Journal of Thermal Analysis, Vol. 32 (1987) 1277–1281

CRITICAL REMARKS ON "ON THE COMPENSATION EFFECT"

J. Zsakó and *K. N. Somasekharan*[*]

DEPARTMENT OF PHYSICAL CHEMISTRY, "BABES-BOLYAI" UNIVERSITY,
3400 CLUJ-NAPOCA, ROMANIA
*DEPARTMENT OF INORGANIC AND PHYSICAL CHEMISTRY,
INDIAN INSTITUTE OF SCIENCE, BANGALORE-560 012, INDIA

(Received November 19, 1986)

A critical assessment of a published paper (by Agrawal) is presented. The procedure proposed and used by Agrawal to distinguish a false compensation effect from a true one is shown not to be correct.

In a recent paper, Agrawal [1] proposed some checkpoints for the drawing of conclusions regarding the occurrence of a true or false compensation effect (CE).

In the introduction he shows that by applying the Arrhenius equation

$$k = A \exp(-E/RT) \tag{1}$$

in the field of heterogeneous kinetics, both A and E have little physical significance. He sees the main cause of this in the lack of a definition for a "mole of solid". It is well known that the application of Eq. (1), valid for homogeneous gas-phase reactions, is an absolutely unjustified extrapolation [2]. Even if the validity of Eq. (1) were proved for certain heterogeneous reactions, the meanings of A and E would be rather obscure, due to the high complexity of the heterogeneous processes involving solid-state reactions, gas evolution, diffusion, etc. How could the definition of a "mole of solid" help? If the rate constant k actually varies with T in the way prescribed by Eq. (1), from the experimental data a magnitude can be derived having the dimension of temperature (let us call it the characteristic temperature Θ), denoted in Eq. (1) by E/R, since it can be transformed into energy per mole by multiplying it by R, or into energy per molecule by multiplying it by the Boltzmann constant. The definition of a mole of solid affects the amount of energy calculated from Θ, but it cannot clarify the physical meaning of this energy.

If a linear relation between ln A and E is observed for a series of related reactions, it is referred to as a CE, formally involving an "isokinetic point", i.e. a temperature T_i at which all reactions would have the same rate constant k_i, since in this case Eq.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

(1), written in the form

$$\ln A = \ln k_i + E/RT_i \tag{2}$$

becomes valid for the whole series, giving a straight line in a $\ln A$ *vs.* E plot, as demanded by the CE.

Such a CE has been reported in many papers, frequently for pyrolysis processes investigated under non-isothermal conditions, mostly when linear temperature programs are used. A great number of calculation techniques have been proposed to derive $\ln A$ and E values directly from TG and DTA curves recorded at constant heating rate. These methods are based on the presumption that pyrolysis processes can be characterized by a single rate constant, depending only on temperature and obeying the Arrhenius equation (1). Since this hypothesis is very arbitrary, the existence of a CE in heterogeneous reactions has been debated, and many authors consider that it arises due to computational artifacts.

Agrawal disputes mainly three reports [3–5]. After re-examining their data by plotting $\ln k$ *vs.* $1/T$ and finding no isokinetic temperature in these plots, he concludes that these are cases of a "false" CE. The significance of the Arrhenius plot $\ln k$ *vs.* $1/T$ in CE studies was advocated particularly by Exner [6–8] and Petersen [9], although it was already known to some earlier workers [10] with all its consequences.

Exner has pointed out that it is not correct to determine the CE by a linear regression of E *vs.* $\ln A$, because these quantities are mutually dependent, both being derived from the original kinetic data. Since k and T are independently determined, and since the two quantities are not a priori mutually dependent, the plot of $\ln k$ *vs.* $1/T$ is correct statistically.

But from where does Agrawal get the k values to make his $\ln k$ *vs.* $1/T$ plot? Chornet and Roy [3] and Zsakó and Arz [4] have reported kinetic parameters (A and E) derived from non-isothermal experiments; neither they nor Alvarez et al. [5] have reported any k values. Agrawal must have calculated his $\ln k$ values, using the Arrhenius relation (1): from the reported A and E values, which are mutually dependent, and which are derived directly from the original non-isothermal data. Therefore, Agrawal's procedure is statistically more objectionable than the use of $\ln A$ *vs.* E plots.

But even if Agrawal's procedure were correct, his conclusions would not be. By producing these "Arrhenius plots", he considers that in the case of a "true" CE one must have 1) a single point of concurrence of the straight lines, and 2) $\ln k_i \neq 0$.

Let us consider the first criterion. For the thermal decomposition of $CaCO_3$, the $\log A$ *vs.* E plot gives a straight line with a correlation coefficient of $r = 0.998$ [4]. "However, the Arrhenius plot shows no single point of concurrence." Consequently, the CE is false, concludes Agrawal. By using Agrawal's procedure of constructing $\ln k$ *vs.* E plots, by calculating them from A and E, a single point of concurrence can be obtained only if $r = 1$, as otherwise the Arrhenius lines intersect each other in some domain $\Delta \ln k.\ \Delta(1/T)$ [11], whose dimensions are determined by r.

In order to illustrate the above statement, we shall take five $\log A$ *vs.* E pairs on the line

$$\log A = -2 + 5 \times 10^{-4} E \tag{3}$$

at equal distances on the A axis.

By means of Eq. (1), from each pair we obtain k as a function of T, giving a straight line in co-ordinates $\log k$ *vs.* $1/T$. The five lines have altogether ten intersections, which are all identical if only solutions of Eq. (3) are used, i.e. in this case one obtains a single point of concurrence.

Let us apply a perturbation consisting of the following: the first and the last pairs are left unchanged, in the second and fourth term $\log A$ is increased by 0.1, and in the third term it is diminished by 0.14. Practically, this perturbation does not affect the slope of the straight line, but it diminishes the correlation coefficient and transforms the point of concurrence of the Arrhenius lines into a domain of intersection. This perturbation has been repeated several times. For each set of five $\log A$ *vs.* E pairs obtained by means of these perturbations, the following magnitudes have been calculated:

— the correlation coefficient, r:

— the ten intersections of the corresponding Arrhenius lines, i.e. ten pairs of $\log k_i$ *vs.* $1/T_i$ values,

— the relative standard deviation of the $\log k_i$ values from their arithmetical mean $\overline{\log k_i}$, i.e. the ratio of the standard deviation to the arithmetical mean: $\Delta_r(\log k_i) = \Delta/\overline{\log k_i}$;

— the relative standard deviation for $1/T_i$: $\Delta_r(1/T_i) = \Delta/1/T_i$;

— the maximum differences between two individual $\log k_i$ values ($\Delta \log k_i$), $1/T_i$ values ($\Delta(1/T_i)$), and T_i values (ΔT_i).

Some of the calculated values are given in Table 1 as functions of the number of perturbations applied (p).

As seen from this Table, in the case of $\Delta_r(1/T_i)$, $\Delta \log k_i$ and $\Delta(1/T_i)$, each perturbation leads to an increase by the same value. It is worth mentioning that a plot of $\log X$ *vs.* $\log(1-r)$, where X stands for $\Delta_r(\log k_i)$, $\Delta_r(1/T_i)$, $\Delta \log k_i$ or $\Delta(1/T_i)$, gives four straight lines, one for each of the magnitudes designated above by X. These lines are parallel with each other, having a slope equal to 0.50785 ± 0.00517, and their linearity can be characterized by a correlation

Table 1 Effect of perturbations upon the intersection of Arrhenius lines (legend in the text)

p	0	1	2	5	10	20
r	1	0.99992	0.99969	0.99806	0.99231	0.97028
$\Delta_r(\log k_i)$	0	0.1942	0.3904	0.9884	2.0114	4.1827
$\Delta_r(1/T_i)$	0	0.02433	0.04853	0.121344	0.24267	0.48534
$\Delta \log k_i$	0	1.44	2.88	7.20	14.4	28.8
$\Delta(1/T_i) \times 10^4$ K^{-1}	0	2.196	4.393	10.98	21.96	43.93
ΔT_i, K	0	42	85	223	545	10,700

coefficient 0.99928 ± 0.00114. Obviously, the area of the domain of intersection is strictly correlated with r.

In the case of the pyrolysis of $CaCO_3$, the correlation coefficient, considered "excellent" by Agrawal, is $r = 0.998$, which entails, according to our above results, a domain of intersection having the width $\Delta(1/T_i) = 1.1 \times 10^{-3}$ K^{-1}, but in the diagram given by Agrawal, the whole length of the $1/T$ axis is only 0.1×10^{-3} K^{-1}. Thus, one must not be surprised that from the 36 intersections of the 9 Arrhenius lines only 13 ones appear (2 of them are not visible in the Figure presented, since the lines d, e and h are not traced up to the $\log k$ axis).

Consequently, Agrawal considers a CE to be true only if $r = 1$ for the $\log A$ *vs.* E plot, which never happens with values derived from experimental data.

The second condition proposed by Agrawal, $\ln k_i \neq 0$, cannot be valid as a scientific criterion for a true CE. It is well known that the function $\ln x$ is defined for $x \in (0, +\infty)$, i.e. the argument x must be dimensionless, and a positive real number. Therefore, instead of $\ln k_i$, correctly one would have to write $\ln (k_i/k_0)$, where k_0 stands for the unit in which k_i is expressed. In other words, Agrawal's condition means that k_i must not be equal to the unit. Since the unit of the rate constant can be chosen arbitrarily, we are able to transform a "false" CE into a "true" one, by changing the unit, e.g. by expressing time not in minutes, but in seconds or hours. In contrast, even if k is determined under isothermal conditions and the $\ln k$ *vs.* $1/T$ plots exhibit a concurrence at the point having the co-ordinates $\ln k_i$ and $1/T_i$, by taking k_i for the unit of rate constants, $\ln k_i$ becomes zero and on the basis of Agrawal's criterion, the CE can be considered to be false.

References

1 R. K. Agrawal, J. Thermal Anal., 31 (1986) 73.
2 J. Zsakó, J. Thermal Anal., 5 (1973) 239.
3 E. Chornet and C. Roy, Thermochim. Acta, 35 (1980) 389.
4 J. Zsakó and H. E. Arz, J. Thermal Anal., 6 (1974) 651.
5 M. R. Alvarez, M. J. Tello and E. H. Bocanegra, Thermochim. Acta, 43 (1981) 115.
6 O. Exner, Nature, 227 (1970) 366.
7 O. Exner and V. Beranek, Collect. Czech. Chem. Commun., 38 (1973) 781.
8 O. Exner, Collect. Czech. Chem. Commun., 37 (1972) 1425.
9 R. C. Petersen, J. Org. Chem., 29 (1964) 3133.
10 G. M. Schwab, Z. Physik. Chem., 5B (1929) 406.
11 A. T. Lesnikovich and S. V. Levchik, J. Thermal Anal., 30 (1985) 237.