[g(\theta) - g(\theta_M)] = I_2 \tag{8}$$

This equation allows the determination of values for $\theta$ against $T$. Meanwhile, from eqns. (1) and (3), we obtain

$$C_n = \frac{C}{C_M} = \frac{f(\theta)}{f(\theta_M)}\exp(x) \tag{9}$$

so that from eqn. (9) we can obtain $C_n$ against $T_n$.

Equations (7) and (8) must be solved numerically for the different desorption mechanism using the corresponding functions $f(\theta)$, $g(\theta)$ and $f'(\theta)$ and, in fact, this is what has been done in particular cases in the literature [5,7].

Table 1 gives functions for some simple desorption mechanisms. Of those mechanisms, Cvetanovic and Amenomiya [5] have solved first order with and without readsorption cases (1W and 1R1 in Table 1), while Konvalinka and co-workers [7] have studied second order with freely occurring readsorption of second order (2R2), as particular cases.

Theoretical curves for second-order desorption without readsorption have not been previously developed to our knowledge, so we have tried to do it by applying the general procedure described above. In this case, using functions of Table 1 for mechanism 2W, we obtain from eqn. (7)

$$\theta_M = \frac{2 - \epsilon_M \exp(\epsilon_M) I_1}{2}\,\theta_i \tag{10}$$

Values of $I_1$ were obtained numerically using Simpson's method for some sets of values of $\epsilon_M$. Corresponding values of $\theta_M$ are given in Table 2.

The theoretical line-shapes of the TPD curve were obtained from eqns. (8)

TABLE 2

$\theta_M$ values for 2W desorption mechanism

| $\epsilon_M$ | $\theta_i$ values | | | |
|---|---|---|---|---|
| | 0.2500 | 0.5000 | 0.7500 | 1.0000 |
| 10 | 0.1445 | 0.2891 | 0.4336 | 0.5782 |
| 12 | 0.1419 | 0.2837 | 0.4256 | 0.5675 |
| 14 | 0.1398 | 0.2797 | 0.4197 | 0.5594 |
| 16 | 0.1383 | 0.2765 | 0.4148 | 0.5530 |
| 18 | 0.1370 | 0.2740 | 0.4109 | 0.5479 |
| 22 | 0.1350 | 0.2701 | 0.4051 | 0.5402 |
| 26 | 0.1336 | 0.2673 | 0.4009 | 0.5346 |

and (9) by the expression

$$C_n = \frac{4}{(2 + I_2)^2} \exp(x) \tag{11}$$

Equation (11) shows that normalized curves are independent of initial coverage, depending only on the parameter $\epsilon_M$. This result shows to be a general one in the case of desorption occurring without simultaneous free

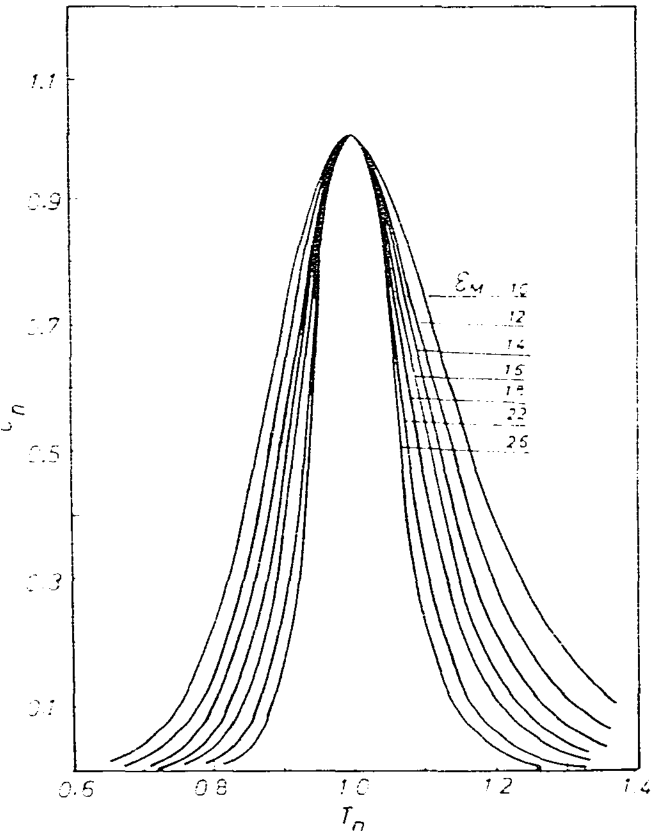

Fig. 1. CA master curves calculated for different values of $\epsilon_M$ for desorption processes following a 2W mechanism.

readsorption of the desorbed species (mechanism 1W and 2W). Theoretical curves obtained for mechanism 2W are shown in Fig. 1, where values of $C_n$ obtained from eqn. (11) for significant values of $\epsilon_M$ with $0.4 \leqslant T_n \leqslant 1.6$ have been plotted once $I_2$-values have been evaluated numerically.

The general procedure stated in this paper to generate "CA master curves" can, in principle, be easily extended to any other case of desorption process, provided that $f(\theta)$ is known.

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