Thermochimica Acta, 124 (1988) 235–239
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

ON THE SENSITIVITY OF SCALE VALUES IN THE ARRHENIUS EQUATION

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(Received 8 May 1987)

ABSTRACT

The sensitivity of parameter scales in the Arrhenius equation was analysed. It was observed that such analysis should make allowances for additional dependences of the compensation effect type between quantities expressed in the equation. It was shown that these additional dependences could significantly change dependences between the investigated parameters of the Arrhenius equation.

INTRODUCTION

In our earlier paper [1] we presented a new interpretation of the Arrhenius equation; in that paper we tried to explain the compensation effect theoretically. The applied method of approach to the problem required the introduction of the notion of a physical quantity scale, a parameter which is usually the real diffeomorphic function. Such a function is mutually univocal (equivalent) and can be differentiated bilaterally, which means that it has its derivative, and its reciprocal function has its own derivative as well.

It is noted from research [2–4] on kinetics of reactions of the type A(solid) $\rightleftharpoons$ B(solid) + C(gas) that the observed sensitivity of the Arrhenius equation to temperature changes would be incomprehensible if there were no compensation between the values of A and E. If there is any linear correlation between ln A and E, when the pressure is a deviation factor of the correlation there will be a pencil correlation between ln k and $1/T$. Thus, at fixed pressure, ln k and $1/T$ are correlated linearly, and small changes of T cause great changes of k, since for the real constants a and b in the equation $\ln k = a + b/T$ the value of b $(= E/R)$ is the gradient of a straight line in relation to the axis $1/T$, so even small changes of T can result in very great changes of ln k.

0040-6031/88/$03.50

The aim of this paper is to analyse the sensitivity of scale values of the Arrhenius equation. Such action, taking into account the limitations presented above, makes it possible to evaluate linear relationships between values referring to this equation.

The Arrhenius equation shows the relation between four values k, A, E, and T, and among these there are correlation relationships [1]. One such relationship is the compensation equation forming the relationship between A and E. In refs. 4 and 5 one can find the false view that the compensation relationship is connected with properties of scale values included in the Arrhenius equation—first of all with properties of the exponential function.

Now we know [1] that the compensation effect is correlated by the existence of the isokinetic pair $(k_0, T_0) = \beta$, occurrence of which results in the specified deviation factor of this correlation, which influences the course of the process. In the case we studied [1], the deviation factor which determined the physical value of the correlation was the pressure of the gas product of the reaction. In other cases, when different deviation factors influence the course of the thermal dissociation process, the compensation process need not occur since then other correlations will take place.

The problem discussed in this paper is a more general one, because, if we assume that among some parameters x, y, z there is a general relationship

$$\mathrm{F}(x, y, z \ldots) = 0 \tag{1}$$

and that under some conditions, there is the following relationship between x and y

$$\mathrm{f}(x, y) = 0 \tag{2}$$

then we can prove that under other conditions

$$\mathrm{g}(x, y) = 0 \tag{3}$$

although the general model F has not been changed.

Thus, the existence of additional relationships $\mathrm{f}(x, y)$ or $\mathrm{g}(x, y)$ does not indicate any possibility of relationships among other parameters of the model F. For instance, if the Arrhenius equation is the general model, then the linear relationship of one pair of values (in proper scales) results in the pencil correlation (in other scales), but it does not mean that additional correlations should be determined only by the Arrhenius equation.

A more precise description of the problems presented above requires the introduction of the following definition

Definition 1 Let us assume that f is a real function, a diffeomorphic one, defined at least in some open section. Let us also assume that x_1 and x_2 are some points belonging to the domain of the function f.

The sensitivity of the function f in points x_1 and x_2 shall be expressed with the following differential quotient

$$-\frac{\Delta y}{\Delta x} = \frac{y_2 - y_1}{x_2 - x_1} = \frac{\mathrm{f}(x_2) - \mathrm{f}(x_1)}{x_2 - x_1} \tag{4}$$

The knowledge of the sensitivity of various scales allows us to establish if linearity occurs between the parameters studied. Applying the method used in ref. 1, let us consider a few ways of calculating the sensitivity of scales.

Example 1 Let us assume that $f(x) = e^x$, then

$$\frac{\Delta y}{\Delta x} = e^{x_1}\left(\frac{e^{\Delta x} - 1}{\Delta x}\right)$$

where $\Delta x = x_2 - x_1$.

Proof Because $\Delta y = y_2 - y_1 = e^{x_2} - e^{x_1} = e^{x_1}(e^{\Delta x} - 1)$, then

$$\frac{\Delta y}{\Delta x} = e^{x_1}\left(\frac{e^{\Delta x} - 1}{\Delta x}\right)$$

which was to be proved.

From Example 1, the sensitivity e^x is great for $x > 0$, since, even if Δx equals almost zero, then $e^{\Delta x} \approx 1 + \Delta x$ and $(e^{\Delta x} - 1)/\Delta x \approx 1$, and $\Delta y/\Delta x \approx e^{x_1}$. So, if x_1 is great, the sensitivity is great as well, and if x_1 equals almost zero, the sensitivity equals almost zero, too.

Example 2 Let us assume that $f(x) = 1/x$, then

$$\frac{\Delta y}{\Delta x} = -\frac{1}{x_1 x_2} = \frac{-1}{x_1^2 + x_1 \cdot \Delta x}$$

Proof Since

$$\Delta y = y_2 - y_1 = \frac{1}{x_2} - \frac{1}{x_1} = \frac{x_1 - x_2}{x_1 x_2} = -\frac{\Delta x}{x_1 x_2}$$

then

$$\frac{\Delta y}{\Delta x} = -\frac{1}{x_1 x_2}$$

which was to be proved.

Thus the sensitivity of this scale is very little for great values of x_1, x_2 and very great for little values of x_1, x_2.

In the Arrhenius equation the temperature T occurs in the hyperbolic scale, and during the thermal dissociation of solids the value of T usually exceeds 200 K. This means that values of $1/T$ are practically stable (± 0.005), so if the analysis of the Arrhenius equation is limited to Example 2, one can accept that the temperature does not influence the value of k.

Example 3 Let us assume that $f(x) = \ln x$, then

$$\frac{\Delta y}{\Delta x} = \ln\left(1 + \frac{\Delta x}{x_1}\right) \cdot \frac{1}{\Delta x}$$

Proof Since

$$\Delta y = y_2 - y_1 = \ln x_2 - \ln x_1 = \ln\left(\frac{x_2}{x_1}\right) = \ln\left(\frac{x_1 + \Delta x}{x_1}\right) = \ln\left(1 + \frac{\Delta x}{x_1}\right)$$

then

$$\frac{\Delta y}{\Delta x} = \frac{\ln\left(1 + \frac{\Delta x}{x_1}\right)}{\Delta x} = \ln\left(1 + \frac{\Delta x}{x_1}\right) \cdot \frac{1}{\Delta x}$$

which was to be proved.

Therefore, as $\Delta x \to 0$, we have $\Delta y / \Delta x \to \ln x_1 = 1/x_1$, and the sensitivity of the logarithmic scale is similar to the sensitivity of the hyperbolic scale. But if $\Delta x \to \infty$, then the convergence of the quotient

$$\frac{\Delta y}{\Delta x} = \frac{\ln\left(1 + \frac{\Delta x}{x_1}\right)}{\Delta x}$$

is analysed by means of the de l'Hospital rule (since we have to do with the quotient ∞/∞); when we differentiate the numerator and the denominator of the quotient, then we obtain

$$\frac{1}{\left(1 + \frac{\Delta x}{x_1}\right)} \cdot \frac{1}{x_1} = \frac{1}{x_1 + \Delta x} = \frac{1}{x_2}$$

Thus, the sensitivity of the logarithmic scale as $\Delta x \to \infty$ is close to the value $1/x_2$, and decreases, since for $\Delta x \to \infty$ we have also $1/x_2 \to 0$.

The examples of relationships which are suitable for numerical analysis in computer languages which include elementary functions as standard (e.g. the language BASIC) allow us to draw the conclusion that for some values of x_1, and for large values of Δx, values of y would be practically stable (± 0.005). What is not met in practice is that the Arrhenius equation is sensitive to changes of T, even at high temperatures. So the analysis of a mathematical model (e.g., the Arrhenius equation) describing empirical relationships must take into account the existence of additional relationships (e.g., the compensation effect) which, though they do not result from the initial model, can significantly change the relationships of the parameters studied in the model. We can also conclude that cautious interpretation of the mathematical models allows us to avoid false hypotheses [6]; in such a case some relationships found empirically (e.g., the compensation effect) are treated as the result of mathematical mistakes and applied computational techniques. False interpretation of experimental correlation results from the fact that the scales in which the studied values occur are sometimes insensitive; but it cannot exclude completely different causes (as we showed in our previous paper [1]), and such correlations do exist.

REFERENCES

1 J. Pysiak and B. Sabalski, J. Them. Anal., 17 (1979) 287.
2 J. Pysiak, Four studies on thermal dissociation reactions of solids, commentary of the DSc thesis, Warsaw, 1975.
3 J. Pysiak and M. Dunikowska-Gawrońska, Application of thermal analysis in research of reaction kinetics. Selected problems of kinetics and mechanism of thermal dissociation of solids. Material for 2nd Polish Conference on Calorimetry and Thermal Analysis, Institute of Physical Chemistry of the Polish Academy of Science, 1976.;
4 E.A. Prodan, M.M. Pavluchenko and C.A. Prodan, Zakhonomernosti topokhimicheskikh reaktzi, Minsk, 1976.
5 P.D. Garn, "Thermal analysis", Proceedings of the 4th ICTA, Budapest, 1975, p. 25.
6 K. Schwethick, Kinetische Methoden zur Untersüchung von Reactionsmechanismen, Berlin, 1971.