

EXPERIENCES IN DEVELOPING AN AUTOMATED FACTOR-JUMP METHOD OF THERMOGRAVIMETRY

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ABSTRACT

We have recently provided details of an apparatus and computer programs to implement the factor-jump method of thermogravimetry. This paper describes the refinement of the technique to the present status of quasi-automatic routine operation. The procedure was worked out using samples of polymethyl-methacrylate, polystyrene and polyurethane polymers. The activation energies obtained are measured to $0.2 \text{ kcal mole}^{-1}$ in favorable cases. This is adequate for diagnosis of changes in mechanism but may sometimes be inadequate for scaling temperature accelerated tests to room temperature.

INTRODUCTION

Following the proposal¹ of the factor-jump method of thermogravimetry for the determination of activation energies, we designed and assembled the computer-driven apparatus described in refs. 2 and 3. Simultaneously, we prepared the computer program described in refs. 4 and 5. The programs were initially tested on simulated experiments using the procedure described in refs. 4 and 5. In this way, the logic and algorithms were shown to be sound and apparently bug-free in idealized situations of no systematic error and no long-term instrumental drift (the magnitudes in the working apparatus were unknown at the time).

The presence of systematic error and long-term drift in the instrument enforced pilot studies, including work described here. To describe the procedure found appropriate, this publication uses a description of an experiment in which polystyrene was oxidized. The procedure applies to both studies of thermal degradation (in vacuo and in N_2) and oxidation (in N_2/O_2 mixtures) of polymers. Some considerations on the minimum rate of weight loss and on the precision needed in the procedure are given.

The computerized thermogravimetry apparatus and the controlling programs have already been described²⁻⁵ in a general fashion. The technique used here consists of subjecting the sample to a series of temperature plateaus and extrapolating the rates of weight loss, r , and temperatures, T , in adjacent plateaus to give values r_1 , r_2 ,

T_1 , and T_2 at a given extent of reaction C_i . These values are used to calculate the activation energy, E_i , at extent of reaction C_i , from the Arrhenius equation as quoted (eqn. (1)) in ref. 5

$$E_i = R \ln(r_{1i}/r_{2i}) / (1/T_{2i} - 1/T_{1i})$$

$$= R [\ln(r_{1i}/r_{2i})] (T_{1i} T_{2i}) / (T_{1i} - T_{2i}) \quad (1)$$

SAMPLE CONSIDERATIONS

In early runs, a coal-scuttle shaped platinum bucket with a flat bottom (10×4 mm) was looped directly over the end of the quartz balance arm. The thermocouple was positioned upstream about 0.5 mm from the bucket and ~ 1 mm above the level of the bucket bottom. The sample position was centered in the furnace along the furnace axis by making the reaction manifold the appropriate size. It was centered radially in the furnace by using a kinked quartz arm in the balance. More recently, we have used a quartz spoon on the end of a quartz rod, with the thermocouple centered under the spoon.

Typically, 15–30 mg of sample are spread evenly over the floor of the bucket or in the spoon. (When lumps of sample retain their shape during the early stages and give undue importance to diffusion processes, powdered samples must be used. This was the case for PMMA). Samples are usually preconditioned under program control for 10–45 min at about 15°C below the temperature of the first plateau, with the actual time being chosen so that (a) the balance mechanism settles down after any recent disturbance such as putting the sample in, (b) any anomalous material such as solvent or monomer is volatilized, and (c) the sample attains a modest rate of weight loss via the degradative process of interest.

DATA COLLECTION

The requirements of data collection are:

(i) plateaus should be fairly short so that the weight–time curve can be fitted well with a second degree polynomial;

(ii) the behavior of the sample should become steady under a new set of conditions before data collection is started, and

(iii) the program should use the sample “equilibration” time to fit polynomials to the weight and factor (temperature, pressure, gas flows) trends with time. Thus, a compromise must be struck between, on the one hand, many closely spaced data and long computational “time-outs” and, on the other hand, few widely spaced data with imprecise but rapid polynomial fits.

Those sources of imprecision in the measured activation energy where the operator has some control or choice are: (a) the time between plateaus, (b) the imprecisions in the various voltages characterizing the levels of the factors, and (c) the contributions of r , σ_r , T , σ_T , r_1/r_2 and ΔT to $\sigma(E_i)$ through eqn. (3) of ref. 5, i.e.

$$\sigma_{E_i}^2 = E_i^2 \left[\frac{\sigma_{r_{1i}}^2}{r_{1i}^2} + \frac{\sigma_{r_{2i}}^2}{r_{2i}^2} \right] \left[\frac{1}{\ln r_{1i}/r_{2i}} \right]^2 + E_i^2 \left[\frac{\sigma_{T_{1i}}^2}{T_{1i}^4} + \frac{\sigma_{T_{2i}}^2}{T_{2i}^4} \right] \left[\frac{T_{1i}T_{2i}}{T_{1i} - T_{2i}} \right]^2 \quad (2)$$

The time between plateaus depends on the apparatus and sample, which should "equilibrate" to new conditions as quickly as possible so that long extrapolations to a common value of C are not needed. It is also a function of the computer program, in that the size of the overlays and speed of execution of the program steps govern the time the computer is involved in its own operations rather than serving the needs of the thermogravimetry apparatus. Finally, the time between plateaus is a function of the hardware, where the choice of mass storage medium governs the speed of reading information or programs into the computer and the choice of multiplication and division by hard-wired devices or software programming governs the computational speed. For a given apparatus, the main influence the operator exerts on the inter-plateau time is to choose an appropriate number of data points to measure and fit; 15-25 points seem to be appropriate.

The imprecisions in the signal voltages can be reduced by averaging several readings together. In the "filtered input" mode on the digital voltmeter, each reading takes $\sim 1/2$ sec. Three readings per average seems ideal to provide an estimate of the standard deviation.

The quantities involved in the variance, $\sigma_{E_i}^2$, of the activation energy, E_i , are various logs and powers, e.g., $\ln(r_i/r_{i+1})$, T^4 , $[T_{1i}T_{2i}/T_{1i} - T_{2i}]^2$ and so on (see eqn. (2)). The values of r depend on T in the form expressed in the Arrhenius equation. They depend in a generally unknown multiplicative fashion on the sample weight since a larger sample loses weight faster. Useful values of T_i and T_{i+1} depend on obtaining a sensible ratio for r_i/r_{i+1} , on ensuring the rates observed are between the user-chosen minimum and maximum values, on the minimum number of E_i values desired before all the sample is consumed, and on the contribution of $\Delta T = T_i - T_{i+1}$ to σ_{E_i} . The main term is ΔT . ΔT values $\geq 10^\circ\text{C}$ generally give reasonably small ($0.3\text{--}0.5$ kcal mole $^{-1}$) contributions to σ_{E_i} , depending on the tuning of the temperature controller. Table 1 shows the effect of E , ΔT and T on the ratio of rates as calculated from eqn. (1). For large activation energies (> 50 kcal mole $^{-1}$), $\Delta T = 8$ seems appropriate. The values of σ_{r_i} and σ_{T_i} depend partly on the number of readings averaged together to give r_i and T_i and partly on the apparatus, especially on the

TABLE 1

RATIOS IN RATES FOR VARIOUS VALUES OF E , ΔT AND T IN EQN. (1)

$\Delta T/T(^\circ\text{C})$	$E(\text{kcal mole}^{-1})$					
	15	20	30	40	50	60
10/250	1.32	1.44	1.73	2.08	2.49	2.99
15/250	1.51	1.73	2.28	2.99	3.94	5.18
10/350	1.21	1.29	1.47	1.67	1.90	2.17
15/350	1.34	1.47	1.79	2.17	2.63	3.19

TABLE 2

SPECIFICATION OF EXPERIMENTAL CONDITIONS AND PROCEDURES

PS in air 7/13/77 24mg sample

Type E thermocouple = NI-CR/CU-NI, expressions good from -0.05 to $+0.04$, 0 to 400 degrees C.
(Table A5.2.3, P.307 NBS Monograph 125, 1974)

Parameters initialised as follows:

NTHCP = E TSCALE = 243.73 SKIP = 30.
 FACTORS = 1 2 0 0 0 0 0 0
 FACFUN = 0 0 0 0 0 0 0 0
 DERIVS = 1 0 0 0 0 0 0 0
 INPUTS = 0 1 2 3 4 5 6 7
 SCALES = 1.000 1.000 0.010 1.000 1.000 1.000 1.000 1.000
 NRRANGE = 3 3 5 5 5 5 5 5
 NREADS = 3 3 3 3 3 3 3 3
 NTERMS = 2 1 0 0 0 0 0 0
 CHI TEST = 3000. 1500. 1000. 1000. 1000. 1000. 1000. 1000.
 PTIMES = 300.0 300.0 300.0 300.0 300.0 300.0 300.0 300.0
 PRECF = 100.00 100.00 100.00 100.00 100.00 100.00 100.00 100.00
 PRECR = 30.00 30.00 30.00 30.00 30.00 30.00 30.00 30.00
 NFACTS = 2 NRATES = 1 TIMLIM = 500. BAD PTS = 8 EQUIL = 200.
 CHECKS = 75 END SIG = 3.0 RATMIN = 10.0 RATMAX = 35.0 TJUMP = 30.0
 TC TO D = 0.17023E-01* -0.22097E-06 0.54809E-11 -0.57670E-16
 10 UNITS = 5 5 3 7 8 1 6
 POLNOM EXP = 1 2 3 4 5
 PRECISION IN E ACT = 25.00

FACTOR LEVELS AND CHANGES FOLLOW:

1 251.000 1.000
 2 800.000 0.000
 3 385.000 0.000
 4 105.000 0.000

DESIGN MATRIX FOLLOWS

1 -11.000 0.000 0.000 0.000
 2 15.000 0.000 0.000 0.000

Steadiness check = 1 where 0 = no, 1 = yes

Input filter to DVM = 1 where 0 = no, 1 = yes

Read other expts = 0 where 0 = no, 1 = yes

Bias voltages and sigmas for factor inputs

Factor	Voltage	Sigma
1	0.0000000E+00	0.9999999E-09
2	0.0000000E+00	0.9999999E-09

Initial and final weights are: 362000. -160000.

Bake time in seconds is 2000.

Bake temperature in degrees Celsius is 220.

Bake pressure in mm HG is 800.

Flow of N2 in scc/min is 385.

Flow of O2 in scc/min is 105.

Facset

220.0 1

14 #D 3632:

* Read as 0.17023×10^{-1}

tuning of the temperature controller. $\sigma_{r,i}$ depends on r in that, even though the sample weight is changing at rate r , it is assumed to be constant for some small window of time during which several sample weight measurements are taken and averaged. $\sigma_{r,i}$ also depends on the variability in T , the effect of which is transmitted to the rate of weight loss in the form given by the Arrhenius equation. The duration of each temperature plateau depends on how many data are needed to supply the precision required in the extrapolations of r and on the number of E_i values desired. Longer plateaus mean fewer E_i determinations for a given sample size.

The operating parameters usually used are given in the first half of Table 2. To some extent, many of their values were forced on us. Trial runs and examination of problems in "real" runs suggested that the sample/apparatus combination needs ~ 200 sec to equilibrate. This is given as the variable EQUIL in Table 2. This time includes equilibration of factors such as temperature control and balance-arm expansion as well as response of the sample to the new conditions. The current speed of the combination of interface, computer, disc and printer makes the length of the temperature and sample weight reading cycle ~ 33 sec when the record of the experiment is printed and ~ 27 sec when it is written on a flexible diskette. This means the variable SKIP must be at least ~ 30 sec. A plateau length of TIMLIM = 500 sec gives 14–17 pairs of temperature/weight readings per plateau, depending on whether the progress of the experiment is logged on the printer or on a disc. This number of points allows all curve-fitting and extrapolations to be done and an activation energy to be calculated in little less than 200 sec, i.e., during the sample re-equilibration time.

The thermocouple in the apparatus is type-E, which gives a large ($\sim 80 \mu\text{V}/^\circ\text{C}$) change of e.m.f. with temperature in the range of interest and has a reasonably linear response. Type-K is not particularly suitable for our application; it has roughly half the temperature coefficient of type-E and suffers from non-linearity because of an order-disorder transition (see ref. 6 and refs. therein). The variable TSCALE scales the thermocouple e.m.f. calculated in the program to a voltage to be output from one of the digital-to-analog converters in the apparatus. TSCALE is an instrumental constant and depends on the amount the output voltage (maximum = 10 V d.c. in our application) is divided down to produce a thermocouple e.m.f.-like voltage (maximum ~ 40 mV here).

The line labeled FACTORS in Table 2 is essentially a heading for the next 11 lines of the table. Thus, the details for factor 1 are coded under the "1" in the FACTOR line and those for factor 2 are under the "2" in the FACTOR line. FACFUN describes whether the voltage reading for a factor is to be transformed to another function or not. The latter is the case here. The transformation possibilities are the logarithm to the base e , the square, and the reciprocal. DERIVS shows by non-zero values which factors are also to be computed as derivatives with respect to time.

INPUTS provides the links between the factors and the voltages which are available at the analog scanner in the interface between the thermogravimetry apparatus and the computer. SCALE carries the scale factors to be applied to the input voltages to transform them to physical units. Column 3 is usually for the pressure;

the voltage representing it will be multiplied by 0.01 to transform the readings to millimeters of mercury. NRANGE denoted the range on the digital voltmeter that should be used in reading each of the various voltages. This range is changed by the program as needed so that precision in the readings will be maximized. NREADS is the number of readings to be averaged together to provide estimates of the mean and standard deviation of a datum. An unusually large estimate of the standard deviation provides some indication of catastrophe. The estimates of the standard deviation of the sample weight are used to test for "end-of-sample", which is defined as occurring when adjacent weight readings do not differ by more than END SIG (= 3 here) pooled estimated standard deviations.

NTERMS is the number of terms to use in the polynomial describing the trend with time. Generally this number should be as small as possible. We use a second-degree polynomial for the weight-time curve and a first-degree polynomial for the temperature-time curve. Pressure and flow rates are not usually monitored by the program but could be and would then be represented by zero-degree polynomials. CHI TEST gives the cutoff value for the χ^2 statistic as calculated from the least-squares fit of the chosen degree of polynomial to the 5 latest averaged readings. Although estimates of the standard deviations are available, they are not worth using in a weighted least-squares fit. Each datum therefore has unit weight in the polynomial fits and in the calculations of χ^2 . Values of χ^2 greater than the cutoff cause data collection to begin again; data accumulated for that particular set of conditions (plateau) are thrown away. If more than BAD PTS (= 8 here) have been thrown away during this plateau, the CHI TEST values are updated. More than 2 updates per plateau cause an error reset, when all data for that plateau are discarded and the next programmed set of conditions is imposed.

PTIME is used mainly in apparatus check out, and is the equilibration time allowed for each factor. This has been more or less replaced by EQUIL at the moment but the PTIME option has been retained until more experience shows whether or not it is useful. PRECF and PRECR are the target precisions, $f/\sigma(f)$, in the factors and rates, respectively. They are used in deciding whether more data are needed under a particular set of conditions.

In our example, the data collection will persist for 500 sec (TIMLIM) with data being measured every 30 sec (SKIP). This provides 17 points per plateau. A check of the currently attained precision is made every CHECK data points; here CHECK is set equal to 75, which, since it can never be attained before the allowed time runs out, is a device to remove it from consideration during this experiment. If CHECK were in the range 3-5 then frequent checks of the attained precision would be made. In practice, both flexible diskettes and the computer are too slow for this to be a realistic approach at the moment and frequent time-outs for reading in new overlays and fitting polynomials, etc., would result in unacceptable loss of data. We believe that impressive improvements will be made when rigid disks and hard-wired integer multiply-divide are added. Floating point hard-wired arithmetic is desirable but is perhaps too expensive.

RATMIN and RATMAX in Table 2 are the minimum and maximum allowable rates of weight loss, as determined directly from the electrobalance readings in $\mu\text{V sec}^{-1}$. Rates outside these limits cause the temperature to be reset by TJUMP degrees Celsius. The choice of minimum rate of weight loss involves yet another compromise. The rate of long-term drift in the electrobalance was found to be $< 0.1 \mu\text{V sec}^{-1}$ under steady conditions at room temperature. The balance drift was difficult to estimate under conditions of changing weight loss, but observations during the degradation of the last few percent of sample and in runs conducted with an empty sample bucket suggested that the apparent drift of the instrument under dynamic conditions may, after extrapolation, sometimes be as high as $0.6 \mu\text{V sec}^{-1}$ ($= \delta_r$) but was often $< 0.1 \mu\text{V sec}^{-1}$. The effect of slight changes in temperature during the temperature plateaus swamped out the other effects and essentially provided an error in the calculated rate of weight loss. Thus the quantity calculated from the polynomial fit to the observed sample weight is $(r' + \delta_r)$, where r' is the "real" rate of weight loss and δ_r is an error arising from both the balance and the rest of the experiment. Given that the activation energy may be calculated from the Arrhenius equation recast in the form

$$E = \frac{RT_1T_2}{T_1 - T_2} \ln \left(\frac{r_1}{r_2} \right)$$

$$= \frac{RT_1T_2}{T_1 - T_2} \ln \left(\frac{r'_1 + \delta_r}{r'_2 + \delta_r} \right) \quad (3)$$

the minimum value of r to give $> 97\%$ precision in E may be estimated by trial to be $\sim 12.5 \mu\text{V sec}^{-1}$, assuming, for example, $\delta_r = 0.6 \mu\text{V sec}^{-1}$, $T_1 = T_2 = 250^\circ\text{C}$, $\Delta T = 15^\circ\text{C}$, $r_2 = 3r_1$ and the error δ_r is always applied additively. This concept will be examined in more detail later. The above value (12.5) for the minimum value of r generally gave reasonable results, whereas values < 10 sometimes gave results which appeared from the context of neighboring activation energies to be spurious.

The line TC to D contains the coefficients, a_i , required in the polynomial to convert a thermocouple e.m.f., t , to temperature, T , in $^\circ\text{C}$ according to the equation

$$T = \sum_i a_i t^i.$$

The Input/Output UNITS for conversation with the operator, the printer, the disc files etc., are given on the next line. The following line, POLNOM EXP, contains the coefficients for the polynomials used in fitting factor trends with time. The last line, PRECISION IN E ACT, contains the target precision, $E/\sigma(E)$, in the activation energy E .

After the operating parameters have been chosen (the procedure of changing the parameters is not shown in Table 2), the sample treatment outlined in the second half of Table 2 is programmed. The starting values are entered on the computer console and are output under FACTOR LEVELS AND CHANGES FOLLOW. The changes to be made to the starting values are given under DESIGN MATRIX

FOLLOWS. The function of the design matrix in controlling the course of the experiment is given in detail in ref. 5.

The bottom part of Table 2 records the choices made for steadiness tests (via χ^2 values) [yes], whether or not filtered voltages are to be input to the digital voltmeter [yes], and whether or not there is to be simultaneous logging of data from other experiments [no]. The experimenter has chosen to specify zero for the bias voltages on the input lines and essentially zero for the associated standard deviations. (These voltages could have been measured by the program but have previously been determined to be very small). The initial and final sample weights are entered in microvolts ($20 \mu\text{V} = 1 \mu\text{g}$) and the bake-out parameters are selected. Control then passes to the program, which will subject the sample to the prescribed bake-out conditions before collecting data.

EXAMPLE OF DATA

Table 3 contains weight and temperature data obtained during a temperature plateau in the oxidation of a sample of polystyrene. The first column in Table 3 is the ordinal number of the point; each point consists of a measurement of those factors previously flagged as pertinent and each factor (enumerated under the F column) occupies a separate line. Thus, the column F denotes the factor number and the column I denotes the input number on the analog scanner (see ref. 3) for that factor. The average of several readings is given in microvolts under the heading READING and the estimate of the associated standard deviation appears under the heading SIGMA. RD gives the numbers of individual readings used in obtaining the average and the estimate of the standard deviation. The individual readings are taken as quickly as possible (typically every 1/2 sec) but the estimate obtained for the standard deviation is only a lower bound to the actual value because there is generally some slow oscillation taking place in the temperature control system. This temperature oscillation affects both the temperature and the weight and has a period of ~ 100 sec.

The remaining columns in Table 3 are the elapsed time in seconds since the end of sample conditioning (i.e., the beginning of the experiment proper), the number of points discarded in the current plateau because of instability, the value of χ^2 for the five most recent measurements including the one under consideration, and the upper limit allowed for these χ^2 values. The plateau begins with point number -3 so that the program can use 5 sets of readings to provide point 1 with a χ^2 value. Points -3 to 0 are used only to calculate χ^2 values, are collected as quickly as possible, and are later discarded.

In the example shown, the sample weight is factor 1, on input 0, and the sample temperature (type-E thermocouple reading) is factor 2 on input 1. The sample weight is read to about $20 \mu\text{V}$ (actually it was changing at $\sim 25 \mu\text{V sec}^{-1}$) and the temperature is read to 1 or $2 \mu\text{V}$. The cutoff values of χ^2 , 3000 and 1500, are taken over 5 readings and, since the fit is not weighted by $1/\sigma_i^2$, represents $\Sigma(y_{i0} - y_{ic})^2$. This allows an average misfit between observed and calculated values of $\sqrt{\chi^2/5}$ or $\sqrt{3000/5}$

TABLE 3

WEIGHT AND TEMPERATURE DATA OBTAINED DURING A TEMPERATURE PLATEAU (READINGS ARE IN μV)

Measurement for plateau number 2

No.	F	I	READING	SIGMA	RD	TIME	BAD	RCHI	TESTCH
-3	1	0	0.1959233E+06*	0.1452967E+02	3	982.	0	0.0	3000.0
-3	2	1	0.1634967E+05	0.3333346E+00	3	982.	0	0.0	1500.0
-2	1	0	0.1956367E+06	0.1763834E+02	3	993.	0	0.0	3000.0
-2	2	1	0.1637067E+05	0.3480103E+01	3	993.	0	0.0	1500.0
-1	1	0	0.1953600E+06	0.2081664E+02	3	1005.	0	0.0	3000.0
-1	2	1	0.1642267E+05	0.8819175E+00	3	1005.	0	0.0	1500.0
0	1	0	0.1950333E+06	0.2027586E+02	3	1017.	0	0.0	3000.0
0	2	1	0.1640767E+05	0.1452965E+01	3	1017.	0	0.0	1500.0
1	1	0	0.1947033E+06	0.2027586E+02	3	1028.	0	287.2	3000.0
1	2	1	0.1636233E+05	0.2027586E+01	3	1028.	0	1156.6	1500.0
2	1	0	0.1938267E+06	0.2333333E+02	3	1064.	0	1036.7	3000.0
2	2	1	0.1640800E+05	0.5773508E+00	3	1064.	0	886.7	1500.0
3	1	0	0.1928467E+06	0.2333333E+02	3	1100.	0	1300.6	3000.0
3	2	1	0.1637767E+05	0.6666676E+00	3	1100.	0	677.9	1500.0
4	1	0	0.1919233E+06	0.2027586E+02	3	1136.	0	1053.1	3000.0
4	2	1	0.1638600E+05	0.1732049E+01	3	1136.	0	509.4	1500.0
5	1	0	0.1909633E+06	0.2027586E+02	3	1174.	0	990.2	3000.0
5	2	1	0.1636333E+05	0.3333346E+00	3	1174.	0	457.1	1500.0
6	1	0	0.1900633E+06	0.2027586E+02	3	1210.	0	126.1	3000.0
6	2	1	0.1638667E+05	0.3333346E+00	3	1210.	0	242.7	1500.0
7	1	0	0.1891367E+06	0.1763834E+02	3	1245.	0	247.0	3000.0
7	2	1	0.1637767E+05	0.8819175E+00	3	1245.	0	118.0	1500.0
8	1	0	0.1882467E+06	0.2333333E+02	3	1280.	0	197.3	3000.0
8	2	1	0.1641733E+05	0.2333346E+01	3	1280.	0	330.6	1500.0
9	1	0	0.1873467E+06	0.1763834E+02	3	1316.	0	316.4	3000.0
9	2	1	0.1636800E+05	0.5773508E+00	3	1316.	0	559.1	1500.0
10	1	0	0.1864733E+06	0.2027586E+02	3	1350.	0	185.6	3000.0
10	2	1	0.1636233E+05	0.8819175E+00	3	1350.	0	509.2	1500.0
11	1	0	0.1855867E+06	0.1763834E+02	3	1386.	0	94.3	3000.0
11	2	1	0.1642200E+05	0.2645751E+01	3	1386.	0	1019.0	1500.0
12	1	0	0.1846267E+06	0.1763834E+02	3	1422.	0	330.3	3000.0
12	2	1	0.1635333E+05	0.3333346E+00	3	1422.	0	1222.3	1500.0
13	1	0	0.1837367E+06	0.1763834E+02	3	1458.	0	514.6	3000.0
13	2	1	0.1636300E+05	0.2309403E+01	3	1458.	0	995.3	1500.0
14	1	0	0.1828267E+06	0.1763834E+02	3	1495.	0	614.7	3000.0
14	2	1	0.1639600E+05	0.5773508E+00	3	1495.	0	1107.5	1500.0

* Read as 0.1959233×10^6 .

$\sim 25 \mu\text{V}$ and $\sqrt{1500/5} \sim 17 \mu\text{V}$, respectively, in sample weight and temperature. These are generous limits and will only be exceeded in cases where some catastrophe in the data collection has made the polynomial fit unacceptably poor.

POLYNOMIAL FITS TO THE DATA

Table 4 shows the results of fitting a second-degree polynomial to the weight data in Table 3. First, the total weight loss (in μV where $20 \mu\text{V}$ corresponds to $1 \mu\text{g}$)

TABLE 4

FIT OF SECOND-DEGREE POLYNOMIAL TO WEIGHT DATA IN TABLE 3

Checks of precision for plateau 2

Weight loss for this plateau = $0.119\text{E}+05$ microvolts with average rate of $0.254\text{E}+02$ microvolts per second

TIME	P	YFIT	SIGMA P	P-YFIT	(P-YFIT)/ SIGP	DEL P
-233.5	0.194703E+06	0.194719E+06	0.203E+02	-0.161E+02	-0.795E+00	0.000E+00
-197.5	0.193827E+06	0.193790E+06	0.233E+02	0.366E+02	0.157E+01	-0.877E+03
-161.5	0.192847E+06	0.192863E+06	0.233E+02	-0.161E+02	-0.688E+00	-0.980E+03
-125.5	0.191923E+06	0.191937E+06	0.203E+02	-0.141E+02	-0.694E+00	-0.923E+03
-87.5	0.190963E+06	0.190963E+06	0.203E+02	0.750E+00	0.370E+01	-0.960E+03
-51.5	0.190063E+06	0.190041E+06	0.203E+02	0.223E+02	0.110E+01	-0.900E+03
-16.5	0.189137E+06	0.189147E+06	0.176E+02	-0.102E+02	-0.581E+00	-0.927E+03
18.5	0.188247E+06	0.188255E+06	0.233E+02	-0.806E+01	-0.346E+00	-0.890E+03
54.5	0.187347E+06	0.187339E+06	0.176E+02	0.775E+01	0.439E+00	-0.908E+03
88.5	0.186473E+06	0.185476E+06	0.203E+02	-0.244E+01	-0.120E+00	-0.873E+03
124.5	0.185587E+06	0.185564E+06	0.176E+02	0.231E+02	0.131E+01	-0.887E+03
160.5	0.184627E+06	0.184653E+06	0.176E+02	-0.267E+02	-0.151E+01	-0.930E+03
196.5	0.183737E+06	0.183745E+06	0.176E+02	-0.837E+01	-0.475E+00	-0.890E+03
233.5	0.182827E+06	0.182814E+06	0.176E+02	0.131E+02	0.744E+00	-0.910E+03

Polynomial coefficients for FACTOR 1

COEFF	SIGMA
0.18872612E+06	0.79009933E+01
-0.25494400E+02	0.36509778E-01
0.74033369E-03	0.28282567E-03

Reduced CHI SQUARE = 388.52

FTEST = 0.21E+06

RMUL = 0.10E+01

R(1) = -0.10E+01

R(2) = 0.10E-01

and the average rate of weight loss encompassed by the data are given. This latter quantity is provided as an initial indication of whether or not the instrumental effects ($\leq 0.6 \mu\text{V sec}^{-1}$) have been overwhelmed. The mid-time of the individual readings is subtracted from the times of the individual readings to distribute estimated errors in extrapolated quantities equally at both ends of the plateau. Note that the times do not have to be evenly spaced.

The quantities P and $YFIT$ in Table 4 are, respectively, the observed weight values and the quantities calculated from the fitted polynomial. The degree of the polynomial was specified in the initialization parameters. $SIGMA P$ is the estimated standard deviation in P and, as was mentioned earlier, is usually too small to be realistic because the oscillation in the temperature is much longer than the 1 sec or so required to take 3 readings of the thermocouple voltage. $P-YFIT$ provides a check of

the appropriateness of the polynomial fit, partly from the magnitudes of the quantities and partly from their signs. Large groups of like signs are a sure indication of systematic misfit.

The quantile $(P-YFIT)/SIGP$ provides a rough indication of the true size of $SIGP$ since for normally distributed errors the absolute values of these quantiles are expected on the average to be less than 0.69 for 75% of the cases and less than 2.1 for 95% of the cases (these values were taken from a t -distribution with 15 degrees of freedom). The larger the period and size of the oscillation in the measured value of the quantity being fitted, the larger these quantiles will be in absolute magnitude, because the estimated standard deviation will then not accurately reflect the actual excursions.

The final quantity in Table 4, $DEL P$, is the arithmetic difference between adjacent values of P . $DEL P$ provides an indication of the smoothness of the data and of the equilibration of the sample. It is a crude estimate of the first derivative with respect to time and in the case of the sample weight can be compared with the extrapolated values of the rate of weight loss provided by the program.

At the bottom of Table 4, we find the coefficients of the polynomial $P = a + bt + ct^2$, with estimates of their standard deviations. The variable t here is the time

TABLE 5

FIT OF FIRST-DEGREE POLYNOMIAL TO TEMPERATURE DATA IN TABLE 3

TIME	P	YFIT	SIGMA P	P-YFIT	(P-YFIT)/ SIGP	DEL P
-233.5	0.163623E+05	0.163823E+05	0.203E+01	-0.200E+02	-0.987E+01	0.000E+00
-197.5	0.164080E+05	0.163822E+05	0.577E+00	0.258E+02	0.446E+02	0.457E+02
-161.5	0.163777E+05	0.163821E+05	0.667E+00	-0.447E+01	-0.670E+01	-0.303E+02
-125.5	0.163860E+05	0.163820E+05	0.173E+01	0.396E+01	0.229E+01	0.833E+01
-87.5	0.163633E+05	0.163819E+05	0.333E+00	-0.186E+02	-0.558E+02	-0.227E+02
-51.5	0.163867E+05	0.163818E+05	0.333E+00	0.484E+01	0.145E+02	0.233E+02
-16.5	0.163777E+05	0.163817E+05	0.882E+00	-0.406E+01	-0.461E+01	-0.900E+01
18.5	0.164173E+05	0.163816E+05	0.233E+01	0.357E+02	0.153E+02	0.397E+02
54.5	0.163680E+05	0.163815E+05	0.577E+00	-0.135E+02	-0.234E+02	-0.493E+02
88.5	0.163623E+05	0.163814E+05	0.882E+00	-0.191E+02	-0.217E+02	-0.567E+81
124.5	0.164220E+05	0.163913E+05	0.265E+01	0.407E+02	0.154E+02	0.597E+02
160.5	0.163533E+05	0.163812E+05	0.333E+00	-0.279E+02	-0.837E+02	-0.687E+02
196.5	0.163630E+05	0.163811E+05	0.231E+01	-0.181E+02	-0.786E+01	0.967E+01
233.5	0.163960E+05	0.163810E+05	0.577E+00	0.150E+02	0.259E+02	0.330E+02

Polynomial coefficients for FACTOR 2

COEFF	SIGMA
0.16381688E+05	0.61206369E+01
-0.27957903E-02	0.42418454E-01

Reduced CHI SQUARE = 524.47

FTEST = 0.43E-02

RMUL = 0.19E-01

R(1) = -0.19E-01

as given in the first column of Table 4. The second-degree coefficient in the example quoted is only just significant. The quality of the fit is indicated by the quantities reduced χ^2 , F test, RMUL and R . See ref. 7 for a discussion of these terms.

Table 5 shows the results of fitting the temperature data during the same plateau. This particular temperature plateau was not particularly well controlled in that there was an oscillation $\leq \pm 1/2^\circ\text{C}$ as judged from the DEL P column. The maximum DEL P value in Table 5 is $69 \mu\text{V} \sim 1^\circ\text{C}$; values of $< 10 \mu\text{V}$ are more typical.

EXTRAPOLATION OF POLYNOMIALS AND CALCULATION OF E_i

After the polynomials have been fitted, the temperature and rate of weight loss must be extrapolated to a time between temperature plateaus to provide the values T_1 , T_2 , r_1 and r_2 needed in eqn. (1). Table 6 shows the results of the extrapolations for the data in Tables 3, 4 and 5. R1 in Table 6 refers to the rate of change of factor 1 (1 is the sample weight). F1 and F2 refer to the extrapolated values of factors 1 and 2 (2 is the temperature). The quantities in these lines are (1) the values when the polynomial is extrapolated backwards in time, (2) the estimate of its associated standard deviation, (3) the value when the polynomial is extrapolated forward in time, (4) the estimate of its associated standard deviation, (5) an estimate of the precision $X/\sigma(X)$ for the values in the backward extrapolation, (6) a similar estimate

TABLE 6

EXTRAPOLATION OF POLYNOMIALS FITTED IN TABLES 4 AND 5

Extrapolation times about mid point of plateau for polynomials

First plateau = -382. 382.

Second plateau = -381. 381.

Real times are 148. seconds on either side of 264. 732. for first plateau, and 1028. 1495. for second

Extrapolated values and sigmas back and forward in time then precisions, = back, forward and requested

	*						
R1	-0.261E+02	0.219E+00	-0.249E+02	0.219E+00	119.	114.	30.
F1	0.199E+06	0.442E+02	0.179E+06	0.442E+02	4496.	4055.	100.
F2	0.164E+05	0.173E+02	0.164E+05	0.173E+02	947.	947.	100.

Activation energy from =ACTIVE=

E	$\hat{\sigma}(E)$	T	$\hat{\sigma}(T)$	rate	$\hat{\sigma}(\text{rate})$
21.414	0.651	224.21	0.20	-0.1363E+02	0.1687E+00
		239.54	0.23	-0.2606E+02	0.2189E+00

Contribution of rate and temperature to variance (=SIGE²)

Rate	Temp
0.244E+00	0.179E+00

Number of points used to get polynomials was 14 and 14 E values, times and sample weights so far:

1	21.414	0.651	880.	0.199058E+06	31.21
---	--------	-------	------	--------------	-------

* Read as -0.261×10^2 .

$X/\sigma(X)$ for the forward extrapolation, and (7) the lowest acceptable levels of these precisions. Failure of the procedure to attain any of these lowest limits of precision will cause the program to return to collect more data unless (a) the assigned measurement time has been used up, or (b) any precision is worsening, as seen from the two latest estimations made under the current set of conditions.

Extrapolated rate of weight loss and temperature values are then used in eqn. (1) to calculate an activation energy. As in the actual output of the program, the calculated activation energy is given in Table 6 with an estimated standard deviation, and with the values of T , $\sigma(T)$, r and $\sigma(r)$ used in the calculations. The temperatures in Table 6 are in °C and the rates are in $\mu\text{V sec}^{-1}$. The contribution of rates and temperature to the estimate of the variance (σ^2) of E_i is given at the bottom of Table 6. The optimum is for these two quantities to be equally small. Usually the rate contribution is the larger.

Provided that $E_i/\sigma(E_i)$ is sufficiently large, or if measurement time has run out, the program determines statistically weighted and unweighted averages from the 10 latest E_i and $\sigma(E_i)$ values, sets a new set of conditions and restarts the data measurement process. If $E_i/\sigma(E_i)$ is too small and measurement time remains, the program will not change the conditions but will measure more data which will be added to those already obtained.

Information on the running averages based on the first 9 activation energies obtained in the oxidation of polystyrene is given in Table 7. (Both here and in the

TABLE 7

SUMMARY OF ACTIVATION ENERGY DETERMINATIONS DURING EXPERIMENT

E values, times and sample weights so far:

No	E	SIG E	Time	Sample Wt.	D.O.C.
1	21.414	0.651	880.	0.199058E+06	31.21
2	22.199	0.870	1643.	0.179461E+06	34.97
3	20.428	3.284	2557.	0.164286E+06	37.88
4	22.307	3.297	3154.	0.146498E+06	41.28
5	21.751	0.654	5459.	0.951671E+05	51.12
6	21.293	0.755	6221.	0.698457E+05	55.97
7	21.785	0.541	6985.	0.541754E+05	58.97
8	20.517	0.757	7751.	0.273903E+05	64.10
9	22.126	0.527	8511.	0.109583E+05	67.25

Weighted mean E is 21.646 + or - 0.244

Reduced CHISQ for E calculation is 0.510 (should be 1.)

Unweighted mean of sigmas is 1.259 calculated over 8. degrees of freedom

Assuming all possible sample means are normally distributed, true weighted mean lies within range 21.166 to 22.125 for 95% confidence level

Unweighted estimate of E and unbiased estimate of SIG E are 21.535 and 0.231 which gives confidence range of 21.083 to 21.988

CHI-SQUARE for unweighted E is 0.54

TABLE 8

SUMMARY OF INFORMATION ON ACTIVATION ENERGIES DETERMINED DURING OXIDATION OF POLYSTYRENE IN AIR

PS run of 7/13/77 in air

1	21.414	0.651	880.	0.199058E+06	31.21	0.1697E+00	14	
			224.21		0.20			-0.1363E+02
2	22.199	0.870	239.54	0.179461E+06	34.97	0.441681E+02	14	
			239.52		0.23			0.199557E+06
			228.39		0.20			-0.2606E+02
3	20.428	3.284	2557.	0.164286E+06	37.88	0.2208E+00	14	
			228.44		0.28			0.198560E+06
			244.73		0.84			-0.2927E+02
			244.73		0.84			0.162829E+06
4	22.387	3.297	3154.	0.146498E+06	41.28	0.1676E+01	5	
			242.99		0.50			-0.2686E+02
			232.46		0.19			0.146056E+06
5	21.751	0.654	5459.	0.951671E+05	51.12	0.2834E+01	5	
			236.28		0.25			-0.1716E+02
			251.72		0.25			0.146899E+06
			251.72		0.25			-0.1825E+02
6	21.293	0.755	6221.	0.698457E+05	55.97	0.369988E+02	12	
			251.77		0.25			0.958499E+05
			240.67		0.21			-0.3434E+02
			240.67		0.21			0.944843E+05
7	21.785	0.541	6985.	0.541754E+05	58.97	0.343245E+02	14	
			240.77		0.21			-0.3163E+02
			255.61		0.19			0.693664E+05
			255.61		0.19			-0.2035E+02
8	20.517	0.757	7751.	0.273903E+05	64.10	0.1707E+00	14	
			255.63		0.19			0.703249E+05
			244.59		0.26			-0.3303E+02
			244.59		0.26			0.268590E+05
9	22.126	0.527	8511.	0.109583E+05	67.25	0.469508E+02	14	
			244.69		0.26			-0.2178E+02
			259.65		0.13			0.279216E+05
			259.65		0.13			-0.2054E+02
10	27.387	6.069	9442.	-0.210176E+05	73.38	0.1311E+00	14	
			259.65		0.19			0.118188E+05
			249.66		0.75			-0.3756E+02
			249.66		0.75			0.100978E+05
						0.327090E+02	14	
					0.19			-0.3222E+02
					0.19			0.2328E+00
					0.19			-0.223508E+05
						0.655307E+02	14	
					0.75			-0.1965E+02
					0.75			0.2006E+01
						0.391067E+03	5	

11	20.196	2.074	10050.		-0.327945E+05	75.63			
			248.15	0.44	-0.2111E+02		0.1141E+01		
					-0.320766E+05		0.127695E+03		5
12	20.899	0.637	10813.		-0.3685E+02				
			263.48	0.23	-0.335124E+03		0.1773E+00		
					-0.586441E+05	80.58	0.357775E+02		14
13	21.542	0.467	10813.		-0.3036E+02				
			263.65	0.23	-0.591515E+05		0.1773E+00		
					-0.1991E+02		0.357775E+02		14
14	21.506	0.853	252.34	0.14	-0.581367E+05				
					-0.728129E+05	83.30	0.1169E+00		
					-0.1714E+02		0.235336E+02		14
15	22.395	0.898	252.98	0.14	-0.722327E+05				
					-0.2987E+02		0.8508E+01		
			267.56	0.21	-0.733932E+05		0.171469E+02		14
16	10.974	42.685	12335.		-0.918636E+05	86.95			
			267.79	0.21	-0.1951E+02		0.8508E-01		
					-0.922093E+05		0.171469E+02		14
17	21.506	0.853	256.73	0.23	-0.1285E+02				
					-0.915178E+05		0.1381E+00		
					-0.100485E+06	88.60	0.280695E+02		14
18	22.395	0.898	256.59	0.27	-0.7583E+01				
					-0.100080E+06		0.1626E+00		
					-0.1583E+02		0.383535E+02		14
19	10.974	42.685	275.58	0.32	-0.100009E+06				
					-0.113928E+06	81.17	0.1955E+00		
					-0.100009E+06		0.459805E+02		14
20	10.974	42.685	15744.		-0.9239E+09				
			275.67	0.28	-0.113873E+06		0.1158E+00		
					-0.0785E+00		0.262568E+02		14
21	10.974	42.685	272.94	0.77	-0.113984E+06				
					-0.113984E+06		0.1316E+00		
					-0.113984E+06		0.298132E+02		14

Quantities are:

1st line: ordinal number, E_i , $\hat{\sigma}(E_i)$, elapsed time, sample weight, degree of conversion.

2nd line: T_1 , $\hat{\sigma}(T_1)$, r_1 , $\hat{\sigma}(r_1)$.

3rd line: w_1 , $\hat{\sigma}(w_1)$, number of "good" data points in plateau 1.

4th line: T_2 , $\hat{\sigma}(T_2)$, r_2 , $\hat{\sigma}(r_2)$.

5th line: w_2 , $\hat{\sigma}(w_2)$, number of "good" points in plateau 2.

lines 1 through 5 repeat for each activation energy.

Energies in kcal mole⁻¹, time in seconds, sample weights in μV , temperatures in $^\circ\text{C}$, rates in $\mu\text{V sec}^{-1}$; 20 μV corresponds to 1 μg .

output of the program, this information is intended only as a guide. The results should be examined critically before the average values are quoted). A summary file containing the pertinent information for each experiment is written on a flexible disc. The summary file for the polystyrene oxidation is shown in Table 8. Note that some instabilities in the experiment resulted in large errors in activation energies 3, 4 and 10. The sample was used up during the determination of activation energy 16.

TEST OF POLYNOMIAL FITS TO WEIGHT-LOSS DATA

Now that we have given an example of the procedure, we turn our attention to choosing the appropriate polynomial form to fit to weight-loss data and to the

TABLE 9

DERIVATIVES FROM POLYNOMIAL FITTED TO WEIGHT-LOSS/TIME CURVE

n^a	X^2	D_i	D_f	s	D_{e1}	D_{e2}	D Curve
1	29	2.09	2.09	0.01	2.09	2.09	
2	17	-0.07	0.07	2.2	-0.12	0.12	
4	10 ⁶	-0.13	0.13	4.3	-0.61	0.61	
1,2	16	-2.16	-2.03	0.02	-2.21	-1.98	
1,3	31	-2.11	-2.11	0.09	-2.14	-2.14	
1,4	18	-2.22	-1.97	0.05	-2.70	-1.49	
1,2,3	18	-2.18	-2.04	0.07	-2.26	-2.03	
1,2,4	18	-2.14	-2.05	0.2	-2.04	-2.15	
1,3,4	20	-2.24	-1.98	0.08	-2.75	-1.54	
2,3,4	10 ⁵	-7.78	-7.68	7.7	-22	-22	
1,2,3,4	20	-2.15	-2.06	0.20	-2.08	-2.20	

^a Weight (w) = $a + \sum_i a_i t^{n_i}$, where t = time.

^b Preferred polynomial.

D_i = dw/dt at beginning of data block; D_f = dw/dt at end of data block; s = computed standard deviation of D_i , D_f ; D_{e1} = value after extrapolation to 200 sec before data block; D_{e2} = value after extrapolation to 200 sec after data block; D curve = approximate shape of dw/dt vs. time.

accuracy with which such a fitted polynomial can be differentiated and extrapolated to obtain useful results. Several polynomials were fitted to a block of weight-loss data taken from the middle of a typical experimental run. The results are given in Table 9. The coefficients of the trial polynomials, given under the column n , ranged between 1 and 4. On the basis of χ^2 , the fit is best for the second-degree polynomial $w = a + bt + ct^2$, where w = sample weight and t = time. The values under the headings D_i and D_f in Table 9 are the derivatives obtained from substituting the times corresponding to the initial and final data in the block; they are to be considered as the earliest and latest "directly observed" values of the rate of weight loss. The extrapolated values are given in the columns D_{e1} for the extrapolation back in time and D_{e2} for the extrapolation forward in time. Because the derivative changed only slowly with time, the extrapolated values should be fairly near the initial and final values.

Several polynomials are immediately seen to be inappropriate because of either no change in the derivative with time, too much change, or nonsensical change, as shown by the overall curve of the trend of the derivative with time in Table 9 (given under the heading "D curve"). The trend should gradually decrease in a smooth fashion with time. There is little to choose between the fit of second- and third-degree polynomials, but the coefficient of t^3 in the third-degree polynomial was only one-third of its estimated standard deviation, and thus the second-degree polynomial is the polynomial of choice. The first-degree polynomial requires a constant derivative and is obviously inappropriate. The column headed " s " in Table 9 is the estimate of the standard deviation of the extrapolated derivatives. Because the time origin was placed in the middle of the data block, both extrapolated derivatives have the same standard deviation. The estimate of the standard deviation is apparently a less reliable estimate

of the appropriateness of the fit of the polynomial to the data than is the χ^2 value, because s for the first-degree polynomial is the lowest value of all.

These and other results show that a second-degree polynomial is generally appropriate for the small sections of the weight-loss curve which we must fit. We now turn our attention to the closeness of the extrapolated derivatives to the values which would have been observed had the data block been part of a larger isothermal plateau. At first precisely this approach was tried. Parts of long isothermal plateaus were fitted with a polynomial and the results were extrapolated out to other regions where the derivatives were compared with derivatives calculated from polynomials fitted to blocks of data which were centered about the extrapolation points. Unfortunately, the whole cumbersome exercise was marred by using data which turned out to have too low a rate of weight loss (see below). It was then decided that a more useful procedure would be to use the usual factor-jump program and procedure except that the program would be changed slightly so that it would be unaware that the temperature was actually not being changed (i.e., a test for nonsensical conditions was removed). Thus the two derivatives and sample weights calculated in the determi-

TABLE 10

EXPERIMENTAL TEST OF DERIVATIVE AND WEIGHT ESTIMATION FROM EXTRAPOLATION OF SECOND-DEGREE POLYNOMIAL^a

% Reacted	Derivative results					Weight results			
	ΔD	\bar{D}	$\hat{\sigma}(\bar{D})$	$100 \Delta D/\bar{D}$	$\Delta D/\hat{\sigma}(\bar{D})$	ΔW	$ \bar{w} $	$\hat{\sigma}(\bar{w})$	$\Delta w/\hat{\sigma}(\bar{w})$
9.0	-0.39	19	0.39	-2.0	-1.0	208	385985	76	2.7
11.8	-0.25	23	0.42	-1.1	-0.6	60	369489	82	0.7
15.0	0.73	27	0.49	2.7	1.5	-117	350282	96	-1.2
18.5	1.01	29	0.43	3.4	2.3	-35	328871	85	-0.4
22.4	0.17	32	0.33	0.5	0.5	-91	305776	64	-1.4
26.4	-0.48	32	0.30	-1.5	-1.6	98	281580	59	1.6
30.6	-0.45	34	0.29	-1.3	-1.5	-176	256336	58	-3.0
34.9	0.19	33	0.36	0.6	0.5	193	230417	71	2.7
39.3	0.65	35	0.35	1.9	1.8	-72	204345	71	-1.0
52.3	0.32	33	0.29	0.9	1.1	-156	126310	56	-2.8
56.4	-0.65	32	0.29	-2.0	-2.2	-13	101856	57	-0.2
60.3	-0.57	30	0.30	-1.9	-1.9	14	78261	58	0.2
64.0	-0.24	29	0.21	-0.8	-1.1	-38	55712	40	-0.9
67.6	-0.32	27	0.16	-1.2	-2.1	34	34465	29	1.1
71.0	0.16	25	0.14	0.6	1.1	76	14294	27	2.7
74.1	-0.62	24	0.17	-2.5	-3.5	103	4408	35	2.9
77.1	-0.37	21	0.21	-1.7	-1.7	-190	22526	46	-4.1
79.8	-0.40	20	0.18	-0.2	-0.2	36	39021	35	1.0
82.2	-0.40	17	0.16	-0.2	-0.3	-11	53225	31	-0.4
84.3	0.59	16	0.13	3.7	4.6	-22	66065	25	-0.9
86.3	0.76	14	0.14	5.4	5.3	-128	77489	28	-4.6
87.9	0.57	12	0.19	4.4	3.1	82	87578	37	2.2
93.6	0.75	22	0.16	3.4	4.8	-83	121716	31	-2.7

^a Data from degradation of polystyrene in vacuum.

w = sample weight in μV ($20 \mu V = 1 \mu g$); D = rate of weight loss in $\mu V \text{ sec}^{-1}$; $\Delta D = D_1 - D_2$;
 $\bar{D} = (D_1 + D_2)/2$; $\hat{\sigma}$ = estimated value of σ .

nation of the activation energy should be directly comparable. Further, the procedure should provide an easily made general check on whether a particular material would be suitable for factor-jump experiments.

Table 10 shows the results of a test of derivative estimation using some results obtained for the degradation of polystyrene in < 1 mm air. The estimation of the derivative and sample weights is satisfactory. The two equivalent estimates of the weight agree within $100 \mu\text{V}$ ($\sim 5 \mu\text{g}$) on the average (i.e., in the Δw column). The two equivalent estimates for each derivative agree within $0.5 \mu\text{V sec}^{-1}$ on the average (see the ΔD column). The agreement appears to be more or less constant regardless of the magnitude of the derivative. The data were measured above a minimum rate of weight loss of $10 \mu\text{V sec}^{-1}$. The error in the derivatives may be estimated as half the spread of the derivatives themselves. On a percentage basis, this is half the value given in column $100 \Delta D/\bar{D}$ and thus ranges from $< \sim 1$ to $\sim 2.5\%$. The effect of error in the derivative can be estimated from Table 12. (The rationale for Table 12 will be given in the following section). An error of 0.2 in a rate of $11 \mu\text{V sec}^{-1}$ for a rate ratio of (say) 4 would give an error of $< 0.5 \text{ kcal mole}^{-1}$ in an individual estimation of the activation energy. This would be a highly satisfactory result given the facts that activation energies are often quoted to $\pm 5 \text{ kcal mole}^{-1}$ and that our estimated standard deviation of the average value contains a factor of $\sqrt{1/N}$. Our conclusion is that a second-degree polynomial can be fitted to the trend of sample weight with time in the factor-jump method and this polynomial can be extrapolated to give satisfactory estimates of the first derivative, i.e., the rate of weight loss with respect to time, for use in the calculation of an activation energy.

TEMPERATURE POLYNOMIAL

The temperature-time behavior is ideally linear and independent of time, i.e., the temperature should be constant. In practice there is a complex damped oscillation approach to equilibrium. We have recognized the slight tendency of the temperature to attain equilibrium only slowly by fitting its trend with time by a first-degree polynomial. Generally, higher coefficients than first are not statistically significant and confer instability rather than improve the precision.

POLYNOMIALS FOR OTHER FACTORS

Generally the remaining factors, the pressure and flow rates, are not changed during the run but are instead held at constant levels. Thus it is appropriate to fit them with a zero-order polynomial, i.e., to a constant value.

ESTIMATION OF MINIMUM RATE OF WEIGHT LOSS

Runs in which the sample was exhausted and other runs carried out with an empty sample pan (and with appropriately initialized parameters so that the run

TABLE II

MINIMUM RATE OF WEIGHT LOSS TO OVERCOME INSTRUMENTAL DRIFT

(Assuming instrumental drift = $0.6 \mu\text{V sec}^{-1}$)

E^a (kcal mole ⁻¹)	r_1/r_2^b	Minimum rate ($\mu\text{V sec}^{-1}$) for allowed error in E of				Actual error in E (kcal mole ⁻¹)			
		4%	3%	2%	1.5%	4%	3%	2%	1.5%
15	1.5	12.5	16	24	> 30	0.6	0.5	0.3	0.2
25	2	11	14	21	29	1	0.8	0.5	0.4
33	2.5	9.5	13	19	26	1.3	1.0	0.7	0.5
40	3	9	12	18	24	1.6	1.2	0.8	0.6
46	3.5	8.5	11	17	23	1.8	1.4	0.9	0.7
51	4	8	10.7	16	21.5	2.0	1.5	1.0	0.8
55	4.5	7.5	10	15.5	20.5	2.2	1.7	1.1	0.8
59	5	7.5	9.7	15	19.7	2.4	1.8	1.2	0.9

^a When r_1/r_2 values from second column, $T_1 \sim T_2 = 250^\circ\text{C}$ and $\Delta T = 15^\circ\text{C}$ are substituted in eqn. (1).

^b Ratio of rates.

would not be ended by the program) showed apparent rates of weight loss of 0.02 to $0.6 \mu\text{V sec}^{-1}$. We took $\delta = 0.6 \mu\text{V sec}^{-1}$ as the maximum contribution of the apparatus to the apparent rate of weight loss. To determine the minimum rate of weight loss to impose on the sample so that this contribution from the apparatus could be considered insignificant, we went through the following exercise. Adding δ to the rates in eqn. (1), we obtain eqn. (3) as stated earlier. (The quantity δ was added for convenience; the effect would be maximized by adding δ in the numerator and subtracting it in the denominator).

The percentage change in E_i can then be estimated from $\ln(r_1/r_2)/\ln(r'_1 + \delta/r'_2 + \delta)$. A suitable program was easily written in BASIC (15 lines). The value of r_1 ranged from 10 to 90 in increments of 10; that of r_2 ranged from 1 to 30 in increments of 1. Results corresponding to ratios of r_1/r_2 ranging from 1.5 to 5 are summarized in Table 11. These values correspond to ratios expected for E values ranging from 15 to 60 kcal mole⁻¹ for $T_1 \sim T_2 = 250^\circ\text{C}$ and ΔT values of $\sim 15^\circ\text{C}$. Thus, a minimum rate of $12.5 \mu\text{V sec}^{-1}$ should measure all activation energies less than 60 kcal mole⁻¹ to 4%, and will measure activation energies less than 35 kcal mole⁻¹ to 3% (this includes most oxidative reactions). To the extent that many of the rates will be above the minimum, one can say that instrumental effects of this kind will in practice produce errors of less than 3% in the individual measured activation energies.

However, the inclusion of $\sigma(E)$ in the Arrhenius equation

$$k = f(c) A e^{-[E + \sigma(E)]/RT}$$

$$= f(c) [A e^{-E/RT}] [e^{-\sigma(E)/RT}]$$

$$= k' e^{-\sigma(E)/RT}$$

(4)

TABLE 12

INTERPLAY OF MINIMUM RATE (r) INSTRUMENTAL DRIFT (D) AND ERROR IN ACTIVATION ENERGY (E)

D	E^a	r_1/r_2	Error (kcal mole ⁻¹)					
			0-0.5 r	0.5-1	1-1.5	1.5-2	2-2.5	2.5-3
0.6	15	1.5	15	7	5	4	3	2
	25	2	>20	11	7	6	4	— ^b
	33	2.5	>20	13	9	7	5	4
	40	3	>20	15	10	7	6	5
	46	3.5	>20	16	11	8	6	5
	51	4	>20	17	11	8	7	6
	55	4.5	>20	17	11	9	7	6
	59	5	>20	18	12	9	7	6
0.5		1.5	12	6	4	3	—	2
		2	18	9	6	5	4	3
		2.5	>20	11	7	6	5	4
		3	>20	12	8	6	5	4
		3.5	>20	13	9	7	5	—
		4	>20	14	9	7	6	5
		4.5	>20	14	10	7	6	5
		5	>20	15	10	7	6	5
0.4		1.5	10	5	3	—	2	—
		2	15	7	5	4	3	—
		2.5	18	9	6	5	4	3
		3	20	10	7	5	4	3
		3.5	>20	11	7	5	4	—
		4	>20	11	8	6	5	4
		4.5	>20	12	8	6	5	4
		5	>20	12	8	6	5	4
0.3		1.5	8	4	3	2	—	1
		2	11	6	4	3	2	—
		2.5	13	7	5	4	3	2
		3	15	8	5	4	3	—
		3.5	16	8	6	4	3	—
		4	17	9	6	5	—	3
		4.5	17	9	6	4	4	3
		5	18	9	6	5	4	3
0.2		1.5	5	3	2	—	1	—
		2	8	4	3	2	—	—
		2.5	9	5	3	—	2	—
		3	10	5	4	3	2	—
		3.5	11	6	4	3	2	—
		4	11	6	4	3	—	2
		4.5	12	6	4	3	—	2
		5	12	6	4	3	—	2

^a From eqn. (1) given corresponding value of r_1/r_2 and assuming $T_1 \sim T_2 = 250^\circ\text{C}$, $\Delta T = 15^\circ\text{C}$.^b No integer value of rate fits these windows.

shows that errors in E enter into the apparent rate constant k as a multiplicative factor applied to the real rate constant, k' . Thus, a more appropriate specification of the minimum rate is in terms of that required to keep the error in the activation energy below a given threshold. Absolute errors in E in kcal mole⁻¹ are given at the right side of Table 11. Absolute errors in E are also given in Table 12, where, for given amounts of instrumental "drift", D , and various rate ratios r_1/r_2 , the minimum rate is given in columns corresponding to the expected error in activation energy in kcal mole⁻¹. Not until the "drift" is as low as 0.2–0.3 $\mu\text{V sec}^{-1}$ is there much hope of measuring an individual activation energy to 0.5 kcal mole⁻¹ or better. For the worst case, i.e., conditions of $D = 0.6 \mu\text{V sec}^{-1}$ and a minimum rate of 12.5 $\mu\text{V sec}^{-1}$, the individual activation energies will only be measured to 1–1.5 kcal mole⁻¹ or better. Since many rates will be above the minimum (perhaps $\geq 15 \mu\text{V sec}^{-1}$) and often the apparent drift will be below the maximum one can reasonably expect many activation energies to be measured to less than 1 kcal mole⁻¹. Table 12 also shows the important effect of reducing instrumental "drift". For a maximum "drift" of 0.2 $\mu\text{V sec}^{-1}$, all activation energies could be measured to better than 0.5 kcal.

PRECISION NEEDED IN ACTIVATION ENERGY

When one considers that physical changes in the sample (such as the formation of crusts or even just the reduction in sample size as the sample loses weight) can make processes such as diffusion change in importance and influence the observed activation energy by several kcal mole⁻¹, activation energies measured to 0.5 to 1 kcal mole⁻¹ are probably sufficient for the purpose of following changes in dominant mechanism.

When the goal is to estimate service life from the results of a test accelerated by temperature, the criterion changes drastically. The activation energy is the parameter which measures the temperature-dependence of a reaction. The rationale of estimating the effect of error in the activation energy on extrapolations of accelerated tests is given below. Given the Arrhenius equation and the supposition that the same processes are rate limiting at both temperatures, we can write

$$\begin{aligned} \frac{r(T_2)}{r(T_1)} &= e^{(E+\sigma)\Delta T/RT_1T_2} \\ &= e^{E\Delta T/RT_1T_2} e^{\sigma\Delta T/RT_1T_2} \end{aligned} \quad (5)$$

as the correspondence between the rates at temperatures T_1 and T_2 , with $\Delta T = T_2 - T_1$. The term $e^{E\Delta T/RT_1T_2}$ in eqn. (5) is the scaling factor, and the term $e^{\sigma\Delta T/RT_1T_2}$ may be interpreted as a term which introduces error into the scaled rate. Table 13 shows the percentage error obtained in the scaled rate when rates measured at 100, 200, 300, 400, and 500°C are scaled to 25°C assuming various errors in the activation energy. The greater the temperature difference between service life and accelerated test, the smaller the error in the activation energy must be for a given error in scaled rate. In our example of the oxidation of polystyrene at various temperatures between 225 and

TABLE 13

EFFECT OF ERROR IN ACTIVATION ENERGY ON ACCELERATED RATE TESTS

(Service temp. = 25°C)

% Error in rate ^a	Error in activation energy (kcal mole ⁻¹)				
	Test temp. (°C) 100	200	300	400	500
1	0.03	0.02	0.01	0.01	0.01
5	0.15	0.08	0.06	0.05	0.05
10	0.28	0.15	0.12	0.10	0.09
25	0.66	0.36	0.28	0.24	0.22
50	1.20	0.65	0.50	0.43	0.39
100	2.05	1.11	0.86	0.74	0.67
250	3.71	2.01	1.56	1.34	1.22

^a Calculated at service temperature from rate observed at test temperature by means of

$$\frac{r(T_2)}{r(T_1)} = e^{E\Delta T/RT_1T_2} e^{\sigma\Delta T/RT_1T_2}$$

where the error factor in the rate is $e^{\sigma\Delta T/RT_1T_2}$, and σ is the error in the activation energy.

275°C, the final averaged activation energy is 21.5 ± 0.2 kcal mole⁻¹, determined at, let us say, 250°C. From Table 13, we can estimate by interpolation that an error of ~15% would be introduced into the calculated rate if the rates observed at ~250°C were scaled to room temperature. This may seem adequate; however, we should recall that a 95% confidence level requires the use of $\sim 2\sigma$, and thus we should interpolate on $2(0.2) = 0.4$ kcal mole⁻¹ error in Table 13. This gives an error of ~35% in the scaled rate. Whether or not this would be a usefully precise rate is beyond the scope of this paper.

The above analysis suggests that the extrapolation to lower temperatures of results obtained in accelerated tests at higher temperatures requires activation energies which are known to great accuracy, i.e., some cases may require that the activation energy be known to within 0.1 kcal mole⁻¹ or better. Apparently such high precision will be rarely attained by the factor-jump method, even by considering average values from many runs, with the factor of \sqrt{N} in the denominator of the estimated standard deviation. To the extent that sample processes themselves cloud the issue, this precision may be unattainable in general. In cases where such precision is required, one must therefore stress extremely modest temperature acceleration. If the rate processes are not sufficiently fast under those conditions one must then look to analysis of rates of production of minute amounts of products or precursors as an alternate method of lifetime prediction.

EXAMPLES OF FACTOR-JUMP DETERMINATIONS OF ACTIVATION ENERGY

Given the limitation of the usefulness of the activation energy as discussed above, to what other uses can the results of the factor-jump process be applied?

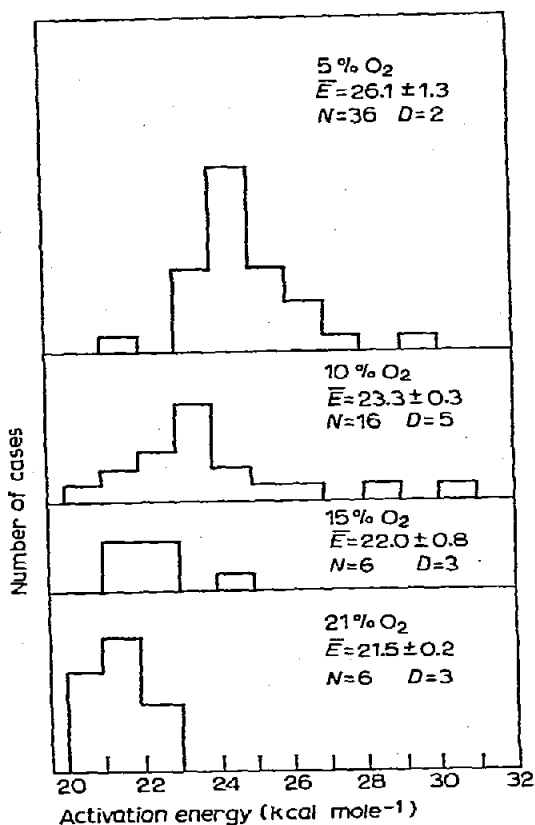


Fig. 1. Histograms of activation energies obtained in the oxidation of polystyrene in various atmospheres flowing at 500 scc min⁻¹.

Several examples will now be given. The first is a crude examination of the effect of oxygen content in the experimental atmosphere on the apparent activation energy of oxidising polystyrene. Figure 1 shows histograms plotted from runs of polystyrene in various N₂/O₂ atmospheres. The total flow rates and pressures were the same in all cases. The relative placings of the histograms clearly show an increase in apparent activation energy with decrease in O₂ content of the atmosphere. This reflects an increase in importance of the nonoxidative degradation mechanism ($E \sim 45$ kcal mole⁻¹, Dickens, unpublished) as the O₂ content of the flowing atmosphere is decreased. The average activation energies supplied in Fig. 1 were calculated over the N values tabulated in Fig. 1 with D values of the original set being discarded for reasons beyond the scope of this paper. These energies are intended as a guide only.

Figure 2 shows the trend with extent of reaction of the activation energy of the in-vacuo degradation of a polymethylmethacrylate molding powder, i.e. PMMA stabilized by being polymerized with a few percent methyl acrylate. In this experiment, the activation energy rose from ~ 33 kcal mole⁻¹ to ~ 41 kcal mole⁻¹. This result is given to illustrate a trend in activation energy and should not be quoted as definitive. We will discuss the degradation of PMMA in a later paper.

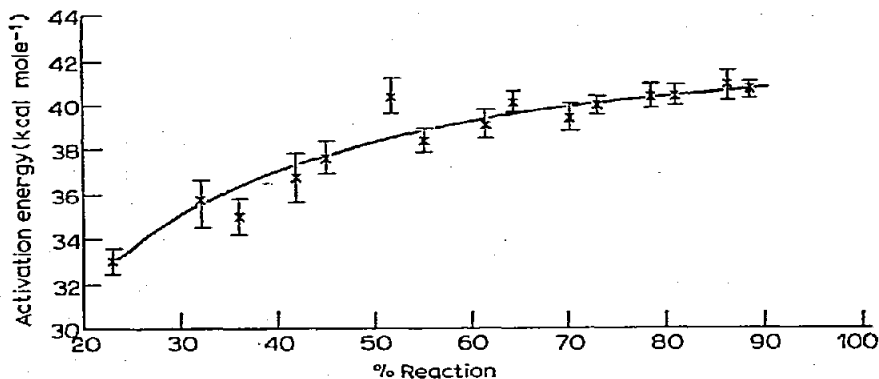


Fig. 2. Plot of activation energy vs. extent of reaction for vacuum degradation of polymethyl methacrylate molding powder (stabilized by copolymerization with acrylate).

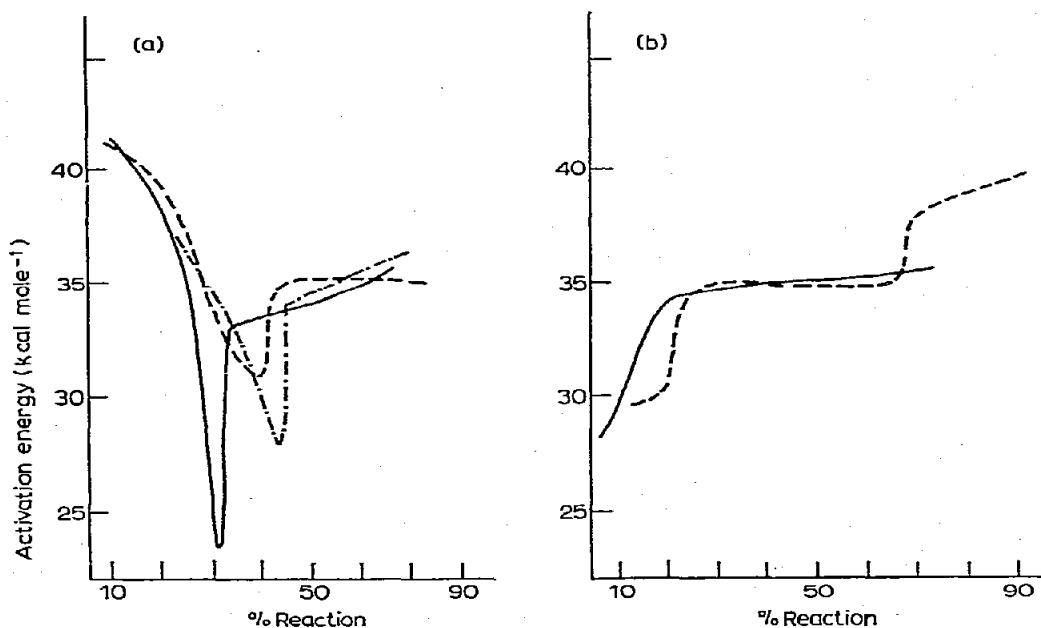


Fig. 3. Plot of activation energies versus extent of reaction for vacuum degradation of (a) methylene diphenyl diisocyanate-polyethylene adipate diol-butane diol polyurethane, and (b) polyethylene adipate diol alone, MW = 1000. —, Small cubes; ---, evaporated film on pan; —.—, evaporated film on gauge.

Figure 3 shows a possible use in the interpretation of the sequence of events during the degradation in vacuum of a methylene diphenyl diisocyanate-polyethylene adipate diol-butane diol polyurethane. The runs produced extensive char from the sample; the best method of sample presentation may be that where a solution of the polymer is evaporated directly in the sample pan. This tends to produce an extensive thin film. Three methods of sample presentation were used in the experiments summarized in Fig. 3(a). However, the essential features are common to all three curves. The activation energy data indicate that the initial process terminates at between 30 to 40% weight loss and the residue decomposes further to produce a final residue

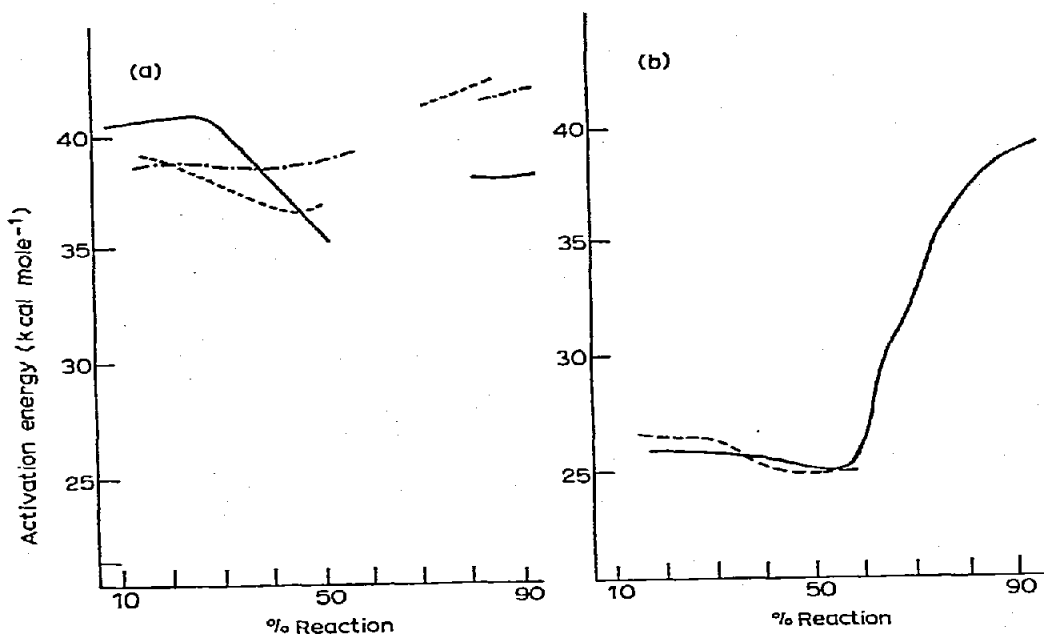


Fig. 4. Plot of activation energy versus extent of reaction for vacuum degradation of (a) methylene diphenyl diisocyanate-polytetramethylene oxide diol-butane diol polyurethane, and (b) polytetramethylene oxide diol alone, MW = 1000.

(seen at the end of the experiment to be a char) involatile in vacuum below 500°C and amounting to about 30% of the initial weight. Comparison of Fig. 3(a) and (b) indicates that the plateau at 45–70% conversion arises from the decomposition of polyester. Thus the early stages may be inferred to be the loss of methylene diphenyl diisocyanate (MDI) from the sample, apparently with an initial activation energy of 40–45 kcal mole⁻¹. However, the parameter-jump method of thermogravimetry as currently implemented consists of a series of temperature plateaus and as such is not suited to examine initial rates (i.e., of <5% extent to reaction). The fact that the activation energy of the first process thus changes from 40 kcal mole⁻¹ to 24–31 kcal mole⁻¹, depending on the sample, suggests increased importance of diffusion (~ 15 kcal mole⁻¹) as the decomposition progresses. A reasonable explanation is that a crust formed on the samples but later cracked as the degradation proceeded.

The activation energies calculated during the in-vacuo degradation of three samples of a methylene diphenyl diisocyanate-polytetramethylene oxide diol-butane diol polyurethane are shown in Fig. 4. The gaps in the curves indicate regions where the temperature had to be increased (under program control) in several steps to force the rate-of-weight loss of the sample above minimum allowed limits. This probably implies a change in process, because final inspections showed the samples were not excessively charred and thus diffusion processes would not be expected to play an increasingly important role as the degradation proceeded. Comparison of Fig. 4(a) with (b) shows that degradation of polyether alone is easily discerned not to be a dominant process in the in-vacuo degradation of the MDI/polyether polyurethanes. However, it is probable that MDI boils out of polyether-based polyurethanes just as

it does from polyester-based polyurethanes. Figure 4(a) suggests that degradation of polyether also occurs during the period when MDI is lost. Otherwise, after considerable or complete loss of MDI, the activation energy would fall to the 26 kcal mole⁻¹ characteristic of polyether degradation. There is some movement in this direction but the lowest activation energy to be measured at sufficiently large rates of weight loss to be realistic is only 35 kcal mole⁻¹, which is not much below the starting value of ~40 kcal mole⁻¹. At 50% reaction, the process changes. We infer this marks the complete loss of MDI and that the later degradation, corresponding roughly to the region 70-90% in Fig. 4(b), is that of the remaining polyether.

The activation energy vs. extent of reaction plots provide useful information on the effects of sample geometry (Fig. 3a), the dominant processes (from a comparison of Fig. 3a and b) and the extent over which these processes occur when they are separated (Fig. 3a) and when they are not (Fig. 4a). The conclusions help to characterize polymer degradations but the inferred nature of the dominant processes must later be confirmed by other techniques, including product analysis. Routine application of the method to all samples is not currently feasible. When heated in vacuo, some samples such as the toluene-diisocyanate-polymethylene glycol-butane diol polyurethane form a bubbly viscous liquid which imparts small shocks to the balance mechanism as the bubbles burst and loses weight in steps as the gaseous content of the bubbles escapes. The way to handle this situation has not yet been resolved. It is possible that the sample will behave simply under different conditions such as atmospheres of N₂, O₂, H₂O, etc., and mixtures thereof.

CONCLUDING REMARKS ON THE FACTOR-JUMP METHOD

The factor-jump method of thermogravimetry has the disadvantage of requiring the estimation of derivatives. This is a notoriously unstable computational procedure. Nonetheless, the work described here shows that in many cases the derivative cannot only be estimated satisfactorily, but can also be extrapolated satisfactorily. Thus the method is computationally feasible.

There are several advantages of the factor-jump method.

(1) Knowledge of the kinetic form of the degradation is not necessary. The only requirement is that the isothermal behavior of the sample be representable over short ranges by a low-degree polynomial. Thus one may study polymer degradations with ease even though the order of reaction construct is not appropriate for degrading polymers. Probably some inference of the kinetic form could be made using the data from the various isothermal sections of the experiment. Up to now, our philosophy has been to put the determination of the activation energy on a firm footing.

(2) The activation energy can be examined over a large extent of reaction using only a narrow temperature range and under the condition of an essentially constant rate of weight loss (within a factor of 2 or 3).

(3) The procedure uses only one sample to estimate a series of activation energies. Comparison of two samples with disparate thermal histories is thus avoided,

and there is no reliance on determining the initial and final sample weights, the extents of reaction and so on.

(4) The single sample is only slightly perturbed by the changes in conditions as the experiment proceeds and soon "re-equilibrates".

(5) Additional advantages in our particular experimental set-up are the control of the procedure by the computer, the real-time processing of the data to obtain final results, estimates of the errors involved and the lack of need of an operator once the run is started.

(6) At the moment the technique has not progressed to the stage where a new material can be characterized every day. Runs in "vacuum" (25–150 μm Hg of air) often show erratic results in the form of scatter in the measured activation energies. It is not presently known whether such erratic results are inherent in the polymer degradations themselves or are caused by the effects of the traces of oxygen present. Efforts are underway to improve the vacuum in the apparatus.

(7) For any results to be considered trustworthy, they must be reproducible and must survive comparison with results obtained by different techniques. To examine the reproducibility, a polymer should be subjected to several factor-jump experiments.

REFERENCES

- 1 J. H. Flynn and B. Dickens, *Thermochim. Acta*, 15 (1976) 1.
- 2 B. Dickens, W. J. Pummer and J. H. Flynn, in C. E. R. Jones and C. A. Cramers (Eds.), *Analytical Pyrolysis*, Elsevier, Amsterdam, 1977, p. 383.
- 3 B. Dickens, *Thermochim. Acta*, 29 (1979) 41.
- 4 B. Dickens and J. H. Flynn, in D. Dollimore (Ed.), *Proceedings of the First European Symposium on Thermal Analysis*, Heyden, London, 1976, p. 15.
- 5 B. Dickens, *Thermochim. Acta*, 29 (1979) 57.
- 6 R. L. Powell, W. J. Hall, C. H. Hyink, Jr., L. L. Sparks, G. W. Burns, M. G. Scroger and H. H. Plumb, *Thermocouple Reference Tables Based on the IPTS-68, Nat. Bur. Stand. (U.S.), Monogr.* 125, 1974.
- 7 P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences*, McGraw-Hill, New York, 1969, Chap. 10.