

## INVESTIGATION ABOUT METHODS OF QUANTITATIVE EVALUATION OF DTA CURVES

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The investigation gives a comparison of the best-known kinetic evaluation methods for DTA curves. With regard to accuracy and error-compensation, the methods of Borchart and Daniels, Coats and Redfern and Šatava and Škvara in particular are to be recommended if simple irreversible reactions are to be evaluated on the basis of homogeneous kinetics. The complete exponential integral method is described which totally eliminates the approximative character of the practical procedure of Coats and Redfern. Hence, it becomes theoretically exact again.

In an estimation of the accuracies and sensitivities of well-known methods of evaluating differential thermal analysis (DTA) or differential thermogravimetric (DTG) curves, it is necessary to compare these procedures using defined curve shapes. It is obvious to apply synthesized model curves, as will be demonstrated very precisely under defined premises by means of a computer. Other subjects of comparison, such as selected experimental DTA or DTG and EGA curves, respectively, are influenced by unknown error sources a priori. Such effects lead to inadmissible generalizations, as in the testing of some evaluation procedures by Chen [1].

The present investigation starts from a homogeneous irreversible first-order model reaction, produced using the computing program DTA-1 for the following parameters, including the Arrhenius equation:

$$\begin{array}{ll} H_R = 40 \text{ kcal mole}^{-1} & q = 3.75 \text{ deg min}^{-1} \\ E = 20 \text{ kcal mole}^{-1} & V = 0.005 \text{ l} \\ k_0 = 10^{12} \text{ min}^{-1} & C_p = 5.714 \text{ cal deg}^{-1} \\ c = 0.1 \text{ mole l}^{-1} & K = 4.0 \text{ cal deg}^{-1} \text{ min}^{-1} \end{array}$$

$$\frac{dx}{dt} = \frac{c}{KA} \left[ C_p \frac{d\Delta T}{dt} + K\Delta T \right], \text{ with } A = \int_0^{\infty} \Delta T dt \quad (1)$$

$$= k_0 \exp(-E/RT)(c - x)^n \quad (2)$$

Figure 1 shows the theoretical DTA curve, as well as one with incidental errors; another curve with larger errors will be presented later. The mean error in  $\Delta T$  amounts to 8 and 14 percent, respectively. The theoretical curve was calculated

down to 0.1 percent of  $\Delta T_{\max}$ , but values down to 10 percent of  $\Delta T_{\max}$  were generally involved in the comparisons.

For the comparisons eight well-known methods were employed. The method of Kissinger [2] was included, although it needed more than two DTA curves at

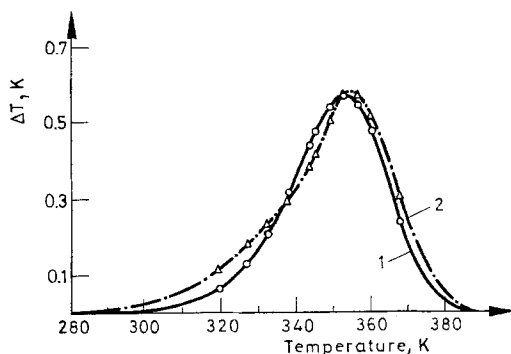


Fig. 1. Theoretical DTA curve (curve 1, o) and DTA curve with incidental errors (curve 2,  $\Delta$ ).

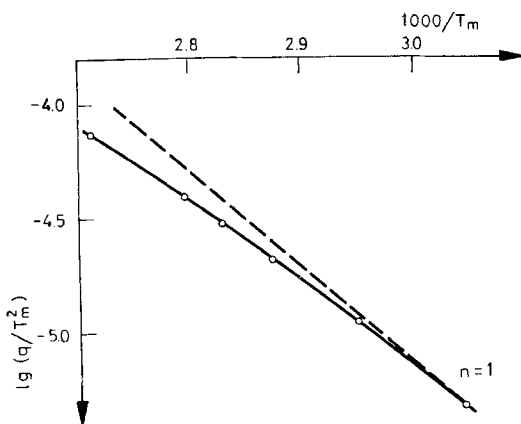


Fig. 2. Plot according to the method of Kissinger.

different heating rates  $q$ , which makes unclear the consideration of error-affected curves. Figure 2 illustrates six exact model curves with variation of  $q$  from 0.5 to 10 degree  $\text{min}^{-1}$ . Relative large deviations from the linearity of Eq. (3) are visible even in the region of low temperatures of the DTA maximum,  $T_m$ :

$$\frac{d \log q/T_m^2}{d(1/T_m)} = -\frac{E}{2.3 R} \quad (3)$$

Putting the temperature of the maximum of the reaction rate  $T_{\text{rm}}$  equal to the temperature of the DTA maximum,  $T_m$ , is still not allowed for  $q = 0.5 \text{ deg min}^{-1}$ ,

the activation energy remaining too small by 6.2 percent. A further simplification was applied to the exponential integral.

In the evaluation of Piloyan et al. [3] the first part of the DTA curve was exploited. The premise for the validity of Eq. (4) is a high heating rate, by which the exponential function related to Eq. (2) becomes important, if  $\Delta T$  is proportional to the reaction rate  $dx/dt$ :

$$\ln \Delta T = -E/RT + \text{const.} \quad (4)$$

As shown in Fig. 3, this method is still not sufficiently usable for  $q = 3.75 \text{ deg min}^{-1}$ . It does not describe the theoretical curve as a linear function. Moreover, experimentally the inaccuracies of the initial slope are larger than near the DTA maximum.

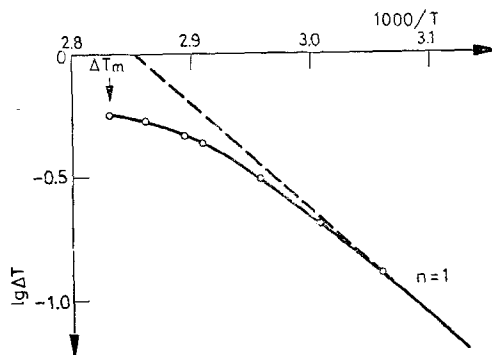


Fig. 3. Plot according to the method of Piloyan et al.

Borchardt and Daniels [4] belong to the pioneers of quantitative DTA. They developed a differential procedure for the establishment of the instantaneous reaction rate,  $dx/dt$ , with a function of the type of Eq. (1). After integration, the rate constant  $k = \frac{dx/dt}{(c-x)^n}$  was formed. If the choice of the reaction order  $n$  is correct, then, after Arrhenius, a straight line appears, from which the reaction parameters  $E$  and  $k_0$  can be obtained:

$$\log \frac{dx/dt}{(c-x)^n} = \log k = -E/2.3 RT + \log k_0 \quad (5)$$

The theoretical DTA curve in Fig. 4 gives a straight line. The errors in curves 2 and 3 are clear in this diagram, but the linear connexion is still not disturbed strongly. A distinction between first and second orders throughout is possible near the maximum,  $T_m$ .

Freeman and Carroll [5] developed a difference procedure which has some obvi-

ous advantages and disadvantages. The advantage consists in not proving the reaction order  $n$ , if, as in Fig. 5, the mathematical exact form of Eq. (6) is plotted:

$$\frac{\Delta \log(dx/dt)}{\Delta \log(c-x)} = -\frac{E}{2.3 R} \frac{\Delta(1/T)}{\Delta \log(c-x)} + n \quad (6)$$

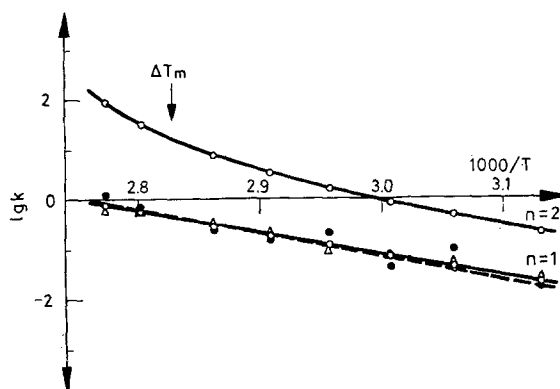


Fig. 4. Plot according to the method of Borchardt and Daniels. ●: from DTA curve with larger errors.

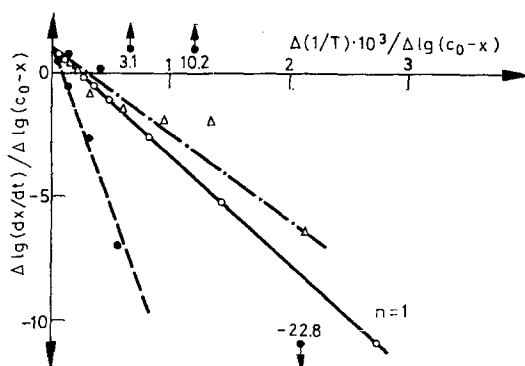


Fig. 5. Plot according to the method of Freeman and Carroll.

However relatively small deviations from the model course result in large deviations, in contrast to the theoretical straight line. Therefore, this procedure calls for high requirements as regards the measuring accuracy, because the ratio of differences of small amounts is to be formed. A further disadvantage is the fact that it is impossible to coordinate the points of the DTA curve to those of Fig. 5, because it is unknown whether the differences are formed from neighbouring or distant points. Therefore, a curve discussion is difficult. The Figure demonstrates that the evaluation of a strongly error-affected curve is not meaningful. A feature

of the described plot is the clustering of the calculated points along the abscissa in the region of small values. Using equal temperature step-widths, this region corresponds to higher temperatures.

In the integrative method of Coats and Redfern [6] an approximation is applied, which results from the treatment of the exponential integral. An asymptotic series evolution for the exponential integral in Eq. (7) is cut off with the second term as shown in Eq. (8):

$$\int_0^x \frac{dx}{(c-x)^n} = g(x) = k_0 \int_0^t \exp(-E/RT) dt = \frac{k_0}{q} \int_0^T \exp(-E/RT) dT \quad (7)$$

$$\log \frac{g(x)}{T^2} = -\frac{E}{2.3 RT} + \log \frac{k_0 R}{qE} \left[ 1 - \frac{2RT}{E} \right] \quad (8)$$

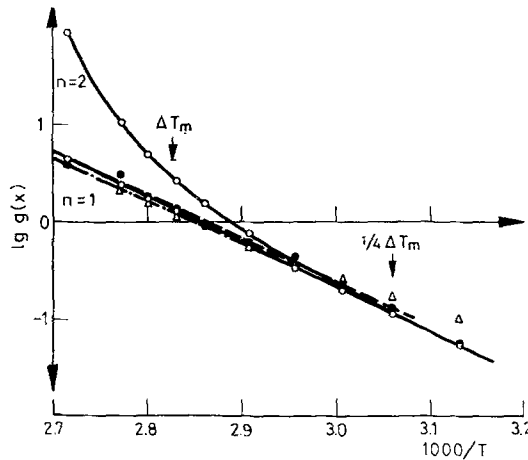


Fig. 6. Plot according to the method of Coats and Redfern.

The remaining temperature-dependence of this expression is neglected. Figure 6 shows that the graph  $\log g(x)/T^2$  vs.  $1/T$  depends strongly on the reaction order near the DTA maximum and at high temperatures, but only slightly in the ascending DTA branch. The erroneous curves are still appropriate for an evaluation, although for the activation energy and the parameter  $k_0$  distinct deviations are to be expected.

The method of Šatava and Škvara [7] consists in a comparison of the  $\log g(x)$  vs.  $1/T$  curve with a family of calculated  $\log p(z)$  vs.  $1/T$  curves with  $E$  as a family parameter. The activation energy ( $z = E/RT$ ) follows from the congruence of two curves. By parallel shifting, one finds the parameter  $k_0$ , because

$$\log g(x) - \log p(z) = \log \frac{k_0 E}{qR} = \text{const.} \quad (9)$$

As visible from Fig. 7, the influence of  $1/T^2$  is hardly noticeable in the model curve, although a soft flexure of the straight line does occur. This is also caused by a correction of the  $\log g(x)/T^2$  function described below for the procedure of Coats and Redfern, which operates in the same direction.

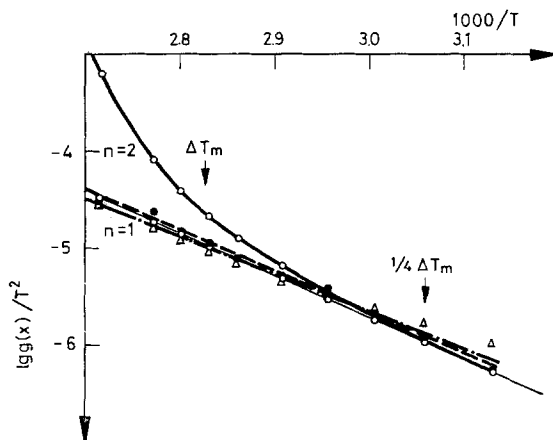


Fig. 7. Plot according to the method of Šatava and Škvara.

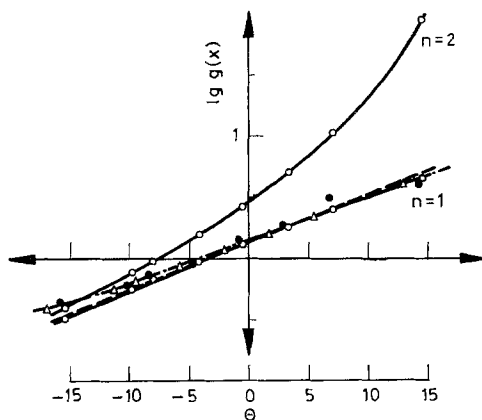


Fig. 8. Plot according to the method of Horowitz and Metzger.

After Horowitz and Metzger [8], in the region of the maximum of the DTA curve relation Eq. (10) is approximately valid, if  $T_{rm}$  is the temperature of the maximum of the reaction rate:

$$\log g(x) = \frac{E}{2.3 RT_{rm}^2} \Theta; \text{ where } \Theta = T - T_{rm} \quad (10)$$

In practice one puts  $T_{rm} = T_m$ . Figure 8 indicates, that the theoretical DTA curve is not a straight line. Because the approximation is obviously linear, near the DTA maximum, a decision as to the reaction order may be very difficult.

An interesting method was proposed by Gyulai and Greenhow [9]. This has the advantage of including the exponential integral totally by numerical integration. One needs at least two DTA curves for different heating rates, and then a temperature pair  $T_{1x}$  and  $T_{2x}$  must be combined according to the same reaction turnover  $x$ . It then follows from Eq. (7) that

$$\frac{g(x)_1}{g(x)_2} = \frac{q_2}{q_1} \frac{I_{11}}{I_{21}} = 1; \quad I_{1x} = \int_0^{T_{1x}} \exp(-E/RT) dT \quad (11)$$

$$\log \frac{q_1}{q_2} = \log \frac{I_{11}}{I_{21}} \quad (12)$$

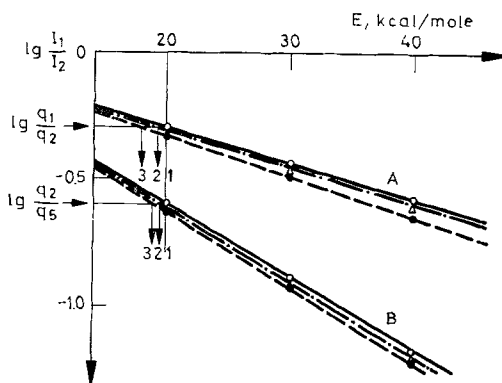


Fig. 9. Plot according to the method of Gyulai and Greenhow

For the temperature pairs  $T_{1x}$  and  $T_{2x}$  the corresponding integrals were taken from tables, and  $\log I_1/I_2$  drawn as a function of the activation energy. The relations constructed are linear. Because of the equality Eq. (12), in Fig. 9 the logarithm  $q_1/q_2$  is introduced. At the point of intersection Eqs. (11) and (12) are fulfilled. The Figure contains a representation of experiments 1 and 2, and 2 and 5, respectively. Despite the mathematical exactness of this procedure, it must be pointed out that it is very sensitive to experimental errors. Thus, an uncertainty of about  $\pm 0.4$  degree in  $T_x$  means a fluctuation of about 10 percent in the activation energy.

The method developed by Székely and Lengyel [10] is an interesting one. In comparison to the procedures described hitherto, it needs both the first and the second derivatives of the turnover with respect to time. Because of these high demands as to the precision of the experiments, in this case the evaluation of error-

Table 1  
Comparison of activation energies with a theoretical value  
 $E = 20 \text{ kcal mole}^{-1}$

	DTA curve 1 (%)	DTA curve 2 (%)	DTA curve 3 (%)
Kissinger	18.76 (6.2)	—	—
Piloyan et al.	18.74 (6.3)	—	—
Borchardt—Daniels	20.00 (0)	19.96 (0.2)	21.15 (5.7)
Freeman—Carroll	19.86 (0.7)	15.60 (22.0)	59.68 (198.4)
Coats—Redfern	20.00 (0)	18.49 (7.5)	19.18 (4.1)
Škvara—Šatava	20.00 (0)	19.30 (3.5)	19.50 (2.5)
Horowitz—Metzger	22.03 (10.2)	18.29 (8.5)	20.24 (1.2)
Gyulai — Greenhow	20.00 (0)	19.21 (4.0)	17.93 (10.4)
Székely — Lengyel	20.00 (0)	—	—

affected curves was without chance of success. On the other hand, the results for the theoretical model curve are in complete agreement with expectations. The plot in the proposed diagram produces a linear correlation.

Table 1 lists activation energies obtained by the different evaluation procedures. It is clear that the methods of Borchardt and Daniels, Coats and Redfern and Šatava and Škvara give the best results, even under extreme conditions. Furthermore, these procedures show relatively good linearization and error compensation. The premises and demands of the other methods prove poorer in practice. This conclusion agrees with that of Zsakó [11] in part, but is in contrast to that of Chen [1], who supported the method of Freeman and Carroll. However, his example diagram is distinctly non-linear and pointed to deficiencies in the experimental data as a basis of comparison. Indeed, the Freeman and Carroll method is a sensitive indicator for deviations from the theoretically exact DTA curve, especially in the region of small reaction turnovers.

### The method of complete exponential integrals

It was seen above that the method of Coats and Redfern is very practicable, although it uses a simplified equation of evaluation; this has often been improved by different corrections [12]. Our earlier investigations [13] succeeded in eliminating the approximation character of this method totally, whereby this procedure becomes theoretically equal with that of Borchardt and Daniels. By integration of the reaction rate expression of Eq. (2) up to time  $t$ , one obtains Eq. (7). After partial integration:

$$g(x) = \frac{k_0 E}{qR} \left[ \frac{e^{-z}}{z} + \int_{\infty}^z \frac{e^{-u}}{u} du \right]; \text{ where } \begin{matrix} u = E/RT \\ z = (E/RT)_x \end{matrix} \quad (13)$$



For large values of  $z$ , an asymptotic series is often used instead of the exponential integral. Cutting off this series yields the expression in Eq. (8). Compared with this, the exact formula is given in Eq. (14):

$$\log \frac{g(x)}{T^2} = -\frac{E}{2.3 RT} + \log [(z)] + \log \frac{k_0 R}{qE} \quad (14)$$

Therefore, the exponential integral was calculated numerically by computer. In fact, a straight line is not to be expected if  $\log g(x)/T^2$  is plotted against  $T^{-1}$ , if the complete exponential integral is involved. Figure 10 shows such a total curve.

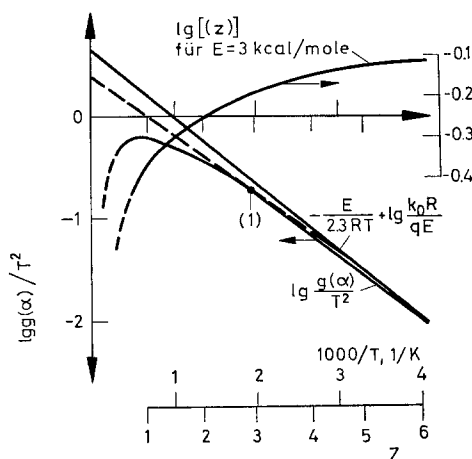


Fig. 10. Plot according to the method of Anderson et al.

Therefore, the tangent at one point gives only an apparent activation energy. From the slope we obtain the real activation energy by differentiation of Eq. (14) with respect to  $T^{-1}$  (see Eq. (15)). The reaction parameter  $k_0$  is now found from Eq. (14) by introduction of  $E(\text{real})$ :

$$\frac{d \log \frac{g(x)}{T^2}}{d(1/T)} - \frac{d \log [(z)]}{d(1/T)} = -\frac{E(\text{real})}{2.3 R} \quad (15)$$

Both required correction values,  $\log [(z)]$  and its derivative with respect to  $T^{-1}$ , are collected in a table (see [13]) as a function of  $z$ . This finishes the discussion of the approximative character of Eq. (8). The exponential integral is now completely available by means of the exact correction. Hence, the qualitative evaluation of DTA curves of simple reactions is possible without approximation. The error in percentage for  $E$  is smaller than for  $k_0$ . It amounts for  $z = 10$  to about  $\Delta E 2.2$  per cent and  $\Delta k_0 30$  per cent. For our model curve with  $z = 28.8$   $\Delta E$  is smaller than 0.1 per cent and  $\Delta k_0$  about 7 per cent. In Table 1 these facts are not considered.

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RÉSUMÉ — L'étude porte sur la comparaison des méthodes les plus connues d'exploitation cinétique des courbes ATD. Du point de vue de l'exactitude et de la compensation des erreurs, on établit que les méthodes de Borchardt et Daniels, de Coats et Redfern ainsi que de Šatava et Škvára peuvent être recommandées pour l'étude des réactions irréversibles simples en cinétique homogène. Dans la seconde partie, on décrit la méthode d'intégration exponentielle complète qui supprime totalement le caractère approximatif de la méthode de Coats et Redfern.

ZUSAMMENFASSUNG — Die Untersuchung beschäftigt sich mit dem Vergleich der bekanntesten kinetischen Auswerteverfahren für DTA-Kurven. Unter Beachtung der Genauigkeit und des Fehlerausgleiches wird festgestellt, daß die Methoden von Borchardt und Daniels, Coats und Redfern sowie Šatava und Škvára besonders empfehlenswert sind, wenn man einfache irreversible Reaktionen auf der Grundlage der Homogenkinetik auswerten will. — Im zweiten Teil wird die Methode des vollständigen Exponentialintegrals beschrieben, die den Näherungscharakter in dem praktikablen Verfahren von Coats und Redfern aufhebt. Dadurch wird es wieder theoretisch exakt.

Резюме — Проведено сравнение самых известных кинетических методов выделения для кривых ДТА. Учитывая точность и компенсационную ошибку, было установлено, что методы Борхардта—Даниэльса, Коутса—Редферна, а также метод Шатавы—Шквары особо рекомендуемы, если простые необратимые реакции могут быть выделены на основании гомогенной кинетики. Во второй части метода описан полный экспоненциальный интеграл, который полностью разрешает приближенный характер практически используемой методики Коутса—Редферна. При этом метод становится снова теоретически точным.