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DETERMINATION OF THE KINETICS OF CURING AND THE HEAT CAPACITY OF AN EPOXY RESIN BY DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

Two techniques were developed for determining the kinetic parameters of chemical reactions from differential scanning calorimeter data. In one technique, variation with time of the heat gain or loss as reactions proceed can be used to determine the order, rate constant, activation energy, and heat of reaction. In the second technique, variation with time of the glass transition temperature of certain materials can be used to determine the order, rate constant, and activation energy. An application has been made to the curing of an epoxy resin.
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SUMMARY

Differential scanning calorimeters (DSC) measure the rate at which energy must be applied to a sample or to a reference holder to maintain them at the same temperature. Two techniques were developed for obtaining kinetic data using a DSC.

If, at a given temperature, a sample is undergoing a reaction involving an energy change, the output of the DSC is proportional to the rate of heat flow due to that reaction. Equations were derived in which the variation with time of the DSC output could be used to determine reaction orders, enthalpy, rates, and activation energies. The exothermic curing of a B-staged epoxy resin (ERL-2258/ZZ1-0820) was studied as an example and was found to follow second-order kinetics with a rate constant of:

\[ k_2 = 959 \ e^{-7448/T} \ \text{g} \ \text{cal}^{-1} \ \text{sec}^{-1} \]

For amorphous materials, a change in heat capacity occurs as they go from a glassy to a liquid state at the glass transition temperature (T_g). The T_g of some materials varies in a regular manner with the extent of polymerization. Equations were derived that relate this variation of T_g with the kinetic parameters. Curing of the B-staged epoxy resin was studied by determining the T_g from DSC heat-capacity curves for samples heat treated for various times and temperatures. The results were found to correlate well with those obtained using the first technique.

The extent of cure was calculated using kinetic data for a typical slow curing cycle. The extent of cure calculated from the T_g measured for a sample heat treated over that cycle corresponded closely with that calculated from kinetic data.
INTRODUCTION

This study was undertaken at the Oak Ridge Y-12 Plant(a) to develop techniques which could be used to determine the kinetic parameters of chemical reactions using a DSC.

Exothermic and endothermic reactions involve heat transfers at rates which decrease with time in the same proportion that the concentrations of the reacting species decrease. The DSC, with its fast response and high sensitivity, is well suited to making kinetic studies of such reactions. Previous workers\(^\text{(1)}\) have reported techniques for determining kinetic parameters from data obtained under nonisothermal conditions. Interpretation of the results is not straightforward\(^\text{(2)}\) and becomes virtually impossible when simultaneous reactions with different activation energies occur. Rogers\(^\text{(3)}\) found that plots of log \(h\) vs \(t\) gave straight lines for first-order, isothermal reactions, where \(h\) is the DSC output and \(t\) is time. Gray\(^\text{(4)}\) determined the fraction of heat evolved at \(t\) by planimeter measurements and equated it with the fraction of cure of an epoxy resin. Comparison was then made with the \(T_g\). In this work, equations were derived which relate \(h\), taken under isothermal conditions, with the kinetic parameters. They were applied in the determination of rate, order, activation energy, and heat of the curing reaction of an epoxy resin.

For many polymers, \(T_g\) varies in a regular manner with molecular weight.\(^\text{(5)}\) Equations were derived which relate \(T_g\) changes with the kinetic parameters and were used to determine the rate, order, and activation energy of the curing of an epoxy resin.

The utility of the data reported herein is that they may be used to calculate rather than measure the degree of cure obtained from a variety of proposed heat-treatment cycles. An example of such a curing cycle is given in which the calculated degree of cure was found to correspond closely with the measured degree.

Effects of changes of stoichiometry and addition of inert diluents upon the determination of the kinetic parameters were also studied.

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(a) Operated by the Union Carbide Corporation's Nuclear Division for the US Energy Research and Development Administration.
KINETICS OF CURING AND HEAT CAPACITY OF AN EPOXY RESIN

APPARATUS AND TECHNIQUES

Thermal measurements and heat treatments were performed on a Perkin-Elmer Model DSC-2 differential scanning calorimeter (DSC). This instrument contains a matched pair of 9-mm-diameter sample holders with integral heating elements and platinum resistance thermometers. Heating-element power is derived alternately at 85 Hz from two sources. The average temperature of the two holders is controlled by a feedback loop and a digital temperature programmer controlling one power supply. The temperature difference between the holders is nulled by the application of power from the second supply and feedback loop to the holder at the lower temperature. The power from this second source, which is the time derivative of the transition or reaction energy or of the heat capacity of the sample, is recorded as a function of time or temperature. Samples of 0.1 to 200 mg can be studied over the range from 100 to 1000 K at heating or cooling rates from 0 to 320 K min\(^{-1}\) and at sensitivities down to 0.01 mcal sec\(^{-1}\). Instrument response is faster, the sample size smaller, and the output more physically meaningful than with conventional differential thermal analysis instruments.

In this work, sample sizes ranged from 4 to 20 mg. Glass transition temperatures (T\(_g\)) were determined at heating rates of 5 deg min\(^{-1}\) and were defined as the temperature at which one half the change in heat capacity (difference between the glass and liquid states) had occurred. The heat of fusion of indium\(^{(6)}\) at 429.8 K and the heat capacity of aluminum oxide\(^{(7)}\) were used as calibrating standards for the determination of the reaction and transition energies and of the heat capacity of the resin.

The epoxy resin used in this study was a 31:9 mixture of ERL-2258/ZZL-0820.\(^{(b)}\) ERL-2258 consists of 50% diglycidyl ether of bisphenol-A (DGEBA) and 50% bis(2,3-epoxycyclopentyl) ether. ZZL-0820 consists of 53% m-phenylenediamine, 34% p,p' methylenediamine and 13% DGEBA. The mixture was heat treated at 358 K for two hours to effect a partial cure, or B-stage.

RESULTS AND DISCUSSION

Three kinds of data were obtained from the DSC thermograms: (1) rates of heat evolution from the curing reaction of the resin, (2) relative and absolute heat capacities, and (3) transition energies. Rates, the order, and the activation energy of the curing reaction were calculated from the rates of heat evolution at different temperatures. Glass transition temperatures were obtained from the relative heat capacities.

Determination of Kinetic Parameters by Heat-Evolution Methods

Samples were heated to 423 or 473 K at 320 deg min\(^{-1}\), and the rate that heat evolved per gram, h, from the isothermal exothermic curing reaction was plotted as a function of time.

---

\(^{(b)}\) A product of the Union Carbide Corporation
Figure 1. RATE OF HEAT EVOLUTION AT TWO TEMPERATURES FOR CURING AN EPOXY RESIN. (The Initial Irregularity in the Curve of the 473 K Run is Due to Slight Temperature Changes in the Heat Sink)

Figure 1 is a graph of the typical data obtained. During the initial 400 seconds of the 473 K run, the instrument heat sink was not close enough to thermal equilibrium for accurate data to be taken at the high sensitivities used. At 5000 seconds into the 423 K run and at 3800 seconds into the 473 K run, the uncertainty in the rate of heat evolution increased because of very slight instrument drift, and the runs were therefore terminated before completion of cure. The area under each of the two curves should be equal to the heat of the curing reaction, ΔH. Planimeter determinations of such areas were found to vary greatly, largely because of the inaccurate curve traced at the start of each run.

However, the shape of the major portions of the curves can be analyzed by equations derived in Appendix A for first, second, and third-order kinetics to yield ΔH, the activation energy E+, and the rate constants for the curing reaction, k_N. For first-order reactions plots of ln h vs t give straight lines according to Equation A-1; but, with this epoxy resin, such plots gave curved lines, indicating that the curing reaction is not first order. Plots of h^{-1/2} vs t give straight lines for second-order reactions according to Equation A-7. As noted in Figure 2, these data lie on straight lines, demonstrating that second-order kinetics are followed. The slight curvature after 3500 seconds for the 423 K heat treatment is due to a very slight instrument drift. These points were not used in calculations of slope and intercept. The points taken before 400 seconds were likewise not used because thermal equilibrium of the heat sink with the sample holders had not yet occurred.
The second-order reaction constant, \( k_2 \), was computed from the squares of the slopes of the lines in Figure 2 and was found to have values of \( 2.07 \times 10^{-5} \) and \( 1.34 \times 10^{-4} \) g cal\(^{-1}\) sec\(^{-1} \) at 423 and 473 K, respectively. The activation energy is thus 14.8 kcal mol\(^{-1}\), and the second-order rate constant at temperature \( T \) is given by:

\[
k_2 = 959 \, e^{-\frac{7448}{T}} \, \text{g cal}^{-1} \, \text{sec}^{-1}.
\] (1)

The reaction half times were computed from the ratio of the intercept to the slope and were 1664 and 202.4 seconds at 423 and 473 K, respectively. The initial rate of heat evolution is the reciprocal of the square of the intercept and is \( 1.742 \times 10^{-2} \) cal g\(^{-1}\) sec\(^{-1} \) at 423 K and \( 1.821 \times 10^{-1} \) cal g\(^{-1}\) sec\(^{-1} \) at 473 K. The area under the curve of Figure 1 is \( \Delta H \), which is the reciprocal of the product of the slope and intercept of the lines in Figure 2, and was computed to be 29.0 cal g\(^{-1}\). Planimeter measurement of that area gave 21.3 cal g\(^{-1}\), but the kinetic-data computation is more reliable because of the uncertainties in \( h \) during the initial part of the runs.

Using the method of Urichenck,(1) attempts were made to obtain kinetic parameters by measuring the areas between the initial and fully cured heat-capacity curves obtained by scanning at 1.25 deg min\(^{-1}\) over the range from 323 to 523 K. A sensitivity of 0.02 mcal sec\(^{-1} \) for a full-scale recorder deflection was required. The area is approximately the sum of
the heat of reaction and the product $\Delta C_p \Delta T$, where $\Delta C_p$ is the difference in heat capacity of the uncured and cured resin and $\Delta T$ is the difference between $T_{g\text{oes}}$ and $T_{g0}$, the final and initial $T_g$ values. However, as a significant portion of the curing reaction had not taken place during this heat treatment, as the slower scan speeds required to get complete reaction require even greater sensitivity, and as higher final temperatures could not be used without degrading the resin, this effort to obtain $\Delta H$ had to be abandoned.

**Determination of Kinetic Parameters by the Glass-Transition-Temperature Method**

Amorphous materials exhibit discontinuous changes in their heat capacities and thermal expansions at the temperature at which they change from the glassy to the liquid state. This temperature (actually a temperature range) is called the "glass transition temperature", $T_g$, here defined as that temperature at which one half the change in heat capacity occurs during a scan of increasing temperature. Because $T_g$ is slightly dependent on the rate of temperature increase (due to finite thermal conductivity), a slow scan speed of five degrees per minute was used.

The heat capacity of the as-received B-staged resin is shown in Figure 3. Heat capacities of the B-staged resin above 373 K cannot be directly determined because the heat given off in the curing reaction significantly changes the apparent baseline. Figure 4 shows the heat capacity after a heat treatment of 25 hours at 423 K. During the initial scan of each sample of B-staged resin through the $T_g$, a large endothermic spike was always found, with an area of 0.838 cal g$^{-1}$. Subsequent scans were devoid of this feature and exhibited the normal S-shaped curve from which the $T_g$ could be determined. This phenomenon is probably a result of a bulk stress relaxation of the material or a molecular-level free-volume effect.[8] The endothermic spike was also seen only on the initial scan through the glass transition region of the heat-treated sample in Figure 4. Note that $T_g$ is greater than the heat treatment temperature, indicating that the curing reaction continues at temperatures below the $T_g$, here accounting for an increase in percent reaction (from 86 to 94%), as determined from $T_g$ and kinetic data. An endothermic spike was also always found whenever the material was held slightly below the $T_g$ for a significant period. Its area appeared to increase with time. Kinetic data for the curing reaction below the $T_g$ could have been determined (vide infra), but were not, due to the lack of time. It is estimated that the reaction rates are decreased one or two orders of magnitude when the heat-treatment temperature is less than the $T_g$. The effects of this continuing cure upon other physical properties should be investigated to determine the suitability of use of this material in each potential application, particularly if optimum physical properties are obtained from material cured less than 100%.

The $T_g$s for many polymers have been shown to be a linear function of the inverse of their molecular weights.[5] Using this assumption, expressions are derived in Appendix B relating the $T_g$ changes with $n^{th}$-order reaction-rate constants. For the resin studied here, a $T_g$ of 473 K was the highest obtained after an overnight heat treatment at 473 K (greater than 98% cured) and was thus used as $T_{g\text{oes}}$. Use of higher heat-treatment temperatures for long time periods showed that $T_g$ went through a maximum at about 473 K, indicating that degradation was occurring. Figure 5 is a first-order plot of the data listed in Table 1 which was obtained by finding the $T_g$ of samples heat treated at 373, 423, or 473 K for various times. The high curvature of the lines demonstrates that the curing reaction is not first
Figure 3. HEAT CAPACITY OF THE 3-STAGED EPOXY RESIN. (The Upper Curve was Obtained from the Initial Heating at 1.25 deg min⁻¹ of the Material through the T_g Region; the Lower Curve was Obtained from the Second Heating.)

Figure 4. HEAT CAPACITY OF A HEAT-TREATED SAMPLE. (Line A was Obtained after a 25-Hour Heat Treatment at 423 K and Shows the Sharp, Endothermic Spike; Line B was Determined Immediately after Obtaining Line A and was Used to Determine a T_g of 444.2 K.)

Figure 5. FIRST-ORDER KINETIC PLOT OF GLASS-TRANSIT (The High Curvature of the Lines at Each Temperature Demonstrates the Rate of the Curing Process.)
Figure 4. HEAT CAPACITY OF A HEAT-TREATED SAMPLE. (Line A was Obtained after a 25-Hour Heat Treatment at 423 K and Shows the Sharp, Endothermic Spike; Line B was Determined Immediately after Obtaining Line A and was Used to Determine a Tg of 444.2 K.)

Figure 5. FIRST-ORDER KINETIC PLOT OF GLASS-TRANSITION-TEMPERATURE DATA. (The High Curvature of the Lines at Each Temperature Demonstrates that First-Order Kinetics are not Followed During the Quenching of this Epoxy Resin.)
order. Figure 6 is a second-order plot of the data. Here, the curvatures are small, indicating second-order kinetics are followed and are due to the uncertainties in the final $T_{g_{oo}}$. The slopes are equal to $k_2d/m$, where $k_2$ is the second-order rate constant, $d$ is the density, and $m$ is the slope of the $T_g$ vs $M^{-1}$ plot (M, mol wt). An activation energy of 11.9 kcal/mol was calculated from the slope of the line in Figure 7.

Using Equation A-10 of Appendix A, the reaction half time at 373 K was calculated to be 17,720 seconds. Equation A-8 was used to calculate from the heat-evolution data the extent of reaction for the samples listed in Table 1. The $T_g$s were plotted against these percentages of reaction in Figure 8. No assumptions concerning the relationship of $T_g$ with molecular weight were used in this figure. The closeness of all but three points to the line is a measure of the quality of the kinetic data. Those three points, marked "a", correspond to samples which were heat treated at times sufficiently long for the $T_g$ to eventually exceed the heat-treatment temperature as the curing reaction proceeded. The unknown, but greatly decreased, reaction rate resulting from this phase change was not determined in this work due to a lack of time and was thus not used in the extent of the reaction calculations.

Comparison of the Two Methods

Equation B-3 (Appendix B) was used to calculate the extent of the reaction based on $T_g$ data. Figure 9 is a plot of the extent of the reaction obtained from heat-evolution data versus that obtained from $T_g$ data. The assumption that $T_g$ is a linear function of the reciprocal of the molecular weight is not valid for this system over the whole interval of the curing reaction, as the points in Figure 9 do not lie on the line of unit slope. The straight portion of the line from 0 to 80% reaction indicates that, over this range, $T_g$ is proportional to $M^{-1}$. If it is assumed that $T_{g_0}$ was measured incorrectly and that a $T_{g_{oo}}$ value of 473 K does not apply to this resin system at less than 80% cure, new values ($T_{g_0}'$ and $T_{g_{oo}}'$) can be calculated from:

$$T_{g_0}' = T_{g_0} + \frac{y(0)}{100} (T_{g_{oo}} - T_{g_0}), \text{ or}$$

$$T_{g_{oo}}' = T_{g_0} + \frac{y(100)}{100} (T_{g_{oo}} - T_{g_0}).$$

(2)

(3)

where $y(0)$ and $y(100)$ are the end points of the straight line in Figure 9 which were determined by least-squares analysis. Using the computed values of 333.1 and 434.4 K for
Figure 6. SECOND-ORDER KINETIC PLOT OF GLASS-TRANSITION-TEMPERATURE DATA. (Slopes of the Lines are k2d/fm; the Slight Curvature of the Lines is Due to an Inaccuracy in the Determination of TgΟ.)

TgΟ and Tgοοο, respectively, the data were replotted in Figure 10 in which the points of less than 80% reaction now lie on the line of unit slope. Physical interpretation of these data without other data is not possible, but it does suggest that there are some parallel, competing chemical reactions occurring in the last 20% of the cure which alter the structure of the material. This possibility is not surprising in view of the complex nature of the components of the resin.

Figures 11 and 12 are the same as Figures 6 and 7 except that TgΟ and Tgοοο were used in the calculations. Note that the lines in Figure 11 are straighter than those in Figure 6. The slope of Figure 12 was used to calculate an activation energy of 14.4 kcal mol⁻¹, in excellent agreement with that calculated from the heat-evolution kinetic data.

**Application of the Kinetic Parameters to the Heat-Treatment Cycles**

In Appendix C an example is given of the use of kinetic data to determine the extent of reaction for a curing heat treatment consisting of a 1.25 deg min⁻¹ increase from 323 to 423 K, a 30-minute hold at 423 K, and a 1.25 deg min⁻¹ decrease from 423 to 323 K. A
Simpson's-rule integration of Equation C.2 was performed for the heat treatment of slow heating to 423 K and holding at 423 K for 30 minutes. From this integration, the curing reaction was calculated to be 64.0% complete; which, from Figure 8, corresponds to a Tg of 399 K. From this value it was estimated that the Tg would be about 403 K after the cooling portion of the heat treatment. A second Simpson’s-rule integration was performed using 403 K as the lower limit on the cooling portion, and this integration resulted in a calculation of 68.5% completion of cure. The calculations were checked by finding the percent cure from the Tg. During the determination of the Tg of the sample after the heat-treatment cycle, a large, very sharp, endothermic spike was noted in the Tg region. A second scan was performed, indicating a Tg of 407 K, which corresponds to a 73.6% cure. The agreement between calculations is very good.

Figure 7. DETERMINATION OF THE ACTIVATION ENERGY FROM GLASS-TRANSITION-TEMPERATURE DATA. (The Activation Energy is the Negative of the Slope Divided by the Gas Constant, R, and is 11.9 kcal mol⁻¹)

Figure 8. CHANGE IN THE GLASS TRANSITION TEMPERATURE WITH THE DEGREE OF CURE. (The Degree of Cure was Calculated from Heat-Evolution Kinetic Data and the Time the Samples were Heat Treated at 373, 423, and 473 K; the Points Marked “a” Correspond to Samples whose Tg’s are Smaller than their Heat-Treatment Temperatures)
Figure 9. COMPARISON OF HEAT EVOLUTION AND GLASS-TRANSITION-TEMPERATURE KINETIC DATA. (Three Heat-Treatment Temperatures were Used: 373, 423, and 473 K; Points Marked "a" and "b" were not Used in Computing the Least-Squares Straight Line)

Figure 10. COMPARISON OF HEAT EVOLUTION AND MODIFIED GLASS-TRANSITION-TEMPERATURE KINETIC DATA. (The Data of Figure 9 were Replotted Using Calculated Values of $T_g = 333.1$ K and $T_g = 434.4$ K; Points Marked "a" and "b" were not Used in Computing the Least-Squares Line)
Effects of Changes of Stoichiometry and Inert Diluents

During the preceding discussion it was assumed that the B-staged epoxy resin consisted only of an epoxide, E, a stoichiometric amount of an active hydrogen compound, H, and some condensed polymer product, P. Because the results were obtained on a per-gram basis, the effect of the presence of P, or any other inert additive for that matter, would be that of a diluent (ie, to decrease ΔH by a factor of 1/(1 + F), where F is the weight fraction of additive, and to decrease reaction rates by a factor of 1/(1 + F)^n, where n is the order of the reaction). Neither the determination of the order of the reaction nor of the activation energy would be affected.
The rate of polymer formation for the second-order kinetic results obtained here is $d[P]/dt$ and is given either by:

$$\frac{d[P]}{dt} = k_2[E][H], \quad (4)$$

$$\frac{d[P]}{dt} = k_2[E]^2, \quad \text{or} \quad (5)$$

$$\frac{d[P]}{dt} = k_2[H]^2, \quad (6)$$

where the brackets designate the concentrations of the species. The rate is measured directly by the DSC, but it is impossible to distinguish between Equations 4, 5, and 6 on the basis of one formulation alone. If a weight, $\Delta W_E$, of E were added in excess of stoichiometric requirements, the concentration of E would then be:

$$[E] = \frac{\Delta W_E}{\frac{1}{M_E} + \frac{\Delta W_E}{d_E} + \frac{M_H}{d_H}}, \quad (7)$$

and the concentration of H would then be:

$$[H] = \frac{1}{\frac{M_E + \Delta W_E}{d_E} + \frac{M_H}{d_H}}, \quad (8)$$

where $M_E$ and $M_H$ are the molecular weights and $d_E$ and $d_H$ are the densities of E and H, respectively.

Rate Expressions 4, 5, and 6 then become:

$$\frac{d[P]}{dt} = k_2 \left( \frac{\Delta W_E}{\left(\frac{M_E + \Delta W_E}{d_E} + \frac{M_H}{d_H}\right)^2} \right), \quad (9)$$
\[
\frac{d[P]}{dt} = k_2 \left( 1 + \frac{\Delta W_E}{M_E} \right)^2 \left( \frac{M_E + \Delta W_E}{d_E} + \frac{M_H}{d_H} \right)^2, \text{ and} \tag{10}
\]

\[
\frac{d[P]}{dt} = k_2 \frac{1}{\left( \frac{M_E + \Delta W_E}{d_E} + \frac{M_H}{d_H} \right)^2}. \tag{11}
\]

respectively, and determination of the rates of reaction of two different formulation ratios of E and H would demonstrate which rate law was followed. The heat of reaction per gram, $\Delta H$, is decreased by a factor expressed as:

\[
\frac{1}{\frac{M_E + \Delta W_E}{d_E} + \frac{M_H}{d_H}}.
\]

The effects of inert diluents on the $T_g$ of polymers cover a wide range from no effect to large changes, which generally decrease the value of $T_g$. Changing the ratio of [E] to [H] from the stoichiometric ratio would decrease the difference between $T_{g_0}$ and $T_{g_{\infty}}$. 
REFERENCES


(4) Gray, A. P.; Thermal Analysis Application, Study 2; Perkin-Elmer Corporation, Norwalk, Connecticut (1972).


(7) Ibid; p 10.

APPENDIX A

DERIVATION OF EQUATIONS FOR DETERMINING KINETIC PARAMETERS FROM ISOTHERMAL DIFFERENTIAL SCANNING CALORIMETRY DATA

Figure 1 shows examples of DSC thermograms for exothermic reactions; here, the curing of a B-staged epoxy resin. If each molecule reacting emits or absorbs the same quantity of energy, then the area under the curve up to time \( t \) is the amount of reaction which has occurred and is given by:

\[
X = \int_0^t f(h) \, dt,
\]

where \( h \) is the instantaneous heat flow rate. The total area under the curve is the heat of reaction, \( \Delta H \):

\[
\Delta H = \int_0^\infty f(h) \, dt.
\]

First-Order Reactions

For first-order reactions:

\[
k_1 t = \ln \left( \frac{\Delta H}{\Delta H - X} \right),
\]

where \( k_1 \) is the first-order rate constant. If it is assumed that \( f(h) \) is of the form:

\[
h = h_0 e^{-k_1 t}, \text{ then (A-1)}
\]

\[
X = \int_0^t h_0 e^{-k_1 t} \, dt = \frac{h_0}{k_1} (1 - e^{-k_1 t}), \text{ and}
\]

\[
\Delta H = \int_0^\infty h_0 e^{-k_1 t} \, dt = \frac{h_0}{k_1}.
\]

Thus:

\[
k_1 t = \ln \left( \frac{\frac{h_0}{k_1}}{\frac{h_0}{k_1} + \frac{h_0}{k_1} (1 - e^{-k_1 t})} \right) = \ln \frac{1}{e^{-k_1 t}} = k_1 t.
\]
Therefore, Equation A-1 is the proper form for first-order reactions. Plots of $\ln h$ vs $t$ give straight lines of slope $-k_1$ and intercept $\ln h_0 = \ln(\Delta H k_1)$. Rogers (3) determined $k_1$ from $\ln h$ vs $t$ plots, but missed the opportunity to calculate $\Delta H$.

**Second-Order Reactions**

For second order reactions, with either initial concentrations of the two reacting species equal or with second-order dependence on one specie:

$$k_2t = \frac{X}{\Delta H (\Delta H - X)}, \quad \text{(A-2)}$$

where $k_2$ is the second-order constant. If $f(h)$ is of the form:

$$h = h_0 (1 + gt)^{-2},$$

where $g$ is a parameter to be determined, then:

$$X = \int_0^t h_0 (1 + gt)^{-2} \, dt = \frac{h_0 t}{1 + gt}, \quad \text{and} \quad \text{(A-3)}$$

$$\Delta H = \int_0^\infty h_0 (1 + gt)^{-2} \, dt = \frac{h_0}{g}. \quad \text{(A-4)}$$

Substituting Equations A-3 and A-4 into Equation A-2 gives:

$$k_2t = \frac{_gt}{1 + gt} \cdot \frac{g (1 + gt)}{h_0} = \frac{g^2 t}{h_0}. \quad \text{(A-5)}$$

Thus:

$$k_2 = \frac{g^2}{h_0}, \quad \text{and}$$

$$h = \frac{g^2}{k_2} \left( \frac{1}{1 + gt} \right)^2, \quad \text{and}$$

$$\Delta H = \frac{g}{k_2}. \quad \text{(A-6)}$$
Equation A-5 can be rewritten:

$$\frac{1}{h^{1/2}} = k_2^{1/2} t + \frac{k_2^{1/2}}{g} \quad (A-7)$$

and a plot of $h^{-1/2}$ vs $t$ will give a straight line of slope $k_2^{1/2}$ and intercept $k_2^{1/2}/g$.

The fraction reacted after time $t$ is:

$$\frac{X}{\Delta H} = \frac{gt}{1 + gt} = \frac{\Delta H k_2 t}{1 + \Delta H k_2 t} \quad (A-8)$$

from which it is easily seen that $g$ is the reciprocal of the half time.

From the Arrhenius equation:

$$k_n(T) = k_n^0 e^{-E^\dagger/RT} \quad (A-9)$$

where $E^\dagger$ is the activation energy and $R$ is the gas constant, the temperature dependence of the $g$ parameter is easily shown to be:

$$g(T) = g_0^0 e^{-E^\dagger/RT} \quad (A-10)$$

The activation energy is normally found from the slope of a plot of $\ln k_n$ vs $T^{-1}$.

**Third-Order Reactions**

Assume a solution of the form:

$$h = h_0 (1 + lt)^{-3/2}$$

where $l$ is a parameter to be determined.

Thus:

$$X = \int_0^t h_0 (1 + lt)^{-3/2} \, dt = \frac{2h_0}{c} \left[ 1 - (1 + lt)^{-1/2} \right], \quad \text{and}$$

$$\Delta H = \int_0^\infty h_0 (1 + lt)^{-3/2} \, dt = \frac{2h_0}{l}.$$
For third-order reactions:

\[
k_3 t = \frac{1}{2} \left[ \frac{1}{(\Delta H - x)^2} - \frac{1}{\Delta H^2} \right] = \frac{i^3_t}{8ho^2}.
\]

Then:

\[
k_3 = \frac{i^3}{8ho^2}, \quad \text{or}
\]

\[
h_o = \left( \frac{i^3}{8k_3} \right)^{1/2}
\]

Thus:

\[
h = \left[ \frac{i^3}{8k_3} \right]^{1/2} (1 + it)^{-3/2}.
\]

Upon raising this expression to the \(-2/3\) power:

\[
h^{-2/3} = \frac{2k_3^{1/3}}{1} (1 + it) = 2k_3^{1/3}t + 2k_3^{1/3}i^{-1}.
\]

Plots of \(h^{-2/3}\) vs \(t\) give straight lines of slope \(2k_3^{1/3}\) and intercept \(2k_3^{1/3}i^{-1}\). The slope-intercept ratio is \(1\). The fraction reacted at time \(t\) is:

\[
\frac{X}{\Delta H} = 1 - (1 + it)^{-1/2},
\]

from which it can be shown that the concentration of the reacting species, \(c\), is:

\[
c = \frac{3}{t_{1/2}},
\]

where \(t_{1/2}\) is the half time of the reaction.

Similar methods can be used to derive equations for other reaction orders. It should be noted that uncertainties in the time of initiation will not affect the determination of the rate and activation energy. Corrections of the other parameters can be made easily by computing intercepts from values of \(\Delta H\) determined by standard techniques.
APPENDIX B

DERIVATION OF EQUATIONS FOR DETERMINING KINETIC PARAMETERS FROM GLASS-TRANSITION-TEMPERATURE DATA

The glass transition temperature, $T_g$, is that temperature (or, more correctly, temperature range) at which, upon heating, an amorphous material changes from a glassy to a liquid state. It can be determined from heat-capacity or thermal-expansion curves.

For many polymers, the empirical formula:

$$T_g = m M^{-1} + b$$

has been found,\(^{(3)}\) where $M$ is the molecular weight, $m$ the slope, and $b$ the intercept. Thus, as $M \to \infty$ and $T_g \to T_{g\infty}$, the $T_g$ at infinite molecular weight, or complete cure, $T_{g\infty}$ must be $b$. Because:

$$M = \frac{d}{c},$$

where $d$ is the density and $c$ the concentration,

$$\frac{d}{c} = \frac{m}{T_g - T_{g\infty}}, \text{ or}$$

$$c = \frac{d}{m} (T_g - T_{g\infty}). \quad (B-1)$$

Initially:

$$\frac{d}{c_0} = \frac{m}{T_{g_0} - T_{g\infty}}, \text{ or}$$

$$c_0 = \frac{d}{m} (T_{g_0} - T_{g\infty}). \quad (B-2)$$

The fraction reacted is thus given by:

$$\frac{(c_0 - c)}{c_0} = \frac{T_{g_0} - T_g}{T_{g_0} - T_{g\infty}}, \quad (B-3)$$

regardless of the kinetic order of the reaction.
For first-order reactions:

\[
\frac{c}{c_0} = e^{-k_1t},
\]

where \(k_1\) is the first-order rate constant, and \(t\) is the time passed since the initiation of the reaction. Substituting Equations B-1 and B-2 (or B-3) into Equation B-4:

\[
\frac{T_g - T_{g\infty}}{T_{g_0} - T_{g\infty}} = e^{-k_1t}.
\]

Plots of \(\ln \left[ \frac{T_g - T_{g\infty}}{T_{g_0} - T_{g\infty}} \right] \) vs \(t\) give straight lines passing through the origin with \(k_1\) as the slope.

For all other reaction orders:

\[
\frac{1}{n-1} \left[ \frac{1}{c^{n-1}} - \frac{1}{c_0^{n-1}} \right] = k_nt,
\]

where \(k_n\) is the \(n\)th order rate constant. Substituting Equations B-1 and B-2 into Equation B-5 gives:

\[
k_n = \frac{m^{n-1}}{d^{n-1}(n-1)} \left[ \frac{1}{(T_{g\infty} - T_g)^{n-1}} - \frac{1}{(T_{g_{0\infty}} - T_{g_0})^{n-1}} \right].
\]

Plots of \((T_{g\infty} - T_g)^{1-n}\) vs \(t\) give straight lines passing through the origin with slopes of \(\frac{k_n d^{n-1}(n-1)}{m^{n-1}}\) and intercepts of \((T_{g\infty} - T_{g_0})^{1-n}\).

The rate constants, \(k_n\), are the same as those in Appendix A. Thus, by determining the density, \(m\) can be determined from a combination of a rate constant obtained from heat evolution data and the term \(k_n d^{n-1}(n-1)/m^{n-1}\) obtained from \(T_g\) data for the same heat-treatment temperature. Thereafter, the molecular weight of a sample can be found from a \(T_g\) measurement.
APPENDIX C

USE OF KINETIC PARAMETERS IN DETERMINING EXTENT OF CURE

Disappearance of a reactant at concentration $c$ is given by:

$$\frac{-dc}{dt} = c^n k^n_0 e^{-\frac{E^+}{R(T + pt)}}, \quad (C-1)$$

where $t$ is the time, $n$ the order of reaction, $k^n_0$ the Arrhenius or frequency factor, $E^+$ the activation energy, $R$ the gas constant, $T$ the initial temperature, and $p$ the rate of temperature change. For isothermal, second order reactions, Equation C-1 may be rearranged and integrated to give:

$$\frac{1}{c} \int_{c_0}^{c} \frac{dt}{c} = k^{2}_0 t e^{-\frac{E^+}{RT}} \int_{0}^{t}, \text{ or}$$

$$\frac{1}{c} - \frac{1}{c_0} = k^{2}_0 t e^{-\frac{E^+}{RT}}.$$  

For second-order, nonisothermal reactions with $p$ constant, but not zero:

$$\frac{1}{c} - \frac{1}{c_0} = \int_{0}^{t} k^{2}_0 e^{-\frac{E^+}{R(T + pt)}} dt. \quad (C-2)$$

Using the series expansion:

$$e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!}.$$  

Equation C-2 may be integrated stepwise to give:

$$\frac{1}{c} - \frac{1}{c_0} = k^{2}_0 \left\{ t - \frac{E^+}{Rp} \ln \left( \frac{T + pt}{T} \right) - \frac{1}{p} \sum_{n=2}^{\infty} \left[ \frac{(E^+)^n}{n!} \frac{1}{(n-1)!} \left( \frac{T + pt}{T} \right)^{1-n} \right] \right\} \quad (d)$$

(C-3)

(c) It was assumed for ease of computation that $k^n_0$ was independent of temperature.
(d) The series in the third term converges slowly and requires carrying a large number of significant digits.
As an example, samples of as-received, B-staged resin were heat treated in the following manner: Heated from 323 to 423 K at $\dot{p} = 1.25$ deg min$^{-1}$, held at 423 K for 30 minutes, and cooled from 423 to 323 K at $\dot{p} = -1.25$ deg min$^{-1}$. It was assumed that the reaction started when the temperature reached $T_g'$ (433 K).

A Simpson's-rule integration of Equation C-2, with $\Delta t = 240$ seconds for the heating and holding parts of the cycle, gives:

$$\frac{1}{c} - \frac{1}{c_0} = \frac{1}{3} \times 240 \left[ K_{333} + K_{423} + 4(K_{338} + K_{348} + \ldots) + 2(K_{343} + K_{353} + \ldots) \right] + k_2^0 \times 1800 e^{-14,800/1.987 \times 423}, \quad (C-4)$$

where the $K_T$s are the values of $k_2^0 e^{-E^+/RT}$ at T.

Equation A-8 can be rewritten as:

$$\frac{X}{\Delta H} = \frac{\Delta H \left( \frac{1}{c} - \frac{1}{c_0} \right)}{1 + \Delta H \left( \frac{1}{c} - \frac{1}{c_0} \right)}. \quad (C-5)$$

The extent of reaction after the 1.25 deg min$^{-1}$ heat and 423 K hold was computed from Equations C-4 and C-5 to be 64.0%. From Figure 8, the $T_g$ at that point was 399 K. It was therefore decided that the reaction would probably cease when 403 K was reached on the cooling portion of the heat-treatment cycle. A third term was added to Equation C-4 to account for the reaction occurring upon cooling to 403 K giving:

$$\frac{1}{c} - \frac{1}{c_0} = \frac{240}{3} \left[ K_{333} + K_{423} + 4(K_{338} + K_{348} + \ldots) + 2(K_{343} + K_{353} + \ldots) \right]$$

$$+ 1800 k_2^0 e^{-14,800/1.987 \times 423}$$

$$+ \frac{240}{3} \left[ K_{423} + K_{403} + 4(K_{418} + K_{408}) + 2 K_{413} \right]. \quad (C-6)$$

The percent of reaction, calculated by substituting the result of Equation C-6 into Equation C-5, was 68.6%. A two-minute anneal at 423 K was needed to eliminate the very sharp exothermic spike found after the heat-treatment cycle, and a $T_g$ of 407.0 K was then obtained in the usual manner. The degree of cure can be determined from $T_g$ in two ways: (1) from Equation B-3, using $T_g' = 333.1$ K and $T_{g_{66}} = 434.4$ K, a $T_g$ of 407.0 K corresponds to a 73.0% cure; (2) from Figure 8, a $T_g$ of 407.0 K corresponds to a 73.6% cure. Both of these ways compare very well with the 68.6% computed from rate-of-heat-evolution data.