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Note

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

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This paper aims to establish a relationship between the heating programme and some particular values of temperature and degree of conversion as their values for the peak of a studied process (i.e. the maximum rate value of the degree of conversion, α_m, and its corresponding temperature, T_m).

The identity

$$\frac{d\alpha}{dt}=\frac{d\alpha}{dT}\cdot\frac{dT}{dt} \tag{1}$$

where α, t, and T have their usual significance, with

$$\frac{dT}{dt}=\beta(T)$$

becomes

$$\frac{d\alpha}{dT}=\frac{1}{\beta}\cdot\frac{d\alpha}{dt} \tag{1a}$$

Also

$$\frac{d\alpha}{dT}=\frac{d\alpha}{d\beta}\cdot\frac{d\beta}{dT} \tag{2}$$

From eqns. (1a) and (2)

$$\frac{d\alpha}{d\beta}=\frac{1}{\beta}\cdot\frac{d\alpha/dt}{d\beta/dT} \tag{3}$$

Equation (3) gives the relationship between the shifts of the degree of conversion and the variation of the heating programme. The problem is now to find the analytical form of $d\beta/dT$, $d\alpha/dt$ being expressed by the

Arrhenius equation

$$\mathrm{d}\alpha/\mathrm{d}t = A\mathrm{f}(1-\alpha)\exp(-E/RT) \tag{4}$$

where A, E and R have their usual significance. Therefore another condition from which the $\mathrm{d}\beta/\mathrm{d}T$ can be derived is necessary, and this is found from

$$\left(\frac{\mathrm{d}^2\alpha}{\mathrm{d}t^2}\right)_{\alpha_\mathrm{m}} = 0 \tag{5}$$

If β is a monotonous function of T, eqn. (5) is rewritten as

$$\left(\frac{\mathrm{d}^2\alpha}{\mathrm{d}T^2}\right)_{\alpha_\mathrm{m}} = 0 \tag{5a}$$

From (4) and (5a)

$$-\frac{\mathrm{d}\mathrm{f}(1-\alpha_\mathrm{m})}{\mathrm{d}T}\cdot\frac{\mathrm{d}\alpha_\mathrm{m}}{\mathrm{d}T} - \mathrm{f}(1-\alpha_\mathrm{m})\cdot\frac{1}{\beta}\cdot\frac{\mathrm{d}\beta}{\mathrm{d}T} + \mathrm{f}(1-\alpha_\mathrm{m})\cdot\frac{E}{RT_\mathrm{m}^2} = 0 \tag{6}$$

which rearranges to give

$$\frac{\mathrm{d}\beta}{\mathrm{d}T} = \frac{\beta}{\mathrm{f}(1-\alpha_\mathrm{m})}\left[\mathrm{f}(1-\alpha_\mathrm{m})\cdot\frac{E}{RT^2} - \frac{\mathrm{d}\mathrm{f}(1-\alpha_\mathrm{m})}{\mathrm{d}T}\cdot\frac{\mathrm{d}\alpha_\mathrm{m}}{\mathrm{d}T}\right] \tag{6a}$$

Introducing (6a) into (3) leads to

$$\frac{\mathrm{d}\alpha_\mathrm{m}}{\mathrm{d}\beta} = \frac{\mathrm{f}(1-\alpha_\mathrm{m})}{\beta}\cdot\frac{\dfrac{\mathrm{d}\alpha_\mathrm{m}}{\mathrm{d}t}}{\mathrm{f}(1-\alpha_\mathrm{m})\dfrac{E}{RT_\mathrm{m}^2} - \dfrac{1}{\beta}\cdot\dfrac{\mathrm{d}\mathrm{f}(1-\alpha_\mathrm{m})}{\mathrm{d}T}\cdot\dfrac{\mathrm{d}\alpha_\mathrm{m}}{\mathrm{d}t}} \tag{7}$$

where "m" means "value measured for the maximum value of $\mathrm{d}\alpha/\mathrm{d}t$".

Equation (7) gives the influence of the heating programme on the shift of the peak of the degree of conversion using measurable data.

Taking into account the reaction order hypothesis, i.e.

$$\mathrm{f}(1-\alpha) = (1-\alpha)^n$$

eqn. (7) becomes

$$\frac{\mathrm{d}\alpha_\mathrm{m}}{\mathrm{d}\beta} = \frac{1}{\beta^2}\cdot\frac{\dfrac{\mathrm{d}\alpha_\mathrm{m}}{\mathrm{d}t}}{\dfrac{E}{RT_\mathrm{m}^2} + \dfrac{1}{\beta}\,\dfrac{n}{1-\alpha_\mathrm{m}}\cdot\dfrac{\mathrm{d}\alpha_\mathrm{m}}{\mathrm{d}t}} \tag{7a}$$

A rough check was made on (7a) considering the right-hand side to be constant and integrating for the decomposition of $\mathrm{Ca(COO)_2 \cdot H_2O}$ with $n = 1$ and $E = 24$ kcal mole [1]. The experimental data for the computation were taken from ref. 2. For the three heating programmes, 2.3, 7.4 and 14.8

K min^{-1} we obtained

	Exptl.	Calcd.	
$\Delta\alpha_1 = \alpha_{2m} - \alpha_{1m}$	0.45	0.3	with $\Delta\beta_1 = 5.1$ K min^{-1}
$\Delta\alpha_2 = \alpha_{3m} - \alpha_{2m}$	0.15	0.15	with $\Delta\beta_2 = 7.4$ K min^{-1}
$\Delta\alpha_3 = \alpha_{3m} - \alpha_{1m}$	0.55	0.7	with $\Delta\beta_3 = 12.5$ K min^{-1}

which are in good agreement.

Equation (6a) provides the second relationship between heating programme and the temperature which corresponds to the peak of $\mathrm{d}\alpha/\mathrm{d}t$. It is obvious that

$$\frac{\mathrm{d}\beta}{\mathrm{d}T} = \frac{1}{\mathrm{d}T/\mathrm{d}\beta}$$

and so

$$\frac{\mathrm{d}T_\mathrm{m}}{\mathrm{d}\beta} = \frac{\mathrm{f}(1-\alpha_\mathrm{m})}{\beta} \frac{1}{\mathrm{f}(1-\alpha_\mathrm{m})\cdot\dfrac{E}{RT_\mathrm{m}^2} - \dfrac{1}{\beta}\dfrac{\mathrm{df}(1-\alpha_\mathrm{m})}{\mathrm{d}T}\cdot\dfrac{\mathrm{d}\alpha_\mathrm{m}}{\mathrm{d}t}} \tag{8}$$

In the reaction order hypothesis eqn. (8) becomes

$$\frac{\mathrm{d}T_\mathrm{m}}{\mathrm{d}\beta} = \frac{1}{\beta\left(\dfrac{E}{RT_\mathrm{m}^2} + \dfrac{1}{\beta}\dfrac{n}{1-\alpha_\mathrm{m}}\dfrac{\mathrm{d}\alpha_\mathrm{m}}{\mathrm{d}t}\right)} \tag{8a}$$

Equation (8a) was tested on the same data as above and the following results were obtained

	Exptl.	Calcd.	
$\Delta T_1 = T_{2m} - T_{1m}$	26	13	with $\Delta\beta_1 = 5.1$ K min^{-1}
$\Delta T_2 = T_{3m} - T_{2m}$	8	6	with $\Delta\beta_2 = 7.4$ K min^{-1}
$\Delta T_3 = T_{3m} - T_{1m}$	34.5	32	with $\Delta\beta_3 = 12.5$ K min^{-1}

The results indicate good agreement with the experimental data, except in the case of ΔT_1 where a value half that of the experimental value was obtained.

REFERENCES

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