Determination of Reaction Rate during the Non-isothermal Oxidation of Organic Compounds

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Summary The maximum rate of pressure change and the temperature change during reaction are related to the maximum rate of consumption of fuel.

THE rate of gas-phase oxidation of organic compounds is often too fast to be measured easily by quantitative chemical analysis of the fuel or oxidant. Thus, commonly, the rate of reaction is determined from the change in total pressure[1–4] or reactant temperature[2–5] as a function of time.

These oxidation reactions are of the degenerate-branched-chain type such that the rate accelerates to a maximum, and subsequently falls to zero as fuel is totally consumed. Usually, special significance is attached to the maximum rate of reaction, this parameter being evaluated from the maxima of either the rate of pressure change[1–3] or the temperature rise[3,5] in the chemical system.

Here we examine the relationship of these measured variables to the true maximum rate of reaction (given by the condition $d^2F/dt^2 = 0$, where F is the concentration of fuel). It is shown that in non-isothermal systems both of these procedures give different (and incorrect) results.

Throughout we will assume perfect gas behaviour so that

$$p = (n/V)\boldsymbol{R}T \qquad (1)$$

the volume (V) being held constant. n is the total number of moles present and is given by

$$n = (F_0 - F)x + F = F(1 - x) + xF_0 \qquad (2)$$

where F_0 = initial concentration of fuel.
F = concentration of fuel at time t.
x = number of product molecules per fuel molecule consumed.

From (2)

$$dn/dt = (1 - x)\,(dF/dt) \qquad (3)$$

The equation for conservation of energy in the system is

$$c(\mathrm{d}t/\mathrm{d}T) = -h(\mathrm{d}F/\mathrm{d}t) - l(T - T_0) \qquad (4)$$

where c = heat capacity of the mixture (assumed constant).
h = molar heat evolved during reaction.
l = heat transfer coefficient between the gas and walls.
$(T - T_0)$ = mean temperature rise of the gas above the temperature of the walls.

Differentiating (1) gives the change of pressure with respect to time, *viz.*

$$\mathrm{d}P/\mathrm{d}t = (\boldsymbol{R}/V)[n(\mathrm{d}T/\mathrm{d}t) + T(\mathrm{d}n/\mathrm{d}t)] \qquad (5)$$

(a) *Isothermal conditions*

$$\mathrm{d}T/\mathrm{d}t = 0$$

From (3) and (5)

$$\mathrm{d}P/\mathrm{d}t = (\boldsymbol{R}T/V)(\mathrm{d}n/\mathrm{d}t) = (\boldsymbol{R}T/V)(1 - x)(\mathrm{d}F/\mathrm{d}t) \qquad (6)$$

Hence, the rate of pressure change is proportional to the rate of consumption of fuel, and $(\mathrm{d}P/\mathrm{d}t)_{\mathrm{max}}$ will coincide with $(\mathrm{d}F/\mathrm{d}t)_{\mathrm{max}}$.

(b) *Non-isothermal conditions*

Differentiating (5) with respect to time and equating to zero gives the condition for maximum rate of pressure change.

$$\mathrm{d}^2P/\mathrm{d}t^2 = (\boldsymbol{R}/V)[T(\mathrm{d}^2n/\mathrm{d}t^2) + 2(\mathrm{d}T/\mathrm{d}t)(\mathrm{d}n/\mathrm{d}t) + n(\mathrm{d}^2T/\mathrm{d}t^2) = 0 \qquad (7)$$

From (3) and (7)

$$n(\mathrm{d}^2T/\mathrm{d}t^2) + 2(1 - x)(\mathrm{d}F/\mathrm{d}t)(\mathrm{d}T/\mathrm{d}t) + T(1 - x)(\mathrm{d}^2F/\mathrm{d}t^2) = 0 \qquad (8)$$

This does not correspond to the condition for maximum rate, $\mathrm{d}^2F/\mathrm{d}t^2 = 0$, nor does it give a simple way of correcting for non-isothermal conditions.

The condition for maximum rate as a function of temperature is given by rearrangement and differentiation of (4) and equating this to zero, *i.e.*

$$h(\mathrm{d}^2F/\mathrm{d}t^2) = -c(\mathrm{d}^2T/\mathrm{d}t^2) - l(\mathrm{d}T/\mathrm{d}t) = 0 \qquad (9)$$

or

$$(\mathrm{d}^2T/\mathrm{d}t^2) = (l/c)(\mathrm{d}T/\mathrm{d}t) \qquad (10)$$

Hence, maximum rate occurs neither at the maximum of the mean temperature rise [as given by the condition $\mathrm{d}T/\mathrm{d}t = 0$ in (4)], nor at the temperature–time inflexion ($\mathrm{d}^2T/\mathrm{d}t^2 = 0$), but at some other time depending on the heat losses. For an adiabatic system ($l \rightarrow 0$) equation (10) shows that a maximum reaction rate occurs at the temperature–time inflexion, as expected.

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