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HALF-WIDTH AND ASYMMETRY OF GLOW PEAKS AND THEIR CONSISTENT ANALYTICAL REPRESENTATION

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The kinetic equation which describes many electronic as well as atomic or chemical reactions under the condition of a steadily linear raise of the temperature, is considered in a mathematically exact and straightforward way. Therefore, the equation has been transformed into a dimensionless form, using with profit the maximum condition for the intensity peak. The two temperatures T_1 and T_2, corresponding to the half-height of the intensity peak, are found as unique polynomials of the small argument $\bar{y} \equiv k\bar{T}/E$ only ($\bar{T} =$ temperature of peak maximum). Thereupon, further combinations give half-width δ, peak asymmetry $A = \delta_2/\delta_1$ or $\bar{A} = \bar{C}/(1 - \bar{C})$ and the maximum of the intensity peak $\bar{J}$; they again all depend only on $\bar{y}$. In some cases this dependence is weak, so that e.g. it is deduced that the half-width energy product divided by $\bar{T}^2$ is an invariant, different for every kinetic order γ:

$$\frac{\delta \cdot E[\text{eV}]}{\bar{T}^2} = \begin{cases} 1/4998\ \text{K for monomolecular processes} \\ 1/3542\ \text{K for bimolecular processes} \\ 1/2872\ \text{K for trimolecular processes} \end{cases}$$

By means of these correlations, activation energy values E [eV] can be determined accurately to within 0.5%, so that for most experiments the inaccuracy of the δ values becomes dominant and limiting. A special nomogram for the express estimation of E from experimentally observed δ and $\bar{T}$ is demonstrated.

Many different physical and chemical processes have been described by the rate equation

$$-\frac{\mathrm{d}c}{\mathrm{d}\tau} = \frac{c^\gamma}{c_0^{\gamma-1}} \cdot K_0 \cdot e^{-\mathrm{R/kT}};\ c_0 = c(\tau_0) \tag{1}$$

with the usual notations: c = concentration of some kind of reactant; γ = kinetic order; K_0 = frequency factor which can include such further quantities as jump number, reaction or trapping cross sections and a distinct own-temperature dependency, but this will not be discussed here; E = activation energy; τ = time; T = temperature, and k = Boltzmann constant.

A special and suitable manner for experimental investigations consists in the observation of the enhancement of such processes when the temperature of the system is raised continuously with a constant heating rate $q = \mathrm{d}T/\mathrm{d}\tau$. It is known that then the exponential term in Eq. (1) is strongly accelerated. At some moment the process rate reaches a maximum and decreases because of the exhaustion of the reactant concentration. Typical effects have been investigated: Thermo-

Stimulated Luminescence, TS Exoelectron Emission, TS Polarization or Depolarization, TS Charge or Capacity effects, TS Desorption, TS Creep, TS Calorimetry or Gravimetric effects, and in many other combinations. Therefore, a correct mathematical solution for the general case is needed, besides the various specified approaches which have been developed for special circumstances for the abovementioned effects.

Concentration and intensity curves, i.e. glow curves, exhibit a characteristic shape, asymmetry and prominent points, which will be discussed and calculated in this note and which are illustrated in Fig. 1 for the particular cases $\gamma = 0$, 1, 2 and 3. Commonly the rate equation is solved directly with respect to the temperature dependence of the concentration and as functions of the process parameters E, K_0 and γ and the experimental condition q [1–4]. It is the aim of this note to deduce some general features of the concentration and the intensity behaviour, and therefore the usual solution procedure should be altered slightly.

Reduced dimensionless reaction equation

From the maximum condition* $\mathrm{d}^2c/\mathrm{d}T^2|_{\bar{T}} = 0$ and with the use of q, one gets

$$\frac{K_0}{q} = \frac{E}{\gamma k\bar{T}^2} \cdot e^{E/k\bar{T}} \cdot \left(\frac{c_0}{\bar{c}}\right)^{\gamma-1} \tag{2}$$

(the dash refers on all symbols to the peak maximum position). Therefore, instead of Eq. (1) it is more easy to use as a starting equation with separated variables

$$-\gamma \cdot \bar{C}^{\gamma-1} \cdot \frac{\mathrm{d}C}{C^\gamma} = \frac{E}{k \cdot \bar{T}^2} \cdot e^{\frac{E}{k\bar{T}}\left(1-\frac{\bar{T}}{T}\right)} \mathrm{d}T. \tag{3}$$

It is the scope of this form of the equation to indicate that its integral should depend only on the following relatives: $y \equiv kT/E$, $t \equiv T/\bar{T} = y/\bar{y}$ and $C(T) \equiv$ $\equiv c(T)/c_0$. Physically, this means some normalization: the actual temperature T is to be related to T and energies E have to be compared with kT. For the considered physical processes it holds without artificial limitations that $y < 0.1$, and the processes occur only in a small temperature interval around T.

Integration of Eq. (3) starting at $t = 0$, $T = 0$, $y = 0$ and $C_0 = 1$ up to $C(T)$ gives:

$$\left.\begin{array}{ll} \text{for } \gamma \neq 1, \neq 0 & \dfrac{\gamma \cdot \bar{C}^{\gamma-1}}{\gamma - 1}\left(\dfrac{1}{C^{\gamma-1}} - 1\right) \\ \text{for } \gamma = 1 & \ln\dfrac{1}{C} \\ \text{for } \gamma = 0 & 1 - C \end{array}\right\} = t^2 \cdot e^{(1-1/t)/\bar{y}} \cdot \eta(y) \tag{4}$$

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* The case $\gamma = 0$ is included, although here an inflection point cannot occur for $C^{(0)}$; here the maximum comes from the absolute exhaustion $C(\bar{\bar{T}}) = 0$ at a moment $\bar{\bar{t}} > 1$, so that the maximum condition reads:

$$\eta(\bar{\bar{y}}) \cdot \bar{\bar{t}}^2 \cdot \exp\,[(1 - 1/\bar{\bar{t}})/\bar{\bar{y}}] = 1.$$

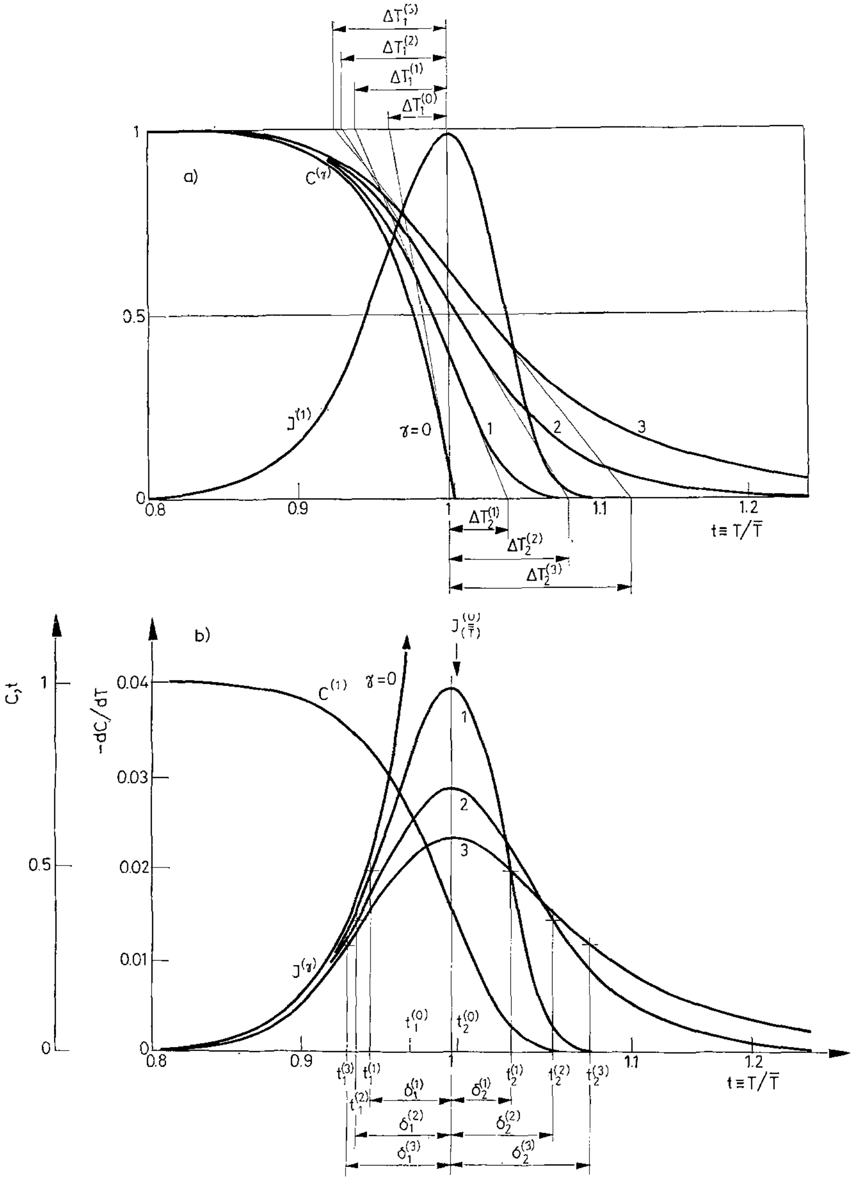

Fig. 1. a) Concentration and b) intensity curves for processes obeying different kinetic orders $\gamma = 0, 1, 2$ or 3, against a common reduced temperature $t \equiv T/\bar{T}$; the numerical scales are chosen for a case $\bar{\gamma} = 0.04$; + : half-height positions; $\delta_1^{(\gamma)}$, $\delta_2^{(\gamma)}$: lower and upper half-widths. Steepest slope (Fig. 1a) in the concentration curves corresponds to the peak maximum in the intensity curves (Fig. 1b). Intercepts $\Delta T^{(\gamma)}$ had been proposed in [8, 16] for use in the systematic analysis methods; in practice the case $\gamma = 0$ can not easily be determined from experimental data. From C curves alone it is difficult to find the position $\bar{t} = 1$; one can make use of systematic similarities and deviations between $\Delta T^{(\gamma)}$ and $\delta_1^{(\gamma)}$ [16].

where
$$\eta(y) \equiv 1 + \sum_{n=1}^{1/\gamma-2} (-1)^{n} \cdot (n+1)! \cdot y^{n}. \tag{5}$$

Although the terms in this last series are very small due to $y < 0.1$, they have to be taken into account for a correct calculation. Several authors admitted some rounding errors in their derivations; we shall not do so, on the consequences of an incorrect account of these small terms in this correction function $\eta(y)$ see [5], which on the other hand is always close to unity: $\eta(y) \leqq 1$.

From (4) it follows that

$$\bar{C} \equiv C(\bar{T}) = \begin{cases} \left(1 - \dfrac{\gamma-1}{\gamma}\bar{\eta}\right)^{1/(\gamma-1)} & \text{for } \gamma \neq 1, \neq 0 \\ e^{-\bar{\eta}} & \gamma = 1 \\ 1 - \bar{\eta} & \gamma = 0 \end{cases} \tag{6}$$

and

$$\frac{C(T)}{\bar{C}} = \begin{cases} \left[\dfrac{\gamma}{\gamma - (\gamma-1)\bar{\eta} + (\gamma-1)\eta t^{2} \cdot \exp\left(\dfrac{1-1/t}{\bar{y}}\right)}\right]^{1/(\gamma-1)} \\ \exp\left[\bar{\eta} - \eta t^{2} \cdot \exp\left(\dfrac{1-1/t}{\bar{y}}\right)\right] \\ \left[1 - \eta t^{2} \cdot \exp\left(\dfrac{1-1/t}{\bar{y}}\right)\right] \Big/ (1-\bar{\eta}) \end{cases} \tag{7}$$

Half-width temperatures $T_i^{(\gamma)}$

Now those two temperature positions $T_i = T_1$ and T_2 should be determined, where the intensity $J(T) \equiv -\mathrm{d}C/\mathrm{d}T$ is half of the maximum intensity. By means of Eq. (1) or (3)

$$\frac{J(T_i)}{\frac{1}{2}J(\bar{T})} = 1 = 2 \cdot \left(\frac{C_i^{(\gamma)}}{\bar{C}^{(\gamma)}}\right)^{\gamma} \cdot e^{\frac{E}{K\bar{T}}\left(1-\frac{\bar{T}}{T_i}\right)} = 2 \cdot \left(\frac{C_i^{(\gamma)}}{\bar{C}^{(\gamma)}}\right)^{\gamma} \cdot \exp\left(\frac{1-1/t_i^{(\gamma)}}{\bar{y}}\right) \tag{8}$$

The superscript (γ) indicates the individual solution for every distinct kinetic order.

Inserting (7) in (8) and with a slight rearrangement, we get the following equations for $t_i^{(\gamma)}$ (and $T_i^{(\gamma)}$):

$$2 \cdot \gamma^{\frac{\gamma}{\gamma-1}} \cdot \exp\left(\frac{1 - 1/t_{\mathrm{i}}^{(\gamma)}}{\bar{y}}\right) -$$

$$-\left[\gamma - (\gamma - 1)\bar{\eta} + (\gamma - 1)\eta_i t_{\mathrm{i}}^{(\gamma)^2} \cdot \exp\left(\frac{1 - 1/t_{\mathrm{i}}^{(\gamma)}}{\bar{y}}\right)\right]^{\gamma/(\gamma-1)} = 0 \qquad (9)$$

$$\text{for } \gamma \neq 1, \neq 0$$

$$\ln 2 + \frac{1 - 1/t_{\mathrm{i}}^{(1)}}{\bar{y}} + \bar{\eta} - \eta_{\mathrm{i}} \cdot t_{\mathrm{i}}^{(1)^2} \cdot \exp\left(\frac{1 - 1/t_{\mathrm{i}}^{(1)}}{\bar{y}}\right) = 0 \qquad (10)$$

$$\text{for } \gamma = 1$$

Let us remember that $y_{\mathrm{i}} = \bar{y} \cdot t_{\mathrm{i}}$, so that

$$\eta_{\mathrm{i}} \equiv \eta(y_{\mathrm{i}}) = \eta(\bar{y} \cdot t_{\mathrm{i}}) = \bar{\eta} + \sum_{n=1}^{1/\bar{y}-2} (-1)^{\mathrm{n}} \cdot (n + 1)!\, \bar{y}^{\mathrm{n}} \cdot (t_{\mathrm{i}}^{\mathrm{n}} - 1). \qquad (11)$$

Finally, this means for every individual γ that if (9) or (10) can be solved with respect to $t_{\mathrm{i}}^{(\gamma)}$, then these solutions should be unique functions of $\bar{y}$, only.

Because $\bar{\eta}$ and η_{i} are polynomials in $\bar{y}$, it is to be expected that the solutions can also be found in the form of a series expansion

$$t_{\mathrm{i}}^{(\gamma)} = 1 + a_{\mathrm{i}1}^{(\gamma)} \cdot \bar{y} + a_{\mathrm{i}2}^{(\gamma)} \cdot \bar{y}^2 + \dots \qquad (12)$$

$$\text{with } a_{11} < 0,\ a_{21} > 0.$$

For a suitable solution procedure, see Appendix I. Numerical results are summarized in Table 1.

Table 1

Temperatures $T_i^{(\gamma)}$, corresponding to the half-height $J_i(T_i) = \frac{1}{2}\bar{J}(\bar{T})$ of the intensity peak

$\bar{\eta} =$	1	$-\ 2 \cdot \bar{y}$	$+\ 6 \cdot \bar{y}^2$	$-\ 24 \cdot \bar{y}^3$	$+\ 120\ \bar{y}^4$	$-+ \dots$
$T_1^{(0)}/\bar{T} = t_1^{(0)} =$	1	$-\ 0.69315\bar{y}$	$+\ 2.48045\bar{y}^2$	$-\ 11.10561\bar{y}^3$	$+\ 51.910\bar{y}^4$	$-+ \dots$
$T_2^{(0)}/\bar{T} = t_2^{(0)} =$	1		$+\ 2\ \bar{y}^2$	$-\ 8\ \bar{y}^3$	$+\ 38.667\bar{y}^4$	$-+ \dots$
$T_1^{(1)}/\bar{T} = t_1^{(1)} =$	1	$-\ 1.46119\bar{y}$	$+\ 3.25246\bar{y}^2$	$-\ 8.6006\ \bar{y}^3$	$+\ 22.641\bar{y}^4$	$-+ \dots$
$T_2^{(1)}/\bar{T} = t_2^{(1)} =$	1	$+\ 0.98520\bar{y}$	$-\ 0.17380\bar{y}^2$	$+\ 0.0412\ \bar{y}^3$	$-\ 0.444\bar{y}^4$	$+- \dots$
$T_1^{(2)}/\bar{T} = t_1^{(2)} =$	1	$-\ 1.76275\bar{y}$	$+\ 5.64697\bar{y}^2$	$-\ 22.8422\ \bar{y}^3$	$-\ 101.863\bar{y}^4$	$-+ \dots$
$T_2^{(2)}/\bar{T} = t_2^{(2)} =$	1	$+\ 1.76275\bar{y}$	$-\ 1.40402\bar{y}^2$	$+\ 1.6274\ \bar{y}^3$	$+\ 0.993\bar{y}^4$	$+- \dots$
$T_1^{(3)}/\bar{T} = t_1^{(3)} =$	1	$-\ 1.97304\bar{y}$	$+\ 7.98120\bar{y}^2$	$-\ 42.4583\ \bar{y}^3$	$-\ 237.592\bar{y}^4$	$+- \dots$
$T_2^{(3)}/\bar{T} = t_2^{(3)} =$	1	$+\ 2.47958\bar{y}$	$-\ 4.08954\bar{y}^2$	$+\ 8.8971\ \bar{y}^3$	$+\ 51.764\bar{y}^4$	$-+ \dots$

Half-width, asymmetry and peak height

Now let us return to the physical situation. Lower, upper and full half-widths of the intensity peak are given for every γ by (see Table 2).

$$\delta_1^{(\gamma)}/\bar{T} \equiv 1 - t_1^{(\gamma)} = -a_{11}^{(\gamma)} \cdot \bar{y} - a_{12}^{(\gamma)} \cdot \bar{y}^2 - \dots \tag{13}$$

$$\delta_2^{(\gamma)}/\bar{T} \equiv t_2^{(\gamma)} - 1 = a_{21}^{(\gamma)} \cdot \bar{y} + a_{22}^{(\gamma)} \cdot \bar{y}^2 + \dots \tag{14}$$

$$\delta^{(\gamma)}/\bar{T} = (\delta_1^{(\gamma)} + \delta_2^{(\gamma)})/\bar{T} = (a_{21}^{(\gamma)} - a_{11}^{(\gamma)}) \cdot \bar{y} + (a_{22}^{(\gamma)} - a_{12}^{(\gamma)}) \cdot \bar{y}^2 + \dots \tag{15}$$

More important, an extremely weak variance with $\bar{y}$ follows for

$$\kappa^{(\gamma)} \equiv \frac{\delta^{(\gamma)} \cdot E}{k\bar{T}^2} = \frac{t_2^{(\gamma)} - t_1^{(\gamma)}}{\bar{y}} = (a_{21}^{(\gamma)} - a_{11}^{(\gamma)}) + (a_{22}^{(\gamma)} - a_{12}^{(\gamma)}) \cdot \bar{y} + \dots \tag{16}$$

and for the peak asymmetry, which is well established experimentally,

$$A^{(\gamma)} \equiv \frac{\delta_2^{(\gamma)}}{\delta_1^{(\gamma)}} = \frac{t_2^{(\gamma)} - 1}{1 - t_1^{(\gamma)}} = \frac{a_{21}^{(\gamma)}}{-a_{11}^{(\gamma)}} \cdot \frac{1 + a_{22} \cdot \bar{y}/a_{21} + \dots}{1 + a_{21} \cdot y/a_{11} + \dots}, \tag{17}$$

For corresponding polynomials see Table 2; in the vicinity of $\hat{y} = 0.04$ the quantities A and κ are practically invariants – see right side of Table 2: $Y \equiv \bar{y} - 0.04$; $|Y| < 0.015$.

It should be noticed that the calculational accuracy should only be limited by the practical demand of precision which is considered in Appendix II. Here, never a term has been neglected and other approximations have not been admitted, never that the rate equation has been solved for the first time in a mathematically full and consistent way.

Previous attempts at a mathematical treatment of experimentally evidenced half-width and peak asymmetry led to crude, but close relations, which could not be well distinguished. Grossweiner [6] found $E \cdot \delta_1^{(1)}/KT_1 \cdot \bar{T} = 1.51$ for the low-temperature shoulder for monomolecular processes; later Dussel and Bube [7] claimed that this value should be better 1.40 ... 1.42 (with some difference in $T_1 < \bar{T}$ this is to be compared with our $-a_{11}^{(1)}$). Lushchik [8] concluded from graphical similarities between δ and ΔT (see Fig. 1) for the high-temperature side that – in our notation – $a_{21}^{(1)} \cong 1$ and $a_{21}^{(2)} \cong 2$.

Other authors developed trial-and-error methods for the evaluation of relations between E and T and δ [9–15]. The best critical examination was given by Chen [13] who showed that for $\gamma = 1$ and $\gamma = 2$ systematic errors arose for δ_1, δ_2 and δ, due to inaccuracies in the treatment of the reaction equation, but which because of their systematic nature can be used as "empirical" correction factors. Another means of correction has been with the aid of the steepest slope in a monomolecular concentration curve and the systematic error in $P/(\Delta T_i)$ [16].

For the first time it was deduced how such relations arise from the reaction equation itself in [17–19], and now details are obtained as to how such correlations are governed by the values $\bar{y} = k\bar{T}/E$ and $\bar{\eta}(y)$, i.e. by the correct account of the exponential integral. Therefore, there is also a demand to determine $\bar{y}$

Table 2

Polynomial representation of peak asymmetry $A^{(\gamma)}(\overline{y})$, half-width energy product $\kappa(\overline{y})$ and reduced half-width δ/T; mention on the right side the special expansion in the vicinity of $\hat{y} = 0.04$

$X(\overline{y}) = X(0) + \overline{y} \cdot B(\overline{y})$	$= X(0.04) \cdot [1 + Y \cdot B'(Y)]$
Asymmetry: $A^{(\gamma)} = \delta_2^{(\gamma)}/\delta_1^{(\gamma)} = (t_2^{(\gamma)} - 1)/(1 - t_1^{(\gamma)})$	
$A^{(0)} = \quad + 2.885\overline{y} - 1.22\overline{y}^2 + 5.2\overline{y}^3 - + ..$	$= 0.1138 \cdot [1 - 25.36Y + 5.2Y^2 - + ..]$
$A^{(1)} = 0.6742 + 1.382\overline{y} - 0.86\overline{y}^2 + 0.1\overline{y}^3 - + ..$	$= 0.7281 \cdot [1 + 1.80Y - 1.2Y^2 + - ..]$
$A^{(2)} = 1 + 2.407\overline{y} - 4.32\overline{y}^2 + 13.3\overline{y}^3 - + ..$	$= 1.0902 \cdot [1 + 1.95Y - 2.5Y^2 + - ..]$
$A^{(3)} = 1.2567 + 3.011\overline{y} - 10.35\overline{y}^2 + 70.9\overline{y}^3 - + ..$	$= 1.3651 \cdot [1 + 1.85Y - 1.4Y^2 + - ..]$
Half-width energy product: $\kappa^{(\gamma)} = (t_2^{(\gamma)} - t_1^{(\gamma)})/\overline{y} = \delta^{(\gamma)} \cdot E/k\overline{T}^2$	
$\kappa^{(0)} = 0.6931 - 0.480\overline{y} + 3.11\overline{y}^2 - 13.2\overline{y}^3 + - ..$	$= 0.678 \cdot [1 - 0.4\ Y - 0.1Y^2 + - ..]$
$\kappa^{(1)} = 2.4464 - 3.426\overline{y} + 8.64\overline{y}^2 - 23.1\overline{y}^3 + - ..$	$= 2.324 \cdot [1 - 1.13Y + 4.9Y^2 - + ..]$
$\kappa^{(2)} = 3.5255 - 7.051\overline{y} + 24.47\overline{y}^2 - 100.9\overline{y}^3 + - ..$	$= 3.276 \cdot [1 - 1.70Y + 3.8Y^2 - + ..]$
$\kappa^{(3)} = 4.4526 - 12.071\overline{y} + 51.36\overline{y}^2 - 185.8\overline{y}^3 + - ..$	$= 4.040 \cdot [1 - 2.19Y + 7.2Y^2 - + ..]$
Reduced half-width:	
$\delta^{(0)}/\overline{T} = 0.693\overline{y} - 0.48\overline{y}^2 + 3.1\overline{y}^3 - + ..$	$= 0.0272 \cdot [1 + 24.7Y - 4\ Y^2 + - ..]$
$\delta^{(1)}/\overline{T} = 2.446\overline{y} - 3.43\overline{y}^2 + 8.6\overline{y}^3 - + ..$	$= 0.0928 \cdot [1 + 23.8Y - 85.4Y^2 + 53Y^3 - + ..]$
$\delta^{(2)}/\overline{T} = 3.526\overline{y} - 7.05\overline{y}^2 + 24.5\overline{y}^3 - + ..$	$= 0.1310 \cdot [1 + 23.3Y - 216\ Y^2 + 63Y^3 - + ..]$
$\delta^{(3)}/\overline{T} = 4.453\overline{y} - 12.07\overline{y}^2 + 51.4\overline{y}^3 - + ..$	$= 0.1621 \cdot [1 + 23.0Y - 36.5Y^2 + 317Y^3 - + ..]$

directly from measured data. This can be done with the help of Eqs (13)–(15), but more straightforwardly with the inverse polynomials (see Appendix III); e.g. it yields

$$\bar{y} = \begin{cases} 0.409 \cdot \delta/\bar{T} \cdot (1 + 0.573\,\delta/\bar{T} + 0.07\,\delta^2/\bar{T}^2 + \ldots) & \text{for } \gamma = 1 \\ 0.284 \cdot \delta/\bar{T} \cdot (1 + 0.567\,\delta/\bar{T} + 0.08\,\delta^2/\bar{T}^2 + \ldots) & \gamma = 2 \\ 0.225 \cdot \delta/\bar{T} \cdot (1 + 0.609\,\delta/\bar{T} + 0.16\,\delta^2/\bar{T}^2 + \ldots) & \gamma = 3 \end{cases} \tag{18}$$

or still more easily

$$\bar{y} = 0.04 + \begin{cases} 0.453\,(\delta/\bar{T} - 0.0928 + \ldots) & \text{for } \gamma = 1 \\ 0.328\,(\delta/\bar{T} - 0.131 \;\; + \ldots) & \gamma = 2 \\ 0.268\,(\delta/\bar{T} - 0.162 \;\; + \ldots) & \gamma = 3 \end{cases} \tag{19}$$

Another quantity of interest is the steepest slope of the concentration curve (see Fig. 1a), i.e. the peak height of the intensity curve:

$$\bar{J}^{(\gamma)} = -\overline{\frac{\mathrm{d}C}{\mathrm{d}T}} = \bar{C}^{(\gamma)} \cdot \frac{E}{k\bar{T}^2} = \bar{C}^{(\gamma)} \cdot \kappa^{(\gamma)}/\delta^{(\gamma)}. \tag{20}$$

The rectangular area $\bar{J} \cdot \delta$ should be comparable to $\int\limits_0^\infty J(T) \cdot \mathrm{d}T = C_0 = 1$. In fact, $\bar{J}^{(\gamma)} \cdot \delta^{(\gamma)}$ is close to unity (see Table 3), but not exactly, due to the typical

Table 3

Variance intervals for the considered properties, according to $0.03 < \bar{y} < 0.05$

	$\gamma = 0$	$\gamma = 1$	$\gamma = 2$	$\gamma = 3$
$C_1^{(\gamma)}$	0.5719 . . 0.5732	0.8126 . . 0.8235	0.8703 . . 0.8806	0.9459 . . 0.9518
$\bar{C}^{(\gamma)}$	0.0553 . . 0.0880 (>0)!	0.3888 . . 0.4017 (>1/e)!	0.5276 . . 0.5440 (>1/2)!	0.6084 . . 0.6261 ($>1/\sqrt{3}$)!
$C_2^{(\gamma)}$	0	0.0750 . . 0.0792	0.1645 . . 0.1761	0.2316 . . 0.2523
$\tilde{A}^{(\gamma)} \; \frac{\bar{C}}{1-\bar{C}}$	0.0585 . . 0.0965	0.6361 . . 0.6715	1.1170 . . 1.1930	1.5540 . . 1.6745
$A^{(\gamma)} = \delta_2/\delta_1$	0.0856 . . 0.1419	0.7149 . . 0.7412	1.0687 . . 1.1112	1.3397 . . 1.3903
$\bar{J} \cdot \delta/\kappa$	(1.0554 . . 1.0889)*	0.3888 . . 0.4017	0.2784 . . 0.2959	0.2252 . . 0.2454
$\bar{J} \cdot \delta$	0.7189 . . 0.7353	0.9142 . . 0.9226	0.9280 . . 0.9534	0.9305 . . 0.9705

* for $\gamma = 0$ the indicated intensity value belongs to $\bar{t} = t_2 > 1$, where the intensity drops from this value to zero

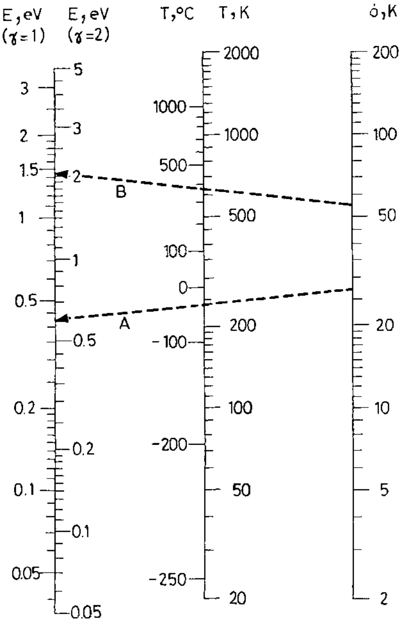

Fig. 2. Nomogram for the correlation $\delta \cdot E/\overline{T}^2 = k \cdot \kappa^{(\gamma)}$ (0.04)
Example A: for $\gamma = 2$, $\delta = 27$ deg, $\overline{T} = 240$ K → $E \cong 0.60$ eV;
Example B: for $\gamma = 1$, $\delta = 55$ deg, $\overline{T} = 360\,°\mathrm{C}$ → $E \cong 1.45$ eV.

curve shapes. Also, other quantities, $C_1^{(\gamma)}(T_1)$ and $C_2^{(\gamma)}(T_2)$, can be treated as characteristic invariants for every γ.

After the verification of the kinetic order γ from the curve shape and asymmetry A (or from $\bar{A} = \bar{C}/(1-\bar{C})$), all the above-given correlations are helpful in analyzing experimental results.

It was shown earlier that a constant half-width energy product, $\delta \cdot E/(kT^2) =$ = const., allows the construction of a nomogram for the first approximation of the activation energy values, which iteratively had to be improved. Now this iteration was already included in our polynomial expansion and we obtained directly usable constants $\kappa^{(\gamma)}(0.04)$, which are lower than $\kappa^{(\gamma)}(0)$ by 5.2% (for $\gamma = 1$) and 7.6% (for $\gamma = 2$), and which are used for the new nomogram (Fig. 2):

$$\begin{aligned} k\kappa^{(0)}(0.04) &= (17115\,K)^{-1} \\ k\kappa^{(1)}(0.04) &= (4998\,K)^{-1} \\ k\kappa^{(2)}(0.04) &= (3542\,K)^{-1} \\ k\kappa^{(3)}(0.04) &= (2872\,K)^{-1}. \end{aligned} \tag{21}$$

Lastly, the frequency factor can be determined by Eq. (2), but again more easily from a relative expression:

$$K_0(\bar{y}) = K_0(0.04) \cdot \frac{\exp(\bar{y}^{-1} - 25)}{(25\bar{y})^2} \tag{22}$$

$$K_0(0.04) \equiv \frac{q \cdot k}{E} \cdot 4.5 \cdot 10^{13} = \frac{q}{E[\mathrm{eV}]} \cdot 3.88 \cdot 10^9 .$$

The only possibility for the experimentalist to influence the reaction consists in the change of the heating rate, which causes a small temperature shift connected by

$$\frac{\mathrm{d} \ln \bar{T}}{\mathrm{d} \ln q} = \frac{\bar{y}}{1 + 2\bar{y}} = \frac{\mathrm{d} \ln \bar{y}}{\mathrm{d} \ln q} \cong \frac{\mathrm{d} \ln (\delta / \bar{T})}{\mathrm{d} \ln q} . \tag{23}$$

Of the same order is the opposite relative change of peak height $\overline{J(\bar{T})}$ on the basis of a temperature scale

$$\frac{\mathrm{d} \ln \overline{J^{(\gamma)}(\bar{T})}}{\mathrm{d} \ln q} = -\frac{2\bar{y}}{1 + 2\bar{y}} . \tag{24}$$

Measured on the basis of a time scale, $\overline{J(\bar{\tau})}$ increases with q:

$$\frac{\mathrm{d} \ln \overline{J^{(\gamma)}(\tau)}}{\mathrm{d} \ln q} = 1 - \frac{2\bar{y}}{1 + 2\bar{y}} \cong 1 . \tag{25}$$

However, quantities having a constant first term in their polynomial representation, such as κ and A, are shifted only by the order of y^2; e.g.

$$\frac{\mathrm{d} \ln \bar{C}^{(\gamma)}}{\mathrm{d} \ln q} = -\frac{\mathrm{d} \ln \bar{\eta}}{\mathrm{d} \ln q} = \frac{2\bar{y}^2}{1 + 2\bar{y}} . \tag{26}$$

This demonstrates once more their relative invariance.

Appendix

I. *Solution for half-height temperatures in polynomial representation*

a) Let us first consider the bimolecular case: $\gamma = 2$ (the special superscript (γ) is omitted for brevity); from Eq. (9) we have to solve the following equation:

$$8 \cdot \exp\left(\frac{1 - 1/t_i}{\bar{y}}\right) - \left[2 - \bar{\eta} + \eta_i t_i^2 \cdot \exp\left(\frac{1 - 1/t_i}{\bar{y}}\right)\right]^2 = 0 . \tag{A1}$$

It was maintained that T_i should be near $\bar{T}$ and that it would be a polynomial function of $\bar{y}$; then it can be described by:

$$t_i = 1 + \sum_{n=1} a_{in} \cdot \bar{y}^n \tag{A2}$$

and therefore

$$f_i(\bar{y}) \equiv \frac{1 - 1/t_i}{\bar{y}} = \frac{\Sigma a_{in} \cdot \bar{y}^{n-1}}{1 + \Sigma a_{in} \cdot \bar{y}^n} = a_{i1} + \sum_{n=1} a'_{in} \cdot \bar{y}^n \tag{A3}$$

where the a'_{in} are given by the a_{in}.

Hence, all expressions t_i, f_i, η_i and $\bar{\eta}$ in Eq. (A1) are in principle ascending power series of the argument $\bar{y}$, and all mathematical operations between them (addition, multiplication, exp) lead to power series in y, too. Now Eq. (A1) is fulfilled only if the coefficients for every power term $\bar{y}^n$ are zero identically. This gives a system of equations for the determination of all a_{in}. For example, the simplest equation at $\bar{y}^0$ reads:

$$8e^{a_{i1}} - [1 + e^{a_{i1}}]^2 = 0 \tag{A4}$$

with two solutions

$$a_{i1} = \ln(3 \mp \sqrt{8}) = \mp 1.762\,747\,.$$

Knowing these first values a_{11} and a_{21} the next a_{12} can be determined from the coefficient at $\bar{y}^1$, and so on. For an easier calculation of the a_{in}, a recursive procedure seems to be suitable.

Let us assume that the first m values $a_{i1} \ldots a_{im}$ have been determined already, especially a_{i1} alone. Then, all expressions in Eq. (A1) should be approximated by a finite series expansion up to terms with $\bar{y}^m$ i.e.

$$t_{im} = 1 + \sum_{n=1}^{m} a_{in} \cdot \bar{y}^n; \quad \bar{\eta}_m = 1 + \sum_{n=1}^{m} \ldots \quad \text{and so on.} \tag{A5}$$

Particularly, with these finite sums it follows that:

$$\frac{1}{\bar{y}}\left(1 - \frac{1}{t_i}\right)\Big/_{m} \simeq \frac{1}{\bar{y}}\left(1 - \frac{1}{t_{im}}\right) + a_{im+1} \cdot \bar{y}^m = f_{im} + a_{im+1} \cdot \bar{y}^m \tag{A6}$$

$$\exp\left(\frac{1 - 1/t_i}{\bar{y}}\Big/_{m}\right) = e^{f_{im} + a_{im+1}\bar{y}^m} \simeq e^{f_{im}}(1 + a_{im+1} \cdot \bar{y}^m) \tag{A7}$$

Inserting these finite polynomials into Eq. (A1) and solving it with respect to a_{im+1}, one gets:

$$a^{(2)}_{im+1} = \frac{1}{2e^{a_{i1}}(e^{a_{i1}} - 3)} \cdot \lim_{\bar{y}\to 0} \left\{\frac{1}{\bar{y}^m}(8e^{f_{im}} - [2 - \bar{\eta}_m + \eta_{im} \cdot t^2_{im} \cdot e^{f_{im}}]^2)\right\} \tag{A8}$$

b) For monomolecular processes the procedure follows the same route for the determining equation coming from (10)

$$f_i + \bar{\eta} - \eta_i \cdot t_i^2 \cdot e^{f_i} + \ln 2 = 0 \tag{A9}$$

At $\bar{y}^0$:

$$a_{i1} + 1 - e^{a_{i1}} + \ln 2 = 0 \tag{A10}$$

$$a_{11} = -1.461\,1863; \quad a_{21} = 0.985\,1998;$$

$$a^{(1)}_{im+1} = \frac{1}{e^{a_{i1}} - 1} \cdot \lim_{\bar{y}\to 0} \left\{\frac{1}{\bar{y}^m}(f_{im} + \bar{\eta}_m - \eta_{im} \cdot t^2_{im} \cdot e^{f_{im}} + \ln 2)\right\}. \tag{A11}$$

II. *Precision of the polynomial expansion with respect to the physically governed smallness of y*

In principle all polynomial $t_i^{(y)}$ can be determined following the procedure deduced in Appendix I up to an arbitrarily high power y^n, and the irrational coefficients a_{in} can be solved to any desired high accuracy.

For the physical processes of our interest the actual variation of y is intrinsically limited to $\bar{y} < 0.1$, and mainly to $0.025 < \bar{y} < 0.05$. The first coefficients, a_{i1}, a_{i2} are of the order of unity; a_{i3} is sometimes of the order of 20, but not very much higher; and so forth. Therefore, the series for t_i, η_i; f_i converge quickly.

In practice, the precision is limited by the experimental conditions and measuring equipment. For example, the deviations for absolute temperature values can be of the order $\Delta T = \pm 1$ K; for relative temperatures within $\Delta T/\bar{T} = 1\% \dots 0.1\%$; but for relative half-width only $\Delta\delta/\delta = 3\% \dots 0.5\%$. Therefore, it would be exaggerated to calculate κ with an accuracy much better than $\Delta\kappa/\kappa = 0.5\%$, and the possible accuracy for the activation energy value will be of the same order. Correspondingly, for $t_i^{(y)}$ it is quite sufficient to take into account only terms up to $n = 4$ and to restrict the number of digits for the individual coefficients $a_{im}^{(x)}$, so that their accuracy is limited by $\Delta a_{im} < \left(\frac{\Delta\kappa}{\kappa}\right) \bar{y}^{m}$.

Further, one can make use of the fact that y is naturally closer to $\bar{y} = 0.025 \dots 0.05$ than to $y = 0$. A re-expansion of the various series $X(y)$ in the vicinity of a mean selected value in this interval, e.g. around $y = 0.04$, as $X/y - 0.04)$, will then tend to a further strong increase of the convergency, so that the necessary number of terms of the polynomial and the number of digits of each coefficient may be lowered still more (see Table 2 — right side).

III. *Inverse polynomial*

Especially for the first determination of $\bar{y}$ by means of experimental observables, for instance by δ and $\bar{T}$, relation (15) can be used, but it will be more straightforward to solve this equation with respect to $\bar{y}$. Very commonly, for a quickly converging series

$$X(\bar{y} - \hat{y}) = A_0 + A_1 \cdot (\bar{y} - \hat{y}) + A_2 \cdot (\bar{y} - \hat{y})^2 + A_3 \cdot (\bar{y} - \hat{y})^3 + \dots \qquad \text{(A12)}$$

In the vicinity of any arbitrarily chosen $\hat{y}$, for instance for $\hat{y} = 0$ or for $\hat{y} = 0.04$, the inverse relation is

$$\bar{y} = \hat{y} + \frac{X - A_0}{A_1}\left\{1 + \frac{A_2}{A_1} \cdot \frac{X - A_0}{A_0} + \left(2\frac{A_2^2}{A_1^2} - \frac{A_3}{A_1}\right) \cdot \left(\frac{X - A_0}{A_1}\right)^2 + \dots\right\}. \qquad \text{(A13)}$$

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RÉSUMÉ — On traite de façon mathématique exacte et directe l'équation cinétique qui décrit de nombreuses réactions électroniques, atomiques ou chimiques dans les conditions d'un accroissement permanent et linéaire de la température. C'est pourquoi on a transformé l'équation sous une forme sans dimensions, en mettant à profit les conditions donnant le pic d'intensité maximale. On a trouvé que les deux températures T_1 et T_2 correspondant à la moitié de la hauteur du pic, sont des polynômes uniques du petit argument $\bar{y} \equiv k\bar{T}/E$ seulement ($\bar{T}$ = température du maximum du pic). Des combinaisons ultérieures ont fourni la demi-largeur δ, l'asymétrie du pic $A = \delta_2/\delta_1$ ou $\tilde{A} = \bar{C}/(1 - \bar{C})$ et le maximum de l'intensité du pic $\bar{J}$, ceux-ci aussi dépendent seulement d'$\bar{y}$. Dans quelques cas cette dépendance est faible, ainsi par exemple, on a déduit que le produit de la demi-largeur par l'énergie, divisé par $\bar{T}^2$, est invariant et différent pour chaque ordre cinétique γ:

$$\frac{\delta \cdot E\,[\mathrm{eV}]}{\bar{T}^2} = \begin{cases} 1/4998\ \mathrm{K} \text{ pour les processus monomoléculaires} \\ 1/3542\ \mathrm{K} \text{ pour les processus bimoléculaires} \\ 1/2872\ \mathrm{K} \text{ pour les processus trimoléculaires} \end{cases}$$

A l'aide de ces corrélations, les valeurs E [eV] de l'énergie d'activation peuvent être calculées avec une exactitude de 0.5%; pour la plupart des expériences, c'est l'inexactitude des valeurs de δ qui devient le facteur dominant et limitatif. On présente un monogramme spécial pour l'estimation rapide des valeurs d'E à partir de valeurs δ et $\bar{T}$ observées par voie d'expériences.

ZUSAMMENFASSUNG — Die kinetische Gleichung, welche viele elektronische sowie atomare oder chemische Reaktionen unter der Bedingung einer gleichmäßigen linearen Erhöhung der Temperatur beschreibt, wird in einer mathematisch exakten und direkten Weise behandelt. Deshalb wurde die Gleichung in eine dimensionslose Form überführt, wobei die Maximumsbedingung für die Intensitätsspitze vorteilhaft angewandt wurde. Die beiden Temperaturen T_1 und T_2, welche der halben Höhe des Intensitätspeaks entsprechen, wurden als eindeutige Polynome des kleinen Arguments $\bar{y} \equiv k\bar{T}/E$ gefunden ($\bar{T}$ = Temperatur des Peakmaximums). Weitere Kombinationen ergaben die Halbwertsbreite δ, die Peak-Asymmetrie $A = \delta_2/\delta_1$ oder $\tilde{A} = \bar{C}/(1 - \bar{C})$ und das Maximum des Intensitätspeaks $\bar{J}$, diese Größen sind ebenfalls nur von $\bar{y}$ abhängig. In einigen Fällen ist diese Abhängigkeit schwach, so daß z. B. abgeleitet wurde, daß das Produkt der Halbwertsbreite und der Energie durch $\bar{T}^2$ dividiert invariant ist und für jede kinetische Ordnung γ verschieden:

$$\frac{\delta \cdot E[\mathrm{eV}]}{\bar{T}^2} = \begin{cases} 1/4998\ \mathrm{K} \text{ für monomolekulare Prozesse} \\ 1/3542\ \mathrm{K} \text{ für bimolekulare Prozesse} \\ 1/2872\ \mathrm{K} \text{ für trimolekulare Prozesse} \end{cases}$$

Anhand dieser Korrelationen können die Werte der Aktivierungsenergie E[eV] mit einer Genauigkeit innerhalb von 0.5% bestimmt werden, so daß für die meisten Versuche die Ungenauigkeit der δ-Werte vorherrschend und begrenzend wird. Ein spezielles Nomogramm für die Schnellbestimmung von E aus experimentell beobachteten Werten von δ und $\bar{T}$ wird aufgeführt.

Резюме — Кинетическое уравнение, описывающее как многие электронные, так и атомные или химические реакции при услови постоянного линейного повышения температуры, решается математически точным и прямым путем. Для этого уравнение было преобразовано в безразмерную форму выгодно используя условие максимума интенсивности пика. Найдено, что две температуры T_1 и T_2, соответсвующие полувысоте интенсивности

пика, являются полиномами только малого аргумента $\bar{y} \equiv k\bar{T}/E$, где $\bar{T}$ — температура максимума пика. Дальнейшие комбинации дают полуширину δ, ассиметрию пика $A = \delta_2/\delta_1$ или $\tilde{A} = \bar{C}/(1-\bar{C})$ и максимум интенсивности пика $\bar{J}$, которые опять таки все зависят от y. В некоторых случаях эта зависимость слабая, так что, например, установлено, что произведение полуширины и энергии разделенное на $\bar{T}^2$ является инвариантным и различным для каждого кинетического порядка γ:

$$\frac{\delta \cdot E[\mathrm{eV}]}{\bar{T}^2} = \begin{cases} 1/4998\ \mathrm{K}\ \text{для мономолекулярного процесса} \\ 1/3542\ \mathrm{K}\ \text{для бимолекулярного процесса} \\ 1/2872\ \mathrm{K}\ \text{для тримолекулярного процесса} \end{cases}$$

С помощью этих корреляций значения энергии активации E[eV] могут быть определены с точностью 0.5%, так что для большинства экспериментов неточность значений δ становится доминирующей и определяющей. Показана специальная номограмма для быстрого установления E из наблюдаемых на эксперименте δ и $\bar{T}$.