

THE ACCURACY OF DETERMINING THE KINETICS CONSTANTS AND THE LAW OF LINEAR COMPENSATION

J. NORWISZ and J. PLEWA

Institute of Non-Ferrous Metals, Gliwice, Poland

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In the light of the data obtained concerning copper oxidation kinetics, the law of linear compensation: $E = E_0 + 2.303 \beta \log Z$ has been examined critically. By the use of different calculation techniques, the existence of a "compensation" dependence has been observed for different pairs of values of the activation energy E and the pre-exponential constant Z , obtained for the same set of experimental data.

The law of linear compensation, frequently occurring in studies of heterogeneous catalysis [1], is usually interpreted as a symptom of the similarity of different reactions

$$E = E_0 + 2.303\beta \log Z \quad (1)$$

where:

E = activation energy, J/mole

E_0 = constant

R = gas constant

β = isokinetic temperature, K

Z = pre-exponential constant, $\text{mg}^2\text{min}^{-1}$

Its existence is in many cases [2] brought into question, and the results obtained are attributed to the particular influence of the experimental error on the result of calculating the activation energy and the pre-exponential constant.

It is assumed [3, 4] that if the value of coefficient β in Eq. (1) approximates the mean harmonic value of the given temperatures used in the calculations, then the obtained dependency (1) is an apparent one, and not the symptom of a real phenomenon. However, Exner [2] maintains that there may occur cases for which β will be essentially different from the average temperature, and yet the dependency (1) will still be an apparent one.

In principle there are no data available which could confirm this hypothesis.

The experimental results obtained on repeating an experiment under slightly changed conditions (e.g. the initial component composition, the nature of the solution, etc. are changed) are the principles for the verification of the foregoing statement.

Thus, it is difficult to distinguish the effect of the measurement error on the result of calculating the activation energy and the pre-exponential constant from

the real effect of the change made. During the analysis of data relating to copper oxidation kinetics, a set of different values of activation energy and pre-exponential constant, depending on the method of their calculation, have been obtained for the same set of experimental data.

If a given phenomenon, here copper oxidation, may be described by a linear equation:

$$Y = AX + B \quad (2)$$

where:

$A, B =$ constants

$Y, X =$ dependent and independent variable, and the constants in Eq. (2) are the familiar functions of the activation energy and the pre-exponential constant: $A = f_1(E, Z)$ and $B = f_2(E, Z)$, then for X and Y different from zero, other values A and B may be obtained by converting Eq. (2) to the form:

$$\frac{X}{Y} = -\frac{B}{A} \frac{1}{Y} + \frac{1}{A} \quad (3)$$

or

$$\frac{Y}{X} = B \frac{1}{X} + A \quad (4)$$

and determining the constants from the above linear equations by means of the method of least squares, assuming the statistic weights of the relative variable [5], or not [6]. The differences of the values of the activation energy E and of the pre-

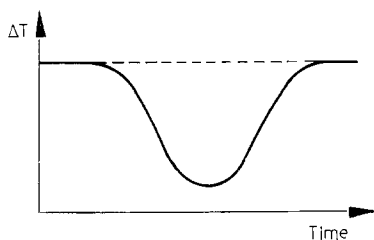


Fig. 1

exponential values Z are the results of a different effect of merely the experimental error on the calculations.

Based on the diffusive oxidation model [7], and assuming Doyle's equation, the following linear equation has been suggested:

$$\log L = 0.5 \left[\log \frac{ZE}{qRc} - 2.315 \right] - \frac{0.4567}{2} \frac{E}{R} \frac{1}{T} = \frac{A}{T} + B \quad (5)$$

where

$L =$ increase of sample mass (TG), mm

$q =$ rate of heating ($q = \text{const.}$), deg/min

Table 1

Forms of transforming the linear Eq. (2), as well as the kinetics parameters: E and Z and their standard deviations for copper air oxidation in the temperature range of 293 – 1073 K

Variant No.	Form of variables of equation $y = mx + b$				Measurement error assumed		Correlation coefficient r	Values of kinetics parameters			
	y	x	m	b	$S(T)$	$S(L)$		$E, \text{J/mole}$	$S(E), \text{J/mole}$	$Z, \text{mg}^2/\text{min}$	$S(Z), \text{mg}^2/\text{min}$
1	$\log L$	$1/T$	A	B	# 0	# 1	0.99011	77.326	1.240	183.173	12.857
2	$1/T$	$\log L$	$1/A$	$-B/A$	# 1	# 0	0.98359	107.720	2.233	8,566.325	864.026
3	$1/\log L$	$1/T \log L$	B	A	# 0	# 1	0.99011	78.877	1.261	227.927	16.471
							0.98659	88.229	1.651	796.969	66.083
4	$1/T \log L$	$1/\log L$	$1/B$	$-A/B$	# 1	# 1	0.99918	67.048	993	38.118	2.748
							0.99733	117.027	2.283	25,061.760	2,583.250
5	$T \log T$	T	$-B/A$	$1/A$	# 1	# 1	0.99918	67.358	997	40.013	2.908
							0.99758	118.045	2.237	27,718.310	2,840.200
							0.99747	88.208	1.651	796.969	66.083
							0.99758	122.226	2.313	45,395.180	4,752.260
6	T	$T \log L$	$-A/B$	$1/B$	# 1	# 0	0.99584	81.470	1.403	328.008	24.296
							0.99464	101.775	2.099	4,107.852	399.956
							0.99539	80.829	1.378	300.418	22.128
							0.99467	107.721	2.233	8,566.325	864.026
							0.99584	82.589	1.416	383.426	28.844
							0.99584	82.589	1.416	383.426	28.844

$S(E)$ — standard deviation

- E = activation energy, J/mole
 Z = pre-exponential constant, $\text{mg}^2\text{min}^{-1}$
 R = gas constant
 c = experimental constant.

This permits calculation of the activation energy and the pre-exponential constant on the basis of the data relating to copper oxidation in the air under the conditions of a linear temperature increase. Eighty measuring points have been taken into account in the calculations.

The calculated values of the correlation coefficient of an adequate equation of the activation energy and the pre-exponential constant and their standard deviations are presented in Table 1 [9, 10]. Those values fall according to Eq. (1) (Fig. 1) on

$$E = -18,207.618 + 2.303 \cdot 950.38 \log Z, \quad r = 0.998590 \quad (6)$$

in which $\beta = 950.38 \text{ K}$, $\epsilon = (910, 990 \text{ K})$ and r = the correlation coefficient. The value β is different from the mean harmonic value $T_h = 806 \text{ K}$ and the arithmetic mean $T_a = 836 \text{ K}$ of the experimental temperatures. The data presented show once again how carefully the experimental data should be interpreted on the basis of the law of linear compensation. The pair of E and Z values obtained are each time determined with apparently high accuracy. This is evidenced by the high correlation coefficient ($r > 0.98$) and by the small values of the respective standard deviations (about 10% of the values determined). However, the effect of the experimental error on the calculation result is explicit. The experimental error has influenced the values E and Z in different ways, depending on the calculation method, "compensating" the changes of the activation energy values through the changes of the pre-exponential values.

It is not true either that the dependence [6] is a real one [3, 4], since the mean temperature values (T_h and T_a) also differ explicitly from the coefficient value β . In this case the only change made is the change of the calculation method, and not an actual change of the investigated reaction parameter.

On the basis of the preliminary elaboration of the experimental data, it has been established that the law of compensation should always be interpreted very carefully. The results obtained should be estimated accurately to determine the real accuracy of the estimated E and Z values, to exclude the possibility of making an error, attributing the dependencies obtained to the actual effect of the change made, whereas it was caused merely by a particular effect of the measurement error on the calculation result.

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