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THE KINETIC COMPENSATION EFFECT

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The criticisms raised by J. Zsakó concerning an earlier paper by this author [J. Thermal Anal. 9 (1975) 101] are in turn examined. The lack of physical significance of n, E, and Z for thermal decompositions is recognized by both authors. The disagreement lies in the value of using these parameters when the complete rate equation is not known.

When a calculated set of parameters does show an apparent kinetic compensation effect, the most probable cause is an irreversible rate limiting process which requires some minimum temperature for initiation of bond breaking.

In recent publications [1, 2] this author has examined the "kinetic compensation effect", hereafter referred to as the *k.c.e.*, and shown that it is a natural consequence of the use of the Arrhenius equation, which relates the observed rate constant (when it has been measured specifically) to an exponential term and a pre-exponential term, then having names adopted from homogeneous kinetics in which statistical behavior can be expected. That is, the change calculated for the "activation energy" for a given reaction under different experimental conditions causes a change in the purported "frequency factor" to compensate for the experimental reality that the rate has really not changed very much. Reactions which display this *k.c.e.*, that is, which fit the equation

$$\log Z = aE + b, \tag{1}$$

appear to be those in which the experimental temperature of the reaction does not change very much but the temperature dependence – over the measured range – does change significantly. The reaction temperature is approximately 1/(2.3 Ra), where a is the coefficient of E in Equation *1*.

More recently, Zsakó [3] has criticized this author's conclusions and attempted to validate the criticism by manipulation of the very equation whose use is being held up for questioning. It is appropriate to examine that defense critically. First the misunderstanding must be clarified.

This present author has not claimed that there is a characteristic temperature for every thermal decomposition. Quite a large fraction of his work has dealt with changes in decomposition temperatures with *known* changes in experimental conditions. Reversible reactions or reactions with a reversible step cannot be

expected to follow such an equation as Eq. 1, although they can probably be made to do so by imposing some experimental conditions.

Both Zsakó [3, 4] and this author [5, 6] have pointed out the lack of physical significance of the "activation energy", "frequency factor" and "order of reaction" in the decomposition of solids. We are in disagreement on the merit of calculating these formal parameters from the Arrhenius equation and the order-of-reaction equation when the quantities are already known to have no clear meaning. It is a source of confusion to see an experimental *temperature coefficient of reaction* referred to as an *activation energy*, a term which has a well-defined meaning in homogeneous kinetics.

The computations performed by Zsakó to demonstrate the validity of the *k.c.e.* comprised the systematic variation of one parameter of the Arrhenius equation while holding another constant and observing the effect upon the third. The procedure is deficient because it employs the equation which is the relationship whose validity is being questioned – in effect, quoting the theory to prove the theory. Also, it uses the fictive concepts of *order of reaction*, *activation energy*, and *frequency factor* which Zsakó recognizes as being purely formal parameters. The figures calculated from the arbitrary parameters have a validity equal to the validity of these parameters – and no more.

We may also view the *k.c.e.* as a mathematical necessity arising from the fact that we hardly ever measure a rate constant over more than two or three orders of magnitude, but calculated Z's often vary by twenty or more orders of magnitude. The Arrhenius equation expresses (for a virtually constant k) a reciprocal relationship between Z and $\exp(-E/RT)$, so that a change in whichever of these is calculated first implies a corresponding (compensating) change in the other. If we look at $\log k = \log Z - E/2.3\,RT$, the effect may be clearer. Now $\log k$ will typically vary by no more than three units, so a variation of 40 kcal per mole in the calculated E will cause a change in $\log Z$ which is far larger than this three-unit change. For example, J. Zsakó's increments of 10 kcal/mole in Table I of Reference *3* cause increases in the "probability of reaction" by factors of one hundred million, at the highest assigned value of a. The possible change in the measured – or even a calculated – rate constant is insignificant. It is therefore clear that Z necessarily changes when the assigned or calculated E changes simply because the mathematics requires it. No other conclusion is supported by the evidence.

We can make one more transformation, recognizing that $\log k$ changes only over a very small (compared to $\log Z$) range. We can state

$$\log Z = \frac{1}{2.3\,RT} \cdot E + \log k. \tag{2}$$

As soon as one realizes that the range of temperatures over which a reaction is studied is normally so small that T is virtually constant (within 2–10%), it becomes obvious that the equation is that of a straight line. Hence, the *appearance* of a linear *k.c.e.* is unavoidable for reactions which meet that criterion.

Restating and slightly extending the conclusion reached in Reference *2*, the *k.c.e.* will appear for reactions which do not take place below some minimum temperature but whose rates then increase abruptly until some rate limit due to heat supply or diffusion of reactants or products is reached. The nature of the temperature dependence of *this* limit may be determined by experimental conditions and hence appear as an extremely inconstant activation energy if the Arrhenius equation is used. If a group of different but related compounds yield values which show the *k.c.e.*, the required temperature is that at which the bond type common to the set can be broken.

To advance the studies of kinetics, the questions which should be raised are:

What is the value in computing parameters already known to be purely formal?

What is the merit in calculating, for a given reaction, a quantity which depends more upon the experimental conditions than upon the reaction itself?

This author [6] has already pointed out that the Arrhenius equation ought to be used only after a valid rate constant has been determined, and this is not done by assigning an arbitrary order of reaction. It is done by testing the reaction to learn whether or not there are effects of geometry or atmosphere. The proper tests comprise (1) a change in sample size – a factor of four ought to be sufficient – and (2) a radical change in geometry and atmosphere. For the latter test, a thin layer on a flat pan should be compared against a compact sample in a confined (but not sealed) space such as in this author's self-generated atmosphere sample holder [7, 8]. If the results vary appreciably, some other parameter is needed in the rate equation. To proceed without finding the complete equation will result in a report on the activation energy associated more with the apparatus than the sample.

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RÉSUMÉ — Réponse aux critiques formulées par J. Zsakó sur un précédent mémoire de l'auteur (J. Thermal Anal., 9 (1975) 101). Les deux auteurs s'accordent pour reconnaître le manque de signification physique de n, E et Z dans le cas des décompositions thermiques. Le désaccord porte sur la valeur de l'utilisation de ces paramètres lorsque l'équation complète de la vitesse n'est pas connue.

Lorsqu'un groupe de paramètres calculés montre un effet de compensation cinétique apparente, la cause la plus probable en est un processus irréversible limitant la vitesse auquel correspond une température minimale nécessaire pour amorcer la rupture des liaisons.

ZUSAMMENFASSUNG — Die kritischen Bemerkungen von J. Zsakó zu einem früheren Artikel des Autors [J. Thermal Anal., 9 (1975) 101] werden der Reihe nach geprüft. Beide Autoren stimmen überein, dass n, E und Z für thermische Zersetzungen keine physikalische Bedeutung haben. Die Meinungsverschiedenheit besteht darin, dass der Wert des Einsatzes dieser Parameter umstritten wird, wenn die vollständige Geschwindigkeitsgleichung nicht bekannt ist.

Wenn ein berechneter Satz von Parametern einen scheinbaren kinetischen Kompensationseffekt zeigt, ist der wahrscheinlichste Grund hierfür ein irreversibler geschwindigkeitsbegrenzender Vorgang, der zur Initiierung des Lösens von Bindungen einer gewissen Minimaltemperatur bedarf.

Резюме — Вновь исследованы критические замечания Я. Жако, касающиеся более ранней статьи автора (J. Thermal Anal., 9 (1975) 101). Отсутствие физического смысла для n, E и Z в случае термических разложений, установлено обеими авторами. Разногласие возникает в значении использования этих параметров, когда полное уравнение скорости реакции неизвестно. Когда вычисленный ряд параметров показывает кажущийся кинетический компенсационный эффект, наиболее вероятной причиной этого является необратимая скорость ограничивающего процесса, который требует некоторого минимума температуры для стимулирования разрушения связи.