Correlation of adiabatic kinetic data

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A reduced-variable plotting method can be used to analyse conversion–time data for certain exothermic reactions, particularly polymerizations. In order to simplify calculations, the activation energy term is modified slightly. This allows for an analytical solution of the conversion–time function. Essentially, the method involves a log–log plot of $(\theta_x-\theta_{0.5})/(\theta_{0.5}-\theta_{1-x})$ *versus* $(1-x)/x$ where θ is time and $(1-x)$ is the degree of conversion. Thus $\theta=0$ at $x=1$ and $\theta=$ infinity at $x=0$ except for a zero-order reaction. To illustrate the method, the adiabatic solution polymerization of acrylamide is used. The plotting scheme may be applied to a single run. However, the results are more impressive when runs varying in monomer and redox couple concentrations and initial temperature are combined. Information extracted included the order of dependence of rate of reaction on reactant concentrations. The energy of activation can be estimated. The method is more powerful than using only initial rates because it utilizes more of the experimental data. However, the number of reactions that are amenable to actual analysis is limited mainly by experimental difficulties such as evaporation, precipitation, and back-diffusion of oxygen.

Keywords Polymerization; acrylamide; adiabatic reaction; graphical solution; kinetics; correlation

INTRODUCTION

Describing a chemical reaction by a mathematical equation has a number of useful purposes. The form of the equation may help explain the mechanism by which the reaction proceeds. Unfortunately, the good fit of a simple law over a wide range of conditions is not very common. In polymerizing systems, various complications occur which give rise to complex theoretical equations or to equally complex empirical correlations. The former may have too many constants to evaluate in a reasonable fashion and the latter may be compatible with no reasonable mechanism. The more general use of kinetic correlations is that of scaling up and predicting performance in industrial operations.

Many polymerizations reported in the literature are only characterized by initial rate of reaction, that is, initial rate of monomer consumption, $(-\mathrm{d}[M]/\mathrm{d}\theta)_0$. The dependence of this rate on initial conditions of concentrations of reactants and on temperature can be estimated by making enough runs. Besides the large number of runs that are needed, there are other disadvantages. One is that the initial rate may be more influenced by impurities than a rate later on. Also, most commercial polymerizations are carried out to conversions of 50 to 99%, so that initial rates are of marginal help in reactor design.

ANALYSIS OF COURSE OF REACTION

The most common method of studying the course of a polymerization is to measure concentration of monomer (or polymer) as a function of time at a constant temperature. Gravimetric titrimetric, dilatometric, and spectroscopic methods are employed. When conversion-time data of very high quality are available, differentiation can be used and $\Delta[M]/\Delta\theta$ can be plotted, for example against $[M]$, the monomer remaining. However, the use of integral data often is safer, especially if data at very low or very high conversions can be given less weight.

When the reaction is thought to be some simple integral order in monomer, and other reactants do not change much in concentration, plotting conversion-time data as zero-, first-, and second-order on appropriate coordinates may allow a decision as to the best fit. Powell[1,2] devised a method for comparing experimental data with a multiplicity of orders on a common plot. The fraction of monomer remaining, x, is plotted against the logarithm of time, θ, or $\theta/(1-x)$. A horizontal shift is used to superpose the data on the line for the most suitable reaction order.

Isothermal methods usually are restricted to rather slow reactions and low polymer concentrations because of the problem of heat removal. Most often, the inside heat transfer coefficient represents the controlling resistance. The inside coefficient for a jacketed vessel varies inversely with the viscosity of the contents to the 1/3 power[3]. A viscosity increase of as much as 100-fold may not be enough to induce the Trommsdorff effect, but it will severely limit the rate of heat removal even in a small laboratory vessel.

An alternative to the isothermal method for fast reactions is the adiabatic reactor. Heat transfer is not a factor. However, maintenance of truly adiabatic conditions is difficult for very slow reactions, the energy of stirring can become a factor, and evaporation or any other phase change can complicate the analysis. Several methods do approximate adiabatic conditions. The common Dewar flask is suitable for fast reactions although the heat capacity of the container has to be taken into account[4]. When large quantities of reactants

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are available, a volume of 2 or 3 litres in an insulated steel kettle will give a high ratio of heat capacity of reactants to that of inert container. The best condition is to have a lightweight reactor surrounded by a shield at the same temperature as the reactants to minimize heat losses[5].

FREE RADICAL POLYMERIZATION

In simple form, free-radical initiation by decomposition of some species I at a rate $k_i[\mathrm{I}]$ followed by propagation and termination reactions leads to an expression for monomer consumption rate:

$$-\mathrm{d}[M]/\mathrm{d}\theta = k_p(k_i/k_t)^{1/2}[\mathrm{M}][\mathrm{I}]^{1/2} \tag{1}$$

where k_p and k_t are rate constants for the propagation and termination reactions. All the rates are assumed to have an Arrhenius-type temperature dependence.

The differential equation in more general terms often is represented by:

$$-\mathrm{d}[M]/\mathrm{d}\theta = K_0\left(\exp - \frac{\Delta E_a}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right)[M]^a[\mathrm{I}]^b \tag{2}$$

where K_0 is a lumped constant referred to temperature T_0. In this case ΔE_a takes into account the temperature dependence of initiation, propagation, and termination.

It would be convenient to have a manner of treating integral adiabatic data in a manner analogous to the Powell plots[1]. The treatment has to be slightly more complicated since an energy of activation, ΔE_a, has to be determined in addition to the order of reaction, a.

To start with, we rewrite the differential equation in terms of the fraction of monomer remaining, x:

$$([M]_0 - [M])/[M]_0 = (1-x) \tag{3}$$

For an adiabatic polymerization in a system with constant heat capacity, there will be a linear relationship between the increase in temperature, T, and the amount of monomer polymerized:

$$\frac{1}{\Delta T_m}\frac{\mathrm{d}T}{\mathrm{d}\theta} = -\frac{1}{[M]_0}\frac{\mathrm{d}[M]}{\mathrm{d}\theta} = -\frac{\mathrm{d}x}{\mathrm{d}\theta} \tag{4a}$$

and

$$\frac{T-T_0}{\Delta T_m} = \frac{[M]_0 - [M]}{[M]_0} = (1-x) \tag{4b}$$

where ΔT_m is the total temperature rise $(T_f - T_0)$ corresponding to complete polymerization of the original charge of monomer, $[M]_0$. The exponential term of equation (2) can be expressed as a function of x.

$$(1/T_0) - (1/T) = (T - T_0)/(T\cdot T_0) = (1-x)(\Delta T_m)/(T\cdot T_0) \tag{5}$$

In the course of any one run, T in the denominator changes from T_0 to T_f. Integration is simplified if we replace T by its geometric mean value, $(T_f\cdot T_0)^{1/2}$. This is not a drastic adjustment. For example, if $T_0 = 293\mathrm{K}$ and $T_f = 313\mathrm{K}$, $T = (T_f\cdot T_0)^{1/2} \pm 3\%$ over the whole range.

The idea of simplifying the temperature dependence of the rate equation is not new. Flynn and Wall[6] reviewed a number of approximations which are useful for the integration of rate expressions in connection with analysis of thermogravimetry. For instance, Horowitz and Metzger[7] suggested the use of a reference temperature in order to ease the plotting of integral conversion data *versus* temperature.

Equation (2) can be recast as:

$$-\mathrm{d}x/\mathrm{d}\theta = K_L(x)^a\exp[\varphi(1-x)] \tag{6}$$

where

$$K_L = K_0[M]_0^{a-1}[\mathrm{I}]^b \tag{7}$$

$$\varphi = (\Delta E_a/R)(\Delta T_m)(T_f)^{-1/2}(T_0)^{-3/2} \tag{8}$$

$$x = (T_f - T)/(T_f - T_0) \tag{9}$$

K_L has the dimensions of $(\mathrm{time})^{-1}$.

INTEGRATION OF SIMPLIFIED ADIABATIC RATE EQUATION

It is easiest to integrate equation (6) for integral values of a and φ and then to estimate intermediate values by graphical methods. Since initiator concentration usually is not measured during the reaction, the common assumption is made that the half-life of the initiator is long compared to the reaction time. The assumption often is, in fact, tenable. The actual plotting method uses ratios of reaction times as a further simplification.

Case 1: $a = 0$

$$e^{\phi}K_L\int_0^{\theta}\mathrm{d}\theta = -\int_1^x \exp(\varphi x)\mathrm{d}x \tag{10}$$

For $\varphi = 0$, $\quad K_L\theta = (1-x)$ (11)

$\varphi > 0$, $\quad e^{\phi}K_L\theta = 1 - \exp[-\varphi(1-x)]$ (12)

Case 2: $a = 1$

$$e^{\phi}K_L\theta = -\int_1^x \exp(\varphi x)(x)^{-1}\mathrm{d}x \tag{13}$$

For $\varphi = 0$, $\quad K_L\theta = -\ln x$ (14)

$\varphi > 0$, $\quad e^{\phi}K_L\theta = E_i(\varphi) - E_i[\varphi(x)]$ (15)

where $E_i(z)$ is the exponential integral of z. The function has been tabulated[8].

Case 3: $a = 2$

$$e^{\phi}K_L\theta = -\int_1^x \exp(\varphi x)(x)^{-2}\mathrm{d}x \tag{16}$$

For $\varphi = 0$, $\quad K_L\theta = (1-x)/x$ (17)

$$\varphi > 0, \quad e^{\phi}K_L\theta = \frac{\exp - \varphi(1-x)}{x} - 1 + \varphi(E_i(\varphi) - E_i(\varphi x)) \tag{18}$$

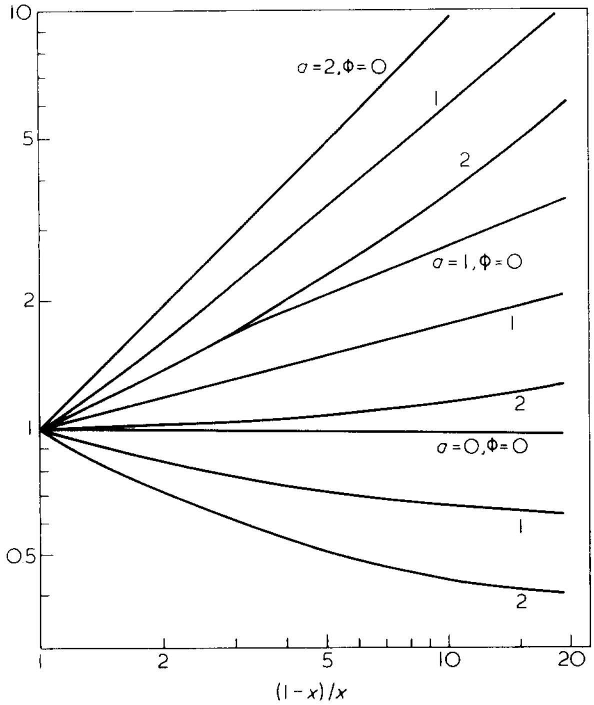

Figure 1 Reduced time ratio Ψ plotted against reduced conversion ratio $(1-x)/x$ for three values of monomer exponent 'a' and three values of the parameter ϕ

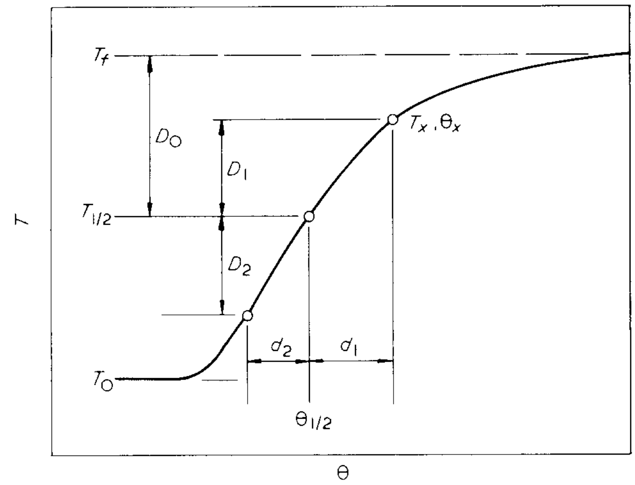

Figure 2 Typical output yields $\Psi = d_1/d_2$ and $(1-x)/x = (D_0+D_1)/(D_0-D_1)$

PLOTS OF REDUCED VARIABLES

There are many possible approaches to using the integrated equations to test experimental data. The closest analogy to the Powell method would be to plot experimental values of θ *versus* $(1-x)/x$ on logarithmic coordinates and use a shift on the time axis to match corresponding curves of $K_L\theta$. However, when a ratio of reaction times is used, the model curves have less overlap and comparison with data becomes simpler. We define a new parameter, Ψ:

$$\Psi = \frac{(\theta_x - \theta_{0.5})}{(\theta_{0.5} - \theta_{1-x})} \tag{19}$$

where the subscripts refer the times within a single run at monomer fractions of x, 50%, and $(1-x)$. The resulting graph (*Figure 1*) is rather symmetrical. The effect of changing either a or φ is relatively linear on this coordinate system. This linearity is of great value in fitting a model.

COMPARISON WITH EXPERIMENTAL DATA

The experimental data can be derived easily from the recorder output (*Figure 2*). Vertical distances D_1 and D_2 are set equal. D_1 is $T-T_{0.5}$ and D_0 is $T_f-T_{0.5}$. Then Ψ is d_1/d_2 and $(1-x)/x$ is $(D_0+D_1)/(D_0-D_1)$. Since K_L is eliminated by equation (19), variations in initial initator concentration should not affect the shape of a plot of Ψ *versus* $(1-x)/x$. That this is indeed the case is borne out by data for polymerization of acrylamide at two concentrations of initiator couple (*Figures 3* and *4*)[9]. Although the reaction is faster at the higher concentration, the reduced plot is the same for both.

In order to determine both ΔE_a and a for the polymerization of acrylamide by persulphate ion, runs at several initial monomer concentrations are required. The major dependence of φ is on the total temperature rise ΔT_m which is, in turn, proportional to initial monomer concentration (assuming that ΔT_m corresponds to complete conversion). The reduced plot (*Figure 1*) has the property that ln Ψ changes almost linearly with φ at a constant value of $(1-x)/x$ and a. A semi-log plot of Ψ *versus* ΔT_m for runs at two monomer concentrations can

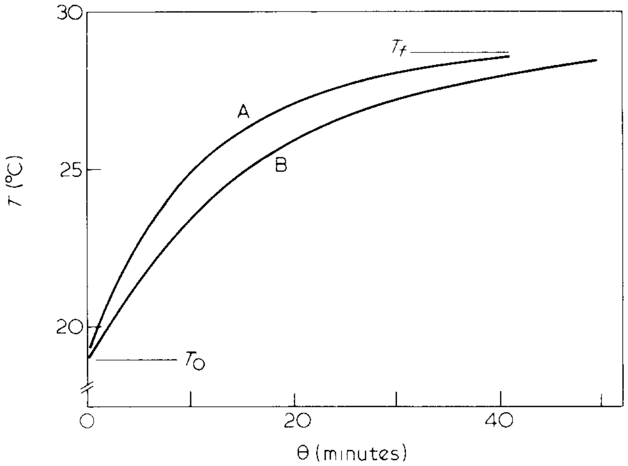

Figure 3 Naider's data[9] for polymerization of acrylamide (0.64 mol l^{-1}) in water. Equimolar concentrations of persulphate and metabiosulphite are (A) 1.6 and (B) 3.2 mmol l^{-1}

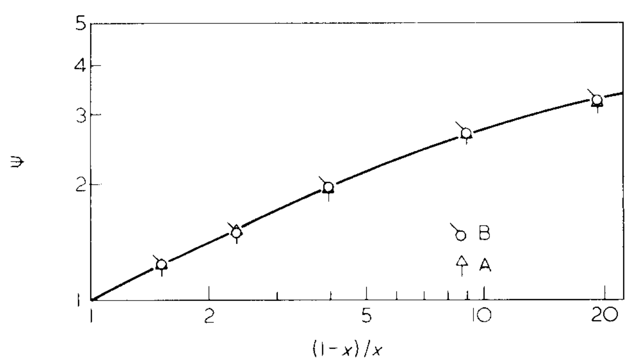

Figure 4 Naider's data (from ***Figure 3***) plotted according to the method of ***Figure 1***

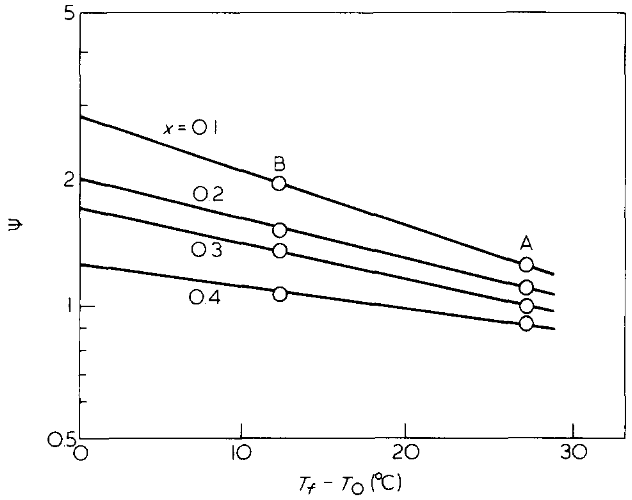

Figure 5 Course of polymerization analysed for two experiments with initial monomer concentrations yielding initial and final temperature of (A) 30.6° and 57.8° and (B) 36.5° and 48.7°C, respectively. In each case persulphate concentration was 17 mmol l^{-1}

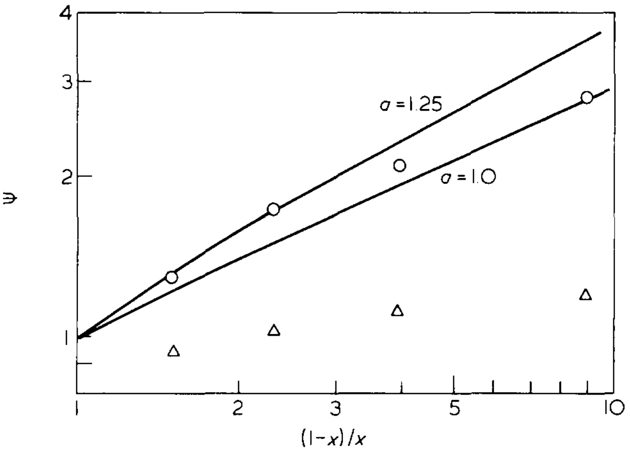

Figure 6 Values of Ψ extrapolated to the isothermal case (○) together with the proposed model at two values of 'a' (and with $\phi = 0$). Also shown are points for the experiment with a total exotherm of 27.2°C (△)

be extrapolated to ΔT_m (and, therefore, φ)$=0$ (*Figure 5*). The data (*Figure 6*) are compatible with the value of $a = 1.25$ found in isothermal polymerizations by Riggs[10]. The adiabatic data were obtained using a 3-litre charge in an insulated steel beaker. The value of φ corresponding to a ΔT_m of 27.2 is about 2.4. ΔE_a calculated from the known starting temperatures thus is 17 kcal mol^{-1}. Riggs reported a value of 16.9 kcal mol^{-1} from isothermal, dilatometric studies[10].

CONCLUSIONS

The graphical method using reduced variables is a fast, convenient method for evaluating certain adiabatic reactions. The order of a polymerization with respect to monomer and the energy of activation are easily estimated with only two or three runs. There are a number of limitations most of which have to do with maintaining truly adiabatic conditions. Complete conversion of monomer and a long initiator half-life are also necessary.

As presented here, the method permits a visualization of the adiabatic polymerization process. Obviously, the method can be adapted to machine computation. Under such circumstances, experimental data might be fed directly to a computer. The linearizing assumption for equation (5) could then be relaxed.

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