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BASIC PROGRAM TO CALCULATE THE KINETIC PARAMETERS OF DECOMPOSITION REACTIONS USING HOROWITZ - METZGER AND COATS - REDFERN METHODS

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Abstract- A BASIC program was introduced to perform kinetic analysis of pyrolitic heterogeneous reactions. The program requires TG data for the calculations. These data then converted to DTG data to calculate reaction order, n, activation energy, E^*, and entropy of decomposition reaction, ΔS^*, pre-exponential factor, A, and correlation coefficient of the linear plots obtained in both Horowitz-Metzger and Coats Redfern methods. The program, which has been tested by known kinetic parameters of $CaCO_3$, gave reasonable results for the thermal decomposition kinetics of some glyoxime and thiourea derivatives and their metal chelates.

Keywords- Computer program, kinetic, calculation, decomposition reactions.

1. INTRODUCTION

Thermal analysis using thermal gravimetric (TG) data gives reliable and adequate information about the thermal behaviors of various compounds under investigation. Thermal analysis employs a gradual decrease or increase in temperature according to a set program followed by measurement of certain physicochemical changes for thermal decomposition reactions. Many researchers perform thermal analysis calculations to examine thermal behaviors of the compounds, which are important for their specific purposes. In such calculations evaluation of TG data and choosing the most proper path for the rest of the calculations requires detailed reasoning and long lasting mathematical operations. A computer program could reduce the time needed for these reasoning and mathematical calculations. There are some programs available for such calculations. Coseac and Segal [1] presented a BASIC program to provide discrimination among thermal decomposition mechanisms. H. Icbudak offered another BASIC program [2] to calculate kinetic parameters of thermal decomposition using Freeman-Carroll method [3].

There are no publications so far about a BASIC program to calculate kinetic parameters of thermal decomposition reactions using Horowitz-Metzger [4] and Coats-Redfern [5] methods in literature. In this study, a BASIC program performing thermo-analytical calculations employing Horowitz-Metzger and Coats-Redfern methods is introduced.

2. EXPERIMENTAL

The differential thermal analysis (DTA) and TG curves are obtained by Shimadzu DT-40 model equipped with DTA and TG units. The thermal analysis system was used over the temperature range of 273-1823 K (0-1550 °C). Analytical reagent purity $CaCO_3$ was placed in Pt crucibles and α-Al_2O_3 was used as the reference material. The measurement was performed by using a dynamic nitrogen furnace atmosphere at a flow rate of 60 mL.min^{-1}. The heating rate was 10 K.min^{-1} and the sample size in mass 5.10 mg.

3. MATHEMATICAL BACKGROUND OF KINETIC CALCULATIONS

The derivation of the mathematical equation of the kinetic problem in general can be found in several publications [4,5]. Two different integral methods on the kinetic calculations can be given under the following headings.

3.1. Horowitz - Metzger method

The rate of the decrease in the concentration of the reactant with respect to time in reaction A → B + C can be given by the equation;

$$\frac{dC}{dt} = -kC^n \qquad (1)$$

Where, k: Specific rate constant, C: the concentration of reactant, n: reaction order and t is time. The dependence of rate to temperature is given by Arrhenius equation (Eq. 2).

$$k = Ae^{-\frac{E^*}{RT}} \qquad (2)$$

Where A: frequency factor (pre-exponential factor), E^*: activation energy, R: universal gas constant and T is absolute temperature in Kelvin.

The equations to calculate kinetics parameters are given in equation below without detailed derivations that can be found elsewhere [4]. The activation energy of the decomposition can be calculated from the relation between C, n, E^*, R and T by the equation;

$$\ln\frac{1-C^{1-n}}{1-n} = \frac{E^*\theta}{RT_s^2} \qquad (3)$$

Here, $C=(W-W_t^f)/(W_o-W_t^f)$ where W is the weight remaining at a given temperature T, W_o and W_t^f are the initial and final weights respectively and θ is the difference of T from a reference temperature T_s ($\theta = T - T_s$). A plot of the logarithm of the left-hand side vs. θ in equation (3) should give a straight line. From the slope of the line E^* is calculated. Pre-exponential factor A, can be calculated from the calculated value of E^* and the intercept [6] by means of equation (4).

$$\frac{E^*}{RT_s} = \frac{A}{\phi}nC_s^{n-1}\exp\left(-\frac{E^*}{RT_s^2}\right) \qquad (4)$$

Finally, the activation entropy ΔS^*, is calculated from equation (5).

$$A = \frac{kT_s}{h}\exp\left(\frac{\Delta S^*}{R}\right) \quad (5)$$

Where k is Boltzman constant and h is Planck constant.

3.2. Coats - Redfern method

In the reaction aA (s) → bB (s) + cC (g) the rate of disappearance of A may be expressed [7] by;

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \quad (6)$$

Where α is fraction of A decomposes at time t, n is order of reaction and k is the rate constant given by the equation (2). Combining Arrhenius equation with Eq. (6) will give equation (7)

$$\frac{d\alpha}{dt} = Ae^{\frac{-E^*}{RT}}(1-\alpha)^n \quad (7)$$

When linear heating rate ($\phi = \frac{dT}{dt}$) is included in this equation then rearranging and integrating α terms from 0 to α and temperature terms from zero to T, the equation (8) is obtained after taking the logarithm of both sides.

$$\log_{10}\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \log_{10}\frac{AR}{\phi E^*}\left[1-\frac{2RT}{E^*}\right] - \frac{E^*}{2.303RT} \quad (8)$$

If the left-hand-sides of last equation is plotted vs 1/T then E^* is calculated from the slope.

$$\text{Slope} = -\frac{E^*}{2.303RT} \quad (9)$$

Pre-exponential factor A can be calculated from the intercept where $1-\frac{2RT}{E^*} \cong 1$.

$$\text{Intercept} = \log_{10}\frac{AR}{\phi E^*}\left[1-\frac{2RT}{E^*}\right] \quad (10)$$

Entropy ΔS^* can be calculated from equation (5).

4. THE PROGRAM

The program first converts TG data to differential thermal gravimetric (DTG) data. By the aid of DTG data (DTG maxima) it uses TG data and calculates kinetic parameters of pyrolitic decomposition reaction employing mass losses at each

temperature change. The program prepares input data to MS Excel program to redraw TG, DTG diagrams as drawn by the software of Thermal Analyzer. The linearisation of the plots obtained by the two methods can then be performed by the program THERMAL ver 1.0. The program can also calculate the correlation coefficients (r) of these linear curves (usually mass loss vs. 1/T or θ).

4.1. The flow chart

The flow chart of the program is given through Figure 1 and 2. The original program includes 1100 lines in full form. The input control, errors control, printer control, screen control and function key definition parts of the program are not included in the flow charts.

The line numbers of the significant sections in the source code of the program (as summarized above) can be correlated to the connection letters appearing in the flow chart as follows.

Line number	200	4900	5500	6000	6500	7000	10000
Connect. Letter	M	F	CRa	HMa	CR1	HM1	END

The program runs in command prompt using a graphical interface but graphical representations of some results are also omitted. The subroutine performing linear regressions is also not included. The main calculations using Horowitz-Metzger and Coats-Redfern methods are given here with the main menu at the beginning of the program being the most significant parts. The program included here only calculates the kinetic parameters as defined by the F6 function key in the main menu. The other choices in the main menu are removed and inactive here. The main menu at the beginning includes seven different choices to study on.

F1 : Permits new data entry
F2 : Performs graphical control of input data
F3 : Allows definition of initial and final temperature limits of decomposition stages (number of stages and sub-stages)
F4 : Produces hard copy of input data
F5 : Calculates reaction order with respect to H.- M. and C.-R. Methods
F6 : Calculates kinetic factors (A, ΔS^*, E^*)
F8 : Terminates the program

4.2. Input data

The required input data for the program consisted of the number of data (number of temperature changes or number of mass losses), initial mass of the sample, mass losses for each temperature changes. These values are given manually in a text file with an extension of *.avd. Meanwhile, another input file for MS EXCEL program was also prepared by the program with an extension *.xls after TG and DTG plot obtained.

4.3. Output data

After calculation of reaction order n, activation energy E^*, pre-exponential factor A, activation entropy ΔS^*, the % mass losses and regression coefficients of the plots drawn for both methods are shown on the screen for each decomposition stages. On screen output of the calculated and input values can also be obtained as printed outputs.

4.4. Use of the program

The program can be installed on a hard disk from a self-installing diskette by means of a batch file. One should type only kur from command prompt to start the installation from diskette (i.e. A:\>kur ↵). The program will be installed to the THERMAL directory of the c: partition.

The THERMAL directory should normally contain the following files;

THERMAL.EXE	: Executable program to start calculation.
README.TXT	: Description of the program and its uses
AVD	: Directory containing input data files (*.avd)
XLS	: Directory containing MS Excel input data files (*.xls)
BVD	: Directory containing internal data files (*.bvd)

The program can be run by typing;

C:\THERMAL>THERMAL ↵

The program asks for the personal and time data to go on with the calculations. A graphical main menu will forward the user to choose the type of operation such that the type of the calculation method, to start inputting data, printing, exiting the program etc. After each type of operation the main menu will meet the user.

The program can calculate the order with respect to three different choices

1. Assuming the reaction order is unity
2. Using the reaction order calculated with the experimental data
3. Using an arbitrarily chosen reaction order

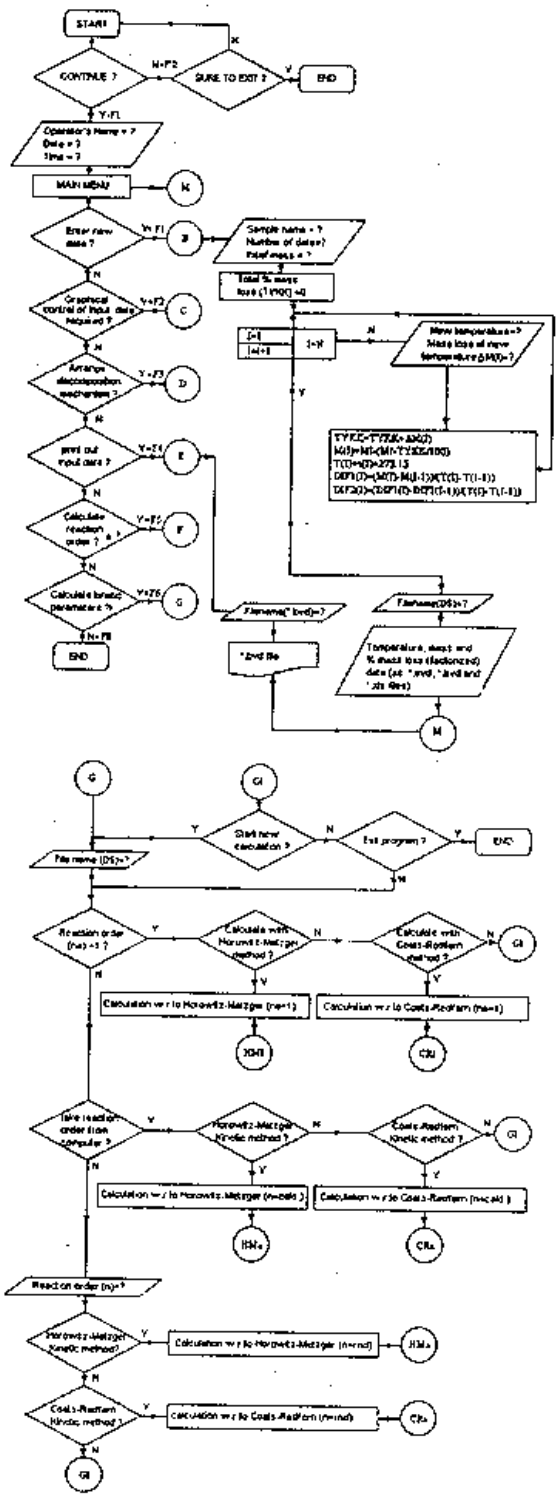

Figure 1. Flow chart of the program "Thermal ver. 1.00".

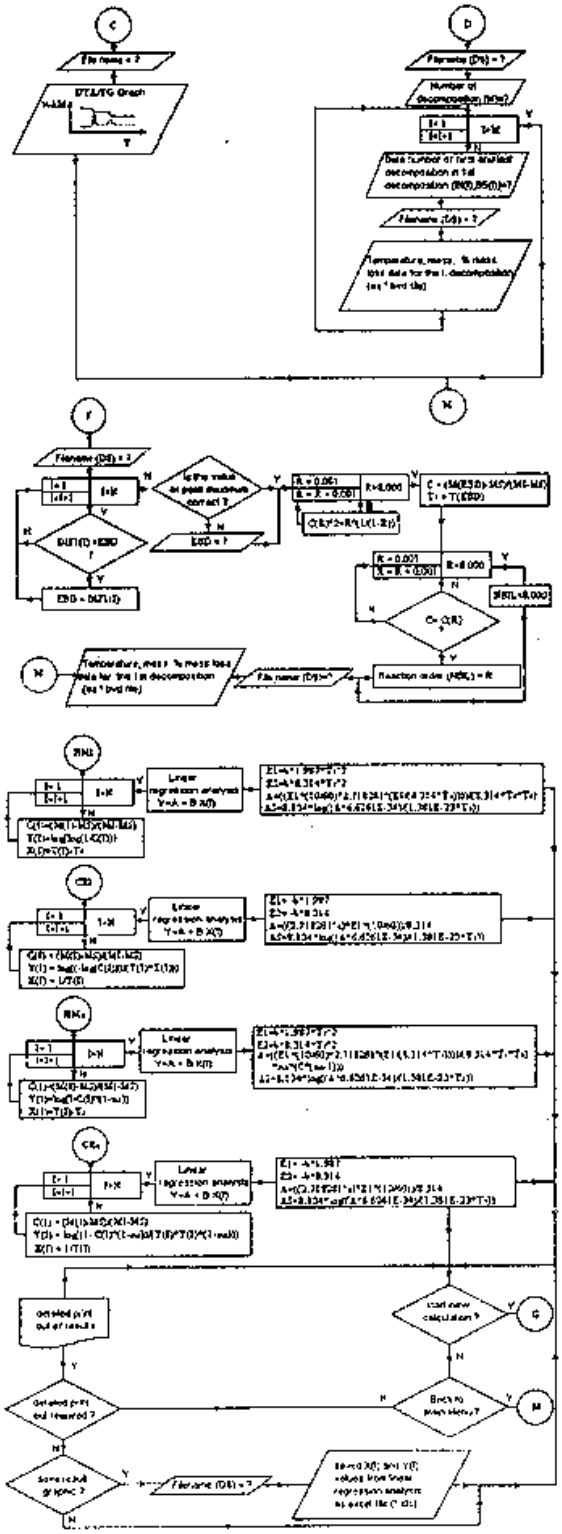

Figure 2. Flow chart of the program "Thermal ver. 1.00"

5. RESULTS

Coats-Redfern [5], examined the kinetics of the pyrolysis reaction of $CaCO_3$. In this study, the same compound was used as the reference and kinetic analysis was performed by the program Thermal ver 1.0 to control the program [8]. The test results of the thermal analysis of $CaCO_3$ calculated with Thermal ver 1.0 are listed on Table 1 for the reaction;

$$CaCO_3\,(s) \xrightarrow{\Delta} CaO\,(s) + CO_2\,(g)$$

Table 1. The results of kinetic analysis of $CaCO_3$ calculated for test purposes.

Kinetic Method	% Decomposition		Reaction Order, n		E^*, kcal/mol		% R.E.
	Lit.	This study	Lit.	This study	Lit.	This study	
Coats-Redfern	44.0	44.0	0.46	0.46	51.7	50.7	1.9
Horowitz-Metzger	-	44.0	-	0.46	-	54.6	-

Abbreviations: Lit. : In the literature [5], R.E. : Relative Error.

The program gave reasonable results for the thermal decomposition kinetics of some glyoxime and thiourea derivatives and their metal chelates [8-13].

RECOMMENDATION

The program permits using a third and more methods for the type kinetic analysis. An easy up; ade can be accomplished by the addition of new subroutines. These additions are planned for the next versions of the program. The program can also be used in combination to the software of a Thermal analyzer if the input data directly saved as an ASCII file on the hard disk.

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