Journal of Thermal Analysis, Vol. 34 (1988) 1141–1149

Letter to the Editor

THE COMPENSATION EFFECT

A reply to Zsakó and Somasekharan's remarks

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(Received January 26, 1988; in revised form April 9, 1988)

This paper is a rebuttal to the paper of Zsakó and Somasekharan. It has been shown that the criticisms of Zsakó and Somasekharan are baseless. The procedure proposed earlier by Agrawal to distinguish between true and false compensation effect is reasonable and gives good results. To establish true c.e., it has been reaffirmed that both T_{iso} and $\ln k_{iso}$ are prerequisite.

In a recent paper, Zsakó and Somasekharan [1] have criticized the procedures proposed by Agrawal [2] to distinguish between the true and false compensation effect (c.e.). Their criticism was directed at four related issues: (i) questioning the use of Arrhenius equation and the definition of mole of solids; (ii) commenting on the calculation of k from A and E obtained from non-isothermal data; (iii) questioning the criterion $\ln k_{iso} \neq 0$, and claiming that this depends on the units of k; and (iv) suggesting that a concurrence point depends on the correlation coefficient. I disagree with all the issues raised by Zsakó and Somasekharan [1]. Since the Editor of Journal of Thermal Analysis did not provide me an opportunity to review and write a timely rebuttal to the article of Zsakó and Somasekharan [1], this paper summarizes my delayed response to the article. It is hoped that the issues raised by Zsakó and Somasekharan [1] can be clarified in this paper.

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Discussion

As their first criticism, citing his own publication [3], Zsakó simply suggests that the Arrhenius equation is an unjustified assumption. The article of Zsakó [3] merely states that the Arrhenius equation is based on an unjustified hypothesis. No reasons for the supposed "unjustification" were given in both the articles. If the Arrhenius equation is an "absolutely unjustified extrapolation", then why does Zsakó use it to demonstrate c.e.? Zsakó's [3] misconception arises from the method he used to simulate the non-isothermal experimental data. He fits the data to a model by adjusting three parameters: the order of reaction *n*, *A* and *E*. As mentioned by Agrawal [2], simulating or extracting three parameters from a single non-isothermal curve leads to non-unique solutions. Due to the non-unique values of *A* and *E*, the data of Zsakó and Arz [4] indicated false c.e. [2]. Since Zsakó used the Arrhenius equation to manipulate the rate constant in order to fit the data and obtained non-unique results, he may have errorneously concluded that the Arrhenius equation is inappropriate. In such a case the fitting technique and not the Arrhenius equation is in question. The study of Flynn and Wall [5] indicates that simulating a non-isothermal curve by just two parameters, *A* and *E*, can lead to problems. For a given value of *A* and *E*, Flynn and Wall [5] found that it was difficult to distinguish between non-isothermal curves obtained from three sets of Arrhenius parameters. The problem is aggrevated if the order of reaction is varied as well. Therefore, it can be concluded that it is not enough to simulate the experimental data assuming a set of *A* and *E*. Instead, to obtain unique and meaningful results, the Arrhenius parameters have to be extracted from the experimental data by one of numerous methods [5–8]. Only for theoretical studies where the effects of various parameters is being studied, using *A* and *E* to generate non-isothermal curve appears justifiable.

As pointed out by Dickens and Flynn [6], Arrhenius equation is not unreasonable. Despite various theories, the Arrhenius equation is *empirical* but accurately represents the experimental rate data as function of temperature for both homogeneous and heterogeneous reactions. The lack of an alternate method to correlate the temperature dependence of the rate constant implies that the Arrhenius equation is universally accepted. Although *A* and *E* are not clearly defined in case of heterogeneous reaction, the application of the Arrhenius equation to heterogeneous systems is limited due to complexity of kinetics which may involve several elementary processes [6, 9, 10]. However, if the rates of individual elementary reactions are comparable and react in overlapping temperature range, then the overall reaction can still be reasonably well represented by the Arrhenius equation [10]. However, for complex cases such as consecutive reactions, the validity of the Arrhenius equation depends on the nature of the overall reaction.

Since the Arrhenius equation is empirical, the limitations of the Arrhenius equation are not theoretical but are related to the linearity problem depending on the value of E and k. The Arrhenius equation appears to be applicable for many chemical reactions as long as $E > 5.2$ kcal/mol and $k < 1.4 \times 10^5$ min^{-1} [12]. Therefore, for many practical cases Arrhenius appears to be applicable to correlate the experimental rate data. Hence, I disagree with Zsakó and Somasekharan [1] that the Arrhenius equation is an "absolutely unjustified extrapolation".

For homogeneous gas phase reactions, the term $\exp(-E/k_B T)$ (where k_B = Boltzmann constant) is a Boltzmann distribution function for the fraction of molecules having an energy E in excess of the average energy $k_B T$. The average energy per molecule ($k_B T$) is converted to average energy per mole ($k_B N_A T = RT$) by multiplying it by the Avogadro number, N_A, which in turn is the number of molecules contained in 22.4 liters of gas at 0 °C and 760 mmHg. In case of solids with three dimensional structures, it is difficult to visualize the significance of N_A. Therefore, the significance for a "mole of solid" is desirable. Zsakó and Somasekharan's thoughts on the use of the ratio E/R to avoid the controversies arising from the lack of understanding of mole is not new and has been discussed before [11]. Unfortunately little efforts have been made in this direction. Despite Zsakó and Somasekharan's statements, it is correct to state that the definition of a mole of solid will not only affect the amount of energy calculated from E/R, *but* it can also provide a physical meaning of this energy. The rate limiting step determines E. E may then be thought to represent the bond breaking energy per "reacting mole" of material or may be related to diffusion [6]. How could the definition of a "mole of solid" help? Clearly a better understanding of a mole of solid could go a long way in understanding reactions of solids and at the least, it can eliminate unnecessary and often unjustified criticism of the Arrhenius equation.

In my paper [2], I have pointed out that Exner [12–14] emphasized plots of $\ln k$ versus inverse temperature rather than $\ln A$ versus E to establish c.e. Apparently, at least three cases referred in my earlier paper [2] ignored the suggestion of Exner. My approach to calculate k from A and E could have been critized if I had demonstrated that the so derived values k had shown a concurrence in a plot of $\ln k$ versus $1/T$ and claimed the occurrence of c.e. From non-isothermal experiments, A and *E are calculated* from the Arrhenius equation. Therefore it is justifyable to back out the rate constant from the Arrhenius parameters. *If the reported values of A and E were mutually dependent, it should have been easier to show a point of concurrence in a plot of $\ln k$ and $1/T$!* Thus, it should have been easier to establish the occurrence of c.e. *Clearly* this did not happen. This implies one of two things: either all cases of c.e. reported from non-isothermal experiments should be discarded as artifacts (as there appears to be no method for testing the accuracy of $\ln k_{\mathrm{iso}}$ for cases in which it is not significantly different from zero); or, if one wishes to establish c.e. from non-isothermal data, a plot of ln k versus $1/T$ (calculated from A and E) should at least exhibit a concurrence. The criticism of Zsakó and Somasekharan [1] of my previous work involving the calculation of k from A and E is therefore unwarranted.

For true c.e., ln k_{iso} should be unique and has to be a real value. If ln k_{iso} is equal to zero or cannot be determined with in the error limits, the Arrhenius equation reduces to

$$\ln A = E/RT_{iso} \tag{1}$$

Therefore, it is but natural that ln A and E will exhibit c.e. If ln k_{iso} is equal to zero, then what is the significance of c.e.? From the definition of c.e., T_{iso} is the temperature at which all rates are equal. If ln k_{iso} cannot be determined, what would T_{iso} characterize? Would it mean that *all reactions* will have an ln $k_{iso} = 0$ at T_{iso}? If so, one can pick and chose a temperature and make ln $k_{iso} = 0$ by simply making sure that the error limits are large enough to make ln k_{iso} not significantly different from zero. This will lead to meaningless results as it is the errors in ln k_{iso} and not ln k_{iso} that determines the value of k_{iso}. This obviously would cause more problems, confusion, and in fact render c.e. meaningless. *Therefore, to establish true c.e., both* T_{iso} *and ln* k_{iso} *are prerequisite.* Due to mathematical limitations, however, when $k_{iso} = 1$, ln $k_{iso} = 0$. In this case if the plot of ln k versus $1/T$ shows a concurrence, then c.e. is real even though the relation ln $k_{iso} \neq 0$ may not be satisfied. This is perhaps the only exception to the rule. This implies that the criterion ln $k_{iso} \neq 0$ can be used as a screening technique for detecting c.e. and plots of ln k versus $1/T$ can be used to confirm c.e. Hence, the suggestion of Zsakó and Somasekharan [1] that ln $k_{iso} \neq 0$ cannot be valid as scientific criterion for true c.e. is too rigid.

Although the criterion that ln $k_{iso} \neq 0$, may appear to depend on the units of time, it is not so. Since the Arrhenius equation is dimensionally balanced, changing the units of k corresponds to changing the units of A. This in turn changes the correlation parameters. Furthermore, for determining c.e. the units of ln A and E should be consistent within the data set. For example, Table 1 summarizes the results for various units of time and ln k_{iso} obtained from the correlation of the data of Zsakó and Artz for the pyrolysis of $CaCO_3$ [2]. The correlation coefficient in all cases listed in Table 1 was 0.9981. The case where the units of k are in sec^{-1} provides the strongest case for the arguments of Zsakó and Somasekharan (as ln k_{iso} is significantly different from zero). However, Figure 1, a plot of ln A versus E, shows that the 95% confidence limits passes through zero, which strengthens the finding of Agrawal [2]. Table 1 indicates that *the error limits of the intercept increases if the change in units cause an increase in ln* k_{iso} *and vice versa.* And, in all cases ln k_{iso} is not significantly different from zero. Obviously, changing the units of A or k did not

Table 1 Value of $\ln k_{iso}$ and its 95% confidence limits as a function of units of k for the pyrolysis of $CaCO_3$

No.	Units of k	$\ln k_{iso}$	95% Conf. interval
1	min^{-1}	-1.1950*	2.1950
2	min^{-1}	-2.7507	4.2466
3	hr^{-1}	1.3404	2.0692
4	sec^{-1}	-6.8436	10.5652
5$^+$	min^{-1}	-4.6^+	3.43

* $\log k_{iso}$

$^+$ Data for Equation 2 and Table 3.

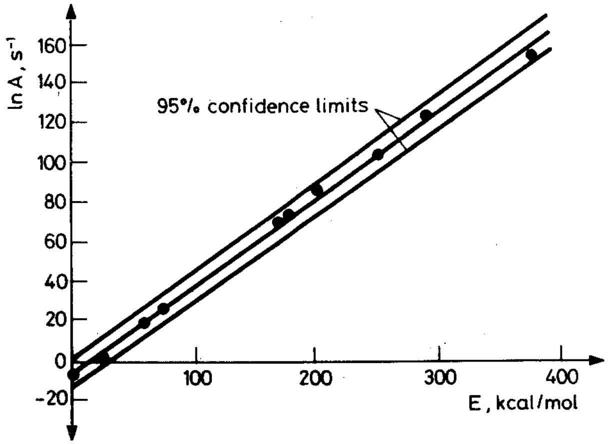

Fig. 1 A plot of $\ln A$ versus E for the pyrolysis of $CaCO_3$ with 95% confidence limits for predictions

change any result. Therefore the concern of Zsakó and Somasekharan that $\ln k_{iso} \neq 0$ depends on the units of k is unfounded.

I disagree with Zsakó and Somasekharan [1] that correlation coefficient decides the criterion for c.e. A correlation coefficient of 0.9981 can be certainly considered to be an excellent fit. But even this high a correlation coefficient is meaningless if the equation is of the form represented in Equation (1). Therefore correlation coefficient does not establish c.e. In case of pyrolysis of $CaCO_3$, the data of Zsakó and Arz [4] was shown by Agrawal [2] to indicate false c.e. False occurrence of c.e. was established as the plot of $\ln k$ versus $1/T$ did not show a point of concurrence. The criticism of Zsakó and Somasekharan [1] that the temperature axis was not wide enough is meaningless as the initial plot of Agrawal [2] covered a temperature range of 140 K. The suggestion of Zsakó and

Somasekharan [1] regarding the "domain of intersection having a width $\Delta(1/T_{iso}) = 1.1 \times 10^{-3}$", implies a temperature range of over hundreds of degrees. What is the significance of this broad a temperature range for comparing k_{iso}? The data of Zsakó and Arz [4] summarized in Table 2 and replotted in Figure 2 shows no convergence. If there is a point of concurrence it should be visible in the expanded temperature range in Figure 2. The temperature range in Figure 2 is $T_{iso} \pm 150$ K. The value of $\ln k_{1137}$ (calculated from the individual set of Arrhenius parameters) varies by an order of magnitude but the rate constant appears to vary by about *four order of magnitude!* Now in actual experimental data, there will be experimental errors in measuring temperature T and computational errors in determining the reaction rate constant k. Due to these errors, even if the system exhibits true c.e., a single point of concurrence may not be observed. Instead the rates should at least

Table 2 Arrhenius parameters used by Zsakó and Arz [4] in establishing compensation effect for pyrolysis of $CaCO_3$ (T_{iso} = 1137 K)

E, kcal/mol	$\ln A$, min^{-1}	$\ln k_{1137}$ min^{-1}	Symbol in Fig. 2
58.7	23.03	−2.952	a
75.5	29.71	−3.709	b
26.3	5.07	−6.571	c
177.3	77.15	−1.328	d
377.5	158.68	−8.413	e
251.7	108.93	−2.480	f
289.4	128.28	0.183	g
169.3	74.16	−0.777	h
201.3	90.28	1.178	i

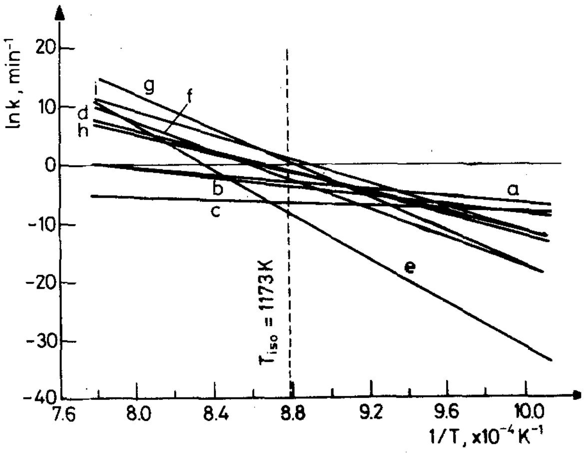

Fig. 2 An Arrhenius plot for the pyrolysis of $CaCO_3$. For a key to symbols see Table 2

appear to converge at T_{iso}. Even within reasonable temperature limits, in Figure 2, no concurrence is observed near T_{iso}. Figure 2 clearly indicates that the new plot does not change the previous finding of Agrawal [2] regarding false c.e. in the data of Zsakó and Arz [4].

To show that the correlation factor is not as important as the convergence in the plot of $\ln k$ versus $1/T$, A and E values were generated using the equation

$$\ln A = -4.60 + 1.135\,E \quad (A \text{ in min}^{-1} \text{ and } E \text{ in kcal/mol}) \tag{2}$$

The values generated by varying A and E (such that the correlation coefficient was about 0.998) are summarized in Table 3. The correlation coefficient is 0.9984 and the intercept is significantly different from zero at 95% confidence limits (see Table 1, row no. 5). This correlation coefficient is comparable to that obtained from the data of Zsakó and Arz [4] previously discussed. Figure 3, a plot of $\ln A$ and E exhibits c.e. and that the 95% confidence limits does not pass through zero. The

Table 3 Arrhenius parameters used to simulate compensation effect (T_{iso} = 443.4 K)

E, kcal/mol	$\ln A$, min^{-1}	$\ln k_{443}$, min^{-1}	Symbol in Fig. 4
20.0	18.0	−4.71	a
30.0	28.5	−5.56	b
40.0	42.0	−3.41	c
50.0	53.0	−3.76	d
60.0	62.5	−5.62	e

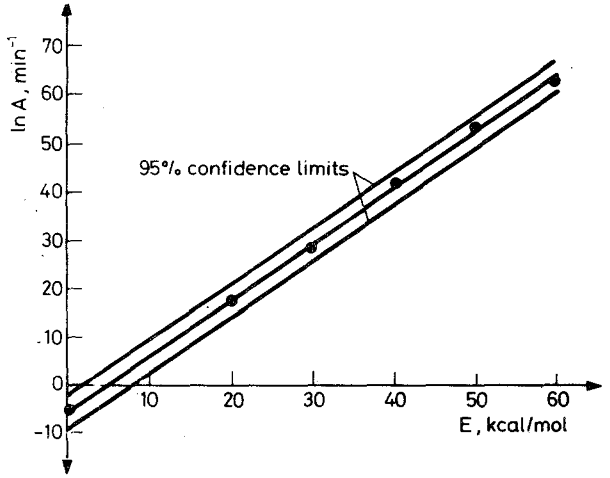

Fig. 3 A plot of $\ln A$ versus E listed in Table 3 with 95% confidence limits for predictions

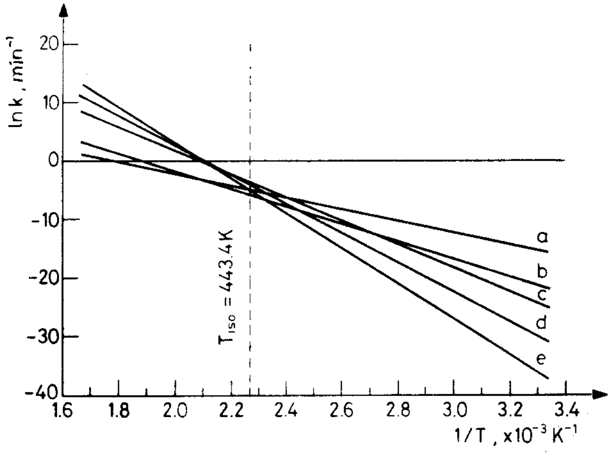

Fig. 4 An Arrhenius plot for values listed in Table 3. For a key to symbols see Table 3

plots of ln k versus $1/T$ generated by the set of Arrhenius parameters in Table 3 are plotted in Figure 4. Clearly for the same correlation coefficient, Figure 4 indicates that there may be "some sort" of c.e. as the rates appear to converge at T_{iso}. This c.e. may be acceptable depending on the errors in T and k. The calculated value of $\ln k_{443}$ are comparable and the rate constant varies by about an order of magnitude. This is more acceptable as for heterogeneous systems, reported values of rate constants vary by over two orders of magnitudes [2]. Comparing Figures 2 and 4, one can at least pause at the suggestion that figure 4 represents true c.e., but Figure 2 certainly does not represent true c.e. Therefore the correlation factor is not the deciding criteria for establishing c.e. as suggested by Zsakó and Somasekharan [1].

Conclusions

The proposals of Agrawal [2] are therefore correct and are not very restrictive. The criticisms of Zsakó and Somasekharan [1] are baseless. For true c.e.: (i) a plot of ln k versus $1/T$ should show a concurrence point at T_{iso} (or the rates should *at least appear to converge* at T_{iso} within acceptable error limits), and (ii) $\ln k_{\text{iso}} \neq 0$. Within acceptable limits of k_{iso} and T_{iso}, criterion (i) should be satisfied for all cases of true c.e. Obviously, criterion (ii) will not be satisfied if $k_{\text{iso}} = 1$. However, in this case for true c.e., criterion (i) has to be satisfied. If criterion (ii) is not satisfied it is highly unlikely that criterion (i) will be satisfied. Therefore criterion (ii) or plots of ln A and E with 95% confidence limits for predictions will be helpful in rapid screening for determining the type of c.e. Most occurrences of c.e. have been reported from non-isothermal experiments. However, the authors of these studies rarely explain the significance of c.e. and merely pass over their discovery. My question to this issue is: So what if the data shows c.e.? Pursuing this question by individual authors will not only benefit their own work but also enhance the acceptability of c.e. True c.e. can prove to be useful in chemical research for: identifying the governing reaction mechanism; predicting effects of various parameters on reactions; predicting Arrhenius parameters when limited data is available; separating the effects of surface and bulk properties; and, optimizing process design [12]. The practice of merely reporting the existence of c.e. without any discussion should be discouraged by the Editors of Journal of Thermal Analysis. Further the Editors of Journal of Thermal Analysis should attempt to at least contact the authors of the papers whose work is being questioned. This procedure will eliminate unnecessary misunderstanding.

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The author would like to thank the reviewer for his constructive criticisms.

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