

ESTIMATION OF THE ACTIVATION ENERGY ON THE BASIS OF THERMAL CURVES BY OZAWA'S METHOD*

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As a result of the development of thermogravimetric methods, thermobalances of steadily increasing accuracy and reliability have been prepared in the last decade. However, experiences show that much of the great many very precise informations furnished by modern balances go to waste without use, because few methods have been available or reported in the literature so far, for computer processing the thermogravimetric results. On the other hand, thermogravimetric curves are often satisfactorily evaluated by reading the weight losses for each process, without making use of the reaction kinetic parameters, which can be calculated from the curves. Many publications have been concerned with the determination of these reaction kinetic parameters, but mostly by graphical methods alone, and seldom suit computer evaluation.

In the course of the presented work, it was attempted to convert the graphical method elaborated by OZAWA [1] to a form suitable for computerized evaluation. The use of this method has the advantage to deliver the activation energy of the reaction, irrespective of the mechanism or of the order of the reaction.

OZAWA's method can be used in all cases where in the expression of the reaction rate the reaction co-ordinate and the temperature dependence can be separated according to Fig. 1.

Applying a heat treatment with linearly increasing temperature, the linear relationship between time and temperature can be used for the explicit elimination of time, and the result shown in Fig. 2 is obtained.

Introducing the approximation of DOYLE, OZAWA [1] obtained the equation shown in Fig. 3.

After rearrangement and logarithmization, a linear relationship is obtained between the reciprocal of the temperature, belonging to identical loss in weight points of thermogravimetric curves, recorded at various heating

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$$-\frac{d\alpha}{dt} = f(\alpha) \cdot Z \cdot e^{-\frac{E}{RT}}$$

$$-\int_{\alpha_0}^{\alpha} \frac{d\alpha}{f(\alpha)} = \int_0^t Z \cdot e^{-\frac{E}{RT}} dt$$

α = extent of reaction; T = temperature; t = time; E = energy of activation; Z = pre-exponential factor; R = gas constant

Fig. 1. Reaction kinetic equation in differential and integrated form

$$T = T_0 + at$$

a = temperature rate

$$-\int_{\alpha_0}^{\alpha} \frac{d\alpha}{f(\alpha)} \equiv g(\alpha) = \frac{Z}{a} \int_{T_0}^T e^{-\frac{E}{RT}} dT$$

Fig. 2. Reaction kinetic equation for non-isothermal reaction at a constant temperature rate

$$\int_{T_0}^T e^{-\frac{E}{RT}} dT = \frac{E}{R} e^{-(2,315 + 0,4567 \frac{E}{RT})}$$

$$\ln a = \ln \frac{ZE}{Rg(\alpha) e^{-2,315}} - 0,4567 \frac{E}{RT}$$

Fig. 3. Ozawa's non-isothermal reaction kinetic equation

rates, and the logarithm of the heating rate. From the slope of this linear relationship the activation energy can be calculated.

According to the graphical method, the losses in weight read from the thermogravimetric curves for various heating rates are plotted as a function of the reciprocal temperature of the sample. From these curves, the logarithm of the heating rate is plotted as a function of the reciprocal temperature belonging to identical losses in weight, and the activation energy is obtained from the slope of the curve.

The greatest problem from the aspect of an computer evaluation was to read off the $1/T$ values belonging to an identical loss in weight from the loss in weight vs. $1/T$ curves because the complicated curve cannot be approximated by any polynomial [2]. The solution was by parabolic approach (Fig. 4). A parabola was fitted to three points of the curve, yielding the $1/T$ value for all the weight loss values between the two extreme points. Next, a point is omitted, a subsequent point is taken and the calculation repeated. The average of the $1/T$ values calculated for identical losses in weight is taken.

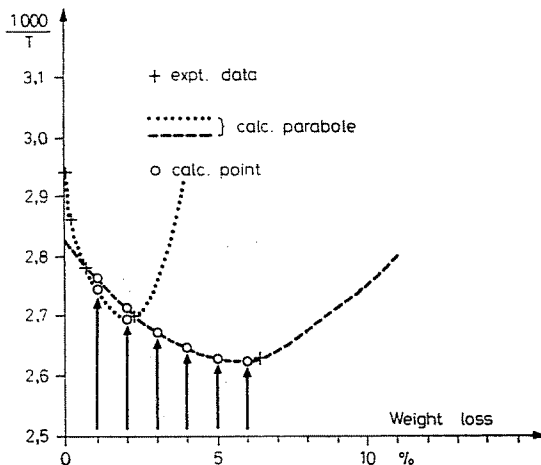


Fig. 4. The method of parabolic approximation

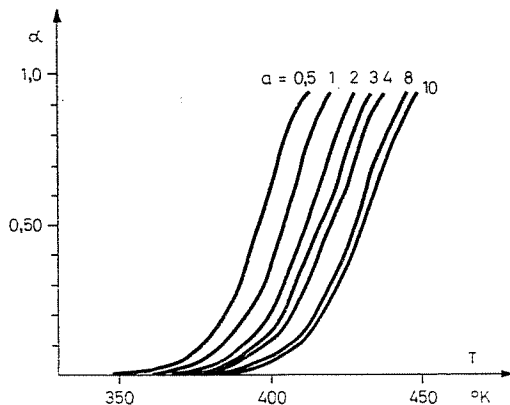


Fig. 5. Simulated thermogravimetric curves of a reaction with an activation energy of 28 kcal and a pre-exponential factor of 10^{+13} for various heating rates

This calculation was then programmed in ALGOL, and run in a RAZDAN-3 computer.

Fig. 5 shows the simulated thermogravimetric curves of a reaction with an activation energy of 28 kcal and a pre-exponential factor of 10^{+13} for various heating rates. An S vs. $1/T$ plot of the curves is shown in Fig. 6. The values plotted were obtained by parabolic approximation, and clearly demonstrate that the approximation yields a completely smooth curve.

From Fig. 7, the activation energy calculated is seen to agree with the value of 28 kcal/mole within the limits of rounding error.

In principle, the method can only be used if the activation energy does not change during the reaction, since, because of the approximation formula

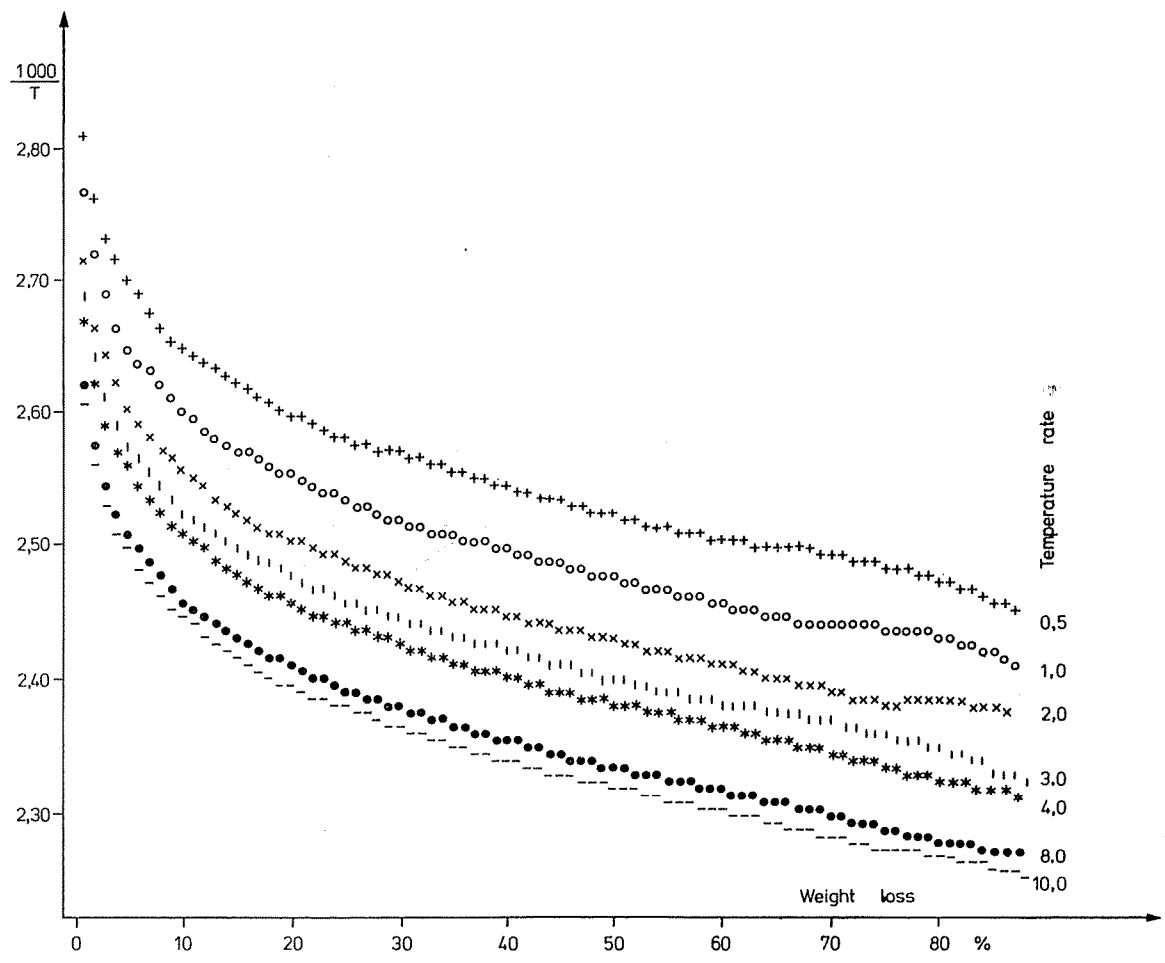


Fig. 6. The weight loss in the simulated reaction vs. $1/T$ curves obtained by parabolic approximation

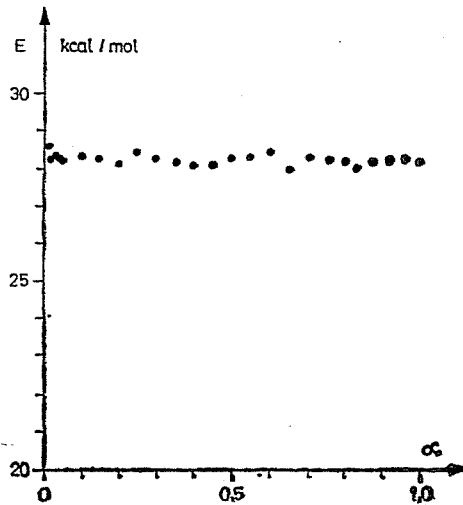


Fig. 7. Activation energy vs. weight loss diagram for the simulated reaction with an activation energy of 28 kcal

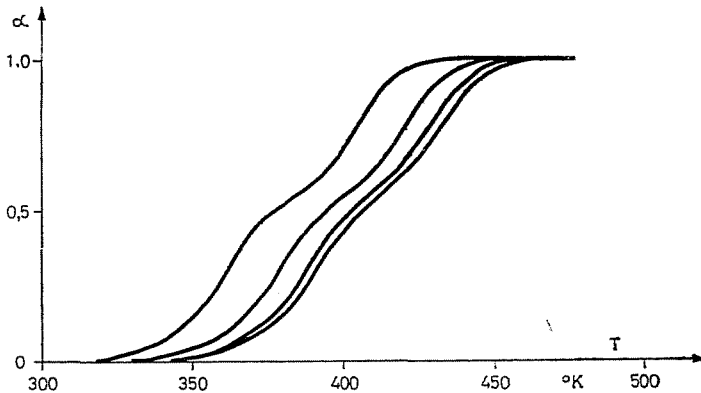


Fig. 8. Simulated thermogravimetric curves of two consecutive reactions with 20, and 28 kcal/mole activation energies and a pre-exponential factor of 10^{+13} for various heating rates

used, the activation energy is not included in the slope. Nevertheless, taking into consideration the approximative character of the method, further the fact that, while the activation energy figures in the slope as an exponent, it is included in the constant term only at the first power, the method can be used also for small changes of the activation energy. To illustrate this, the simulated thermogravimetric curves of two consecutive processes of 20, and 28 kcal/mole activation energy, respectively, and a pre-exponential factor of 10^{+13} have been prepared and are shown in Fig. 8. The curvature corresponding to the transition of the two separated processes is little appears on the curve at temperature rate 1, 4, 8 and 10. The activation energy calculated with the

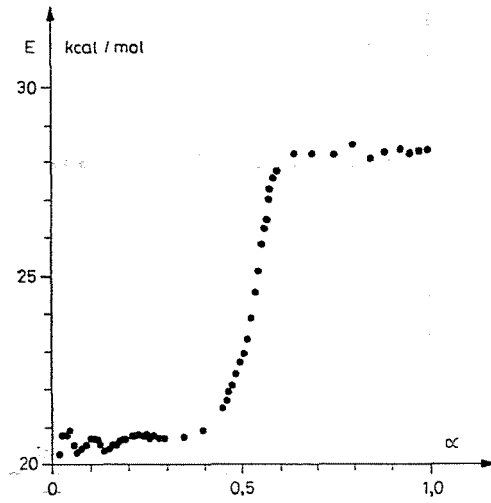


Fig. 9. Activation energy vs. weight loss diagram for the simulated consecutive reactions with 20 and 28 kcal/mol activation energies

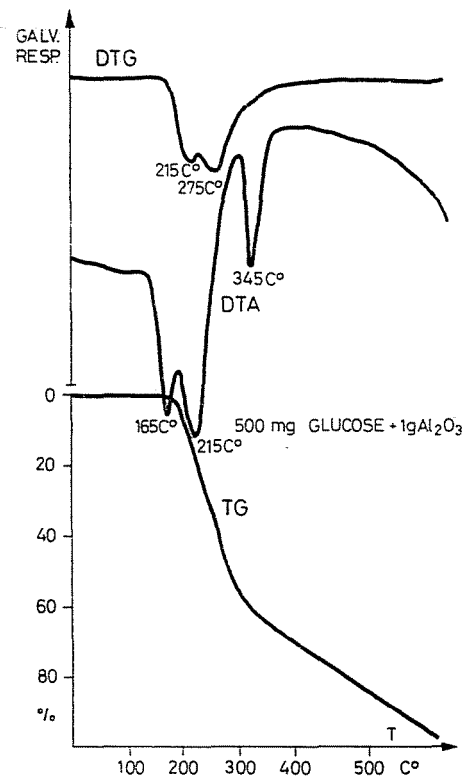


Fig. 10. Thermal curves of glucose

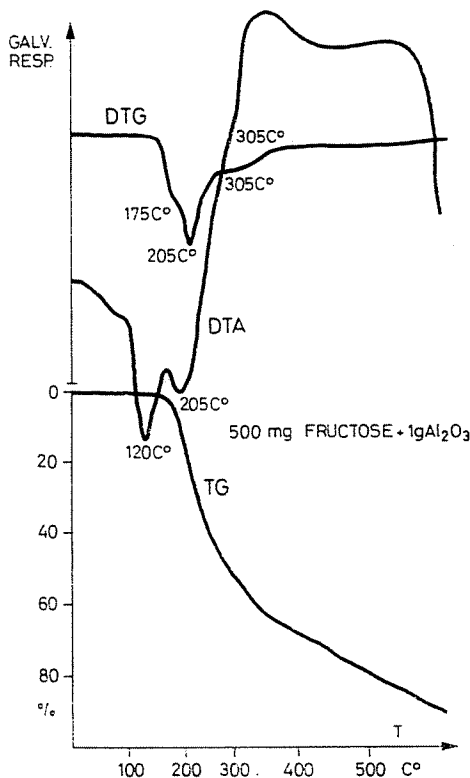


Fig. 11. Thermal curves of fructose

method described is shown in Fig. 9 as a function of the loss in weight. The initial 20 and final 28 kcal/mole values are seen to agree well with the activation energies of the processes taking place.

The method has been applied for investigating the thermal decomposition of glucose and fructose.

In our earlier investigations [4] glucose and fructose mixed with aluminium oxide, heated at a rate of 6 °C/min melt, were found to decompose at a loss of weight of about 25 per cent into brown colour substances. Above 300 °C, the formed caramel colour substances are pyrolysed, and then completely burnt. The method described has been applied in the initial section of the decomposition, up to 250 °C.

In Figs 10 and 11 the derivatograms of glucose and fructose are shown. The reaction investigated kinetically is the first endothermal reaction after melting. In the case of glucose this seems to be a single, uniform process, while in the case of fructose it proceeds in two sections of different rate, which can be distinguished primarily on the basis of the DTG curves [3].

The samples, prepared identically, were heat-treated at heating rates of 0,5 to 8,0 °C/min, the activation energies were calculated from the values read from the derivatograms, and have been plotted in Fig. 12 as a function of the loss in weight.

Two identical curves have been obtained for glucose and fructose, the difference little exceeding the standard deviation of ± 2 kcal/mole.

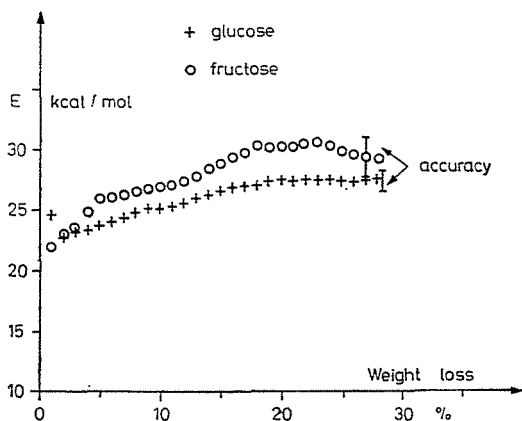


Fig. 12. Activation energy vs. weight loss diagram

The activation energy is seen to decrease from the initial value of 26–28 kcal/mole to 22 kcal/mole, then to increase again to an average value of 26 to 28 kcal/mole for both sugars.

This value is in good agreement with the activation energy of 28 kcal/mole, observed for the decomposition of glucose under isothermal conditions, further with the value of 30 kcal/mole, determined in the case of both sugars for the formation of 5-hydroxymethyl furfural.

The minimum observed for the activation energy at the beginning of the decomposition can be ascribed to the alkali ions dissolved by the sugars from the aluminium oxide.

According to the flame-photometric investigation of the melt, about 1 mg of sodium ion is leached out from 1 g of aluminium oxide. To enhance the effect, anhydrous sodium carbonate, corresponding to about a tenfold of sodium ions, was added to the glucose–aluminium oxide mixture, and the above test and calculations were repeated. The modified activation energy curve is shown in Fig. 13.

The relatively large quantity of alkali ions is to have reduce the activation energy to a value of 21 kcal/mole. When using pure aluminium oxide, the curve returns to its original value of 26 kcal/mole, because the acids formed bind the alkali ions in form of salts, while this is impossible at a tenfold quantity.

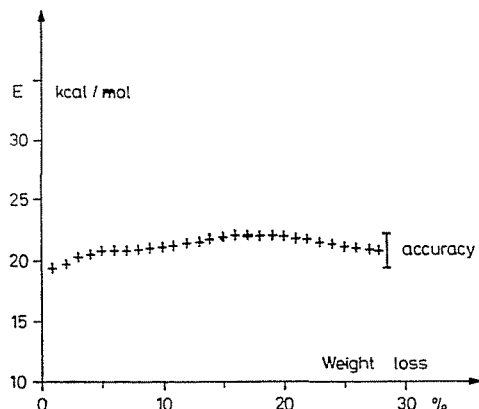


Fig. 13. Activation energy vs. weight loss diagram for a mixture of 100 mg glucose + 20 mg Na_2CO_3 + 1 g Al_2O_3

Thus, the method described gave values for the activation energy in good agreement with the results of isothermal investigations, and the activation energy proved to be suitable for characterizing the catalytic effect of additives affecting the reactions.

Summary

OZAWA worked out a graphic method for computing the kinetic parameters of any thermal reaction from the thermal gravimetric curves taken at various heating rates.

This method was transformed for the estimation of the activation energy by a computer program.

The method and the results are shown on some models and are used for the thermal decomposition of glucose and fructose.

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