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Note

ON THE EXISTENCE OF A MAXIMUM IN THE REACTION RATE FOR THE NON-ISOTHERMAL AUTONOMOUS ADIABATICALLY ISOLATED REACTIONS OF THE TYPE aA → PRODUCTS

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In a previous paper [1], we analysed reactions of the type

$$a\text{A} \rightarrow \text{products} \tag{1}$$

whose non-isothermicity is due only to the fact that their thermal effect occurs in adiabatically isolated conditions. Such reactions have been described as non-isothermal autonomous adiabatically isolated. For such reactions

$$T = q(\alpha) \tag{2}$$

The most usual explicit form of relationship (2) is

$$T = T_0 + q_0\alpha \tag{3}$$

T_0 being the initial temperature, and

$$q_0 = aQ/C \tag{4}$$

where Q is the thermal effect (exothermic or endothermic) corresponding to one mole of A considered as constant, a is the number of moles of reactant A and C is the heat capacity of the system, considered as constant.

The rate equation for the considered reaction is

$$\mathrm{d}\alpha/\mathrm{d}t = Af(\alpha)\ \mathrm{e}^{-E/R(T_0+q_0\alpha)} \tag{5}$$

We shall assume constant kinetic parameters, namely

$$A = \text{const.} \tag{6}$$

$$E = \text{const.} \tag{7}$$

$$f(\alpha) = (1-\alpha)^n, \qquad n = \text{const.} \tag{8}$$

i.e. classical conditions [2].

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Considering the second derivative of α with respect to t

$$d^2\alpha/dt^2 = A\ e^{-E/R(T_0+q_0\alpha)} d\alpha/dt\left\{f'(\alpha) + f(\alpha)\left[Eq_0/R(T_0 + q_0\alpha)^2\right]\right\} \quad (9)$$

From the condition of the maximum of the reaction rate

$$d^2\alpha/dt^2 = 0 \quad (10)$$

one obtains

$$f'(\alpha_m) + f(\alpha_m)\left[E/R(T_0 + q_0\alpha_m)^2\right] q_0 = 0 \quad (11)$$

where the subscript m denotes maximum. For $f(\alpha)$ given by eqn. (8), eqn. (11) takes the particular form

$$-n(1-\alpha_m)^{n-1} + (1-\alpha_m)^n\left[Eq_0/R(T_0 + q_0\alpha_m)^2\right] = 0 \quad (12)$$

or, after performing the calculations and rearranging the terms

$$\alpha_m^2 + (2x + y)\alpha_m + x^2 - y = 0 \quad (13)$$

where

$$T_0/q_0 = x \quad (14)$$

and

$$E/Rq_0n = y \quad (15)$$

It should be noted that the determination of a maximum reaction rate is meaningful only for exothermic reactions which take place via a temperature increase, i.e for $q_0 > 0$. For endothermic reactions, the temperature decreases with time and, accordingly, the reaction rate decreases.

For exothermic reactions, the solution of eqn. (13) is

$$\alpha_m = \left[-(2x + y) + \left(y^2 + 4xy + 4y\right)^{1/2}\right]/2 \quad (16)$$

The degree of conversion corresponding to the maximum reaction rate is submitted to two more conditions, namely

$$\alpha_m > 0 \quad (17)$$

which gives

$$y > x^2 \quad (18)$$

and

$$\alpha_m < 1 \quad (19)$$

which gives

$$0 < (x + 1)^2 \quad (20)$$

Taking into account relationships (14) and (15), inequality (18) leads to

$$\frac{E}{Rq_0 n} > \frac{T_0^2}{q_0^2} \tag{21}$$

i.e.

$$\frac{Eq_0}{Rn} > T_0^2 \tag{22}$$

or, taking into account relationship (4)

$$\frac{EaQ}{RnCT_0^2} > 1 \tag{23}$$

This inequality could be treated as a condition for the existence of a maximum reaction rate for non-isothermal autonomous adiabatically isolated reactions.

REFERENCES

1 E. Urbanovici and E. Segal, Thermochim. Acta, 125 (1988) 261.
2 E. Urbanovici and E. Segal, Thermochim. Acta, 135 (1988) 193.