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LUMPED PARAMETER EQUATION AND THERMOANALYTICAL CURVES

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ABSTRACT

The importance of knowing either an approximate value of the activation energy or the reaction mechanism prior to the analysis of DSC curves using the relation

$$\ln g(\alpha) - \ln p(x) = \ln \frac{ZE}{\beta R}$$

is emphasised on the basis of the results obtained for the decomposition of sodium bicarbonate. The iteration of activation energy in the neighbourhood of an approximate value determined independent of the reaction mechanism eliminates the necessity to carry out a separate isothermal experiment to determine the reaction mechanism. A computer program suitable for the purpose is presented. Comparison of theoretical curves based on the above equation, with experimental α vs. T curves, shows good agreement for α values greater than 0.1. The conclusions, although derived from DSC curves, are general in nature since the treatment is based on α vs. T curves.

INTRODUCTION

The last two decades of progress in thermal analysis witnessed an increasing use of these techniques for the study of the kinetics of solid state reactions. Progress in this direction was, however, hampered by the ambiguity of results obtained due to the oversimplification of mathematical derivations and imprecise definition of experimental conditions. The application of one of the most general methods for DSC curves is considered in this paper. The results obtained are general in nature and hence are worthy of consideration in the treatment of other thermoanalytical curves.

The basic expression for the integral methods of analysis of thermoanalytical curves, proposed by Doyle [1], is given by

$$g(\alpha) = \frac{ZE}{\beta R} p(x) \tag{1}$$

where $g(\alpha)$ is a function of the fraction decomposed, α, and $p(x)$ is a function of $x = E/RT$. Z, E, R, β and T is the pre-exponential factor of the Arrhenius equation, activation energy, gas constant, heating rate and temperature, respectively. Zsako [2] and Skvara and Satava [3] used the above equation in logarithmic form expressed as

$$\ln g(\alpha) - \ln p(x) = \ln \frac{ZE}{\beta R} \tag{2}$$

The right-hand side of eqn. (2) is constant for a given reaction at a constant heating rate, and hence it has been pointed out that plots of ln g(α) vs. T and ln p(x) vs. T should be identical in shape, provided the mechanism of the reaction and the activation energy assumed for calculating g(α) and p(x), respectively, are correct. All three terms in eqn. (2) are unknown for a given system. The kinetic parameters Z and E are "lumped" together to form an ill-defined constant difference between two uncertain quantities. Such a formulation is likely to be ambiguous. Several authors [4—6] have recently pointed out that variations of eqn. (2) do not yield a unique set of values for the kinetic parameters, and have suggested that the results from TG measurements should be supplemented by at least one isothermal experiment to enable determination of the reaction mechanism. However, these earlier treatments were based on simplified expressions for p(x) whereby the function is treated as linearly dependent on $1/T$. Analysis of DSC curves for the decomposition of sodium bicarbonate, without resorting to the assumption of linear dependence of p(x) upon $1/T$, is presented in this paper. Instead of determining the reaction mechanism from a supplementary isothermal experiment, unambiguous values of kinetic parameters have been obtained from TG curves alone by calculating an approximate value of the activation energy, prior to the application of eqn. (2).

Coats and Redfern [7] and Piloyan and Novikova [8] suggested a simple method for the determination of the activation energy, independent of reaction mechanism, from TG curves. This method was utilised for obtaining the activation energy from DSC curves. The approximate value thus obtained was further refined by iteration with eqn. (2) to obtain better estimates of the activation energy, pre-exponential factor and the reaction mechanism, as illustrated in this paper.

EXPERIMENTAL

DSC curves were recorded with a Perkin-Elmer model DSC-1B differential scanning calorimeter. The apparatus was calibrated with standard samples of indium, tin and lead supplied with the unit. Sodium bicarbonate (B.D.H., AnalaR) was sieved, and DSC curves were obtained with 9.5 ± 0.1 mg of —150, +240 mesh samples at heating rates of 2.1, 4.2, 8.3 and 16.7°C min^{-1}.

RESULTS AND DISCUSSION

Since analysis of the data by eqn. (2) involves an iterative procedure, a computer program was written in CERN FORTRAN for use with a BESM-6 computer to facilitate the application of the expression to DSC curves. The

TABLE 1

Models of solid state reactions used for analysing DSC curves for the decomposition of sodium bicarbonate

Kinetic model	$f(\alpha)$	$kt = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = g(\alpha)$
1. Power law	$\frac{1}{r}\alpha^{1-r}$	$\alpha^r, (r = \frac{1}{4}, \frac{1}{3}, \frac{1}{2}, 1, \frac{3}{2} \text{ or } 2)$
2. Nucleation and nuclei growth:		
(a) random nucleation (Mampel, unimolecular law)	$1-\alpha$	$-\ln(1-\alpha)$
(b) Avrami—Erofeev nuclei growth	$\frac{1}{r}(1-\alpha)[-\ln(1-\alpha)]^{1-r}$	$[-\ln(1-\alpha)]^r, (r = \frac{1}{4}, \frac{1}{3}, \frac{3}{2} \text{ or } \frac{2}{3})$
3. Diffusion-controlled:		
(a) Jander, three-dimensional diffusion	$(1-\alpha)^{1/3}[(1-\alpha)^{-1/3}-1]^{-1}$	$\frac{3}{2}[1-(1-\alpha)^{1/3}]^2$
(b) Anti-Jander, three-dimensional counter-diffusion	$(1+\alpha)^{1/3}[1-(1+\alpha)^{-1/3}]^{-1}$	$\frac{3}{2}[(1+\alpha)^{1/3}-1]^2$
(c) Brounshtein—Ginstling, three-dimensional diffusion	$[(1-\alpha)^{-1/3}-1]^{-1}$	$\frac{3}{2}[1-\frac{2}{3}\alpha-(1-\alpha)^{2/3}]$
(d) Valensi, two-dimensional diffusion	$[-\ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha)+\alpha$
4. Phase boundary:		
(a) contracting sphere	$(1-\alpha)^{2/3}$	$3[1-(1-\alpha)^{1/3}]$
(b) contracting cylinder	$(1-\alpha)^{1/2}$	$2[1-(1-\alpha)^{1/2}]$
5. Reaction order	$\frac{1}{r}(1-\alpha)^{1-r}$	$1-(1-\alpha)^r, (r = 2, 3 \text{ or } 4)$

fraction decomposed, α, was calculated from

$$\alpha = \frac{a}{A} \tag{3}$$

where A is the total area enclosed by the DSC peak and its baseline and a is the area swept at time t (or temperature, T). The trapezoidal rule was used to calculate A and a from the input values of $\mathrm{d}H/\mathrm{d}t$ and t. The α vs. T data thus obtained were converted to $\ln g(\alpha)$ vs. T for various models listed in Table 1. Values of $\ln g(\alpha)$ were calculated only for α above 0.08, since the values below this were not reliable.

Three values at intervals of 1000 cal mole^{-1} were used on either side of the approximate value of the activation energy to facilitate iteration with respect to E. A modified version of the routine EXPINT, for the evaluation of the exponential integral [9,10] (available in the computer library) was used to calculate $\ln p(x)$ vs. T data. The standard deviation, σ, of the difference, D, equal to $\ln g(\alpha) - \ln p(x)$ for temperatures in the reaction interval was calculated for each pair of $p(x)$ and $g(\alpha)$ representing a kinetic model. Since D is a constant for the correct choice of activation energy and reaction mechanism, the activation energy, E', corresponding to the minimum standard deviation was selected and a series of four values at intervals of 100 cal mole^{-1} was generated on either side of E'. The iteration was then repeated. When the minimum σ corresponded to an extreme value in the array of E considered, the array was further expanded by including values at the desired interval and the calculations were repeated. The value of E and the reaction mechanism corresponding to the minimum standard deviation as

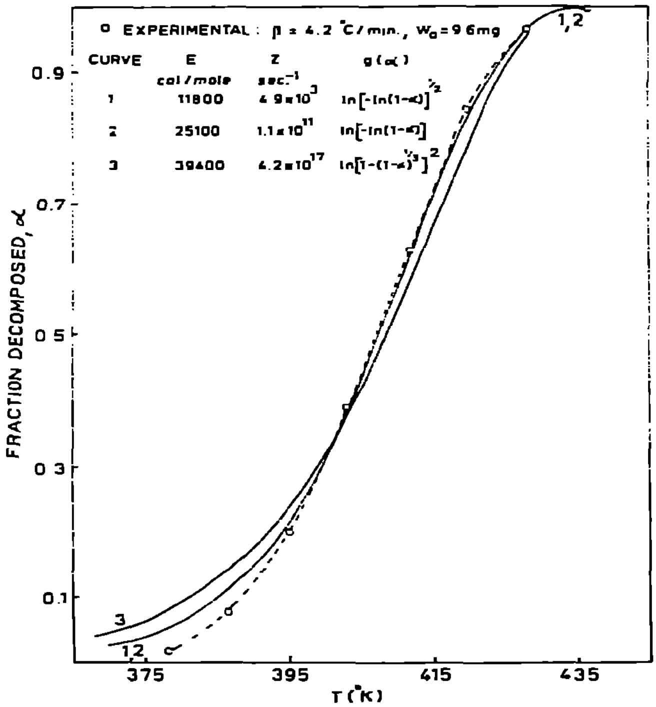


Fig. 1. Theoretical vs. experimental curves for the decomposition of sodium bicarbonate.

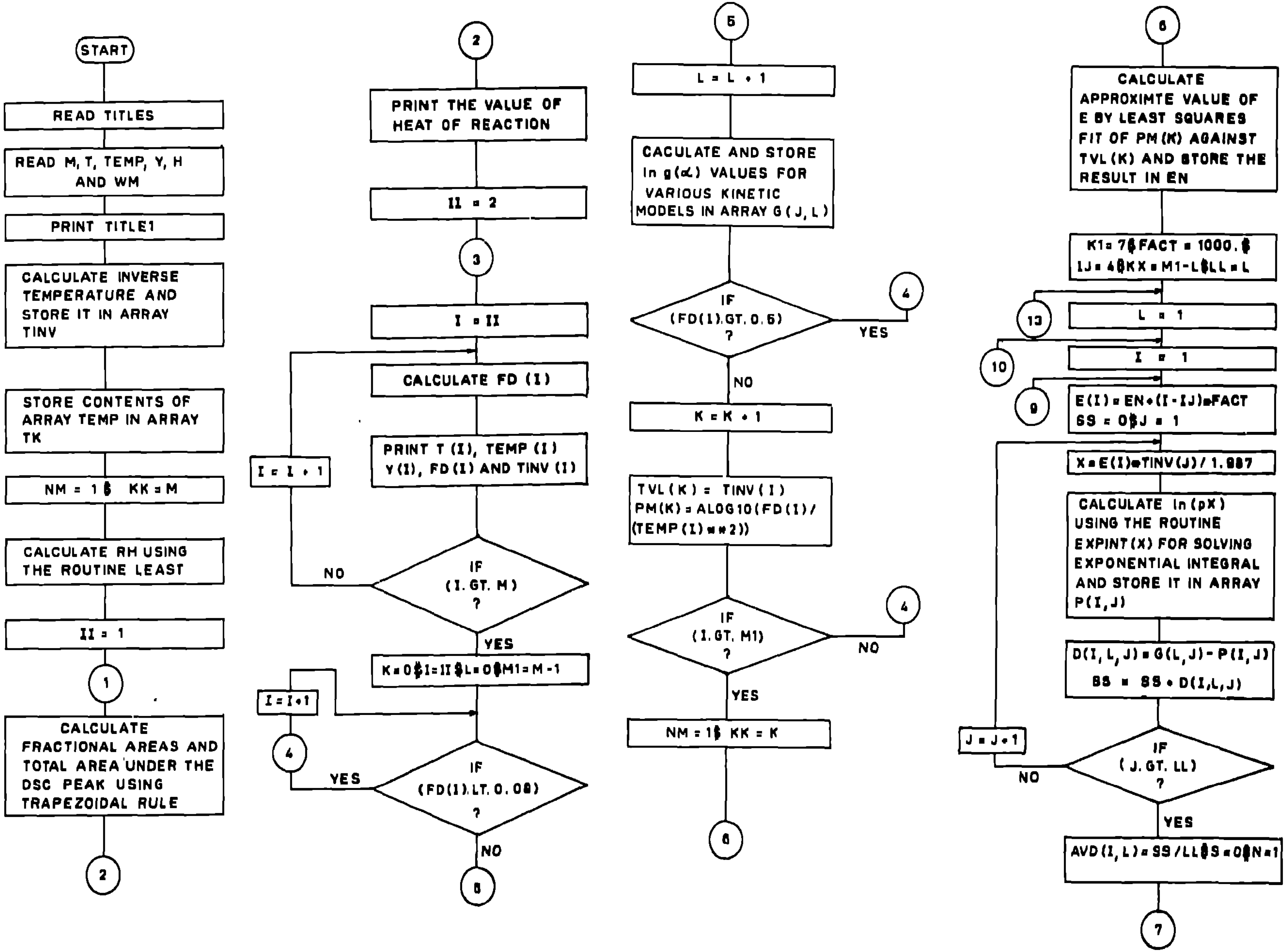
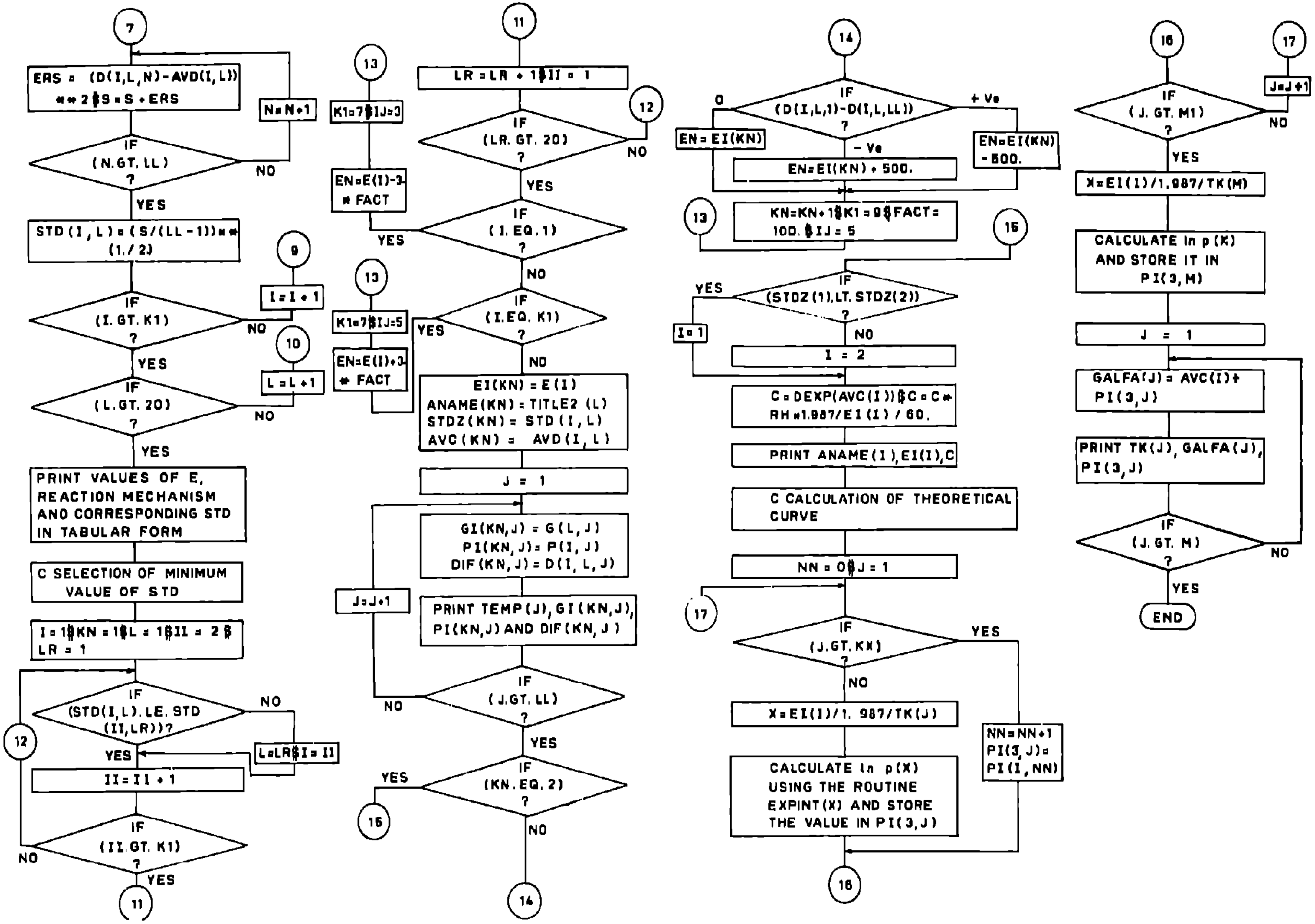

START
READ TITLES
READ M, T, TEMP, Y, H AND WM
PRINT TITLE1
CALCULATE INVERSE TEMPERATURE AND STORE IT IN ARRAY TINV
STORE CONTENTS OF ARRAY TEMP IN ARRAY TK
NM = 1$ KK = M
CALCULATE RH USING THE ROUTINE LEAST
II = 1
1
CALCULATE FRACTIONAL AREAS AND TOTAL AREA UNDER THE DSC PEAK USING TRAPEZOIDAL RULE
2
2
PRINT THE VALUE OF HEAT OF REACTION
II = 2
3
I = II
CALCULATE FD (I)
PRINT T (I), TEMP (I) Y(I), FD(I) AND TINV (I)
I = I + 1
NO
IF (I. GT. M) ?
YES
K=0$I=II$L=0$M1=M-1
I=I+1
4
YES
IF (FD(1).LT. 0.08) ?
NO
5
5
L = L + 1
CACULATE AND STORE ln g(α) VALUES FOR VARIOUS KINETIC MODELS IN ARRAY G(J, L)
IF (FD(1).GT. 0.6) ?
YES
4
NO
K = K + 1
TVL(K) = TINV(I)
PM(K) = ALOG10(FD(I)/(TEMP(I)**2))
IF (I. GT. M1) ?
NO
4
YES
NM = 1$ KK = K
6
6
CALCULATE APPROXIMTE VALUE OF E BY LEAST SQUARES FIT OF PM(K) AGAINST TVL(K) AND STORE THE RESULT IN EN
K1= 7$FACT = 1000.$
IJ= 4$KX = M1-L$LL = L
13
L = 1
10
I = 1
9
E(I) = EN+(I-IJ)*FACT
SS = 0$J = 1
X = E(I)*TINV(J)/ 1.987
CALCULATE ln(pX) USING THE ROUTINE EXPINT(X) FOR SOLVING EXPONENTIAL INTEGRAL AND STORE IT IN ARRAY P(I,J)
D(I,L,J) = G(L,J) - P(I,J)
SS = SS + D(I,L,J)
J = J+1
NO
IF (J. GT. LL) ?
YES
AVD(I,L) = SS/LL$S = 0$N = 1
7

Fig. 2, continued)



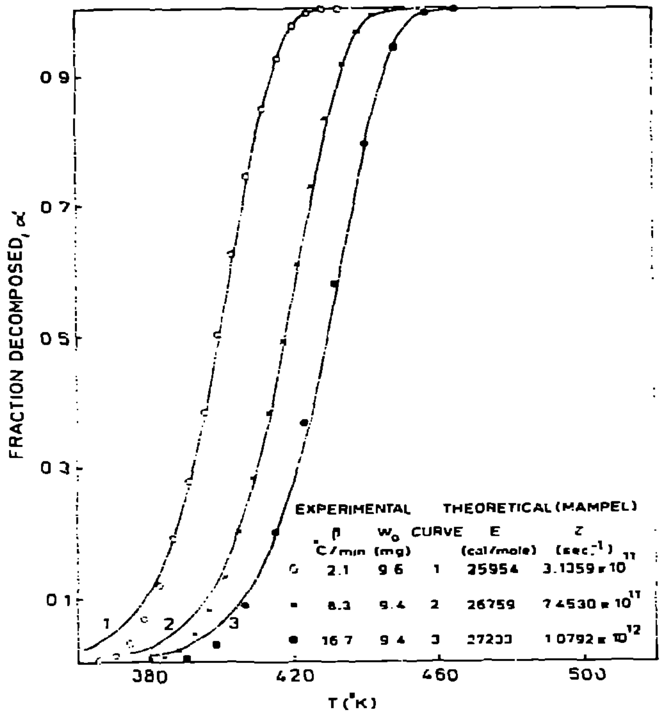


Fig. 3. Theoretical vs. experimental curves for the decomposition of sodium bicarbonate.

well as the pre-exponential factor, from the corresponding average value of D, were printed out.

Theoretical ln g(α) values were calculated from E and Z. Since the reaction mechanism is known, these values can be used to predict α vs. T curves. Some predicted curves are compared with an experimental curve in Fig. 1. It was observed in this case that depending on the choice of reaction mechanism, eqn. (2) yielded minimum standard deviation for D at three values of E ranging from 9000 to 43 000 cal mole^{-1}. The pre-exponential factor was also different. Although the comparison enables elimination of the Jander equation, both the Avrami and Mampel equations yielded identical theoretical curves agreeing with the experimental curve in the range $0.2 < \alpha < 1.0$.

This uncertainty was overcome by modifying the program such that the iteration is done only in the neighbourhood of the approximate value of E obtained from

$$\ln \frac{\alpha}{T^2} = \ln \frac{ZR}{\beta E} - \frac{E}{RT} \quad 0.08 < \alpha < 0.5 \tag{4}$$

Fig. 2. Flow chart of the program for the analysis of DSC curves. M, Number of data; T, time (sec); TEMP, temperature (K); Y, rate of change of heat content with time (dH/dt); H, interval at which data are read (sec); WM, molecular weight of the reactant: TITLE1, contains the titles of the experiment; TITLE2, contains the abbreviations of the names of reaction mechanisms used for the analysis; RH, heating rate; FD, fraction decomposed; E, activation energy (cal mole^{-1}); STD, standard deviation of log $ZE/\beta R$; GALFA, contains theoretical values of g(α); NM, KK, indices of the first and last points of the data subjected to least squares fit.

The flow chart for the computer program is given in Fig. 2. This program can also be used for analysing TG curves after deleting the portion between connectors 1 and 3. All the experiments indicated the Mampel Unimolecular Decay Law as the mechanism for the decomposition of sodium bicarbonate. Some of the theoretical curves generated using the Mampel Law are compared with the experimental curve for α vs. T in Fig. 3, wherein the values for the kinetic parameters are also indicated. These values compare well with the activation energy of 24 kcal mole^{-1} and reaction mechanism according to the Mampel Law proposed [11] on the basis of isothermal weight loss measurements on sodium bicarbonate.

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