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POLYMERIZATION KINETICS BY MEANS OF DIFFERENTIAL THERMAL ANALYSIS

PART II. DERIVATION OF RATE AND ENTHALPY EQUATIONS

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FOREWORD

This report was prepared by the Polymer Branch of the Nonmetallic Materials Division. The work was initiated under Project No. 7340, "Nonmetallic and Composite Materials", Task No. 734004, "New Organic and Inorganic Polymers." It was administered under the direction of the AF Materials Laboratory, Research and Technology Division, with Dr. W. E. Gibbs acting as project engineer.

This report covers work from November 1962 to November 1963.

ABSTRACT

Rate equations and enthalpic parameters were derived for use in differential thermal analysis (DTA) of polymerization reactions. General free radical polymerization kinetics are discussed and the existence of a "stationary state" under DTA conditions was demonstrated, by comparison of a theoretical computer curve, based on stationary state assumption, with actual experimental conditions. These curves appear to be almost superimposable.

This technical documentary report has been reviewed and is approved.

William E. Gibbs

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INTRODUCTION

Differential thermal analysis techniques have in recent years been extended to encompass the field of solution reactions. Borchardt and Daniels (Reference 1) were successful in measuring the heat of reaction and in determining the kinetic parameters for the decomposition of benzene diazonium chloride and the reaction of N, N-dimethyl aniline and ethyl iodide in solution. This technique has now been adapted for use in determining polymerization kinetics and thermodynamic parameters. In Part I of this report (Reference 2) the apparatus and necessary modifications are described. In the present report the derivation of the rate expression and enthalpy relationship are presented, which permit the extension of Borchardt and Daniels' work to polymerization systems.

Borchardt and Daniels (Reference 1) have given the scheme by which rate of reaction and enthalpy data can be obtained by differential thermal methods from simple first-order and pseudo-first-order reactions taking place in solution. Starting with the assumption that in a dilute solution the heat capacities (at constant pressure) of solvent and that of solvent plus reactants are very nearly the same, the heat generated or absorbed by a chemical reaction is given by:

$$dH = C_p \, d\Delta T + K \Delta T \, dt \tag{1}$$

where K is the cell constant, and ΔT is the height of the curve in degrees C. Integration of this equation between $t = 0$ and $t = \infty$ gives the total heat transferred, ΔH.

$$\Delta H = C_p (\Delta T_\infty - \Delta T_0) + K \int_0^\infty \Delta T \, dt \tag{2}$$

Since ΔT is zero both at $t = 0$ and $t = \infty$, the first term is also zero, reducing the equation to:

$$\Delta H = KA \tag{3}$$

A being the total area under the curve. This condition expresses then the enthalpy of the reaction. A typical DTA curve is shown in Figure 1.

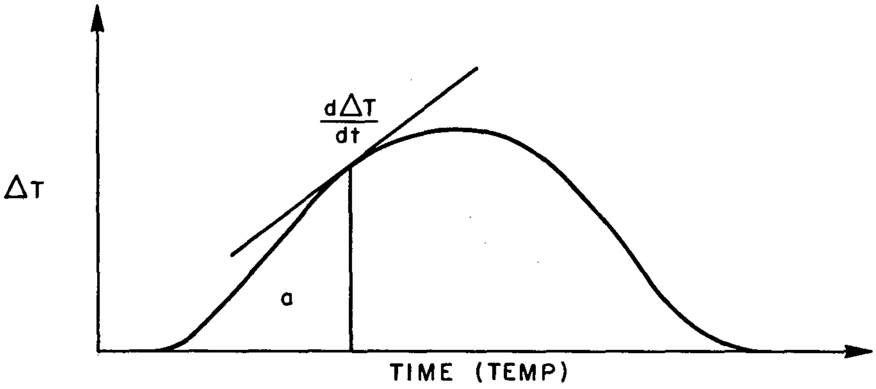

Figure 1. Typical DTA Curve

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Assuming that the heat evolved during a small time interval is directly proportional to the number of moles reacting during that time:

$$dH = -\frac{KA}{n_r}\, dn, \tag{4}$$

(n_r = total number of moles that react), then substitution of equation (4) into equation (1) gives:

$$-\frac{dn}{dt} = \frac{n_r}{KA}\left(C_p \frac{d\Delta T}{dt} + K\Delta T \right) \tag{5}$$

where $\frac{d\Delta T}{dt}$ is the slope and ΔT the height of the curve (Figure 1). The number of moles unreacted (n) at any instant is equal to the initial moles (n_o) minus the number of moles that have reacted:

$$n = n_o - \int_0^t -\frac{dn}{dt}\, dt \tag{6}$$

Substituting equation (5) into equation (6) and integrating gives:

$$n = n_o - \frac{n_r}{KA}\,(C_p\Delta T + Ka) \tag{7}$$

The quantity a is shown in Figure 1. The expression for the rate constant of a reaction of order x with respect to one component is:

$$-\frac{dn}{dt} = \frac{kn^x}{V^{x-1}}, \quad \text{and} \quad k = -\frac{V^{x-1}\frac{dn}{dt}}{n^x} \tag{8}$$

where k = reaction rate constant, V = volume, and n = moles. If $n_o = n_r$ then substitution of equations (5) and (7) into equation (8), and rearranging gives:

$$k = \left[\frac{KAV}{n_o}\right]^{x-1} \frac{C_p \frac{d\Delta T}{dt} + K\Delta T}{\left[K(A-a) - C_p\Delta T\right]^x} \tag{9}$$

For a first order reaction this becomes:

$$k = \frac{C_p \frac{d\Delta T}{dt} + K\Delta T}{K(A-a) - C_p\Delta T} \tag{10}$$

The relative magnitude of the terms in equation (10) is such that those involving C_p are usually much smaller than the quantitites from which they are added or substracted. By neglecting C_p, equation (10) may, therefore, be simplified to:

$$k = \frac{\Delta T}{A-a} \tag{11}$$

This is essentially the equation used by Borchardt and Daniels, and their kinetic results are in good agreement with data obtained by conventional methods. They also obtained enthalpy data on the reactions mentioned, but no comparisons are possible since no literature values are available.

These same authors further extended their derivations to include reactions between several components of the form $\ell L + mM \longrightarrow$ products, for which the rate expression becomes:

$$\frac{dz}{dt} = (L - z)^{\ell} \left(M - \frac{m}{\ell} z\right)^{m} \tag{12}$$

in which case equation (10) is expanded to

$$k = \frac{\left[\frac{KAV}{L_o}\right]^{\ell + m - 1} \left[C_p \frac{d\Delta T}{dt} + K\Delta T\right]}{\left[K(A-a) - C_p\Delta T\right]^{\ell} \left[\left(K\frac{M_o}{L_o} A - \frac{m}{\ell} a\right) - C_p\Delta T\right]^{m}} \tag{13}$$

POLYMERIZATION KINETICS

The above formalization is based upon stoichiometric reactions and cannot as such be used to describe free radical polymerization. It will be necessary, therefore, to develop the required relationships for these systems. The series of reactions which make up the overall process of free radical polymerization may be written as:

1. Generation of Initiator Fragments: $I_2 \longrightarrow 2I\cdot$; $R_f = 2fk_d[I_2]$
2. Chain Initiation: $I\cdot + M \longrightarrow M\cdot$; $R_I = k_i[I\cdot][M]$
3. Chain Propagation: $M\cdot_i + M \longrightarrow M\cdot_{i+1}$; $R_p = k_p[M\cdot][M]$
4. Chain Termination: $M\cdot_i + M\cdot_j \longrightarrow$ Inactive Products: $R_t = 2k_t[M\cdot]^2$

where f is the efficiency of initiator fragments. Because of lack of knowledge of the conditions in this experiment, f was assumed to be 1.

The overall rate of polymerization, the disappearance of monomer, or the formation of polymer is given by:

$$\frac{-d[M]}{dt} = k_I[I\cdot][M] + k_p[M\cdot][M]$$

If the kinetic chain length is reasonably high, the loss of monomer by the chain initiation step is negligible compared with that lost during propagation and the rate of polymerization may be taken as equal to the rate of propagation:

$$\frac{-d[M]}{dt} = k_p[M\cdot][M]$$

In general, the heat evolved or absorbed during polymerization is made up of the heats liberated or absorbed by each of the several reactions which take place:

$$\Delta H_T = \sum(\Delta H_d + \Delta H_i + \Delta H_p + \Delta H_t + \Delta H_{ct} + \ldots\ldots\ldots\ldots),$$

where ΔH_T is the total heat and the subscripts refer to initiator decomposition, chain initiation, propagation, termination, and chain transfer, respectively. Even though the heat generated or absorbed per mole for all these reactions may be significant, due to the fact that the number of initiator decomposition, chain initiation, chain termination, and chain transfer reactions that occur per propagation step is very small (about equal to the reciprocal of the number average degree of polymerization) the heat generated during polymerization is with very small error due to the propagation reaction alone.

Equation (14) contains two easily measured quantities, $-d[M]/dt$ and $[M]$, one quantity which is difficult to measure, $[M\cdot]$, and one quantity, the rate constant, the determination of which is one of the objectives of this work. Free radical concentrations generally are quite small, in the 10^{-8} to 10^{-10} region, and no accurate methods are available for their measurement. It is possible to circumvent the measurement of this quantity by use of the stationary state assumption. This assumption may be stated as: the rate of change of radical concentration is very much smaller than either its rate of formation or rate of disappearance. Since the rate of formation of $[M]$ is:

$$\frac{+d[M\cdot]}{dt} = k_i [I\cdot][M] \tag{15}$$

and its rate of disappearance is:

$$\frac{-d[M\cdot]}{dt} = 2k_t [M\cdot]^2 \tag{16}$$

the instantaneous $M\cdot$ concentration is:

$$\frac{d[M\cdot]}{dt} = k_i [I\cdot][M] - 2k_t [M\cdot]^2 \tag{17}$$

According to the stationary state assumption $d[M\cdot]/dt$ is very much smaller than either $k_I [I\cdot][M]$ or $2k_t [M\cdot]^2$, therefore:

$$k_i [I\cdot][M] \cong 2k_t [M\cdot]^2$$

and

$$[M\cdot]^2 = \frac{k_i [I\cdot][M]}{2k_t} \tag{18}$$

A similar stationary state assumption may be used to replace the $I\cdot$ in the expression $d[I\cdot]/dt = 2fk_d [I_2] - k_I [I\cdot][M]$; therefore

$$2fk_d [I_2] = k_i [I\cdot][M] \tag{19}$$

Combination of equations (18) and 19) and substitution into equation (14) lead to:

$$-\frac{d[M]}{dt} = k_p[M]\left[\frac{fk_d[I_2]}{kt}\right]^{\frac{1}{2}} \tag{20}$$

The validity of the stationary state assumption has been borne out by numerous experiments conducted at constant temperature. It has been subjected recently to a critical review and the general criterion has been derived for its use in isothermal experiments (Reference 3). However, little is known of the validity of the assumption under differential thermal analysis conditions where the temperature changes continually throughout the reaction. It is,therefore, necessary to examine this in some detail.

CONSIDERATION OF "STATIONARY STATE ASSUMPTION" UNDER CONSTANTLY INCREASING TEMPERATURE CONDITIONS

For the investigation of the applicability of "stationary state" under conditions here, the polymerization of styrene initiated by AIBN was selected, since its rate constants are better known and the initial and final concentrations and the heating rate could be experimentally determined. Values for k_p and k_t were taken from the literature (Reference 4). Initiator decomposition parameters were determined at this laboratory. Five values covering the range of 10^6 to 10^8 were assigned to k_i, assuming it to be of the same general order of magnitude as the propagation rate constants. These data are summarized in Table 1.

TABLE I

Rate Constants in Styrene Polymerization

Reaction	Rate Constant	A_i	E_i, cal.
Initiator decomposition	k_d	6.2×10^{15}	32,000
Termination	k_t	1.32×10^9	2,400
Propagation	k_p	2.2×10^7	7,800
Initiation	k_{i-1}	2.2×10^7	7,800
	k_{i-2}	10^6	10,000
	k_{i-3}	10^6	6,000
	k_{i-4}	10^8	10,000
	k_{i-5}	10^8	20,000

The initial initiator concentration I_o was 5.25×10^{-3} mole/1, the initial monomer concentration $M_o = 1.5$ mole/1, the heating rate $dT/dt = 1.027 \times 10^{-2}$ °K/sec. The reaction visibly started at T_o = 341.5°K and ended (T_∞) at 390°K (approx. duration 4800 sec); $T_\infty - T_o = T_R$ is therefore 48.5°K and

$$0 \leq \frac{T_R}{T_o} \leq \frac{48.5}{341.5} = 0.142 \tag{21}$$

The exponential term of the Arrhenius equation was rearranged to:

$$\exp\left\{-\frac{E}{R}\,\frac{1}{T_o + \Delta T_R}\right\} = \exp\left\{-\frac{E}{RT_o}\,\frac{1}{1 + \frac{T_R}{T_o}}\right\} \tag{22}$$

to allow simplification in the calculations; $\dfrac{1}{1 + \frac{T_R}{T_o}}$ in turn, is very nearly equal to $1 - \dfrac{T_R}{T_o}$. The data in Table 2 show the error introduced by this assumption.

TABLE 2

Percent Error Introduced by Assuming $1 - \dfrac{T_R}{T_o} = \dfrac{1}{1 + \frac{T_R}{T_o}}$

T°K	Percent Error
0	0.00
10	0.09
20	0.35
30	0.78
40	1.39
48.5	2.06

This approximation results in a considerable simplification of subsequent calculations, thereby more than offsetting the small error introduced.

Accordingly,

$$\exp\left\{-\frac{E}{RT}\right\} \approx \exp\left\{-\frac{E}{RT_o}\right\} \exp\left\{\frac{ET_R}{RT_o^2}\right\} \tag{23}$$

Since $T_R = (dT/dt)t$, the rate constants can be expressed in the following form:

$$k_i = B_i e^{h_i t} \tag{24}$$

where

$$B_i = A_i e^{-\frac{E_i}{RT_o}}, \text{ and } h_i = \frac{E_i \frac{dT}{dt}}{RT_o^2}$$

B_i and h_i are constants for a particular experiment and their values may vary depending on the heating rate, dT/dt, and the initial temperature of the reaction, T_o.

The rate constants were then calculated and are given in Table 3.

TABLE 3

Rate Constants - Approximate Form

Rate Constants	B_i	$h_i \times 10^4$
k_d	2.8×10^{-5}	14.0
k_t	3.9×10^{7}	1.06
k_p	2.4×10^{3}	3.43
k_{i-1}	2.4×10^{3}	3.43
k_{i-2}	4.8×10^{-1}	4.4
k_{i-3}	1.5×10^{2}	2.6
k_{i-4}	4.8×10^{1}	4.4
k_{i-5}	2.9×10^{-5}	1.76

Since $-\frac{d[I_2]}{dt} = k_d [I_2]$, integration of this equation gives:

$$[I_2] = I_o \exp\left\{-\int_o^t k_d dt\right\} ;$$

denoting $2 f k_d [I_2]$ as g, we obtain:

$$g = 2 f k_d I_o e^{-\int_o^t k_d dt} \tag{25}$$

The exact rate expressions were calculated:

$$g = 3.0 \times 10^{-7} f \exp\left\{1.4 \times 10^{-3} t - 2 \times 10^{-2} e^{1.4 \times 10^{-3} t}\right\} \tag{26}$$

$$\frac{d\,[I\cdot]}{dt} = g - k_i\,[I\cdot][M] \tag{27}$$

$$\frac{d\,[M\cdot]}{dt} = k_i\,[I\cdot][M] - 7.8 \times 10^{7} \times e^{1.06 \times 10^{-4} t}[M\cdot]^2 \;; \tag{28}$$

$$\frac{d\,[M]}{dt} = -2.4 \times 10^{2} \times e^{3.43 \times 10^{-4} t}[M\cdot]\,[M] \;. \tag{29}$$

For the approximate equations using the stationary state assumption the following equation was used in lieu of equations (27) and (28):

$$g = 7.8 \times 10^{7} \times e^{1.06 \times 10^{-4} t}[M\cdot]^2 = k_i\,[I\cdot][M] \tag{30}$$

These two sets of equations, (a) (26-29) and (b) (26), (30) and (29) were solved independently for k_i by digital computer. For purposes of calculation f was assumed to be 1. Figure 2 shows the functions g, $[M\cdot]$, $\frac{d\,[M]}{dt}$, $[I\cdot]$, (for k_{i-1}), and $[I\cdot_5]$ (for k_{i-5}) as calculated by computer. The function d $[M]/dt$ was calculated from data obtained by computer for the function $[M]$. Figure 3 describes the functions $[M]$ and $[M\cdot]$ showing both exact as well as approximate equations.

The functions obtained from the two sets of equations were practically identical. The maximum deviation of the function $[M]$ was approximately 0.15 percent and that of $[M\cdot]$, 0.4 percent, the mean deviations being negligible. The deviations of $[I\cdot]$ calculated from both sets of equations and their effect on $[M\cdot]$ and $[M]$ were so small that they could not be detected by the 8-digit computer and may, therefore, also be considered negligible.

The plot of the functions $[M\cdot]$ and -d $[M]/dt$ shows an abrupt increase shortly after the start of the reaction coinciding thereafter closely with the curve derived from the stationary state assumption. The evaluation of the rate constants from experimental curves will have to take this into account by curve fitting in this region and adjustment of the base line. This condition is shown in Figure 4 by the slanted base line of the experimental curve.

Assuming proportionality of ΔT and [M] as well as the adjusted base line, the experimental curves were plotted by means of the least squares method. The resulting curve was superimposed on the theoretical curve of [M] (Figure 4). Except for the aforementioned abrupt shift at the beginning of the reaction there is good agreement between the two curves. The deviation of the experimental curve from the calculated values indicates that the reaction must have started in a very gradual manner before it reached the point indicated by the thermocouple as the start of the reaction. This analysis has, nevertheless, shown that the stationary state assumption is quite valid within the general conditions of the experiment.

DERIVATION OF RATE EQUATION

By neglecting the C_p term, as before, equation (5) may be reduced to:

$$-\frac{dn}{dt} = \frac{n_r \Delta T}{A} \tag{31}$$

The decomposition of the initiator which essentially goes to completion (i.e.,$n_r = I_o$) may be stated as:

$$-\frac{d\left[I_2\right]}{dt} = k_d\left[I_2\right] = \frac{f I_0 \Delta T'}{VA'} \tag{32}$$

where T' and A' are used to distinguish the initiator contribution from the rest of the reaction terms. For practical purposes T' and A' are determined in a separate run of initiator decomposition conducted under the same conditions as the polymerization reaction.

Since the disappearance of monomer is equal to the formation of polymer:

$$-\frac{d\,[M]}{dt} = \frac{d\,[P]}{dt} = \frac{P\Delta T}{VA} \tag{33}$$

where P is the total amount of polymer formed. Similarly to equations (6) and (7), the monomer concentration at any given point is again equal to its initial concentration, M_o, less the amount of polymer formed:

$$[M] = \frac{1}{V}\left[M_0 - \frac{Pa}{A}\right] = \frac{M_0 A - Pa}{VA} \tag{34}$$

It has already been pointed out (equation 14), that the propagation rate, now expressed as dP/dt may be assumed to be equal to the overall rate,

$$\frac{d[P]}{dt} = k_p\,[M]\,[M\cdot]$$

Rearrangement of equation (20) and substitution of equations (33) and (34) then gives:

$$\frac{k_p}{k_t^{\frac{1}{2}}} = \frac{P\Delta T}{(M_0A - Pa)\,(fk_d\left[I_2\right])^{\frac{1}{2}}} \qquad (35)$$

Substitution of equation (32) into the above equation gives the final expression for the polymerization rate constant:

$$\frac{k_p}{k_t^{\frac{1}{2}}} = \frac{C\Delta T}{(M_0A - Pa)\,(\Delta T')^{\frac{1}{2}}} \qquad (36)$$

where the constant C is:

$$C = P\left(\frac{VA'}{fI_0}\right)^{\frac{1}{2}} \qquad (37)$$

Reintroduction of the heat capacity term expands equation (36) to:

$$\frac{k_p}{k_t^{\frac{1}{2}}} = \frac{C(C_p\frac{d\Delta T}{dt} + K\Delta T)}{(\Delta T')^{\frac{1}{2}}\left[K(M_0A - Pa) - PC_p\Delta T\right]} \qquad (38)$$

UNITS AND DIMENSIONS

The reaction rate $k_p/k_t^{1/2}$ is in liters, mole $^{-1}$, sec $^{-1}$; M_o, I_o, and P in moles; V in liters; A, A' and a in °Csec, ΔT and $\Delta T'$ in °C; C_p in calories °C^{-1}; $d\Delta T/dt$ in °Csec^{-1}; and K in calories °C^{-1} sec^{-1}.

The cell constant K needs only be evaluated once from a reaction with known enthalpy. C_p is the total heat capacity of the solvent and monomer, but since we are dealing with a dilute system the heat capacity of the solvent is usually assumed to be equal to that of the system. $d\Delta T/dt$ is the slope of the DTA curve. The enthalpy ΔH is in calories mole^{-1}.

The rate constants are plotted in the usual manner as -log k vs. 1/T°K and from the activation energy plot the activation energy $E_p - E_t/2$ and the frequency factor $A_p/A_t^{1/2}$ can then be obtained.

This work demonstrates the feasibility of extending DTA into the realm of polymerization kinetics. It has been shown that stationary state conditions prevail when reaction is subjected to a moderate heating rate. The present heating capacity of the apparatus lies between approximately 0.5 and 2.5°/min and while it is to be expected that some increase in the heating rate beyond this limit should upset the stationary state the exact practical limits are still to be determined.

The relative ease with which kinetic parameters as well as enthalpy can be determined by means of DTA reduces the amount of work involved from that extending over a period of weeks and even months to one day.

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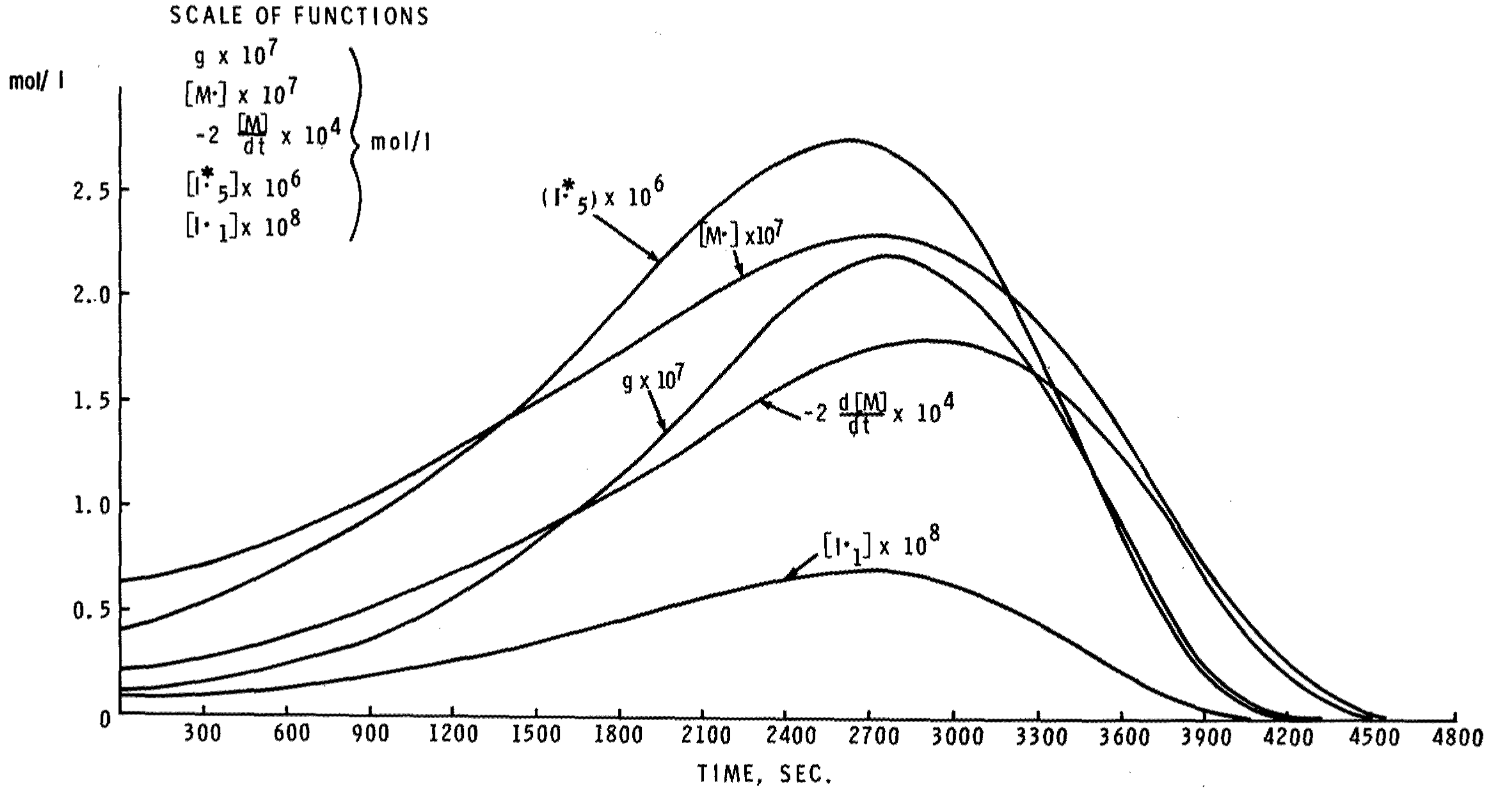

Figure 2. The functions g; $[M^{\cdot}]$; $\frac{d\,[M]}{dt}$; $[I\cdot_1]$ and $[I\cdot^{*}_5]$ from values obtained by computer

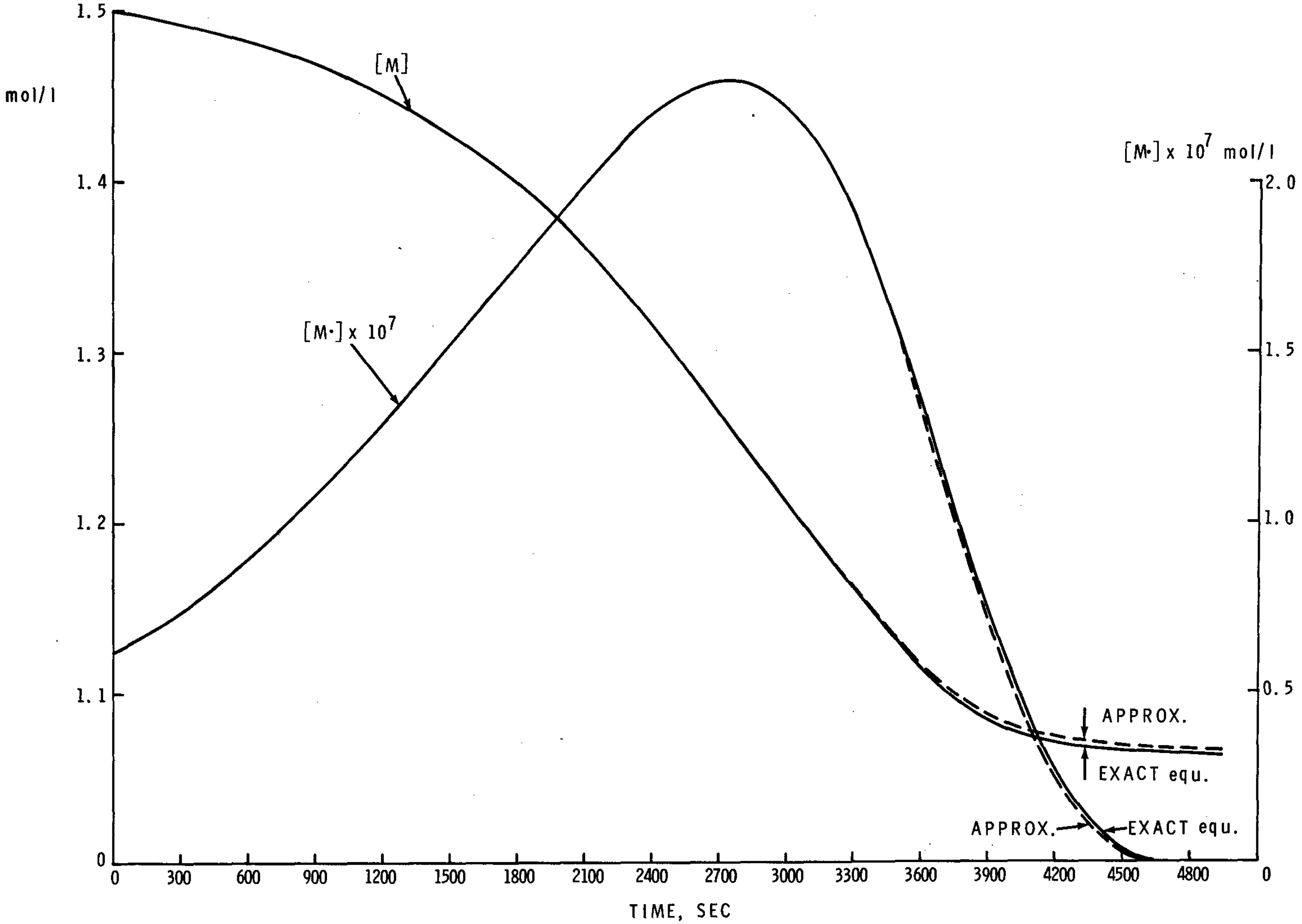

Figure 3. The functions [M] and [M·] from computer data

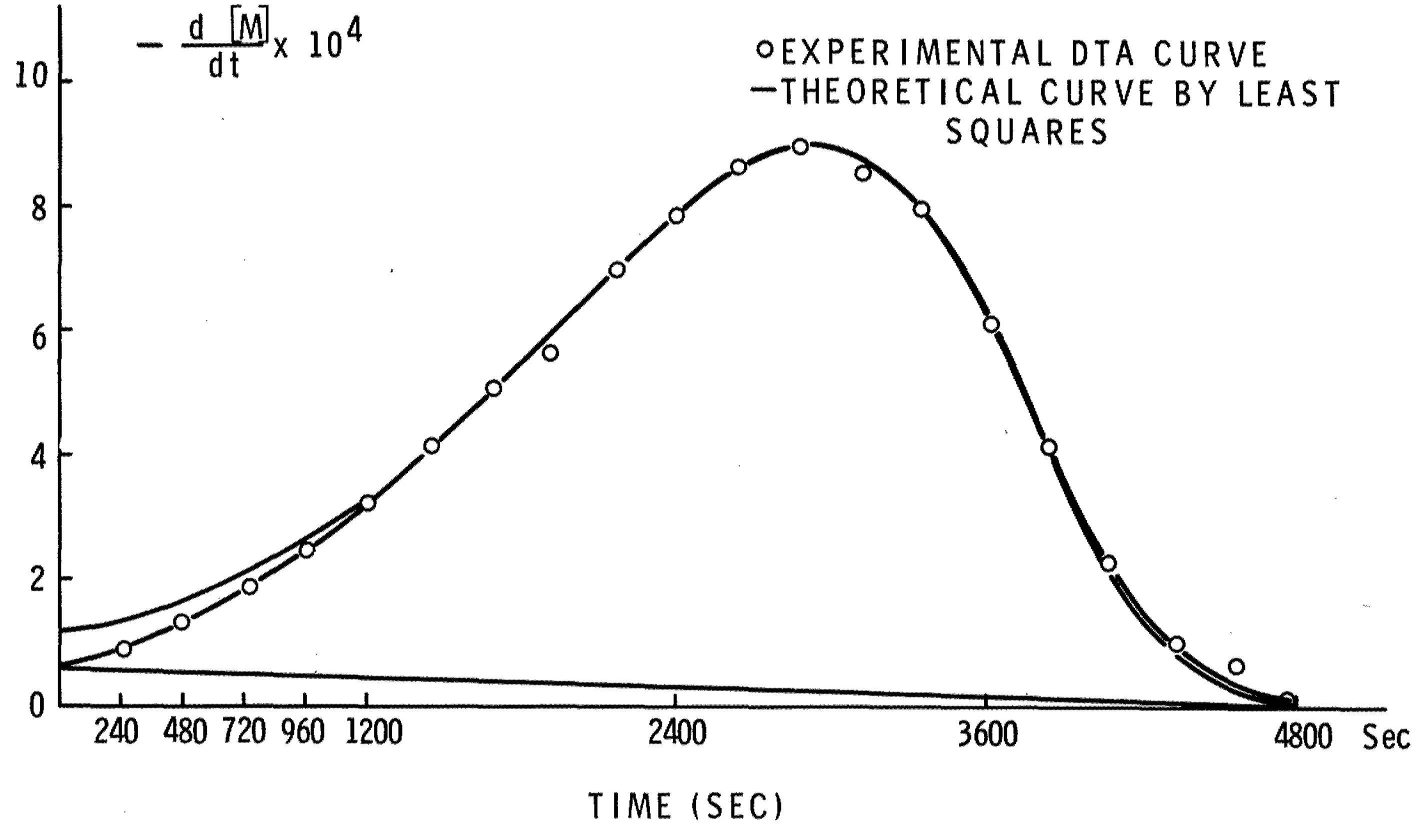

Figure 4. The theoretical and experimental function - $\frac{d[M]}{dt}$.