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NEW THERMOGRAVIMETRIC RELATIONSHIPS FOR STUDYING THE PYROLYSIS OF POLYMERS

Prepared by:
Hugh C. Anderson

ABSTRACT: Two thermogravimetric methods were developed to show whether rate of weight loss varies with extent of pyrolysis of a polymer. The first of these, a kinetic technique, involves obtaining (at various degrees of degradation) the activation energy, the order of decomposition, and the Arrhenius pre-exponential factor by solving three simultaneous equations. The data for these equations are obtained by performing three thermogravimetric experiments at three constant heating rates. The second method, which involves cycling the polymer between 25°C and a fixed higher temperature, is based on the compound interest law. If the rate of weight loss changes with extent of decomposition, the experimental points deviate from the theoretical curve; if the rate does not vary, the experimental points coincide with the curve. Both techniques show that rate of weight loss does not change appreciably with degree of pyrolysis of Teflon. For a copolymer of tetrafluoroethylene and hexafluoropropylene, these methods show that rate of weight loss does vary with degree of pyrolysis.

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NEW THERMOGRAVIMETRIC RELATIONSHIPS FOR STUDYING THE PYROLYSIS OF POLYMERS

This report contains a description of two new thermogravimetric techniques and a discussion of their application to the study of two model polymers (polytetrafluoroethylene and a copolymer of polytetrafluoroethylene and hexafluoropropylene). This work was performed under Task PR-6 as part of a general polymer pyrolysis investigation directed toward the acquisition of a more fundamental understanding of the thermal decomposition of polymers and related substances.

The most significant outcome of the research described herein is that it produced two simple thermogravimetric relationships that reveal whether rate of pyrolysis varies with extent of degradation of a polymer. Whether or not this variation in rate occurs is one of the most important questions confronting a polymer degradation chemist.

R. E. ODENING
Captain, USN
Commander

Albert Lightbody
ALBERT LIGHTBODY
By direction

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INTRODUCTION

1. If a polymer is decomposed to an extent of 10% (as determined by weight loss), the structure of the residue may be different from that of the original material. Then, if the residue is decomposed another 10%, the structure of this second residue could be different from those of the original polymer and of the first residue. These changes in structure can alter the mechanism and rate of decomposition as the material is further pyrolyzed. Since the usual thermogravimetric method (refs. (a) and (b)) yields rates averaged over wide degradation ranges, it may fail to reveal rate changes due to modifications in the structure of the residue.

2. The purpose of the work described herein was to develop methods to indicate whether the rate of decomposition changes as the polymer is pyrolyzed. A study of the problem led to two likely approaches. The first of these, a kinetic method, was possible because of our ability to perform thermogravimetric experiments at various constant heating rates. Based upon the use of three heating rates, an equation was derived for calculating the activation energy, the order of decomposition, and the Arrhenius pre-exponential factor. For the second approach, an equation based on a modification of the compound interest law (ref. (c)) was derived. It was then possible to use a thermogravimetric cycling procedure to show if rate of decomposition changes with extent of pyrolysis. These two techniques were applied to polytetrafluoroethylene (DuPont's Teflon 5) and a FEP copolymer (DuPont's Teflon 100) of tetrafluoroethylene and hexafluoropropylene.

THEORETICAL

3. For the kinetic method, equation (4) in Figure 1 was derived. It contains the three kinetic parameters: E, activation energy; n, order of decomposition; and A, Arrhenius pre-exponential factor. In order to solve for these parameters, data are required for three simultaneous equations. Since rate of weight loss and heating rate are dynamic processes, weight-loss curves will shift along the temperature axis (Fig. 2) when obtained at different constant heating rates. With three such curves, all the necessary data become available for the required solution.

4. The thermogravimetric cycling experiments for the second method were performed on the following assumption. When a polymer is decomposed partially by repeated cycling between 25°C and a fixed higher temperature, W_r/W_i for each cycle should follow a curve of $W_r/W_i = (1 - W/W_i)^M$, in which W_r = weight of polymer remaining after cycle M, W_i = initial weight, and W = weight loss during the first cycle (see Fig. 3).

EXPERIMENTAL

5. Figure 4 shows a modification of the weighing chamber for the thermogravimetric apparatus described previously (refs. (d) and (e)).

Approximately 9 to 11.5 mg. samples of 100-mesh Teflon 5 and Teflon 100 powder were pyrolyzed at a pressure of 1×10^{-3} mm. Hg. The heating rates were controlled to within ± 10%. Precision of the weight-loss measurements was ± 0.02 mg., and the temperature was measured to ± 0.5°C. Heating rates of 1, 2 and 4°C per minute between 25 and 620°C were used for the kinetic experiments. For the cycling experiments, the theoretical curves in Figure 7 were obtained by heating the polymer for the first time at a rate of 4°C/minute up to the temperatures indicated. The fractional weight remaining (W_r/W_i) was then calculated by assuming the initial fractional weight-loss to be constant. For these experiments, W/W_i was 0.11 ± 0.01.

RESULTS AND DISCUSSION

A. Kinetic Experiments

6. Data necessary for solving for E, n, and A were obtained from typical curves for Teflon 5 (Fig. 5) and Teflon 100 (Fig. 6). An IBM 7090 computer was used to solve the simultaneous equations, and the gauss reduction method (ref. (f)) was used to spot check the results. The calculated kinetic values are given in Table I for Teflon 5 and in Table II for Teflon 100.

7. That the kinetic values in Table I do not differ appreciably for various fractions of weight loss indicates that the rate of degradation of Teflon 5 does not change with degree of pyrolysis. These results agree with the following generally proposed mechanism (ref. (l)) of Teflon pyrolysis. Initiation occurs by random splitting of a C-C bond into a pair of free radicals. These radicals remain in the vicinity of the site where they are formed and depropagate by step-wise ejection of monomer molecules from the radical ends. Monomer then diffuses rapidly away from the reaction site in vacuum pyrolysis. The results also show that the rate of decomposition is independent of the molecular weight of the polymer.

8. Curves in Figure 6 and kinetic values in Table II indicate that there are at least two stages in the decomposition of Teflon 100 copolymer. The initial stage of decomposition suggests a lower stability of chain segments containing hexafluoropropylene units. Wall (ref. (k)) reported that a similar copolymer produced less light volatiles than pure Teflon; 75 to 84% as compared to about 95% for the latter. The main components of these volatiles were C_3F_6 and C_2F_6, C_3F_6 being more abundant in the early stages of pyrolysis. At 10% degradation, the light volatiles contained 85% C_3F_6 and 9% C_2F_4, whereas at 92% decomposition the volatiles contained 19% C_3F_6 and 68% C_2F_4.

B. Cycling Experiments

9. The average results of the cycling experiments are shown in Figure 7. The close agreement between the experimental points and the theoretical curve for Teflon indicates further that the rate of weight loss

does not change appreciably with degree of decomposition. For the early stages of degradation of the copolymer, the large deviations of the experimental points from the theoretical curve show a definite change in rate of weight loss with increasing decomposition. In fact, after the third cycle, W_r/W_i remained constant through two additional 500°C cycles. For the second stage of degradation, the deviations of the experimental values of W_r/W_i from the theoretical curve are not as great as they were for the first step. The theoretical curve for the second stage of decomposition was obtained by taking the amount of polymer remaining after the fifth cycle in the first stage as the initial weight (W_i).

CONCLUSIONS AND RECOMMENDATIONS

10. Either the kinetic or cycling experiment can be used to tell whether the rate of weight loss varies with extent of pyrolysis. The latter method is preferred for this purpose because it is much simpler. The kinetic method can then be used to obtain precise kinetic data at selected extents of pyrolysis.

11. The author recommends that these methods be applied to an investigation of the effect of the position of aromatic substituents on the thermal stability of model epoxide polymers. These polymers could be synthesized from resorcinol diglycidyl ether, hydroquinone diglycidyl ether, and catechol diglycidyl ether with o-, p, and m-phenylenediamines being used as coreactants.

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TABLE I

KINETIC VALUES FOR PYROLYSIS OF TEFLON 5 HOMOPOLYMER

W/W_i	E(kcal)	n	$A(1/min)10^{-20}$
0.1	77	1.00	3.7
0.2	78	1.00	4.3
0.3	77	1.00	3.7
0.4	77	0.99	3.7
0.5	76	1.02	4.8
0.6	78	1.00	3.8
0.7	78	1.01	3.7
0.8	76	1.01	3.8
0.9	77	1.07	4.8
Average	77.0	1.01	4.0
Madorsky (ref. (g))	80.5	1.00	2.8
Siegle (ref. (h))	83.0	1.00	27.0
Anderson (ref. (i))	75.0 ± 4	1.02 ± 0.07	-
Doyle (ref. (j))	67.0	-	-

NOTE: Each group of values for E, n, and A is the average of three determinations. Maximum average deviations were: E, ± 7%; n, ± 10%; and A, ± 20%.

TABLE II

KINETIC VALUES FOR PYROLYSIS OF TEFLON 100 COPOLYMER

W/W_i	E(kcal)	n	$A(1/min)10^{-13}$
0.1	34.8	0.93	0.0004
0.2	44.4	0.88	0.1
0.3	60.2	0.91	222.0
0.4	55.6	0.90	48.0
0.5	48.2	1.00	4.0
0.6	42.3	1.09	1.0
Average	48	0.95	46.0
Wall (ref. (k))	55	1.00	6.0

NOTE: Each group of values for E, n, and A is the average of three determinations. Maximum average deviations were: E, ± 5%; n, ± 10%; and A, ± 15%.

$$(1)\ \frac{dx}{dt} = k(a-x)^n;\ (2)\ \frac{dx}{(a-x)^n} = \frac{dw}{(w_i-w)^n};\ (3)\ k = A\exp\left(-\frac{E}{RT}\right).$$

BY COMBINING EQUATIONS (1), (2), AND (3) AND MULTIPLYING THE LEFT SIDE OF THE RESULTING EQUATION BY dT/dT AND TAKING THE LOGARITHM, WE OBTAIN:

$$(4)\ \mathrm{LOG}\left(\frac{dT}{dt}\cdot\frac{dw}{dT}\right) = \mathrm{LOG}\ A + n\mathrm{LOG}(W_i - W) - \frac{E}{2.3RT}$$

a = INITIAL NO. OF MOLES OF SAMPLE;
x = NO. OF MOLES LOST AT TEMP., T (°K);
w_i = INITIAL WEIGHT OF SAMPLE;
w = WEIGHT LOSS AT TEMP., T.

FIG. 1. DERIVATION OF THERMOGRAVIMETRIC RATE EQUATION

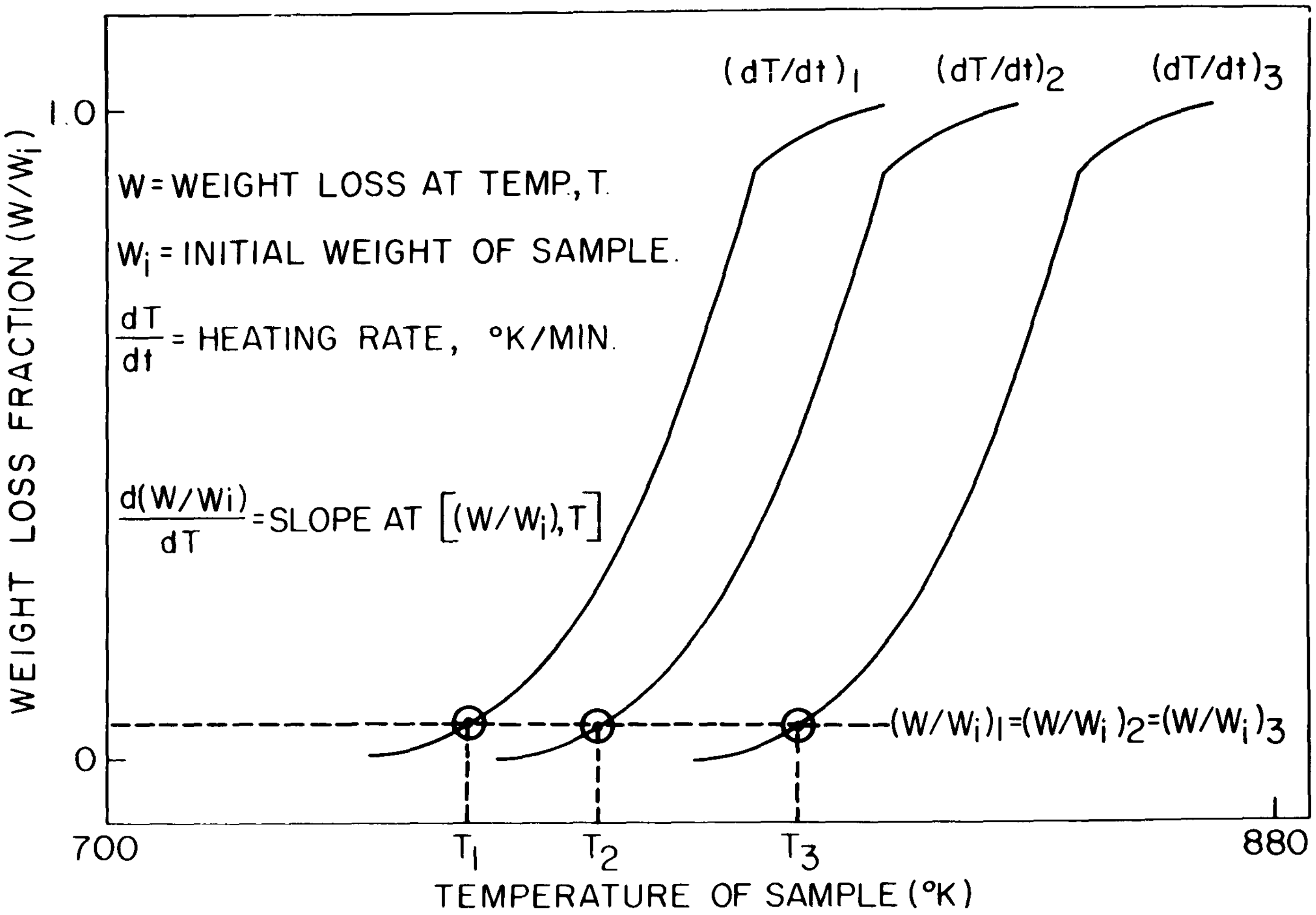
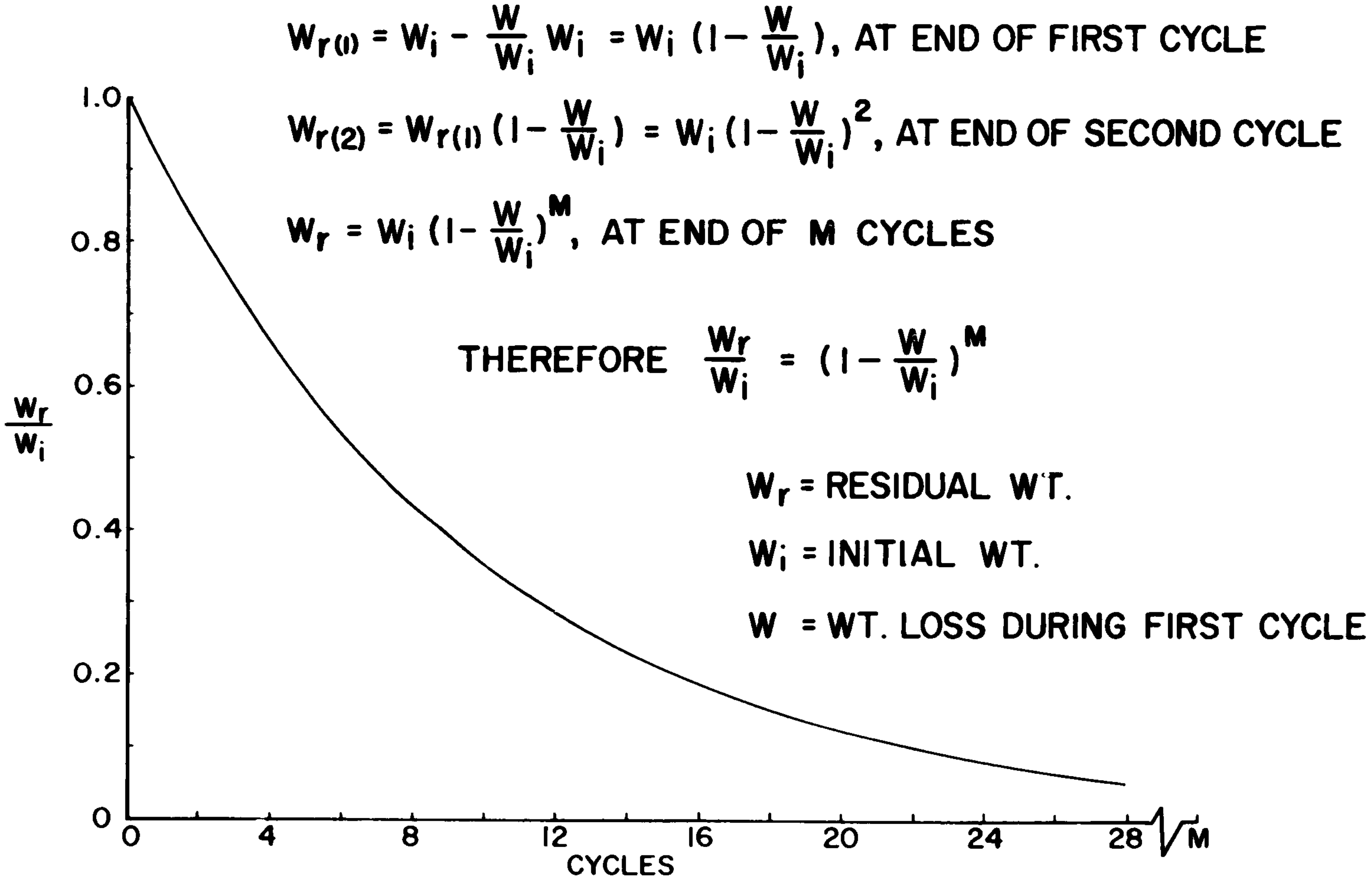


FIG. 2. HYPOTHETICAL THERMOGRAVIMETRY OF A SINGLE POLYMER



$$W_{r(1)} = W_i - \frac{W}{W_i} W_i = W_i \left(1 - \frac{W}{W_i}\right), \text{ AT END OF FIRST CYCLE}$$

$$W_{r(2)} = W_{r(1)} \left(1 - \frac{W}{W_i}\right) = W_i \left(1 - \frac{W}{W_i}\right)^2, \text{ AT END OF SECOND CYCLE}$$

$$W_r = W_i \left(1 - \frac{W}{W_i}\right)^M, \text{ AT END OF M CYCLES}$$

$$\text{THEREFORE } \frac{W_r}{W_i} = \left(1 - \frac{W}{W_i}\right)^M$$

W_r = RESIDUAL WT.

W_i = INITIAL WT.

W = WT. LOSS DURING FIRST CYCLE

FIG. 3. HYPOTHETICAL THERMOGRAVIMETRIC CYCLING CURVE

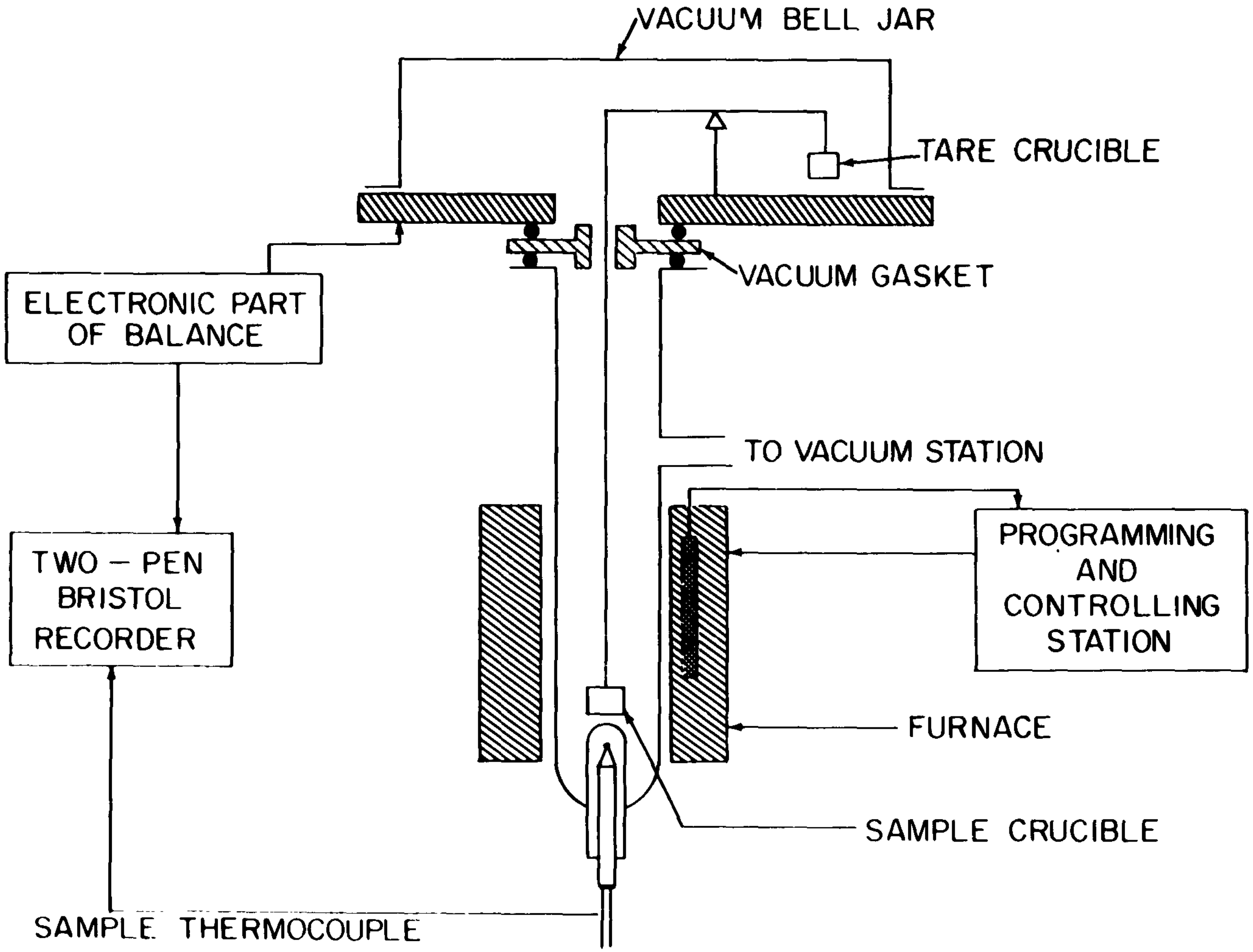


FIG. 4. THERMOGRAVIMETRIC EXPERIMENTAL ARRANGEMENT

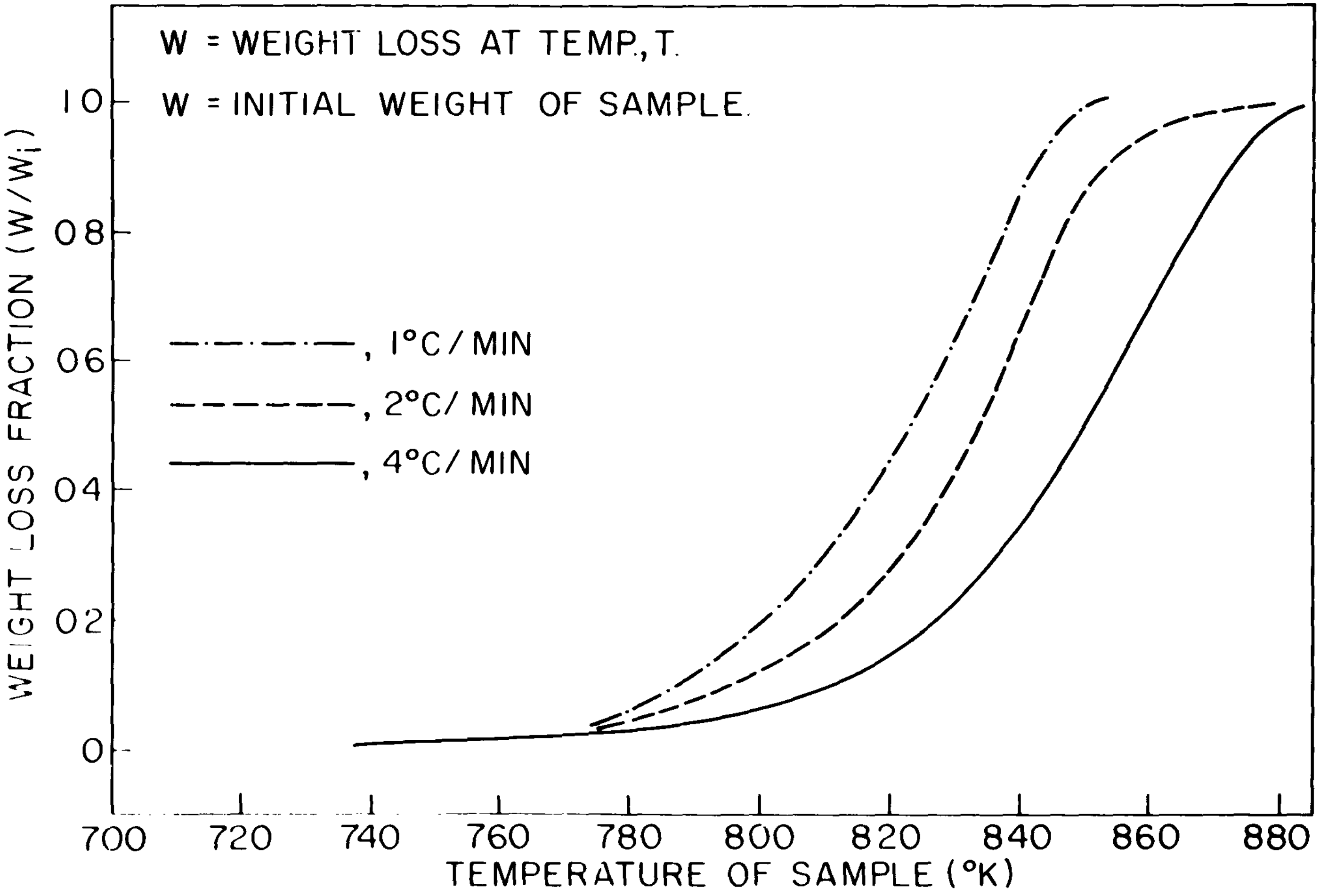


FIG. 5. THERMOGRAVIMETRY OF POLYTETRAFLUOROETHYLENE

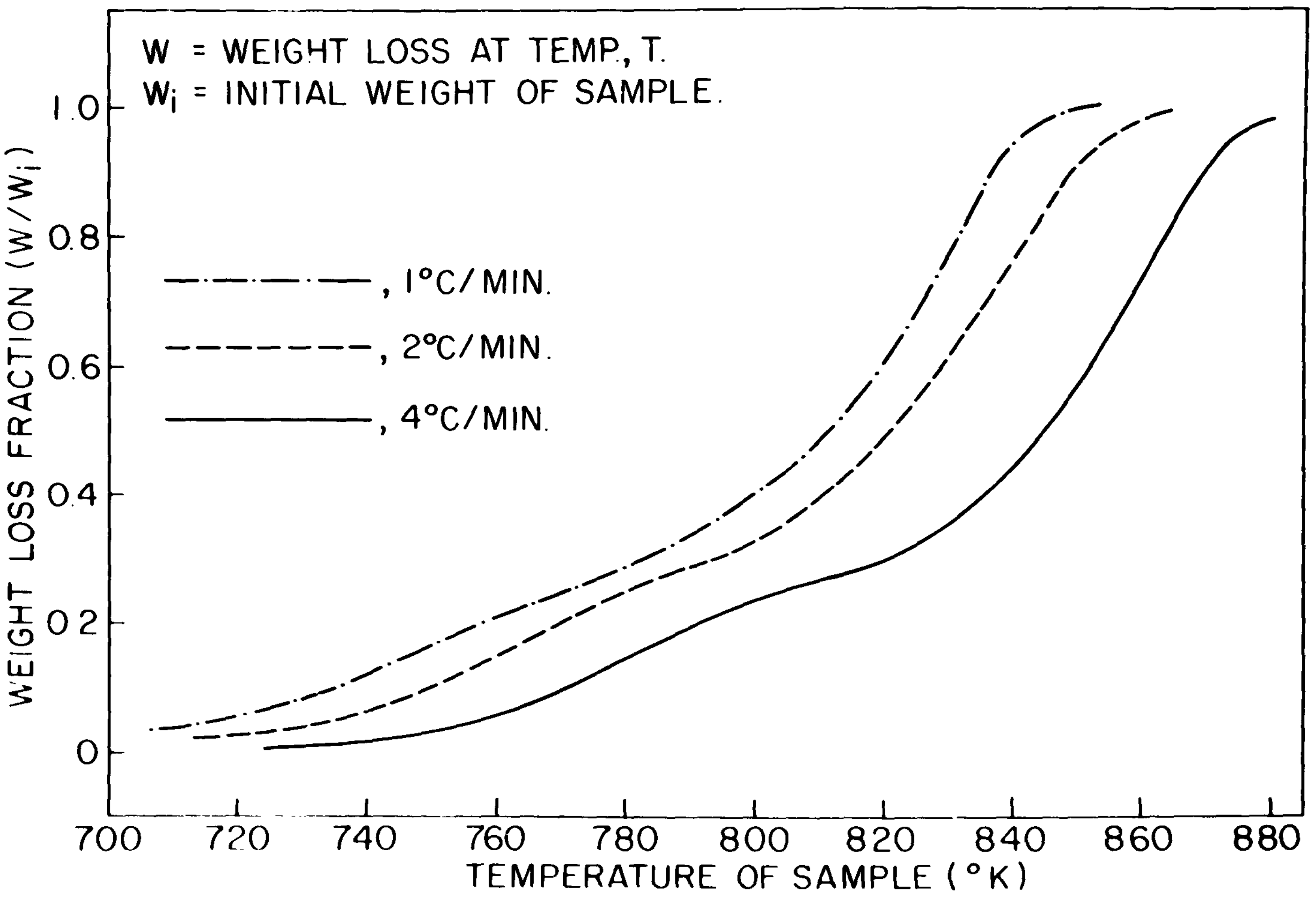


FIG. 6. THERMOGRAVIMETRY OF A COPOLYMER OF TETRAFLUOROETHYLENE AND HEXAFLUOROPROPYLENE

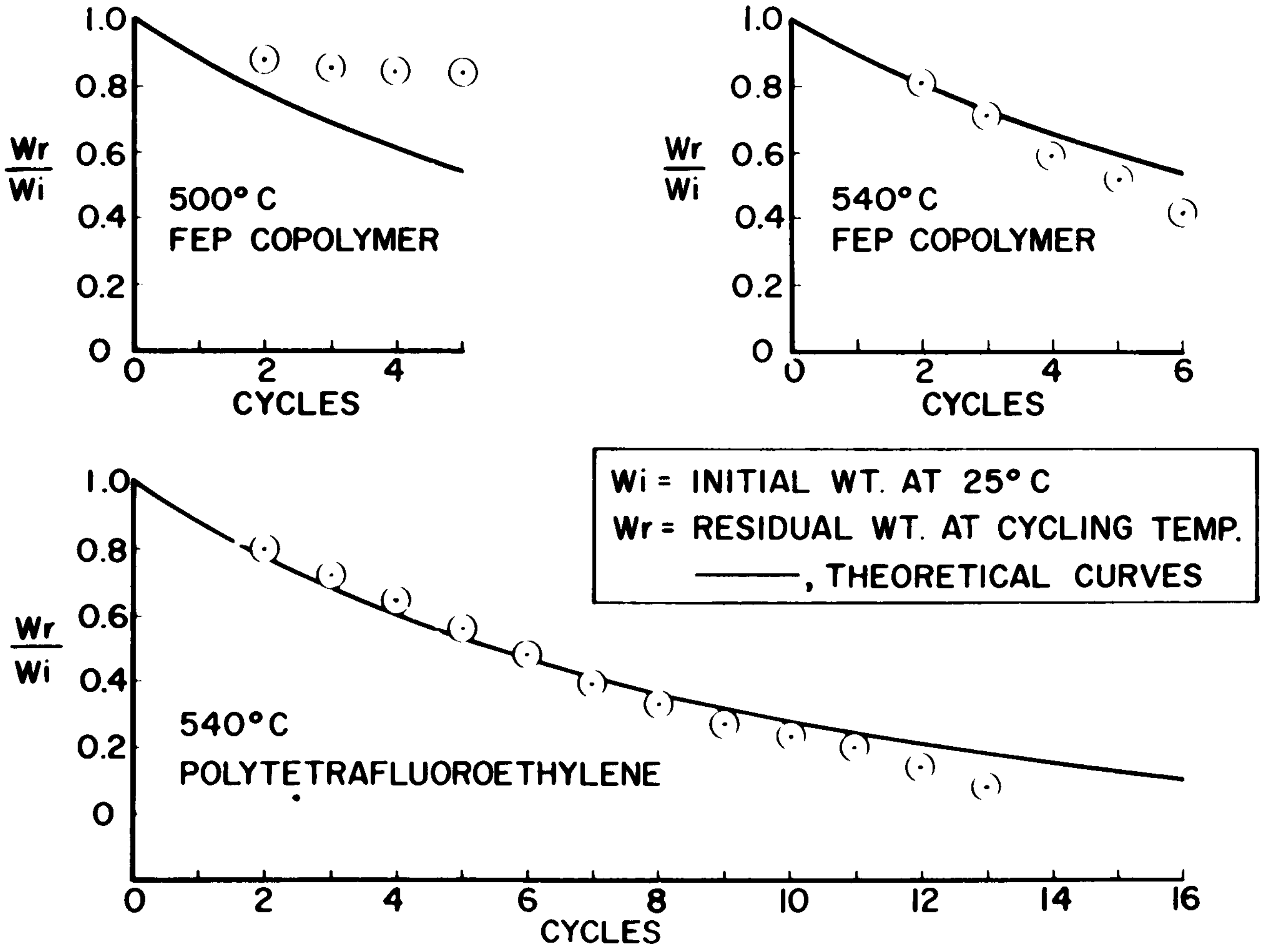


FIG. 7. THERMOGRAVIMETRIC CYCLING CURVES

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SUBJECT ANALYSIS OF REPORT

DESCRIPTORS	CODES	DESCRIPTORS	CODES	DESCRIPTORS	CODES
Thermogravimetric	THEG	Energy	ENER	Teflon	TEFL
Relationships	RELT	Decomposition	DECM	Copolymer	COPO
Pyrolysis	PYRL	Arrhenius	ARRH	Tetra	TERA
Polymers	POLY	Simultaneous	SIMT	Fluoro	FUOR
Methods	METD	Equations	EQUA	Ethylene	ETHY
Kinetic	KINE	Heating	HEAT	Hexa	HEXA
Technique	TECN	Rates	RATE	Propylene	PROY
Cycling	CYCE	Temperature	TEMP		
Variation	VART	Plastics	PLAS		
Weight	WEIG	Experiment	EXPE		
Loss	LOSS	Theory	THEY		
Activation	ACTV	Degradation	DEGR		

[illegible]

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NEW THERMOGRAVIMETRIC RELATIONSHIPS FOR STUDYING THE PYROLYSIS OF POLYMERS (U), by Hugh C. Anderson. 8 July 1963. 6p. charts. Task PR-6.

UNCLASSIFIED

Two thermogravimetric (TG) methods were developed to show whether rate of weight loss varies with extent of pyrolysis of a polymer. The first of these, a kinetic technique, involves obtaining the activation energy, the order of decomposition, and the Arrhenius pre-exponential factor by solving three simultaneous equations. The second method, which involves cycling the polymer between 25°C and a fixed higher temperature, is based on the compound interest law.

1. Plastics - Pyrolysis
2. Plastics - Thermogravimetric analysis
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