

## KINETICS FROM THERMOGRAVIMETRIC DATA AND GAS CHROMATOGRAPHIC DATA

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### ABSTRACT

The equation of reaction kinetics derived from thermogravimetric data is given as

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{Z}{\beta} \int_{T_0}^T \exp(-E/RT) dT$$

On the left-hand side of the equation, the integration is determined from the corresponding weight loss and temperature for approximate values of the reaction order: 1, 5/4, 3/2, 7/4 and 2, which are obtained from quantitative analysis of gas chromatography during isothermal decomposition. On the right-hand side of the equation, approximations of the exponential integral are derived and consist of four patterns dependent on  $E/RT$ .

(1)  $0.01 \leq u \leq 0.06$

$$p_1(u) = \frac{\exp(-u)}{u} \frac{u^2 + 46u + 23}{u^3 + 48u^2 + 115u + 23.3006}$$

Relative error = 0.010–0.650% ( $u = E/RT$ ).

(2)  $0.07 \leq u \leq 0.22$

$$p_2(u) = \frac{\exp(-u)}{u} \frac{u^2 + 22u + 54}{u^3 + 24u^2 + 122u + 58}$$

Relative error = 0.015–0.625%.

(3)  $0.23 \leq u \leq 0.47$

$$p_3(u) = \frac{\exp(-u)}{u} \frac{u^2 + 11u + 16}{u^3 + 13u^2 + 38u + 18}$$

Relative error = 0.015–0.220%.

(4)  $0.48 \leq u$

$$p_4(u) = \frac{\exp(-u)}{u} \frac{u^2 + 11u + 16}{u^3 + 13u^2 + 36u + 19}$$

Relative error < 0.531%.

### INTRODUCTION

In order to investigate the thermal decomposition and degradation of various materials, thermogravimetric analysis has been used and general

considerations discussed by Flynn and Wall [1] and Šesták et al. [2]. Reaction kinetics are meaningful in characterizing the decomposition and degradation of a number of organic compounds and metallic salts. Many methods have been proposed to estimate the activation energy, but in non-isothermal decomposition the activation energy calculated for a system where the reaction order changes is erroneous, as Flynn and Wall [1] pointed out.

There are two theoretical methods for determining the reaction order. In Ozawa's method [3], the reaction order is evaluated by thermogravimetric curves which are plotted as weight loss (%) against the logarithm of  $(ZE/RT)^p(E/RT)$ , only as integer numbers. In Friedman's method [4], the logarithm of  $Zf(\alpha/\alpha_0)$  is substituted in the kinetic equation  $f(\alpha/\alpha_0) = [(\alpha - \alpha_f)/\alpha_0]^n$ , where  $\alpha_f$  = weight of char. This reaction order gives a value over a whole decomposition reaction.

The kinetic equation includes an exponential integral that represents the greatest difficulty for solving the integration. For its solution, approximations have been proposed by Coats and Redfern [5], Gorbachev [6], Zsakó [7] and Senum and Yang [8], and discussed and compared with each other for  $E/RT \geq 0.5$  by Senum and Yang [8]. The results suggest that the Senum–Yang approximations (2nd and 3rd degree) are extremely superior to the others in the extent of the relative error.

In this paper, activation energy is estimated from the slope of a straight line plot of the logarithm of heating rates against reciprocal absolute temperatures, and reaction orders were estimated from the the results of gas chromatography.

In addition, an approximation of the exponential integral is tried, and the evaluation of reaction kinetics will be discussed by use of data on isothermal decomposition to complement the results from non-isothermal gravimetric data.

## REACTION KINETICS

The rate of disappearance may be given as

$$d\alpha/dt = k(1 - \alpha)^n \quad (1)$$

the Arrhenius function,  $k = Z\exp(-E/RT)$  and the heating rate,  $\beta = dT/dt$ , where  $\alpha$  = fraction of decomposed material,  $k$  = rate constant,  $n$  = reaction order,  $Z$  = pre-exponential factor,  $E$  = activation energy,  $R$  = gas constant,  $T$  = absolute temperature and  $t$  = time.

Combining eqn. (1), the Arrhenius function and the heating rate, rearranging and integrating, we get

$$\int_0^\alpha \frac{d\alpha}{(1 - \alpha)^n} = \frac{Z}{\beta} \int_{T_0}^T \exp(-E/RT) dT \quad (2)$$

where  $T_0$  is the value of  $T$  at  $t = t_0$ . As the rate of a reaction is very small at low temperatures, the following equation is given

$$\frac{Z}{\beta} \int_{T_0}^T \exp(-E/RT) dT = \frac{Z}{\beta} \int_0^T \exp(-E/RT) dT \quad (3)$$

The right-hand side of eqn. (3) is expressed as

$$\frac{Z}{\beta} \int_0^T \exp(-E/RT) dT = -\frac{ZE}{\beta R} \int_{\infty}^u u^{-2} e^{-u} du \quad (4)$$

where  $u = E/RT$ ,  $du = -(E/RT^2) dT$ .

$$-\frac{ZE}{\beta R} \int_0^u u^{-2} e^{-u} du = \frac{ZE}{\beta R} \left( u^{-1} e^{-u} - \int_0^u u^{-1} e^{-u} du \right) \quad (5)$$

$$= \frac{ZE}{\beta R} p(u) \quad (6)$$

Then  $p(u)$  is defined as

$$p(u) = u^{-1} e^{-u} - \int_0^u u^{-1} e^{-u} du = u^{-1} e^{-u} - E_1(u) \quad (7)$$

where the values of  $E_1(u)$  are given in the mathematical handbook as Senum and Yang [8] have elucidated. The  $p(u)$  function cannot be represented in an unique equation, so that its several approximations [5–10] have been proposed in the restricted extent of  $u$ . The function consists of  $\exp(-u)/u$  and  $E_1(u)$  as shown in eqn. (9) and their relationship is drawn in Fig. 1.

Some attempts were tried for  $u \leq 7$  in  $p(u)$ , and four approximations have been derived as follows

$$(1) 0.01 \leq u \leq 0.06$$

$$p(u) = \frac{\exp(-u)}{u} \frac{u^2 + 46u + 23}{u^3 + 48u^2 + 115u + 23.3006}$$

$$(2) 0.07 \leq u \leq 0.22$$

$$p(u) = \frac{\exp(-u)}{u} \frac{u^2 + 22u + 54}{u^3 + 24u^2 + 122u + 58}$$

$$(3) 0.23 \leq u \leq 0.47$$

$$p(u) = \frac{\exp(-u)}{u} \frac{u^2 + 11u + 16}{u^3 + 13u^2 + 38u + 18}$$

$$(4) 0.48 \leq u$$

$$p(u) = \frac{\exp(-u)}{u} \frac{u^2 + 11u + 16}{u^3 + 13u^2 + 36u + 19}$$

The extent of  $u$  is restricted in the  $p_1(u)$ ,  $p_2(u)$ ,  $p_3(u)$  and  $p_4(u)$  approximations described above. The relative errors of these four approximations are shown in Table 1. In the relative error, the  $p_4(u)$  approximation

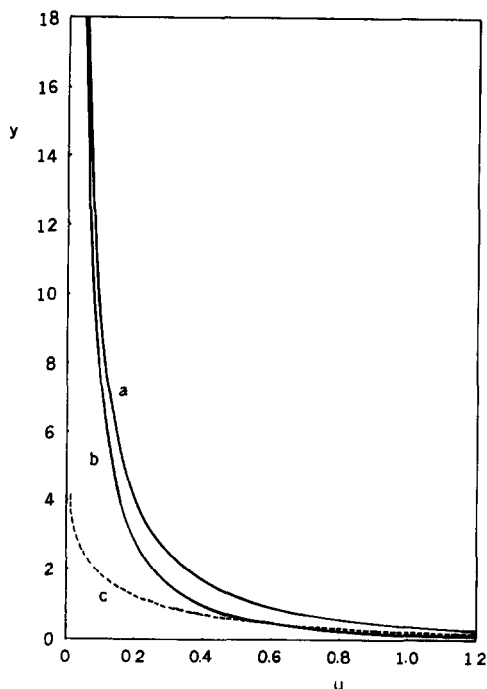


Fig. 1. The three function curves of the exponential integral: (a)  $y = \exp(-u)/u$ ; (b)  $y = p(u)$ ; (c)  $y = E_1(u)$ .  $y = E_1(u)$  from ref. 11.

is compared with six others and has the lowest relative errors for  $0.5 \leq u \leq 7$  as shown in Table 2. For  $u \geq 8$ , the superior order of seven approximations in the relative errors is drawn up in the Senum–Yang (3rd degree), Senum–Yang (2nd degree),  $p_4(u)$ , Balarin, Zsakó, Gorbachev and Coats–Redfern approximations. However if a  $u$ -value is large enough, values of these approximations, even the Coats–Redfern one, become approximately equivalent to each other, because the first two terms of expansion of every approximation are equal to those of the Coats–Redfern one which is expressed as  $[\exp(-u)/u](1 - 2/u)$ , and is the simplest. This approximation gives the relative error ( $5.886 \times 10^{-2}\%$  for  $u = 100$  [8],  $1.485 \times 10^{-2}\%$  for  $u = 200$  and  $6.623 \times 10^{-3}\%$  for  $u = 300$ ) and is able to be used at least for  $u \geq 100$ , as for the others. For the range  $8 \leq u \leq 100$ , in the Senum–Yang (3rd degree) and  $p_4(u)$  approximations, relative errors of  $10^{-2}\%$  may be applied. These facts suggest that every approximation plays a respective part under the region of  $u$  which is suitably large enough.

Expanding and integrating the left-hand side of eqn. (2), the following equation is obtained

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \alpha + \frac{n}{2}\alpha^2 + \frac{n(n+1)}{6}\alpha^3 + \frac{n(n+1)(n+2)}{24}\alpha^4 + \dots \quad (8)$$

TABLE 1  
Relative errors of four approximations (%)

$u$	Rel. error	$u$	Rel. error
	$p_1(u)$		$p_2(u)$
0.01	$9.02 \times 10^{-3}$	0.07	0.625
0.02	0.227	0.08	0.389
0.03	0.157	0.10	0.071
0.04	0.052	0.12	0.098
0.05	0.332	0.14	0.159
0.06	0.649	0.16	0.143
		0.18	0.068
		0.20	0.049
		0.22	0.200
	$p_3(u)$		$p_4(u)$
0.23	0.220	0.48	0.042
0.24	0.158	0.50	0.029
0.26	0.056	0.60	0.282
0.28	0.021	0.70	0.423
0.30	0.076	0.80	0.495
0.32	0.115	0.90	0.526
0.34	0.138	1.00	0.531
0.36	0.150	2.00	0.290
0.38	0.152	3.00	0.128
0.40	0.145	4.00	0.055
0.42	0.131	5.00	0.021
0.44	0.112	6.00	$4.84 \times 10^{-3}$
0.46	0.088	7.00	$2.76 \times 10^{-3}$
0.47	0.074	8.00	$6.27 \times 10^{-3}$
		10.00	$8.09 \times 10^{-3}$
		20.00	$3.75 \times 10^{-3}$
		30.00	$1.71 \times 10^{-3}$
		40.00	$8.49 \times 10^{-4}$
		100.00	$7.72 \times 10^{-5}$

where  $\alpha$  corresponds to about 0.3 [12]. This value means that thermal decomposition of organic materials terminates near the temperature of a second endotherm in the DTA curve at which the weight loss of a material is about 0.3. The thermal decomposition of D-glucose terminates near the second endotherm and at 0.3 weight loss as shown by Örsi [13]. Then the  $\alpha^4$  and higher terms are below  $8.1 \times 10^{-3}$  and negligible, so that the following equation is obtained

$$\alpha + \frac{n}{2}\alpha^2 + \frac{n(n+1)}{6}\alpha^3 = \frac{ZE}{\beta R} p(u) \quad (9)$$

It thus suggests that the thermal decomposition of organic materials is facilitated in the temperature region between the first and second endotherms of their DTA curves.

TABLE 2  
Relative errors of the seven approximations (%) in the range of  $u$  from 0.5 to 10

$u$	$P_{CR}(u)$	$P_G(u)$	$P_Z(u)$	$P_B(u)$	$P_{SY-2}(u)$	$P_{SY-3}(u)$	$P_4(u)$
0.5	1214.11	25.73	21.57	23.79	9.66	4.33	$2.88 \times 10^{-2}$
0.6	872.77	23.57	13.27	19.61	8.23	3.45	0.282
0.7	660.62	21.74	8.67	16.50	7.09	2.81	0.398
0.8	519.46	20.10	5.91	14.16	6.13	2.29	0.495
0.9	420.25	18.68	4.11	12.30	5.36	1.63	0.526
1	347.74	17.42	2.91	10.79	4.72	1.58	0.531
2	100	9.86	0.157	4.09	1.66	0.370	0.290
3	48.02	6.43	0.163	2.09	0.761	0.124	0.128
4	28.42	4.55	0.219	1.24	0.403	$5.10 \times 10^{-2}$	$5.45 \times 10^{-2}$
5	18.86	3.40	0.200	0.799	0.235	$2.39 \times 10^{-2}$	$2.08 \times 10^{-2}$
6	13.46	2.64	0.138	0.549	0.147	$1.23 \times 10^{-2}$	$4.84 \times 10^{-2}$
7	10.11	2.11	$6.29 \times 10^{-2}$	0.395	$9.71 \times 10^{-2}$	$6.84 \times 10^{-3}$	$2.76 \times 10^{-3}$
8	7.87	1.73	$8.35 \times 10^{-3}$	0.294	$6.68 \times 10^{-2}$	$4.02 \times 10^{-3}$	$6.27 \times 10^{-3}$
9	6.31	1.45	$6.83 \times 10^{-2}$	0.225	$4.75 \times 10^{-2}$	$2.47 \times 10^{-3}$	$7.70 \times 10^{-3}$
10	5.18	1.22	0.115	0.176	$3.47 \times 10^{-2}$	$1.58 \times 10^{-3}$	$8.09 \times 10^{-3}$

CR, Coats and Redfern; G, Gorbachev; Z, Zsako; B, Balarin; SY, Senum and Yang.

For the reaction order, quantitative analysis by use of gas chromatography was carried out on products of isothermal decomposition of D-glucose and will be described in detail later. The results show that the reaction order shifts approximately from  $n = 1$  to 2, according to elevation by an interval of  $10^\circ\text{C}$  of heating in isothermal decomposition between the first and second endotherms. Consequently, the relationship between reaction order and heating temperature may be approximately assumed as follows

$$n = 1 \quad t_{1st} \leq t < t_{1st} + \Delta t = t_2$$

$$n = 5/4 \quad t_2 \leq t < t_2 + \Delta t = t_3$$

$$n = 3/2 \quad t_3 \leq t < t_3 + \Delta t = t_4$$

$$n = 7/4 \quad t_4 \leq t < t_4 + \Delta t = t_5$$

$$n = 2 \quad t_5 \leq t \leq t_{2nd}$$

where  $t_{1st}$  is the temperature at the beginning of the weight loss near the first endotherm,  $t_{2nd}$  is the temperature at the termination of decomposition of a material near the second endotherm, and  $\Delta t = (t_{2nd} - t_{1st})/5$ . Then the values of the left-hand side of eqn. (9) are determined by use of the corresponding temperature and reaction order.

Logarithms of heating rates are plotted against reciprocal absolute temperatures for identical weight loss, then straight lines are determined by the least-squares method. Activation energies are estimated from the slopes of the lines, and pre-exponential factors are calculated from eqn. (9).

## EXPERIMENTAL

D-Glucose (GR grade), meso-erythrite (GR grade) and pyridine (GR grade) were purchased from Wako Junyaku Co. Ltd. Pyridine was dried with sodium hydroxide and distilled at 115.5°C. Trimethylchlorosilane and hexamethyldisilazane (gas chromatographic grade) were from Kanto Kagaku Co. Ltd.

Thermogravimetric measurements were carried out by use of 30 mg of D-glucose at heating rates of 0.5, 1, 2, 5, 7 and 10°C min<sup>-1</sup> in air on a Shimazu TG 20.

Samples of the isothermal decomposition products of D-glucose were prepared such that 50 mg of the sugar were heated at temperatures of 155, 165, 175, 185, 195, 205, 215 and 225°C, and kept for 5–120 min in a DTA furnace on a Shimazu DTA 20B after elevating to these temperatures at a heating rate of 10°C min<sup>-1</sup>. Samples were immediately removed and placed into a desiccator cooled at -2°C [14]. These samples were dissolved in 0.3 ml of pyridine and trimethylsilylated [15] with 0.2 ml of hexamethyldisilazane and 0.1 ml of trimethylchlorosilane. The solutions were stirred and allowed to stand for 30 min. Gas chromatography was performed by injection of 1 μl of a solution on a Shimazu GC 4CT equipped with TCD detectors and stainless-columns (3 mm × 3 m) packed with SE 30 silicon gum supported by chromosorb W (80–100 mesh). The columns were operated with a temperature programme from 120 to 230°C at a heating rate of 5°C min<sup>-1</sup>.

In order to determine quantitative amounts of the sugar in the decomposition products, meso-erythrite was used an internal calibration standard similar to that described in ref. 14. The peaks of the sugar appeared at 29.3 min (retention time) for the α-anomer and 30.5 min for the β-anomer. From the results of gas chromatography, the calibration curve was plotted as the

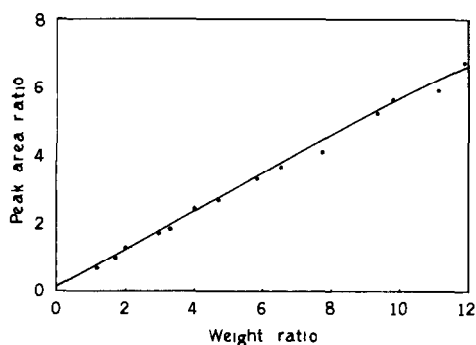


Fig. 2. Calibration curve of peak area ratio against weight ratio between D-glucose and the internal standard.

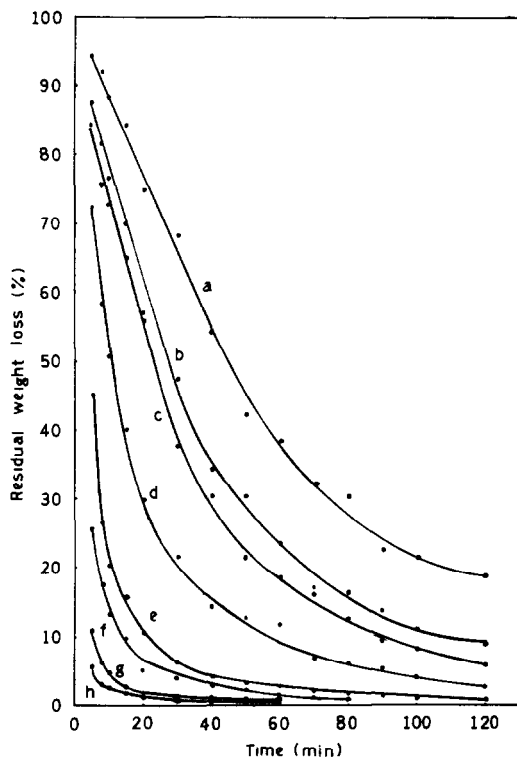


Fig. 3. Relation between the residual weight (%) of D-glucose and isothermal decomposition time. Heating temperature: (a) 155; (b) 165; (c) 175; (d) 185; (e) 195; (f) 205; (g) 215 and (h) 225°C.

ratio of total peak area (of  $\alpha$ - and  $\beta$ -anomer) of the sugar versus peak area of the internal standard against the ratio of the weight of the sugar versus the weight of the standard in Fig. 2.

Residual weight percentages of the sugar in the decomposition products were determined by use of the calibration curve in Fig. 3.

## RESULTS AND DISCUSSION

Thermal decomposition of organic compounds takes place mainly between the first and the second endotherms as Órsi [13] has shown for D-glucose, its decomposition begins at 145°C and terminates at 240°C. From the gas chromatographic data, which were the results of the isothermal decomposition of D-glucose, the reaction order and rate constant were estimated from the relationship between residual weight of the sugar and heating time (5–120 min) at the heating temperature (155–225°C).



TABLE 3  
Kinetic parameters obtained from gas chromatographic data

Heating temp.(°C)	Reaction order	Rate constant	ln $k$	1000/ $T$	ln $Z$
155	0.8	$2.299 \times 10^{-4}$	-8.378	2.336	29.98
165	1.1	$4.487 \times 10^{-4}$	-7.709	2.283	29.77
175	1.3	$5.774 \times 10^{-4}$	-7.457	2.232	29.19
185	1.5	$1.273 \times 10^{-3}$	-6.667	2.183	29.18
195	1.6	$3.724 \times 10^{-3}$	-5.593	2.137	29.49
205	1.7	$7.078 \times 10^{-3}$	-4.951	2.092	29.39
215	1.8	$2.213 \times 10^{-2}$	-3.811	2.049	29.83
225	1.9	$4.498 \times 10^{-2}$	-3.102	2.008	29.86

In the equation  $k = [1/(n-1)t][1/(1-\alpha)^{n-1} - 1]$ , the reaction order should be selected such that the rate constant is given a constant value. Consequently, during the isothermal decomposition of the sugar, the results of the estimation of reaction orders and rate constants are shown in Table 3.

Taking logarithms of the Arrhenius function gives  $\ln k = \ln Z - E/RT$ . The logarithms of the rate constants are plotted against the reciprocal absolute temperature in Fig. 4. The straight line was determined by the least-squares method and its slope was  $-16.42$ . The activation energy was  $32.62 \text{ kcal mol}^{-1}$ , and  $\ln A$  was estimated as 29.59. The results show that both the reaction order and rate constant became larger with increase in heating temperature by an interval of  $10^\circ\text{C}$  in isothermal decomposition as shown in Table 3. This fact suggests that the relationship between reaction

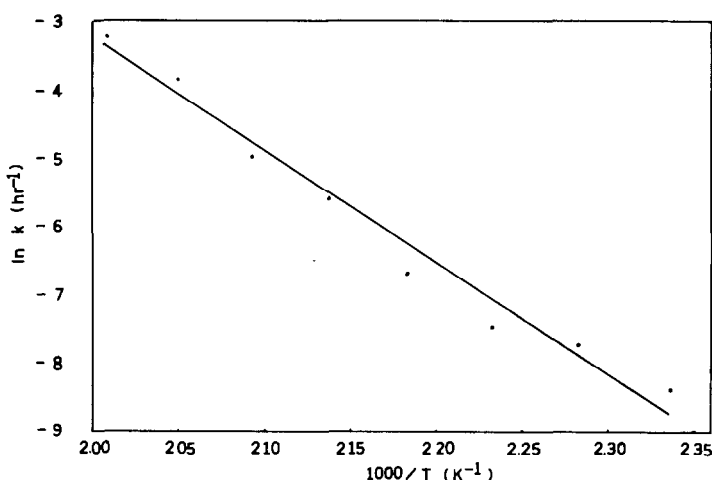


Fig. 4. Arrhenius plots of logarithms of  $k$  against the reciprocal absolute temperature.

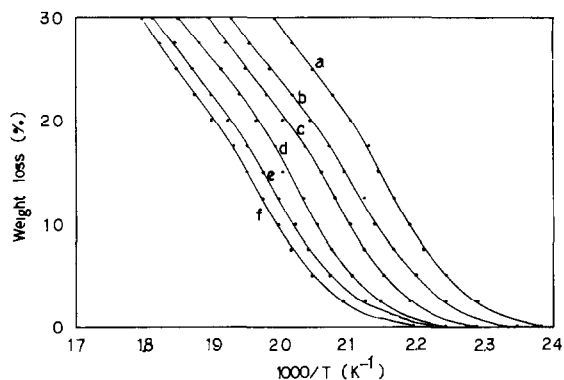


Fig. 5. Thermogravimetric curves of D-glucose against the reciprocal absolute temperature at heating rates ( $^{\circ}\text{C min}^{-1}$ ) of (a) 0.5; (b) 1; (c) 2; (d) 5; (e) 7.5 and (f) 10.

order and heating temperature may approximately be shown as

$n = 1$	$147^{\circ}\text{C} \leq t < 165.6^{\circ}\text{C}$
$n = 5/4$	$165.6^{\circ}\text{C} \leq t < 184.2^{\circ}\text{C}$
$n = 3/2$	$184.2^{\circ}\text{C} \leq t < 202.8^{\circ}\text{C}$
$n = 7/4$	$202.8^{\circ}\text{C} \leq t < 221.4^{\circ}\text{C}$
$n = 2$	$221.4^{\circ}\text{C} \leq t \leq 240^{\circ}\text{C}$

where  $147^{\circ}\text{C}$  is the melting temperature and/or the beginning of the weight loss, and  $240^{\circ}\text{C}$  is the temperature at which the thermal decomposition of the sugar terminates [13]. The relationship described above will be defined under the condition which possesses the first and the second endotherms in the DTA curve in the thermal decomposition of organic compounds.

The weight loss in thermogravimetry is plotted against the reciprocal absolute temperature at various heating rates in Fig. 5.

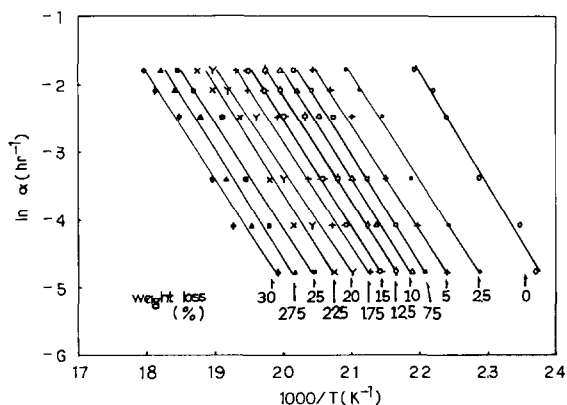


Fig. 6. Plots of logarithms of  $\alpha$  against the reciprocal absolute temperature.

TABLE 4  
The kinetic parameters of the decomposition of D-glucose

Weight loss (%)	Activation energy (kcal mol <sup>-1</sup> )	ln Z	Reaction order	Temp.(°C) at β = 0.5°C min <sup>-1</sup>
2.5	30.01	31.80	1	164
5	29.49	31.18	1.25	173
7.5	30.32	32.00	1.25	180
10	30.60	32.31	1.25	184
12.5	30.03	31.54	1.5	189
15	28.81	30.02	1.5	194
17.5	29.73	30.93	1.5	198
20	29.09	30.06	1.75	203
22.5	29.46	30.19	1.75	209
25	30.05	30.48	1.75	216
27.5	30.62	30.77	2	223
30	29.84	29.75	2	229
mean	29.84	30.92		

Taking logarithms of eqn. (9) and rearranging, the following equation is obtained

$$\ln \beta = \ln \frac{Z}{\alpha + \frac{1}{2}n\alpha^2 + \frac{1}{6}n(n+1)\alpha^3} \frac{E}{R} \frac{u^2 + 11u + 16}{u(u^3 + 13u^2 + 36u + 19)} - \frac{E}{RT} \quad (10)$$

The logarithms of the heating rates are plotted against the reciprocal absolute temperatures in Fig. 6. The straight lines were determined by the least-squares method. Activation energies were estimated from the slopes of the lines which were equal to  $-E/R$ , and the mean is 29.94 kcal mol<sup>-1</sup>. As  $u$ -values lie in the region 29.98–34.56, the approximation  $p_4(u)$  may be applied to estimate the kinetic parameters. The values of reaction order in eqn. (10) were used for the corresponding temperature and weight loss. The logarithms of  $Z$  were also calculated by eqn. (10) and the mean is 30.92. The results of the parameters estimated are shown in Table 4.

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