Thermochimica Acta, 82 (1984) 387–389
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

VARIATION OF THE MAXIMUM RATE OF CONVERSION AND TEMPERATURE WITH HEATING RATE IN NON-ISOTHERMAL KINETICS. PART II

C. POPESCU

Centrul de Cercetări Materii Prime, Auxiliari şi Ape Reziduale, Str. Siret 95, Bucharest (Romania)

E. SEGAL

Polytechnical Institute of Bucharest, Institute of Chemistry, Department of Physical Chemistry and Electrochemical Technology, Bd. Republicii nr. 13, Bucharest (Romania)

(Received 16 July 1984)

In a previous paper [1] two equations were proposed to express the variation of the maximum rate of conversion and temperature with heating rate, namely

$$\frac{d\alpha_m}{d\beta}=\frac{f(1-\alpha_m)}{\beta^2}\,\frac{(d\alpha/dt)_m}{f(1-\alpha_m)\dfrac{E}{RT_m^2}-\dfrac{1}{\beta}f'(1-\alpha_m)\left(\dfrac{d\alpha}{dt}\right)_m} \tag{1}$$

and

$$\frac{dT_m}{d\beta}=\frac{f(1-\alpha_m)}{\beta}\,\frac{1}{f(1-\alpha_m)\dfrac{E}{RT_m^2}-\dfrac{1}{\beta}f'(1-\alpha_m)\left(\dfrac{d\alpha}{dt}\right)_m} \tag{2}$$

where the symbols have their usual meanings and subscript m indicates a maximum rate value. By separation of the terms and appropriate integration of either of these two equations one obtains

$$-\frac{E}{R}\left(\frac{1}{T_{m2}}-\frac{1}{T_{m1}}\right)-\ln\frac{f(1-\alpha_{m2})}{f(1-\alpha_{m1})}=\ln\frac{\beta_2}{\beta_1} \tag{3a}$$

or, rearranging the terms and changing the base of the logarithm

$$\log\frac{\beta_2}{\beta_1}+0.4343\frac{E}{R}\left(\frac{1}{T_{m2}}-\frac{1}{T_{m1}}\right)=-\log\frac{f(1-\alpha_{m2})}{f(1-\alpha_{m1})} \tag{3b}$$

where subscripts 1 and 2 indicate the different values obtained for two different heating rates, β_1 and β_2, respectively.

Equation (3b) is formally identical with that of Ozawa [2], the difference occurring in the numerical coefficient of E/RT, which is stated in ref. 2 as being 0.457, which is 5% greater than the coefficient in eqn. (3b).

Plotting three or more thermograms in the (α, T) plane (see Fig. 1) two parallels to the two axes, through the inflexion point of the curve (β_1), i.e.

α_{m1} = constant

T_{m1} = constant

will change eqn. (3a) into the following two equations

$$\ln\frac{\beta_2}{\beta_1} = 0.4343\frac{E}{R}\left(\frac{1}{T_{m1}} - \frac{1}{T_2}\right) \tag{4a}$$

$$\ln\frac{\beta_2}{\beta_1} = \ln\frac{f(1-\alpha_{m1})}{f(1-\alpha_2)} \tag{4b}$$

If the reaction-order hypothesis is assumed, eqn. (4b) becomes

$$\ln\frac{\beta_2}{\beta_1} = n\ln\frac{1-\alpha_{m1}}{1-\alpha_2} \tag{4c}$$

where T_2 and α_2 are the temperature and conversion on the second thermogram, corresponding to α_{m1} and T_{m1}, respectively (see Fig. 1).

Solving eqns. (4a), (4b) or (4c) will give the kinetic parameters E and n, with β_1, β_2, α_{m1}, α_2, T_{m1} and T_2 as measured values.

Note. In a recent paper, Tang and Chaudri [3] criticized our previous communication [1]. Their first objection refers to our accidental mistake in writing eqns. (7) and (8) (eqns. (1) and (2) in the present paper). The problem could have been avoided if the calculus had been followed step by step. In their more important objection, they affirm that α cannot be treated as a function of T, β, or any other variable. This statement means, mathematically, that $d\alpha/dT$, $d\alpha/d\beta$, or any other derivative of α, is zero, which is quite wrong. In fact, α cannot be treated as a state function of any variable

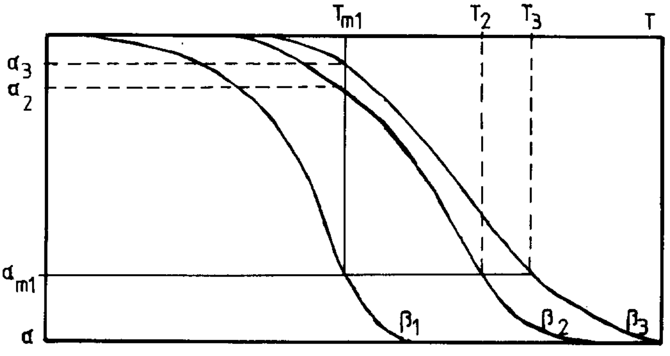

Fig. 1. Thermograms plotted in the (α, T) plane.

[4,5], and we agree this point of view, but it does not exclude that α may be a function of certain variables. Moreover, experience shows that for $T = ct$, α depends on β, and for $\beta = ct$, α depends on T.

REFERENCES

1 C. Popescu and E. Segal, Thermochim. Acta, 63 (1983) 381.
2 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.
3 T.B. Tang and M.M. Chaudri, Thermochim. Acta, 73 (1984) 241.
4 T.B. Tang, Thermochim. Acta, 58 (1982) 373.
5 J.R. MacCallum, Thermochim. Acta, 53 (1982) 375.