LOW TEMPERATURE ISOTHERMAL PYROLYSIS OF CELLULOSE

A. Broido and M. Weinstein*

Pacific Southwest Forest and Range Experiment Station
Forest Service, U.S. Department of Agriculture
Berkeley, California 94701 U.S.A.

ABSTRACT

By providing continuous weight measurement, thermogravimetry, even for isothermal experiments, offers a major advantage over the classical methods of determining weight-change curves in complex pyrolysis reactions. Thus, even minor weight changes, readily detectable on a continuous record, furnish clues concerning the reaction sequences and indicate conditions under which confirmatory experiments may be undertaken. Unfortunately, such perturbations are frequently ignored, being considered part of the "experimental error" which they often represent in the traditional experiments. This paper illustrates the utility of looking at the minor weight deviations, too large to be random experimental error, in a 1,000-hour isothermal pyrolysis experiment on high purity cellulose paper at 226°C. Resolution of the curve into the minimum number of consecutive and competing reactions required to fit within instrumental accuracy yields previously unrecognized characteristics of the pyrolysis behavior, applicable at other temperatures as well.

INTRODUCTION

Current attempts to determine an acceptable nomenclature in thermal analysis have not yet resulted in agreement on a definition for that most basic term--thermogravimetry (1). The most restricted definition of the term limits its use to techniques in which a thermobalance is "necessary"--excluding the use of a thermobalance in isothermal experiments which have been performed classically by a sequential process of heating for a fixed interval, then cooling and weighing. This classical procedure is performed in one of two ways: either (a) by repeated heating of the same sample or (b) by using a series of samples heated over different time intervals.

If only gross information is desired, or if the substance being analyzed undergoes a simple, well-defined reaction sequence, the only real advantage in tying up an expensive thermobalance for any length comes from the fact that the thermobalance, by eliminating the cooling and reheating steps in the first classical procedure, can supply an answer much sooner than can that procedure. By providing the information on a single sample, the

*Present address: Weizmann Institute of Science, Rehovot, Israel

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thermobalance can furnish the needed data with much less sample than is required for the second classical procedure.

However, by providing continuous weight measurement on a single sample, the thermobalance eliminates the small errors introduced in the first classical procedure as the result of additional sample handling, and in the second classical procedure as the result of sample inhomogeneity. Thus, when the material undergoes an unknown, complex sequence of reactions in which even small weight losses can be highly informative, the advantage of using the thermobalance instead of the classical isothermal procedures may be sufficiently great to qualify this use as one for which a thermobalance is "necessary".

This paper provides an illustration of the advantage of the use of the thermobalance in attempting to identify the complex reaction sequence occurring when high purity cellulose paper is pyrolyzed isothermally.

BACKGROUND

Because of its obvious pertinence to the well recognized problems of fire and air pollution, the thermal decomposition of cellulose has received considerable attention in recent years (2-4). Even when pure cellulose is pyrolyzed in an inert atmosphere, at least two competing sequences of reactions occur--in proportions dependent on such factors as purity of the sample (5) and its crystallinity (6). In different temperature ranges, various pyrolysis reactions predominate, and thus for a certain restricted set of conditions, simplified degradation schemes can adequately describe the pyrolysis behavior. However, the conditions amenable to relatively simple laboratory experimentation only remotely resemble those of real interest (e.g. conditions in a forest fire), and the simple models do not lend themselves to extrapolation beyond very narrow limits. What is needed, then, is a model sufficiently detailed to permit meaningful extrapolation to a wide variety of conditions.

The determination of kinetic parameters from weight change curves obtained on samples continuously heated through a programmed temperature regime takes advantage of the speed and convenience of such a procedure at the expense of the greater accuracy normally obtained in an isothermal experiment. However, for a reaction in which the reactants are "pre-mixed" (including all pyrolysis reactions), isothermal experiments cannot be carried out (except at a negligible rate at low [i.e., room] temperature) without going through a nonisothermal heating period during which the reaction behavior of the sample is ill-defined. To minimize those conflicting aspects of the pyrolysis behavior of cellulose which could be attributed to the rather long nonisothermal heating periods of earlier pyrolysis studies, Lipska and Parker (7) developed an apparatus for rapidly heating (heating time < 1 minute) a sample to an accurately controlled temperature and then rapidly returning the sample to room temperature for subsequent weighing (and further analysis). At each reaction temperature, then, a series of samples could be exposed

for progressively longer times to obtain a curve that relates weight decrease to time of exposure.

Lipska and Parker (7) used their apparatus to study the isothermal pyrolysis of cellulose in the range 250-300°C. For the present discussion, we chose their results at 250°C (Figure 1) for two reasons: First, their lowest temperature minimizes uncertainties due to reaction in the nonisothermal heating period. Second, for several measurements at a higher temperature, they first preheated their samples for 1.5 hours at 250°C, and those experiments provide a measure of the reproducibility of their techniques.

Since Lipska and Parker found an ultimate weight loss of 77% at 250°C, the ordinate in Figure 1 was computed as 100 (W-23)/77. The variation in the four points at 1.5 hours is about 1%, and all the other experimental points fall comfortably within 1% of a single straight line, corresponding to a single first order pyrolysis reaction. The only inconsistency in these data seems to be that the line does not extrapolate to 100% at zero time. In comparing their measurements at other temperatures, we note two additional anomalies which indicate that a single first-order reaction represents a questionable simplification: (a) an abrupt initial weight loss ranging from 2% at 250°C to 6.5% at 298°C and (b) a change in ultimate char ranging from about 23% at 250°C to only 16% at 298°C.

The initial check-out experiments of our thermogravimetry apparatus (8) provided us with a convenient opportunity to conduct a long isothermal experiment on pure cellulose paper. Therefore, we decided to conduct this experiment at a temperature of 225°C, for which weight loss would be negligible even during our much longer heat-up time (15-30 minutes). The initial results were so provocative that we decided to let the experiment continue while we turned our efforts to other problems not requiring the use of this apparatus. Before terminating this experiment, then, we managed to obtain a pyrolysis curve of 1,000 hour (nearly 6 week) duration. As will be seen later, there is reason to wish the experiment had been continued even longer. However, in this paper we wish to focus particular attention on the early portion of the curve.

APPARATUS

Experimental weight loss data

The thermogravimetry apparatus is illustrated schematically in Figure 2. The output of the Cahn "RG" electrobalance was recorded by a Varian Model G14 millivolt recorder.[1] The cellulose sample, about 3x5 cm in cross section and weighing about 90 mg, was cut from Whatman #541 "ashless" filter paper (ash content = 0.008%) and suspended from the balance beam by hooking a nichrome

[1]Brand names and commercial products or enterprises are mentioned solely for information. No endorsement by the U.S. Department of Agriculture is implied.

hang-down wire through a small hole near the top of the sample. The system was evacuated to 10^{-3} - 10^{-4} mm Hg overnight, then heated to 226°C as measured by a 20-gauge chromel-alumel thermocouple mounted adjacent to the sample. Prior measurements indicated that the sample was safely within a region of the furnace in which the temperature was uniform to ± 1°C, and frequent measurements during the run (at the fixed thermocouple location) indicated a temperature constant to well within ± 1°C.

Even after overnight pumping at room temperature, cellulose samples lose additional extraneous volatiles (e.g. water) on gentle heating (8). In addition, programmed heating with inert samples attached to the balance indicate a significant zero drift during the heating period. On the other hand, once isothermal conditions are attained, the weight of inert samples remains constant to ± .01 mg. Since repeated programmed heating at 5°C/min from room temperature indicates a negligible weight change in pure cellulose up to temperatures of 250°C, the "true" original weight of the sample could safely be considered the weight recorded when the temperature first reached 226°C.

Empirical fitting of weight loss curve:

From prior information, the simplest reaction scheme (minimum number of reactions) was postulated and the mathematical expressions for this scheme programmed on an Electronic Associates, Inc. Pace TR 20 analog computer. With the experimental curve plotted on the oscilloscope face of the Repetitive Operation Display Unit, the coefficient attenuators representing the rate constants and normalized molecular weights for each reaction step could be rapidly and continuously varied to modify the analog output until it matched the experimental curve. Agreement between the computed and experimental curves could be further refined by the slower process of displaying the analog output on a Moseley 7030A X-Y recorder. When the uncertainty in the analog output (∿1%) was too large for the problem, a digital computer was used to obtain an exact numerical solution. The "good fit" parameters from the analog were fed into the digital computer to compare calculated and experimental results. Whenever any step in the curve fitting procedure could not provide a sufficiently close fit to the experimental curve, the reaction scheme was modified by including an additional reaction step and the procedure repeated. The procedure, then, provided the minimum number of reaction steps required for any predetermined degree of fit and the sets of values of rate constants and normalized molecular weights required for the particular scheme.

RESULTS AND DISCUSSION

To illustrate the results which would have been obtained had this experiment been conducted by the classical procedure, the continuous weight curve was read at a number of discrete times and the results plotted in Figure 3. Even at 1,000 hours, the sample was still losing weight, and it was necessary to extrapolate to an ultimate weight loss estimate of about 72%. Thus, the ordinate in Figure 3 was computed as 100 (W-28)/72. As in

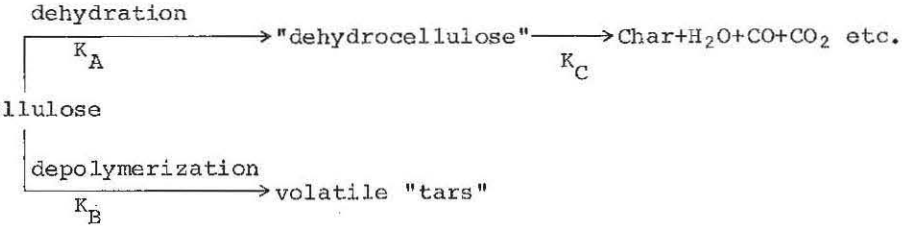
the results reported by Lipska and Parker (7), the points seem to fall well on a single straight line.

One "improvement" in Figure 3 over Figure 1 is readily apparent. Since the weight loss due to extraneous volatiles (occurring principally near 100°C) is eliminated when the weight at temperature is taken as 100%, the curve in Figure 3 does pass through the origin. Elsewhere, as was true in Figure 1, the data seem to fit within about 1%.

However, these data were obtained from a continuous curve obtained on a single sample kept continuously at the reaction temperature. With a 10 mg range as full scale on the recorder, the data trace can be read to 0.01 mg (for a 90 mg sample, then, to about 0.01%). As the pen moves down the chart, non-linearity of the recorder and chart paper introduce complications. As the sample loses sufficient weight that it becomes necessary to change the Cahn "Mass Dial" setting, additional and larger errors are introduced. Still, we estimate that over the entire weight range of the experiment, the relative error is less than 0.3%, and for small weight losses perhaps an order of magnitude better. Thus, agreement to 1% can easily mask some highly significant features of the curve.

The entire experimental curve is illustrated in Figure 4 and the first 100 hours of the curve are redrawn on an expanded scale in Figure 5. It is readily apparent that for the first 24 hours or so the curve is convex, i.e., the weight loss was accelerating. Subsequently the curve becomes concave, so that while, overall, it roughly fits the linear approximation of Figure 3, the deviations are clearly outside the experimental uncertainty.

Kilzer and Broido (9) had previously proposed a minimum pyrolysis scheme as



Such a scheme is shown as curve S in Figures 4 and 5 with all reactions first order and with parameter values as follows:

$K_B = 1.54 \times 10^{-3}$/hour

$K_A = 3.10 \times 10^{-3}$/hour

$K_C = 1.88 \times 10^{-3}$/hour

normalized molecular weight of cellulose = 1

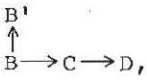
normalized molecular weight of dehydrocellulose = .89
(representing loss of one H_2O per anhydroglucose monomer)

normalized molecular weight of char = .355
(i.e., $W_\infty = .355\ K_A/(K_A + K_B)$)

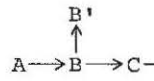
Again curve S fits the experimental data with 1%. Further, the value for K_B is consistent with the value $3 \pm 1 \times 10^{-5}$/min which may be computed for K_B at 226°C from the activation energy (54.9 kcal/mole) and pre-exponential factor (3.15×10^{19}/min) obtained by Broido and Weinstein (8) at higher temperatures using ammonia-swelled cellulose. Nevertheless, this computed curve also lacks some of the characteristic features of the experimental curve.

In particular, the initial "incubation" period, if real, requires one or more precursor reactions with essentially no weight loss preceding the weight loss reactions. If such a reaction does in fact occur, it should be detectable by some measurement other than weight loss. For example, one possible reaction is that leading to the sharp drop in length of the cellulose molecule (degree of polymerization or DP) reported to occur early in the pyrolysis of cellulose. Measurements of the DP of cellulose were undertaken (10) and confirmed the fact that the sharp drop in DP preceded any detectable weight loss. Results of additional experiments, still in the preliminary stage, suggest that a carbonyl peak in the infrared spectrum of cellulose appears early in the pyrolysis sequence; however, it is possible that such results are simply another measure of the end groups produced in the shortening of the cellulose molecule and are not evidence of a subsequent reaction affecting the internal monomer units.

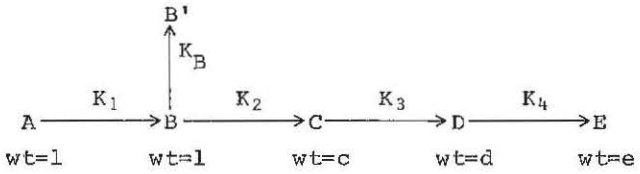
If, then, the original reaction scheme is diagramed as



the introduction of the "precursor" reaction changes the scheme to



In fact, to fit the experimental data within the estimated experimental error, one additional step is needed, thus:



Unfortunately, with 8 parameters available (5 rate constants and 3 effective molecular weights), it would be somewhat surprising if only a single solution were found, and other data then must be invoked to confirm or exclude any particular solution. To date, two solutions, each deviating by less than ± 0.25 mg from the experimental curve (a deviation too small to show up in Figure 4), have been found.

The first solution (Curve 1 in Figure 5) has the following values:

$K_B = 1.20 \times 10^{-3}$/hour
$K_1 = 5.50 \times 10^{-2}$/hour
$K_2 = 3.25 \times 10^{-2}$/hour
$K_3 = 9.20 \times 10^{-3}$/hour
$K_4 = 2.95 \times 10^{-3}$/hour
$c = .893$
$d = .830$
$e = .296$

Here, the value of c corresponds to the loss of 1 molecule of water per cellulose monomer, d corresponds to the loss of an additional water molecule for every 2 monomer units and e corresponds almost exactly to a 4-carbon residue per monomer.

This solution is appealing for a number of reasons. The consistencies with other data in the early portion of the curve have already been discussed. Tang and Bacon (11) have previously obtained data which led them to postulate that, in the carbonization of cellulose fibers, each monomer unit yields a 4-carbon residue which serves as a "building-block" for repolymerization into a "carbon polymer". Houminer and Patai (12), in studying the thermal decomposition of specifically-labelled D-glucose, found that "the volatile fragments are formed preferentially with the involvement of C-1 and C-2". Pending confirmation of these results with specifically-labelled cellulose, their findings, too, imply a 4-carbon C-3 to C-6 residue. Finally, the proposed structure of "dehydrocellulose" does leave the C-3 position of one anhydroglucose ring conveniently close to the C-6 position of an adjoining molecule. Consequently, a direct sequence of reactions can produce a graphite structure without requiring a breakdown to small 4-carbon units which subsequently recombine.

On the other hand, one disturbing aspect to this solution is the implication that even at 226°C a somewhat longer pyrolysis will yield a pure carbon residue. Normally, carbonization must be carried out at much higher temperatures to remove the last fractions of hydrogen and oxygen. Coals which presumably have been formed at relatively low temperature over many thousands of years still hold appreciable amounts of the other elements. Thus, it would be most surprising if pyrolysis at 226°C for a year or less would, in fact, yield a relatively pure graphite residue.

The second solution found to date (Curve 2 in Figure 5) has the following values:

$K_B = 1.58 \times 10^{-3}$/hour
$K_1 = 0.156$/hour
$K_2 = 1.04 \times 10^{-2}$/hour
$K_3 = 4.44 \times 10^{-3}$/hour
$K_4 = 5.90 \times 10^{-3}$/hour.
$c = .890$
$d = .840$
$e = .355$

Here c and d are essentially the same as in the first solution. The value of e corresponds reasonably well to a $C_4H_2O_{.5}$ residue, with a carbon content of 83%--in good agreement with that usually found in low temperature chars.

However, as with the first solution, this second solution requires that only relatively little additional weight loss would occur on additional heating of the residue. In fact, on termination of the run, the residue was heated to 370°C for an additional 2 hours and lost another 35% of its weight in the process. For values of e approaching those in the above two solutions, this loss implies a large fraction of the sample (as much as 40%) reacting by the depolymerization process. Such a large K_B/K_2 ratio would be rather surprising when the combustion behavior at these low temperatures is considered. In any case, the search for additional solutions is continuing, and additional experiments to clarify the situation are being planned.

SUMMARY

Classical isothermal pyrolysis experiments provide data which, while adequately describing cellulose pyrolysis behavior under the restricted set of conditions of the experiment, do not permit extrapolation to other, quite different, conditions. For continuous thermobalance measurements on a cellulose sample kept at 226°C for 1,000 hours, a relatively simple pyrolysis model agrees with the experimental data within 1% over the entire range, but this agreement is significantly outside the experimental error in the measurements. The more complex model which fits the data within an experimental error of 0.2 - 0.3% does not yield a unique solution, but does provide clues to other experiments. The "incubation" period at the start of the experiment implied precursor reactions involving little or no weight loss, and such reactions have now been confirmed. The ultimate development of a completely consistent model should resolve the many apparently conflicting results observed through the years and permit meaningful extrapolations to more severe conditions.

ACKNOWLEDGMENTS

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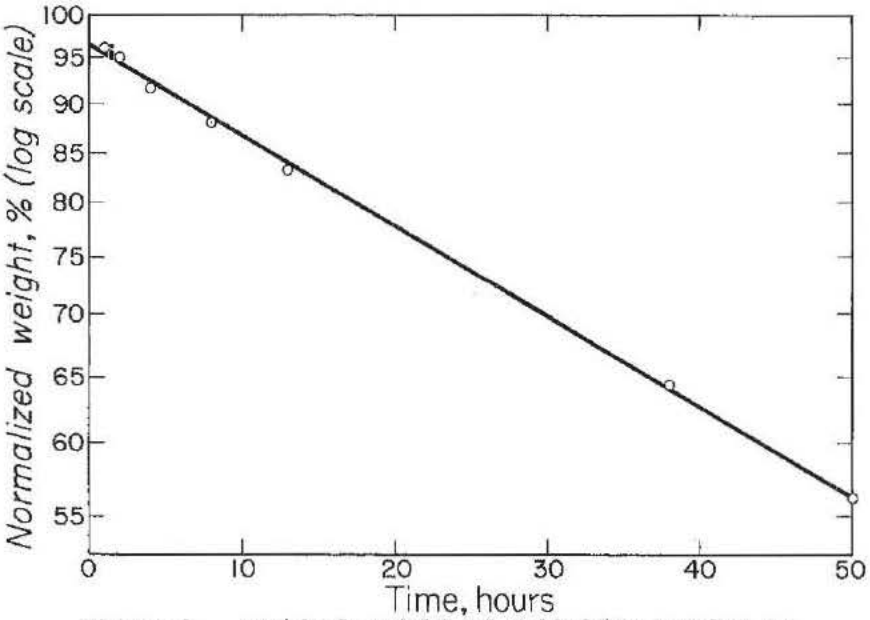

Figure 1. Residual weight of cellulose samples vs. time at 250°C [from Lipska and Parker (7)]. Circled points represent their values tabulated for 250°C; the four uncircled points are their "preheated" samples.

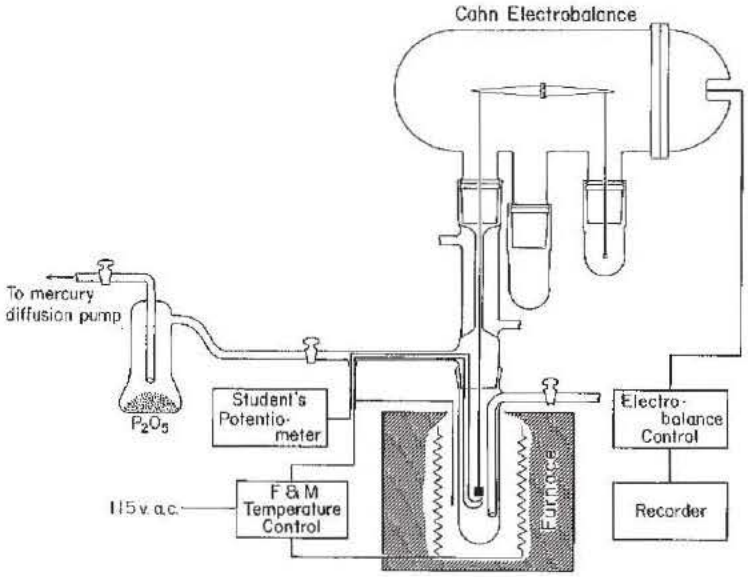

Figure 2. Schematic of thermogravimetric analysis apparatus.

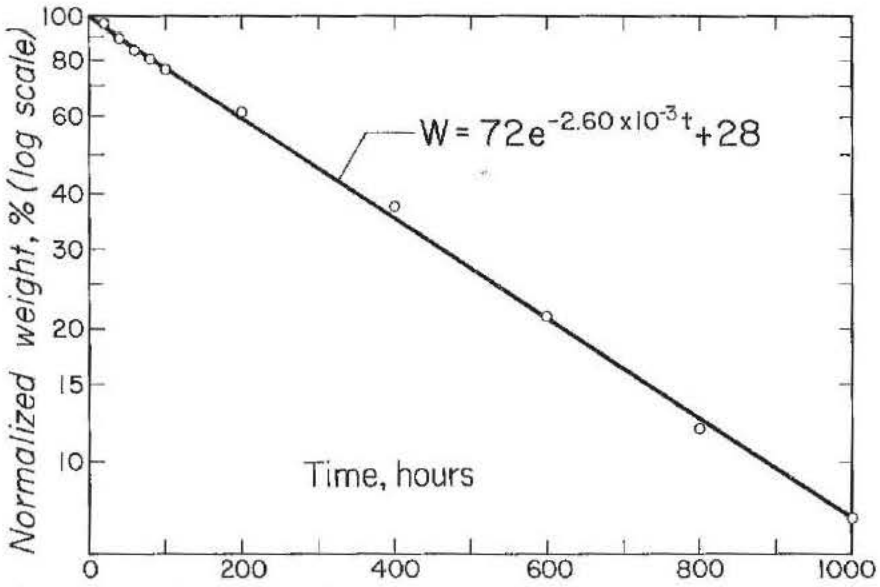

Figure 3. Discrete values of weight vs. time at 226°C (from continuous thermobalance recording).

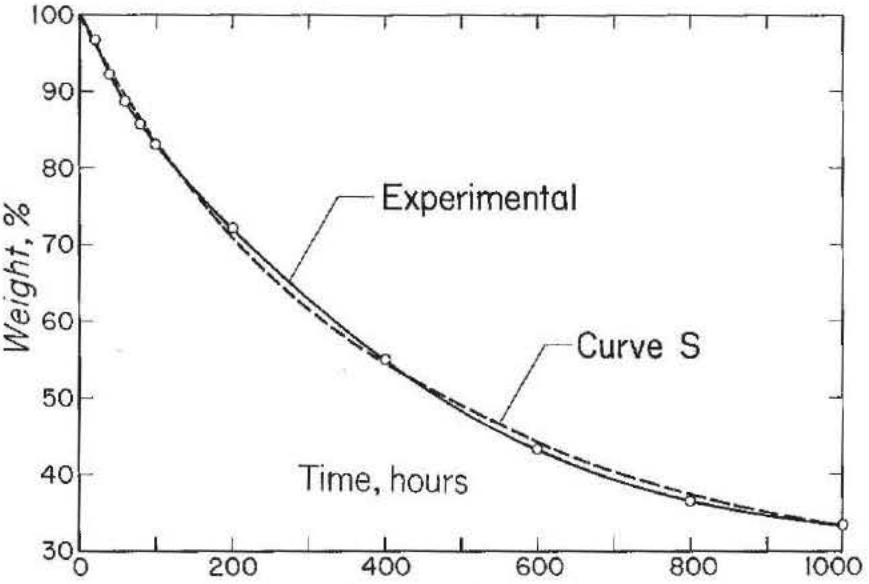

Figure 4. Residual weight of cellulose sample vs. time at 226°C. Comparison of experimental curve with simple mathematical model.

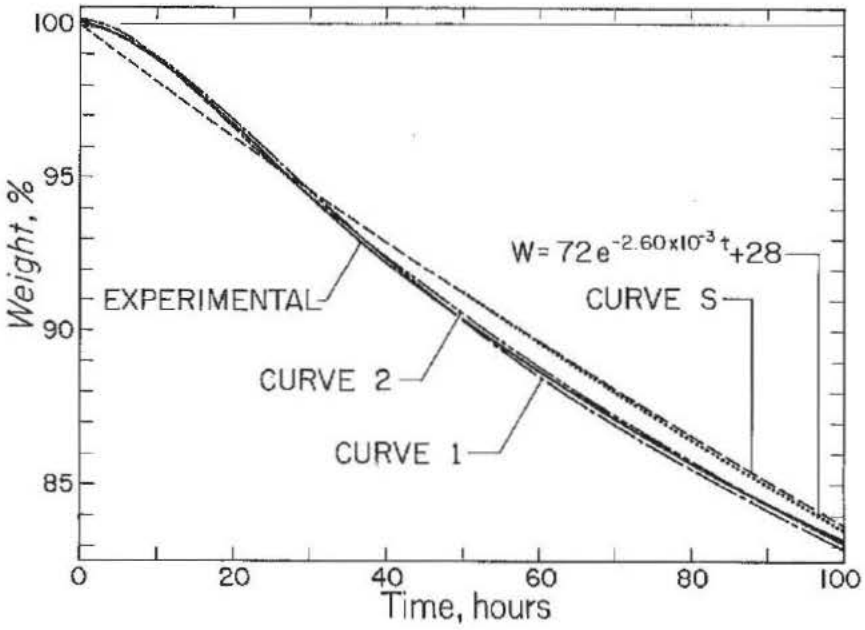

Figure 5. Expanded scale of first 100 hours of experimental curve in Figure 4. Comparison with four mathematical models.