

## Note

## IS KISSINGER'S RULE TRUE?

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(Received 31 October 1978)

There is a strange discrepancy. For a bimolecular reaction in a non-isothermal, time-dependent heating experiment, each expert feels that the shape index, given as the ratio  $s = a/b$ , should be close to unity (for  $a$  and  $b$ , see inset within Fig. 1). But the rule numerically approximated by Kissinger [1,2] as

$$s^{(n)} = 0.63n^2 \quad (1)$$

gives  $s^{(2)} = 2.52$ .

Kissinger's rule hitherto has not been seriously objected to, and it was often used if further kinetic parameters were to be determined and if, therefore, an unknown kinetic order  $n$  was replaced by the experimentally observed shape, i.e. by the inverse Kissinger relation,  $n = 1.26 s^{1/2}$ . But an incorrect value for  $n$  would lead to incorrect values for the activation energy  $E$  and frequency factor  $K_0$ . In this sense Kissinger's rule should be re-examined.

For objectivity, it should be mentioned that Kissinger defined the shape index primarily in the form

$$s = \frac{|d^2x/dT^2|_b}{|d^2x/dT^2|_a} \quad (2)$$

and deduced from the reaction rate equation

$$\frac{dx}{dT} = (1-x)^n \times \frac{K_0}{q} \times e^{-E/kT} ; \quad q \equiv dT/dt \quad (3)$$

the next derivatives and the inflection points  $a$ ,  $b$  from the condition  $d^3x/dT^3|_{a,b} = 0$ , so that

$$s = \frac{\left[ \frac{dx/dT|_b}{dx/dT|_a} \times \frac{\frac{E}{kT_b^2} - \frac{n}{1-x_b} \times \frac{dx}{dT}|_b}{\frac{E}{kT_a^2} - \frac{n}{1-x_a} \times \frac{dx}{dT}|_a} \right]}{\left[ \frac{E}{kT_b^2} - \frac{n}{1-x_b} \times \frac{dx}{dT}|_b \right]} = \frac{3-\alpha}{3+\alpha} \times \frac{4n-5+\alpha}{4n-5-\alpha} \times \frac{1-x_b}{1-x_a} \times \frac{T_a^4}{T_b^4} \quad (4)$$

with

$$\alpha \equiv \sqrt{1 + 4/n + 8y(2 - 1/n)} ; \quad y \equiv kT/E$$

Although Kissinger has already mentioned the fact that the second inflection point at position  $a$  disappears for all values of  $n < \frac{1}{2}$ , he gave no limi-

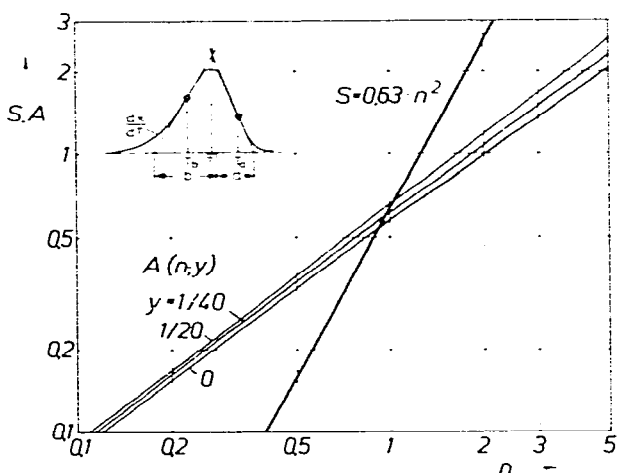


Fig. 1. Plot of  $A(n; y)$  vs.  $n$  for  $y = 0, 1/40$  and  $1/20$  for comparison with Kissinger's  $s = 0.63 n^2$ .

tation for his rules (1) or (2). Further, he calculated the numeral approximation for few examples with  $0.6 < n \leq 1$  only, and on the other hand he did not record rate curves for cases with a kinetic order much higher than unity. Also, his estimation that  $T_a/T_b \cong 1.08$ , independent of  $n$ , is roughly fulfilled only for the very restricted range for  $n$  he had chosen. These are some difficulties for the choice of  $(1 - x_a)$  close to zero for small  $n$  and  $dx/dT|_a$  from experimental curves and for the phenomenological estimation of the shape index.

Now it seems that another procedure is more readily obtainable and significant for the characterization of the shape of the rate curve, but which can also be interconnected with the ratio  $a/b$ .

The asymmetry  $A$  can be considered in the form of the ratio of the areas under the rate curve above and below the peak maximum

$$A = \frac{\int_{\bar{T}}^{\infty} (dx/dT) dT}{\int_0^{\bar{T}} (dx/dT) dT} = \frac{1 - \bar{x}}{\bar{x}} \cong \frac{a}{b} \quad (5)$$

With the result that from ref. 3

$$\bar{x} = 1 - n^{1/(1-n)}(2 - \bar{\eta}) \quad (6)$$

and ref. 4

$$\bar{\eta}(\bar{v}) = 1 - \sum_{m=1}^{\infty} (-1)^{m+1} (m+1)! \bar{v}^m \quad (7)$$

(Kissinger limited this series to the first two terms) one obtains

$$A(n; y) = \frac{1}{\frac{n^{1/(n-1)}}{2 - \bar{\eta}(\bar{v})} - 1} \quad (8)$$

This dependence of  $A(n; y)$  is demonstrated in Fig. 1 for the realistic cases  $y = 1/20 \dots 1/40$  and also for the simplified case  $y = 0$ .

Over the range  $n = 0.1 \dots 5$  and also for higher values, the numerical approximation

$$A = 0.65n^{0.85} \quad (9)$$

can be well established and rearranging

$$n = 1.54A^{1.18} \quad (9a)$$

Comparison with theoretical curves both for small  $n < 1$  and high  $n = 2 \dots 4$  revealed a much better agreement for shape index, defined by the slopes by eqn. (2), with asymmetry  $A$ , than with rule (1). The values for asymmetry and shape index coincide for  $n \approx 1$ , naturally.

Finally, true shape index and asymmetry rise more slowly than by direct proportionality with respect to kinetic order, whereas Kissinger's rule predicted an overestimated quadratic relationship.

#### NOTE ADDED IN PROOF

Comparing calculated test curves for  $n = 0.5, 1, 1.5$  and  $2$ , van Heek and Jüntgen [5] (see their fig. 5) confirmed that Kissinger's rule fails for  $n > 1$ .

#### REFERENCES

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