

Evaluation of Kinetic Parameters from TVA Data. A Computer Simulation Approach

RODNEY S. ROCHE, *Department of Chemistry, The
University of Calgary, Calgary, Alberta, Canada*

Synopsis

A simple computer simulation of linear temperature-programmed thermal volatilization analysis (TVA) provides useful insights into the effects of the order of reaction n , the Arrhenius preexponential factor A , the overall activation energy ΔE , and the linear rate of heating β on the position and shape of TVA thermograms. Analysis of the numerical results of simulation experiments leads to a method for evaluating ΔE , A , and n from TVA data. The computer-simulation approach can easily incorporate mechanistic complexity. The latter possibility is applied to cases where n and ΔE are changing during the course of reaction, and it is shown that the proposed method gives good recovery of ΔE for such reactions.

INTRODUCTION

The use of the dynamic molecular still in kinetic studies of the thermal degradation of high polymers was pioneered by Grassie and Melville¹ in their classical study of the degradation of poly(methyl methacrylate). The principle of the method is the following. If a sample of a polymer is heated to degradation temperatures in a continuously evacuated vessel in which a liquid nitrogen trap is interposed between the hot reaction zone and the pumps, a readily measurable transient pressure will be created by those degradation products volatile enough to distil molecularly to the liquid nitrogen trap. Up to pressures of the order of 0.1 torr, the transient pressure is linearly proportional to the rate of volatilization. Under isothermal degradation conditions, therefore, the dynamic molecular still is capable of providing the same data as a derivative thermogravimetric curve with the added advantage of experimental simplicity. Under a linearly programmed temperature regime, the dynamic molecular still provides analogous data to that obtained by dynamic derivative thermogravimetric analysis (DDTGA).

The latter use of the dynamic molecular still was developed by McNeill^{2,3} and has been termed thermal volatilization analysis (TVA). In a number of very careful and elegant studies, McNeill⁴⁻⁶ has clearly elucidated the factors determining the optimum design of the apparatus for TVA and the effect of the experimental variables on the TVA thermograms obtained. The analogies between DDTGA and TVA have been recognized for some

time, and this has prompted Cameron and Fortune⁷ to examine the applicability to TVA data of the methods⁸ developed for deriving kinetic parameters from TGA data. In this paper, the same question is examined using a computer-simulation approach which simplifies the discussion of the problem significantly and leads to a method of evaluating Arrhenius parameters from TVA thermograms which obviates the problems associated with the need to calibrate the Pirani gauge and accurately measure rates of volatilization.

COMPUTER SIMULATION OF THE TVA EXPERIMENT

The TVA experiment is very simply simulated if the linear increase in temperature is approximated by a series of equal temperature steps at each of which the reaction is assumed to proceed isothermally. The length of time spent at each temperature is defined by $\beta^{-1}\Delta T$, where β^{-1} is the reciprocal of the linear heating rate and ΔT is the temperature step length. In this way we avoid the problem, which has been the focus of much earlier work,⁸ of finding suitable integral approximations to the TGA equation⁹:

$$\ln(W/W_0) = \frac{A\Delta E}{\beta R} \left[\int_0^\infty \frac{e^{-x}}{x} dx - \frac{e^{-x}}{x} \right] \quad (1)$$

where $x = -\Delta E/RT$ and all other symbols have their usual meaning. In the sense that the approach adopted here provides a numerical integral approximation to eq. (1), it is completely analogous to earlier attempts to develop techniques for the evaluation of kinetic parameters from TGA and TVA data using eq. (1) or one of its differential variants.

However, by focusing on the processes occurring in the TVA experiment itself, our approach lends itself in a straightforward way to the inclusion of any level of mechanistic complexity in the calculation of TVA thermograms. For example, changes in n , the order of reaction, or ΔE , the overall activation energy, as the reaction proceeds, which can conceivably arise in the degradation of complex systems such as high molecular weight polymers, are very readily programmed into the computer simulation procedure.

We follow established practice by assuming that a given volatilization process is accurately described throughout its course by the Arrhenius equation:

$$-d(W/W_0)/dt = A \exp(-\Delta E/RT)(W/W_0)^n \quad (2)$$

A CDC 6400 computer was programmed, using FORTRAN IV, to select n , A , ΔE , and β over a range of values and to calculate, from eq. (2), the rate, in weight per cent volatilized per minute, and W/W_0 , the residual weight fraction at the end of each step, for a series of isothermal reaction steps occurring at temperature intervals ΔT of 0.1°K for equal intervals of time given by $\beta^{-1}\Delta T$ min, where β^{-1} is the reciprocal of the linear heating rate and ΔT is the temperature interval in the simulation. The residual weight fraction at the end of one step was carried over as the initial weight

fraction for the next isothermal reaction step. In this way, the linearly increasing temperature regime of the TVA experiment can be simulated for a variety of conditions.

It has long been recognized in the TGA and DTA fields that data obtained at different heating rates are the best basis for obtaining Arrhenius parameters from such experiments.⁸ We have therefore run a large number of simulations, systematically varying the linear heating rate β for a range of values of n , A , and ΔE , in order to explore in numerical detail suitable approaches to obtaining kinetic parameters from the TVA experiment. We have applied the methods so developed to a variety of data, and the results are reported here.

A Calcomp plotter was used to draw TVA thermograms showing the dependence of shape, amplitude, and position on n , A , ΔE , and β . For the latter purpose, a 1.0°K step in the simulation program was found to be adequate. A 0.10°K step was used routinely in order to achieve more precision in the numerical experiments. In order to minimize computer time, we visually located extrema and other features of interest in the calculated TVA output. This approach proved to be particularly useful in the development of procedures for evaluating kinetic parameters from TVA data. The values of T_M and $(W/W_0)_M$ (the maximum temperature and the residual weight fraction at the maximum of the calculated TVA thermogram) were substituted into eq. (3) [cf. eq. (9) of Kissinger¹⁰]:

$$\frac{\Delta E \beta}{RT_M^2} - An(W/W_0)_M^{n-1} \exp(-\Delta E/RT_M) = 0. \quad (3)$$

This equation contains all the variables of interest and provides a good check on numerical accuracy. The "residuals" found were of the order of 5×10^{-4} in most simulation experiments.

EXPERIMENTAL

The TVA apparatus used in this laboratory is similar to that described by McNeill.³ Samples for TVA were placed in the dynamic molecular still and pumped to 10^{-4} torr. After establishment of a stable background pressure, the temperature-programmed oven (Perkin Elmer F11) was switched on and stabilized at 40°C, in order to provide a good temperature reference point before starting the linear temperature increase. The Pirani gauge (Bendix GP001) was coupled to a CVC Type G1C-111A Ionization Gauge Amplifier, the output of which was fed to a Hewlett Packard recorder Model 7102A. All TVA studies on a given material were performed at linear heating rates of 1, 2, 3, and 5°C/min.

RESULTS AND DISCUSSION

A typical computer-simulated TVA thermogram, illustrating the negligible effect on its characteristics of the size of the temperature increment used in the simulation program, is shown in Figure 1. The effect

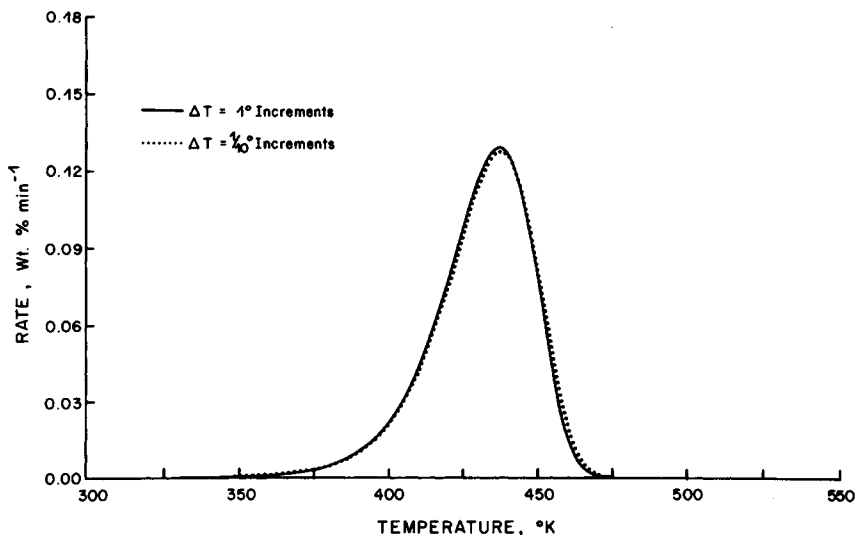


Fig. 1. Computer-simulated TVA thermograms. Effect of increment size in simulation program; $n = 1$, $\Delta E = 25$ kcal/mole, $A = 10^{12}$ min $^{-1}$, $\beta = 5^\circ$ /min.

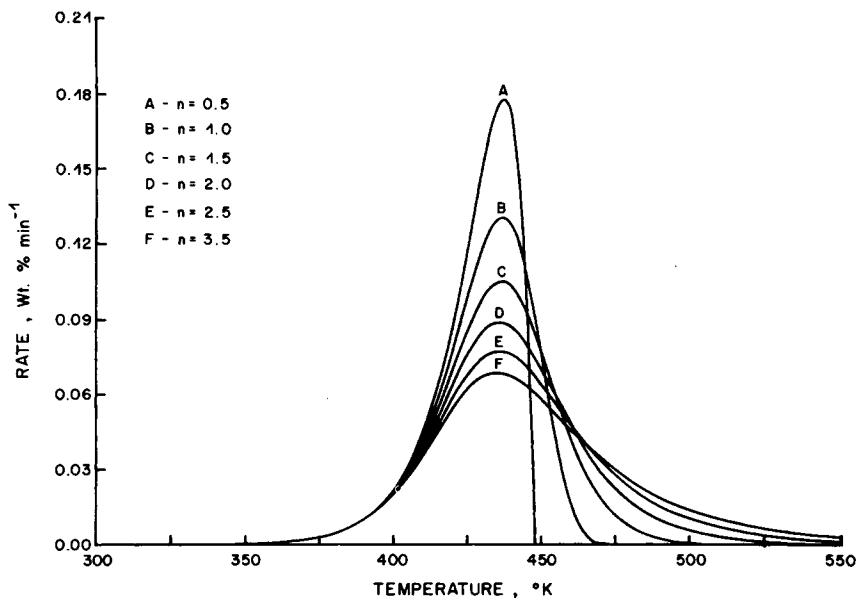
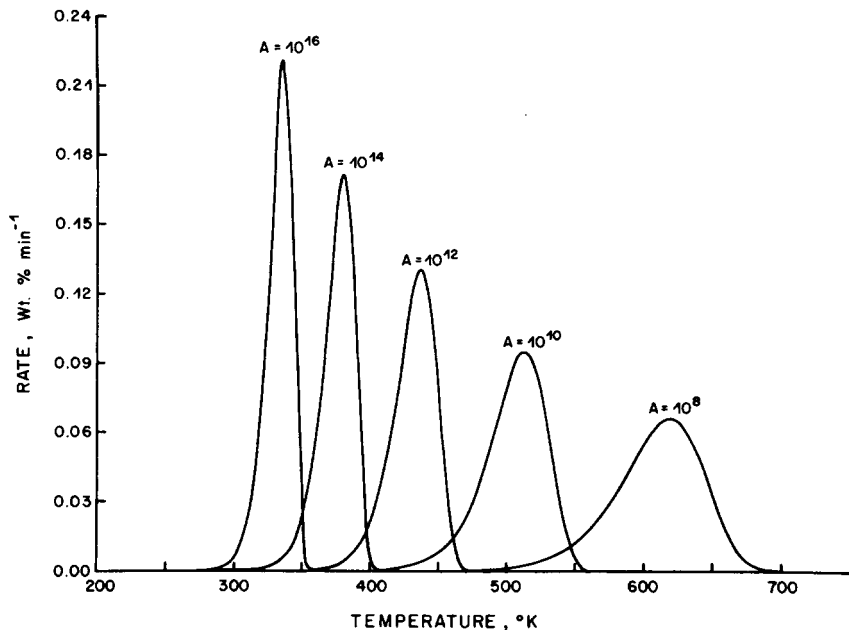


Fig. 2. Computer-simulated TVA thermograms. Effect of order of reaction; $\Delta E = 25$ kcal/mole, $A = 10^{12}$ min $^{-1}$, $\beta = 5^\circ$ /min.

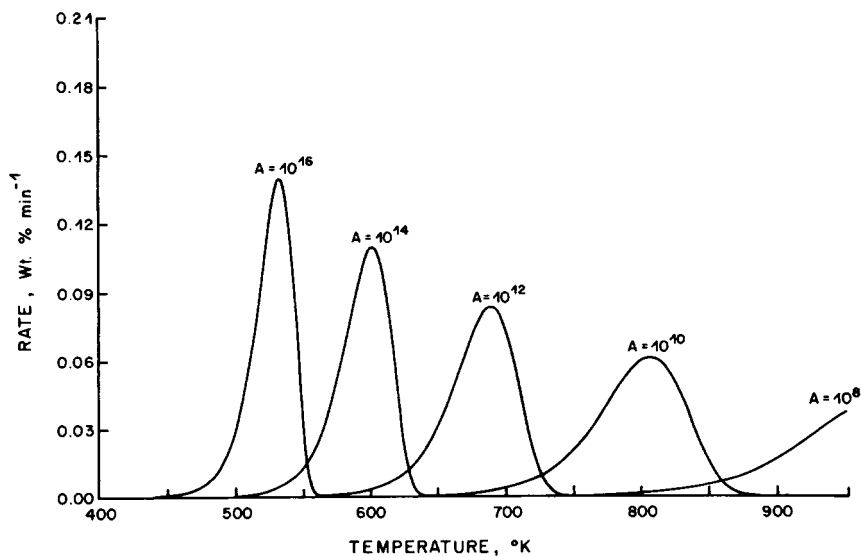
of the order of the reaction n on the shape and amplitude of a typical TVA thermogram is shown in Figure 2. These curves are similar in shape to those reported by Flynn and Wall^{8a} for a different set of Arrhenius parameters and using Doyle's⁹ integral approximation to eq. (1). One noteworthy feature of Figure 2 is that, while the shape and amplitude of the TVA thermogram are sensitive to n , the value of T_M is not. Detailed numerical analysis revealed that the maximum shift in T_M , for a given set of

A , ΔE , and β , was 3.3°K when the order is varied between $n = 0.5$ and $n = 2.0$ (Table I).

It is clear from Figures 3 and 4 that, even with data obtained at a single heating rate, considerable insight into the volatilization process can



(a)



(b)

Fig. 3. Computer-simulated TVA thermograms. Effect of Arrhenius preexponential factor: (a) $n = 1$, $\Delta E = 25$ kcal/mole, $\beta = 5^\circ/\text{min}$; (b) $n = 1$, $\Delta E = 40$ kcal/mole, $\beta = 5^\circ/\text{min}$.

TABLE I
Numerical Simulation of the TVA Experiment in the Temperature Range of 200–1000°K

A, min ⁻¹	ΔE	n	$T_M, \text{ }^\circ\text{K}$										$\left\langle \left(\frac{W}{W_0} \right) \right\rangle$	$\left[\frac{-\Delta \ln \beta / \Delta(T_M^{-1})}{\times 10^3} \right]$	$\left(\frac{-\Delta \ln \beta / \Delta(T_M^{-1})}{\times 10^3} \right)$
			$\beta = 0.1$	$\beta = 0.6$	$\beta = 1.1$	$\beta = 1.6$	$\beta = 2.1$	$\beta = 21.0$							
10 ¹⁰	25	0.5	448.2	476.2	487.0	493.7	498.6	544.9	0.265	13.501	13.501	24.311			
		1.0	447.7	476.0	486.4	493.0	497.9	543.0	0.392	13.519	13.519				
	2.0	446.8	474.9	485.2	491.8	496.7	541.8	0.533	13.543	13.543					
	35	0.5	620.6	659.4	673.6	682.7	689.5	752.0	0.266	18.910	18.910				
		1.0	619.9	658.6	672.8	681.8	688.6	751.2	0.393	18.921	18.921				
	2.0	618.6	657.1	671.2	680.2	686.8	749.1	0.533	18.969	18.969					
	45	0.5	791.3	840.4	858.4	869.9	878.5	957.4	0.267	24.278	24.278				
		1.0	790.4	839.4	857.3	868.8	877.3	956.1	0.393	24.297	24.297				
	2.0	788.9	837.6	855.4	866.8	875.2	954.0	0.533	24.357	24.357					
	55	0.5	960.8						0.266						
1.0		959.8						0.391							
2.0	957.9							0.531							
10 ¹²	25	0.5	388.4	409.7	417.4	422.4	426.1	459.6	0.263	13.365	13.365	24.092			
		1.0	388.1	409.3	417.2	422.0	425.6	459.0	0.387	13.412	13.412				
	2.0	387.4	408.6	416.3	421.2	424.8	458.1	0.529	13.394	13.394					
	35	0.5	538.5	567.8	578.4	585.2	590.2	635.9	0.263	18.712	18.712				
		1.0	538.0	567.2	577.9	584.6	589.6	635.0	0.389	18.712	18.712				
	2.0	537.2	566.3	576.8	583.5	588.5	634.0	0.529	18.770	18.770					
	45	0.5	687.4	724.5	737.9	746.5	752.8	811.0	0.264	24.086	24.086				
		1.0	686.8	723.8	737.2	745.8	752.1	810.2	0.389	24.086	24.086				
	2.0	685.7	722.6	735.9	744.4	750.7	809.0	0.529	24.105	24.105					
	55	0.5	835.3	880.1	896.4	906.7	914.4	984.5	0.264	29.398	29.398				
1.0		834.6	879.4	895.6	905.9	913.5	983.6	0.389	29.419	29.419					
2.0	833.3	877.9	894.0	904.2	912.0	982.2	0.529	29.399	29.399						

TVA DATA

3561

10 ¹⁴	25	0.5	342.4	359.0	364.9	368.7	371.5	397.5	0.260	13.308	13.314
		1.0	342.1	358.6	364.6	368.4	371.2	397.0	0.386	13.286	
		2.0	341.8	358.2	364.1	367.9	370.7	395.2	0.524	13.347	
	35	0.5	475.2	498.0	506.2	511.4	515.3	557.2	0.258	18.591	18.585
		1.0	474.8	497.6	505.8	511.0	514.9	555.4	0.387	18.561	
		2.0	474.2	496.9	505.1	510.3	514.1	554.2	0.525	18.602	
	45	0.5	607.0	636.0	646.4	653.0	657.9	703.1	0.260	23.886	23.920
		1.0	606.6	635.5	645.9	652.5	657.4	702.0	0.387	23.899	
		2.0	605.9	634.7	645.0	651.6	656.4	701.2	0.525	23.977	
	55	0.5	738.2	773.2	785.8	793.8	799.7	854.8	0.259	29.224	29.199
		1.0	737.6	772.6	785.2	793.2	799.1	853.7	0.387	29.178	
		2.0	736.7	771.6	784.1	792.1	798.0	852.5	0.525	29.197	
	65	0.5	868.7	909.8	924.5	933.8	940.8	940.8	0.260	34.510	34.481
		1.0	868.1	909.1	923.8	933.2	940.1	940.1	0.387	34.509	
		2.0	867.0	908.1	922.7	932.0	939.0	939.0	0.525	34.424	
10 ¹⁶	25	0.5	305.9	319.1	323.9	326.9	329.1	350.6	0.255	13.211	13.209
		1.0	305.7	318.9	323.7	326.7	328.9	349.3	0.382	13.194	
		2.0	305.4	318.6	323.3	326.3	328.5	348.2	0.521	13.222	
	35	0.5	424.9	443.2	449.7	453.9	456.9	485.1	0.255	18.470	18.481
		1.0	424.7	442.9	449.4	453.6	456.6	484.0	0.383	18.507	
		2.0	424.2	442.4	448.9	453.0	456.1	483.7	0.522	18.465	
	45	0.5	543.2	566.4	574.7	579.9	583.8	619.5	0.256	23.780	23.764
		1.0	542.9	566.1	574.3	579.6	583.5	618.4	0.383	23.754	
		2.0	542.3	565.4	573.7	578.9	582.8	617.2	0.523	23.759	
	55	0.5	660.8	689.0	699.0	705.4	710.1	752.2	0.256	28.977	29.032
		1.0	660.5	688.6	698.6	704.9	709.6	751.0	0.384	29.061	
		2.0	659.8	687.8	697.8	704.1	708.8	750.1	0.522	29.057	
	65	0.5	778.0	811.0	822.8	830.3	835.7	886.7	0.258	34.306	34.309
		1.0	777.6	810.5	822.3	829.8	835.2	885.4	0.384	34.327	
		2.0	777.0	809.8	821.5	829.0	834.1	884.1	0.521	34.296	

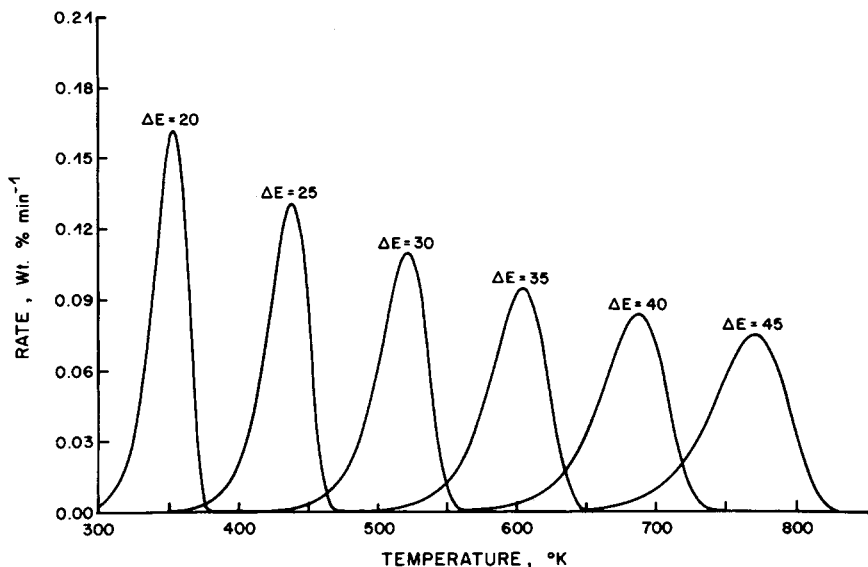


Fig. 4. Computer-simulated TVA thermograms. Effect of activation energy; $n = 1$, $A = 10^{12} \text{ min}^{-1}$; $\beta = 5^\circ/\text{min}$.

be gained from an examination of the position and shape of the TVA thermogram, without the necessity of calibrating the Pirani gauge used to measure transient pressures in the dynamic molecular still. The single heating rate experiment is critically dependent on the accurate measurement of temperature, a measurement which has to be made with some care.³ For the latter reason, we have not explored in detail the possibility of retrieving Arrhenius parameters from TVA thermograms obtained at a single fixed value of β and instead have explored in more detail the use of several β values for such purposes. It is perhaps worth pointing out, however, that the width $\Delta T_{1/2}$ at half-height is directly proportional to ΔE and that $\log \Delta T_{1/2}$ is inversely proportional to $\log A$. Thus, given that $\Delta T_{1/2} = 35^\circ\text{C}$ (for $n = 1$, $A = 10^{12} \text{ min}^{-1}$, $\Delta E = 25 \text{ kcal/mole}$, and $\beta = 5^\circ \text{ min}^{-1}$) and that $\langle \Delta \log \Delta T_{1/2} / \Delta \log A \rangle$, averaged over $\Delta E = 25\text{--}40 \text{ kcal/mole}$ and $A = 10^8\text{--}10^{14} \text{ min}^{-1}$, is approximately -0.06 , it is possible to set up a single-thermogram analysis yielding approximate values for A and ΔE from data obtained at $\beta = 5^\circ \text{ min}^{-1}$.

Evaluation of A and ΔE from TVA Thermograms for "Normal" Reactions

The advantages of doing experiments at a number of different heating rates have been pointed out by several authors.⁸ We have therefore explored the effects of β on TVA thermograms in some detail. The effect of increasing β over a 25-fold range is shown qualitatively in Figure 5. It is clear that the sensitivity of the method is increased by increasing β . In the range of values up to $\beta = 25^\circ\text{C}/\text{min}$, the sensitivity increases approximately with $\beta^{0.9}$. However, the choice of β should be made with care

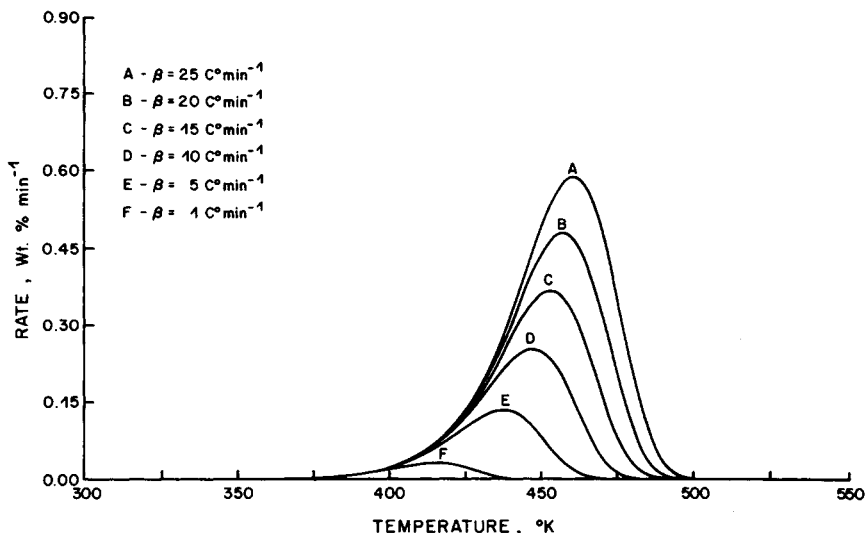


Fig. 5. Computer-simulated TVA thermograms. Effect of heating rate; $n = 1$, $\Delta E = 25$ kcal/mole, $A = 10^{12}$ /min.

in view of the temperature lag of the sample behind the linearly increasing temperature of the oven, which becomes quite large at high β .³ We have observed lags as high as 40°C at $\beta = 25$ min⁻¹. Because the observed lag is much lower at lower β , heating rates in the range of 1°–5°C are routinely used in this laboratory.

The results of the numerical simulation experiments clearly reveal the utility of varying β in a TVA study of a given system. In Table I, we present in summary form some of the results of simulation experiments in which the simulation temperature step was 0.10°K and in which the model system is assumed to behave uniformly, with constant n , A , ΔE , and β , throughout the course of the reaction. We define such a reaction as a "normal" reaction.

In Table I, attention is focused on the behavior of the maximum of the TVA thermogram. A number of useful features of the behavior of the TVA experiment are revealed by these results. The exact linearity of the plot of $\ln \beta$ versus T_M^{-1} °K over a 210-fold range of β values, the slope of which is proportional to ΔE , provides the basis for a method for evaluating the latter parameter from TVA experiments conducted at a number of different heating rates. For all values of A and ΔE examined, the results of Table I reveal that the slope of $\ln \beta$ versus T_M^{-1} °K plots are virtually independent of the order of reaction and lie within 0.2% of the values averaged over $n = 0.5$ to 2.0 for a given set of A and ΔE values within the ranges of $A = 10^{10}$ – 10^{16} min⁻¹ and $\Delta E = 25$ –65 kcal/mole.

Within the precision of the numerical procedures used here, it is reasonable to further conclude, from the results presented in Table I, that the plot of the slope of $\ln \beta$ versus T_M^{-1} , $\Delta \ln \beta / \Delta(T_M^{-1})$ versus ΔE is also

TABLE II
 Values of $[\Delta \log_{10} A / \Delta(T_M^{-1})] \times 10^3$ from Computer-Simulated TVA Data in
 the Temperature Range of 200–1000°K^a

ΔE	n	$[\Delta \log_{10} A / \Delta(T_M^{-1})] \times 10^3$					
		$\beta = 0.1$	$\beta = 0.6$	$\beta = 1.1$	$\beta = 1.6$	$\beta = 2.1$	$\beta = 21$
25	0.5	5.780	5.793	5.802	5.805	5.808	
	1.0	5.807		5.809		5.869	
	2.0	5.817		5.845		5.820	
35	0.5	8.084	8.110	8.117	8.126	8.126	
	1.0	8.127		8.196		8.164	8.168
	2.0	8.139		8.174		8.146	
45	0.5	10.395	10.423	10.433	10.437	10.441	
	1.0	10.445		10.438		10.490	10.487
	2.0	10.457		10.452		10.466	
55	0.5	12.652	12.692	12.696	12.709	12.712	
	1.0	12.708		12.703		12.761	12.728
	2.0	12.721		12.718			
65	0.5	14.921	14.936	14.959			
	1.0	14.960		14.968		14.978	14.933
	2.0						

^a Derived in the range of $A = 10^{10}$ – 10^{16} min^{-1} .

linear. The slope of the latter plot, $\Delta \ln \beta / \Delta(T_M^{-1})\Delta E$, is not very sensitive to A over the range of $A = 10^{10}$ – 10^{16} min^{-1} . All values of $\Delta \ln \beta / \Delta(T_M^{-1})\Delta E$ lie within 2% of the global average of 5.313×10^2 . We can, therefore, propose a method for determining ΔE which is dependent only on *accurately* determining the maximum temperature T_M of TVA thermograms run at several different β values. The value of ΔE can be read off a plot of $\Delta \ln \beta / \Delta T_M^{-1}$ versus ΔE using the appropriate values given in Table I.

The noteworthy feature of this method is that accurate measurement of the rate of volatilization at T_M which, as Cameron and Fortune⁷ have pointed out requires careful calibration of the Pirani gauge, is not required. The method described here is applicable, perhaps with reduced accuracy, even in the nonlinear part of the Pirani response curve because this non-linearity will only have the effect of flattening the maximum of the TVA thermogram. Clearly, because of the need for the highest accuracy in locating T_M , it is preferable to operate in the linear range of the Pirani gauge.

The evaluation of A is also straightforward. For a given value of ΔE , our results indicate that the plot of $\log_{10} A$ versus T_M^{-1} is linear, the slope of which is not very sensitive to β or n . The results presented in Table II can be used to evaluate A once a value for ΔE has been established using the method described above.

Evaluation of ΔE for Complex Reactions

So far in this discussion of the results of our simulation experiments, we have emphasized the behavior of the extremum of the TVA thermogram

TABLE III
Simulation of TVA Experiment with Changing Order of Reaction in the Temperature Range of 200–1000°K^a

ΔE	$T_M, ^\circ\text{K}$					$[\Delta \ln \beta / \Delta (T_M^{-1})] \times 10^3$	$(W/W_0)_M$	ΔE_{out}^b
	$\beta = 0.1$	$\beta = 0.6$	$\beta = 1.1$	$\beta = 1.6$	$\beta = 2.1$			
25	386.2	407.3	415.0	419.8	423.4	13.3825	0.4024	24.986
35	535.5	564.5	575.0	581.6	586.6	18.7154	0.4022	34.971
45	683.6	720.3	733.6	742.0	748.3	24.0709	0.4026	44.961
55	830.7	875.1	891.1	901.4	908.9	29.3949	0.4030	54.981
65	977.2	—	—	—	—	—	—	—

^a $n = 0.5 + 0.5[1 - (W/W_0)]$; $A = 10^{12} \text{ min}^{-1}$.

^b ΔE_{out} is the value recovered by the $\ln \beta$ -versus- T_M^{-1} method.

TABLE IV_a
Results of Simulation of TVA Experiment with Changing Activation Energy^a

β	$T_M, ^\circ\text{K}$	$(W/W_0)_M$
1	590	0.543
2	602	0.548
5	620	0.544
10	634	0.544

^a $\Delta E_{\text{IN}} = 35 + 5[1 - (W/W_0)]$; $n = 1$; $A = 10^{12} \text{ min}^{-1}$; $\Delta T = 1.0^\circ\text{K}$ in simulation program. ΔE_{IN} is the input value for ΔE to the simulation program.

and have proposed a method for evaluating A and ΔE which relies on locating T_M . It is trivial to demonstrate, for what we have defined as "normal" reactions, that A and ΔE values are recoverable from the $\ln \beta$ -versus- T^{-1} plot at *all* values of W/W_0 . The TVA study of complex systems in which n and ΔE are changing throughout the course of the reaction requires equally reliable methods for evaluating n , A , and ΔE . The computer-simulation approach is particularly useful for dealing with complex systems. All that is required is a minor modification of the simulation program which systematically modifies either n or ΔE as a function of $[1 - (W/W_0)]$, the extent of reaction.

We have chosen to vary n or ΔE linearly with the extent of reaction in order to evaluate the $\ln \beta$ -versus- T^{-1} method for recovering the input- ΔE value. The results of such a simulation are presented in Table III for the case where the order of the reaction changes from 0.5 to 1.0 as the reaction proceeds. In this case, $n = 0.5 + 0.5[1 - (W/W_0)]$. It is clear from the results of Table III that the $\ln \beta$ -versus- T_M^{-1} method is applicable in situations where the order of the reaction is changing as the reaction proceeds. It is also clear that the simulation technique can provide a predictive basis for a TVA study designed to confirm a complex volatilization mechanism that may be suggested by the results of other experimental approaches.

We have also tested the $\ln \beta$ -versus- T^{-1} method for the situation in which the activation energy ΔE increases as the reaction proceeds. The results of such a test are presented in Tables IV_a and IV_b. The $\ln \beta$ -versus- T^{-1} method is therefore shown to be reliable for two typical complex situations. It is clear from Table IV_b, however, that if the TVA maximum method is used, only the ΔE at the maximum is obtained. Although this value will be reliable, it can in no way reveal the complexity of the reaction if ΔE is changing during the course of the reaction. It is therefore necessary to apply the general $\ln \beta$ -versus- T^{-1} method at various extents of reaction in order to detect complexity in ΔE . In practice, this requires either complementary TGA data or, at least, the experimental verification that the Pirani response is linear. If the latter condition is met and the composition of the volatile phase does not change appreciably during the course of the reaction, then it is possible to assess quite accurately the value of $[1 - (W/W_0)]$ from the integration of the TVA thermogram using standard techniques and hence ΔE as a function of conversion (Table IV_b).

TABLE IVb
 Recovery of ΔE by $\ln \beta$ -Versus- T^{-1} Method for the Simulation Experiment of
 Table IVa at Various Extents of Reaction

$1 - (W/W_0)$	ΔE_{IN}	ΔE_{OUT}
0.1	35.50	35.37
0.2	36.00	36.20
0.3	36.50	36.47
0.4	37.00	37.16
0.455 ^a	37.276	37.10
0.5	37.50	37.49
0.6	38.00	38.02
0.7	38.50	38.30
0.8	39.00	39.29
0.9	39.50	39.40
1.0	40.00	

^a $1 - \langle (W/W_0)_M \rangle$.

The Evaluation of the Order of Reaction n

Because the position of the TVA thermogram on the temperature axis is not sensitive to the order of the reaction (Fig. 2; Tables I and II), we cannot derive a value for n from T_M measurements. It is obvious from Figure 2, however, that the shape of a given thermogram is fairly sensitive to the order of the reaction. In this connection, the analogy to DTA thermograms is clear, and the shape index defined by Kissinger for DTA data is applicable to TVA as well. However, the residual weight fraction at the maximum, $(W/W_0)_M$, is a more sensitive index of n for "normal" reactions (see Table I). The average values for this quantity, $\langle (W/W_0)_M \rangle$, are fully consistent with the earlier observations of Kissinger,¹⁰ Horowitz and Metzger,¹¹ and, more recently, of Gyulai and Greenhow.¹² Perhaps the best experimental approach to evaluation of n is to use a combination of methods⁸ with TVA as an adjunct providing a sensitive and accurate localization of T_M .

It is clear from the results of Tables III and IV that the $(W/W_0)_M$ method is misleading for complex reactions, and more detailed analysis would be required in order to properly define n in such cases.

Application of the $\ln \beta$ -Versus- T_M^{-1} Method

There is a dearth of published data for reactions conducted at various heating rates. The data of Kissinger on the DTA of magnesite, calcite, and brucite are presented in such a way that the method proposed here can be directly compared with his method. Kissinger reports three sets of T_M data at five values of β . We have found that his data give reasonably good linear $\ln \beta$ -versus- T_M^{-1} °K plots which thus indicate that his temperature measurements are accurate. From the slopes of these plots, we evaluated ΔE for each compound using the data of Table I. We compare the results of our method for ΔE with those reported by Kissinger in Table V. The

TABLE V
Results of $\ln \beta$ -Versus- T_M^{-1} K Method Applied to Kissinger's¹⁰ DTA Data

	ΔE , kcal/mole	
	Kissinger's method	Our method
Magnesite	32.4	34.72
Calcite	43.7	43.92
Brucite	31.4	34.42

TABLE VI
 ΔE Values Obtained from TVA Compared with Literature Values

Sample	ΔE , kcal/mole	
	This work	Literature values
Polyformaldehyde (Delrin)	40.4	20-52 ¹³
Poly(methyl methacrylate)	29.7	29.5-52 ¹³
Polystyrene (MW 863,000)	56.8	55 ¹³
CaC ₂ O · H ₂ O (dehydration)	18.5	20.2 ¹¹

agreement between the two methods is satisfactory and illustrates the applicability of the $\ln \beta$ -versus- T_M^{-1} method to DTA as well.

In Table VI, we summarize the results of a number of TVA studies conducted in this laboratory and compare the values obtained for ΔE by the $\ln \beta$ -versus- T_M^{-1} K method with literature values. The comparisons presented in Table VI do not, of course, provide a very reliable check on our method, but the results obtained with well-characterized samples such as calcium oxalate suggest that it is valid.

CONCLUSIONS

The insights into the potentialities of the TVA method provided by the computer-simulation results presented here prompt us to suggest that the TVA technique could be more widely exploited than it is at present. The analogy between DTG and TVA is complete, the latter method having the marked advantage of being a direct differential method.

The exact linearity of $\ln \beta$ versus T_M^{-1} K, or T^{-1} K at a given extent of reaction, provides a basis for evaluating ΔE in a straightforward way for reactions of any complexity. Similarly, the linearity of $\ln A$ versus T_M^{-1} K for a given ΔE and β provides the basis for evaluating A once ΔE has been established.

The determination of the order of reaction is less straightforward when the reaction is complex, and in such cases recourse to complementary methods such as isothermal TGA is advisable. The latter comments notwithstanding, the widely ignored diagnostic value of $(W/W_0)_M$ ^{10,11,12} provides a simple and direct evaluation of n for "normal" reactions. The simplicity of the computer simulation technique outlined here allows the prediction of the TVA characteristics of reactions involving any level of mechanistic

complexity in a straightforward way. For the latter reason, the TVA technique has a largely unexploited potential for the evaluation of the Arrhenius parameters of polymer degradation reactions.

The author acknowledges the able technical assistance of Mr. Henry Bertram. This work was generously supported by the Defence Research Board of Canada under Grant No. 1028-47.

References

1. N. Grassie and H. W. Melville, *Proc. Roy. Soc.*, **A199**, 1, 14, 24, 39 (1949).
2. I. C. McNeill, *J. Polym. Sci. A-1*, **4**, 2479 (1966).
3. I. C. McNeill, *Eur. Polym. J.*, **3**, 409 (1967).
4. I. C. McNeill and D. Neil, in *Thermal Analysis*, R. F. Schwenker and P. D. Garn, Eds., Academic Press, New York, 1969, p. 353.
5. I. C. McNeill, in *Thermal Analysis*, R. F. Schwenker and P. D. Garn, Eds., Academic Press, New York, 1969, p. 417.
6. I. C. McNeill, *Eur. Polym. J.*, **6**, 373 (1970).
7. G. G. Cameron and J. D. Fortune, *Eur. Polym. J.*, **4**, 333 (1968).
8. (a) J. H. Flynn and L. A. Wall, *J. Res. Nat. Bur. Stand.*, **70A**, 487 (1966); (b) L. Reich and D. W. Levi, *Macromol. Rev.*, **1**, 173 (1967); (c) L. Reich, *Macromol. Rev.*, **3**, 49 (1968); (d) L. Reich and S. S. Stivala, *Elements of Polymer Degradation*, McGraw-Hill, New York, 1971.
9. (a) C. D. Doyle, *J. Appl. Polym. Sci.*, **5**, 285 (1961); (b) *idem.*, *Nature*, **207**, 290, (1965).
10. H. E. Kissinger, *Anal. Chem.*, **29**, 1702 (1957).
11. H. H. Horowitz and G. Metzger, *Anal. Chem.*, **35**, 1464 (1963).
12. G. Gyulai and E. J. Greenhow, *Thermochim. Acta*, **6**, 254 (1973).
13. Grassie, N., in *Polymer Handbook*, J. Brandrup and E. H. Immergut, Eds., Interscience, New York, 1966.

Received April 29, 1974

Revised June 7, 1974