Journal of Thermal Analysis, Vol. 33 (1988) 237–242

CRTA: A MATHEMATICAL DESCRIPTION OF REVERSIBLE THERMAL DISSOCIATION REACTIONS IN THE Q-DERIVATOGRAPH

V. A. Bir and *V. A. Logvinenko*

INSTITUTE OF INORGANIC CHEMISTRY, NOVOSIBIRSK, 630090, U.S.S.R.

For the analysis of experimental data, an elemental process model is suggested, which considers the kinetic and thermodynamic parameters of the reaction, its topochemical mechanism, and the mass exchange between the reaction zone and the external medium. The proposed model is fully based on the principal assumption that the duration of the experiment is much greater than the relaxation time for all the heat transfer processes in the sample volume.

The thermal analysis of solid substances by means of the Q-derivatograph gives important information about their thermal decomposition processes [1–3]. At the same time, this information at present remains qualitative in nature; this is connected with the lack of detailed formalized theoretical concepts on the nature of the processes under the quasi-equilibrium operating conditions. The designs of commercial Q-derivatographs are largely based on practical considerations, but not on theoretical requirements [2]. In view of this situation, we set out to study the general factors affecting the kinetics of reversible reactions under quasi-equilibrium conditions, and to propose a fairly simple scheme for the processes taking place in agreement with the experimental data.

Let us discuss a one-step reversible reaction:

$$A_s \rightleftarrows B_s + C_{\text{gas}}$$

proceeding in derivatograph crucibles. In our reasoning, we proceed from the simple assumption that the total experimental time τ can be written as

$$\tau = m_o / q \tag{1}$$

where m_o is the total quantity of gas evolved during the reaction, and q is the controlled rate of gas evolution; τ is much longer than the characteristic times (of relaxation) for the processes of mass and heat transport in the sample layer and in the free volume of the sample holder:

$$\tau \gg \tau_m ,\ \tau \gg \tau_H \tag{2}$$

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

The fulfilment of requirements (2) results in the approximate equality of the partial pressure of the evolved gas within the whole crucible reaction volume; the temperature gradients are small. This is valid largely for the labyrinth holder; it is impossible to ignore the complications arising in the multiplate holder. Requirements (2) give the grounds for the following assumption: the direct and reverse reactions are localized only on the interphase boundary A_s/B_s. We can write the kinetic equation in the known form:

$$d\alpha/dt = k(T)\,[1 - \frac{p_o}{p^*(T)}]\,f(\alpha) \tag{3}$$

where $k(T)$ is the rate constant of the direct reaction, p_o is the partial pressure of the gaseous product in the crucible, $p^*(T)$ is the equilibrium pressure, and $f(\alpha)$ is the topochemical mechanism function of the reaction, proportional to the interface area. The process is considered to be a quasi-steady one, and the rate can be written as $d\alpha/dt = q/m = 1/_T$.

We get the final expression:

$$1/_T = k(T)\,[1 - \frac{p_o}{p^*(T)}]\,f(\alpha) \tag{4}$$

This expression, together with the Arrhenius equation

$$k(T) = k_o \exp\,(^{-E}/_{RT}) \tag{5}$$

and the van't-Hoff equation

$$p^*(T) = \exp\,(^{\Delta S}/_R - {}^{\Delta H}/_{RT}) \tag{6}$$

unambiguously designate the desired relationship $(1-\alpha)$ *vs.* T, observed in the experiments.

It is generally accepted that the pressure p_o is unambiguously connected with the sample holder design [2]. Partial pressure of ~1 atm is assigned to the labyrinth holder, one of ~0.8 atm to the conical crucible, etc. [3]. Let us consider the simplified model for the mass exchange, which is practically exact for the conical and labyrinth sample holders (Fig. 1).

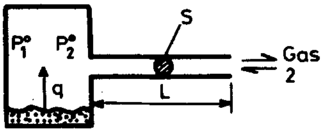

Fig. 1 Chart of the mass-exchange model for the labyrinth and conical holders.

Gas 1 is created in the sample holder volume at a rate q. The mass exchange with the outer medium (inert gas 2) proceeds through the tube with cross-section S and length L. The partial pressures of the first and second gases (p_1^o and p_2^o) are fixed in this volume under steady conditions. Let us find these pressures. A diffusion mechanism for mass exchange is inadequate, because the moving force for the removal of the second gas from the reaction volume to the outer medium is negative, and the steady-state is not maintained.

Therefore, it is necessary to suppose the existence of convection flow towards the outer medium.

This flow is due to the excess pressure in the crucible, arising because gas 1 is produced in the reaction volume. Our estimations show that this excess pressure is very small ($\sim 10^{-4}$ atm), and the partial pressure sum in the crucible, is equal to the atmospheric pressure $\bar{p}$ with satisfactory accuracy:

$$p_1^o + p_2^o = \bar{p} \tag{7}$$

Taking into account the molar concentrations of the gases, C_1^o and C_2^o, we have:

$$C_1^o + C_2^o = C^o = \bar{p}/_{RT} \tag{8}$$

For the steady process, the following equations must hold for any cross-section along L:

$$I_1 = -D\,\mathrm{d}C_1/\mathrm{d}L + VC_1 = q/S \tag{9}$$

$$I_2 = -D\,\mathrm{d}C_2/\mathrm{d}L + VC_2 = 0 \tag{10}$$

I_1 and I_2 are the flows of the corresponding gases through the cross-section S; D is the diffusion coefficient for gases 1 and 2; and V is the linear rate of convection flow.

The boundary conditions are:

$$C_1\Big|_{L=0} = C_1,\ C_1\Big|_{L=L} = C_1^L,\ C_2\Big|_{L=0} = C_2,\ C_2\Big|_{L=L} = C_2^L$$

The set of Eqs (8–10) is closed, and unambiguously determines the desired concentrations C_1^o and C_2^o. From Eqs (8) and (9), we have (if $C^o = C_1^o + C_2^o$):

$$V = q/F\cdot C^o \tag{11}$$

For simple boundary conditions (no gas 1 in the outer medium), $C_1^L = 0,\ C_2^L = C^o/,\ p_1^o \equiv p_o$:

$$p_o = 1 - e^{-aq}\,[\mathrm{atm}],\ a = \frac{LRT}{M_1 \cdot D_{Fp}} \cdot \frac{10^{-6}}{60}\ [\mathrm{min/mg}] \qquad (12)$$

Here q is in mg/min , and M_1 is the molecular mass of the evolved gas 1. Equation (12) shows that the crucible design really does determine the value of p_o (through the ratio L/S), but p_o also depends on many other factors. The pressure p_o is plotted as a function of the decomposition rate q for the first stage of decomposition of $CuSO_4 \cdot 5H_2O$ in Fig. 2.

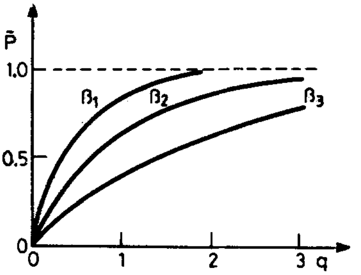

Fig. 2 Partial pressure of the evolved vapour as a function of the rate of mass loss (for the labyrinth holder).

For the above example, $a \sim T^{-0.8}$. Therefore, the partial pressure of the evolved gas in the crucible is practically constant, if the regime is kept isothermal during the experiment under quasi-equilibrium conditions.

Equations (4–6) and (12) fully define our simple model. Let us show how this model describes the appearance of the isothermal regions for the experimental curves $(1-\alpha)$ *vs.* T. From Eq. (4), p_o = const, but it does not follow that T = const, so that $f(\alpha)$, the region surface area, changes during the experiment. If follow from Eq. (4) that:

$$\frac{1}{f(\alpha)} = \tau \cdot \frac{k(T)}{p(T)}\,[p^*(T) - p_o] = \tau \cdot k^-(T) \cdot \Delta p \qquad (13)$$

where $k^-(T)$ is the rate constant of the reverse reaction and Δp is the difference between the equilibrium pressure p^* and the partial pressure in the crucible. Equation (13) can be rewritten as

$$f(\alpha) = B(T), \qquad B(T) = \frac{1}{\tau \cdot k^-(T) \cdot \Delta p(T)} \qquad (14)$$

The solution of Eq. (14) will give us the desired function $(1-\alpha)$ *vs.* T.

The function $B(T)$ is defined only at $T > T_*$ $(\Delta H > 0)$, where T is the equilibrium temperature, and $p^* (T_*) = p_o$ (see Eq. (8)). The function $B(T)$ becomes infinity at $T \to T_*$, as follows from Eq. (14). Giving the value $B = B(T + \epsilon)$, we will have $\delta T = T - T_* \leqslant \epsilon$, so that $f(\alpha) \geqslant B_\epsilon$. Therefore if the condition $f(\alpha) \geqslant B$ is satisfied, a region of α exists where the deviation of the temperature from the equilibrium one will not surpass a preset value ϵ. As an illustration, consider the example in Fig. 3.

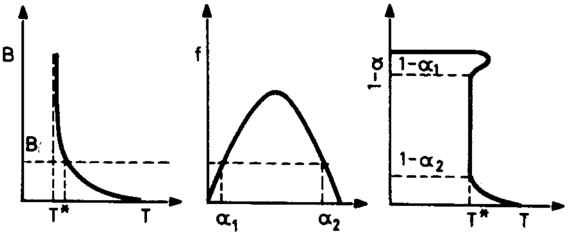

Fig. 3 Appearance of the quasi-isothermal regions on the mass loss curve under the quasi-equilibrium regime.

The availability and the extent of the quasi-steady region (where the deviation $(T - T_*)$ does not exceed ϵ and is not fixed visually) depend on the form of the function $f(\alpha)$. The quasi-equilibrium region does not exist if B_ϵ is larger than the maximum value of $f(\alpha)$. Such a dependence exists for other parameters.

The expansion of the left side of Eq. (13) into a Taylor's series with respect to T_* gives:

$$\frac{1}{f(\alpha)} = \left(\frac{\Delta H}{RT_*^2} \cdot \tau \cdot k_*\right) \Delta T + \left[k_* \cdot \tau \left(\frac{\Delta H}{RT_*^2}\right)^2 \left(\frac{2E}{\Delta H} - 1 - \frac{2RT_*}{\Delta H}\right)^2\right] \Delta T^2 + \ldots \quad (15)$$

For the small deviations ϵ and neglecting the non-linear term on the right side of Eq. (15), we have that the ϵ quasi-equilibrium is satisfied under the conditions:

$$f(\alpha) \geqslant L/\epsilon, \quad L = \frac{R \cdot T_*^2 \cdot q}{\Delta H \cdot k_* \cdot m_o} \quad (16)$$

where k_* is the rate constant for the direct reaction at the equilibrium temperature T_*. It follows from Eq. (16) that the larger the heat of the endothermic reaction, and the lower the rate q, the longer the quasi-isothermal region τ. The proposed model was qualitatively verified by special experiments under quasi-equilibrium conditions. In particular, the dependence of the quasi-equilibrium temperature (and therefore the partial pressure p_0) on the decomposition rate q and the medium gas type is observed for the labyrinth sample holder.

References

1 V. A. Logvinenko, L. I. Myachina, G. V. Gavrilova, J. Thermal Anal., 29 (1984) 1095.

2 F. Paulik and J. Paulik, Hung. Sci. Instr., 28 (1973) 1.

3 F. Paulik and J. Paulik, Thermochim. Acta, 4 (1972) 189.

Zusammenfassung – Ein einfaches Modell für eine reversible thermische Dissoziationsreaktion wird aufgestellt, das kinetische und thermodynamische Parameter der Reaktion, ihren topochemischen Mechanismus und den Gasaustausch zwischen der Reaktionszone und dem externen Medium berücksichtigt. Das Modell beruht auf der Annahme, dass die (quasi-isotherme, quasi-isobare) Versuchsdauer viel länger ist als die Relaxationszeit aller Transportvorgänge im Probenvolumen.

РЕЗЮМЕ — Предложена модель анализа экспериментальных данных какого-либо элементарного процесса, учитывающая кинетические и термодинамические параметры реакции, ее топохимический механизм, также как и массообмен между реакционной зоной и внешней средой. Предложенная модель полностью основывается на главном предположении, что время эксперимента намного больше времени релаксации всех процессов теплопереноса в объеме образца.