Thermochimica Acta, 124 (1988) 385–387
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

DISCUSSING COEFFICIENT VALUES OF THE COMPENSATION FOR THERMAL DISSOCIATION REACTIONS OF THE TYPE A(SOLID) ⇌ B(SOLID) + C(GAS)

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(Received 8 May 1987)

While analysing the Arrhenius equation the values of coefficients a and b in the compensation equation have been theoretically proved, and conditions for k and T were determined, which enabled the coefficient b to be treated as constant.

In papers by Pysiak [1,2] and in many others (see ref. 3 and references quoted therein) dealing with the thermal dissociation of solids, it has been found experimentally that coefficients of the compensation equation

$$\ln A = a + bE \tag{1}$$

where A and E (parameters of the Arrhenius equation) mostly take the values $a = 0$ and $o < b < 1$.

In this paper we show that values of coefficients a and b can be proved theoretically while analysing the Arrhenius equation

$$k = A\ \mathrm{e}^{-E/RT} \tag{2}$$

One can conclude on the basis of the character of the parameters occurring in eqn. (2) that usually $A,\ E,\ T,\ R > 0$, so we can obtain at once the simple

Lemma 1. Let us assume that $k = A\mathrm{e}^{-E/RT}$ and $A,\ E,\ T,\ R > 0$, then $k > 0$.

Proof. It results from the properties of the exponential function that we always have $\mathrm{e}^{-E/RT} > 0$, so $A\mathrm{e}^{-E/RT} > 0$, since $A > 0$. Thus $k > 0$, which was to be proved.

Lemma 2. Let us assume that parameters A and k are connected with the Arrhenius equation (2) such that $A > k$.

Proof. Since $E/RT > 0$, then $\mathrm{e}^{-E/RT} > \mathrm{e}^0 = 1$, since the exponential func-

0040-6031/88/$03.50

tion rises. Therefore $Ae^{-E/RT} > A$, and $A > Ae^{-E/RT} = k$, which was to be proved.

Lemma 3. Let us assume that $\ln A = bE$, then in such a case

$$0 < b < 1 \text{ if and only if } 1 < A < e^E \quad (3)$$

$$b_1 < b < b_2 \text{ if and only if } e^{b_1 E} < A < e^{b_2 E} \quad (4)$$

Proof. We can show the correctness of eqn. (4) since eqn. (3) is a special case: it is enough to substitute values for $b_1 = 0$ and $b_2 = 1$ in eqn. (4) in order to obtain eqn. (3).

Let us assume that $b_1 < b < b_2$. Then we have $b_1 E < bE < b_2 E$. From the assumption that $\ln A = bE$ we obtain $b_1 E < \ln A < b_2 E$ and $e^{b_1 E} < e^{\ln A} < e^{b_2 E}$, and on basis of the definition of the logarithmic function we can obtain $e^{\ln A} = A$. That is $e^{b_1 E} < A < e^{b_2 E}$, which was to be proved.

Lemma 4. $k = Ae^{-E/RT} \Leftrightarrow A/k = e^{E/RT} \Leftrightarrow \ln(A/k) = E/RT \Leftrightarrow E = RT \ln(A/k)$

Proof. It can be proved immediately by means of simple mathematical transformations.

Now we can express the theorem.

Theorem 1. Let us assume that $\ln A = bE$ and $k > 1$; then we obtain $0 < b < 1$.

Proof. From Lemma 2 it is known that $A > k$, so we obtain $\ln A > \ln k$, because the logarithmic function rises and $k > 1$ was assumed.

Hence, if $\ln k > \ln 1 = 0$, then in this expression

$0 < \ln k < \ln A$, thus $1 < (\ln A/\ln k)$ and $1/[1 - (\ln A/\ln k)] < 0$.

Simultaneously, from Lemma 3 it is known that in order to obtain $b \in (0, 1)$ it is enough that we can obtain both $1 < A < e^E$ and then $E = RT\ln(A/k) = \ln(A/k)^{RT}$on the basis of Lemma 4.

Hence if $A < e^E \Leftrightarrow A < e^{\ln[(A/k)RT]} = [(A/k)/RT] \Leftrightarrow \ln A < RT \ \ln(A/k)$, and since $1 < k < A$ (on the basis of Lemma 2), then $1 < (A/k)$ and $0 = \ln 1 < \ln(A/k)$. Therefore on the basis of the inequality $\ln A < RT \ln(A/k)$ one can obtain the inequality $[\ln A/\ln(A/k)] < RT$, since $\ln(A/k) > 0$. Taking into account the fact that $[\ln A/\ln(A/k)] = [\ln A/(\ln A - \ln k)] = 1/[1 - (\ln k/\ln A)] < 0$, then the inequality $\ln A/\ln(A/k) < RT$ always occurs (since $T \geqslant 0$), and $1 < A < e^E$; therefore (on the basis of Lemma 3) $0 < b < 1$, which was to be proved.

Hence if we assume that $k > 1$, then on basis of the Arrhenius equation (2) we calculate that coefficient b in the compensation equation (1) falls between 0 and 1 which, of course, does not mean that it is stable [4].

Therefore the considerations we present here do not explain the problem of stability of the coefficient b, they only allow us to evaluate initially the values of coefficients a and b in eqn. (1).

Similar considerations can be used to support Theorem 1, and then we find that

Theorem 2. Let us assume that $\ln A = bE$ and $RT > 1$ (i.e. $T > 1/R$), so then we have $0 < b < 1$.

Proof. If $k > 1$, then the thesis results directly from eqn. (1). So we assume that $0 < k < 1$ (there is no other possibility: cf. Lemma 1). Because $k = Ae^{-E/RT}$, therefore $Ae^{-E/RT} < 1$ and $A < e^{E/RT}$. We also know that $RT > 1$, therefore $1/RT < 1$, then $0 < A < e^{E/RT}$, which means (on the basis of Lemma 4) that we have $0 < b < 1$, which was to be proved.

The considerations presented here may be continued in order to determine which conditions parameters k and T should meet in order to give $b_1 < b < b_2$, where b_1 and b_2 represent any real numbers. We intend to find conditions for parameters k and T, so that if they are met one could treat the coefficient b as constant.

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