

LETTER TO THE EDITOR

Reply to "Comments on A. Corma *et al.*, 'On the Compensation Effect in Acid–Base Catalyzed Reactions on Zeolites' "

There are many kinetic studies on heterogeneous catalysis which claim the existence of a compensation effect, defined as a good correlation between the activation energy, E_a , and the logarithm of the frequency or preexponential factor, A (1):

$$E_a = a + b \ln A. \quad [1]$$

In this equation, a and b are constants, called "compensation parameters." The activation enthalpy (ΔH^*) and activation entropy (ΔS^*) can also be used to show the presence of a compensation effect:

$$\Delta H^* = C + d \Delta S^*. \quad [2]$$

While application of Eqs. [1] and [2] should, in principle, be possible, there is no doubt that the estimation of the parameters in Eqs. [1] and [2] by fitting experimental results presents serious problems of a statistical nature (2) because the two variables involved are usually affected by considerable error and (what is more important) they are always mutually dependent.

In the case of the acid–base catalyzed reactions on zeolites studied by us (3), the final results are the outcome of a sequence of four computational steps during the analysis of data (4):

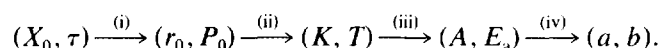
(i) Measured initial conversions (X_0) – contact times (τ) at a constant reaction temperature, are fitted to a straight line ($X_0 = r_0 \tau$) in order to obtain the initial reaction rate (r_0).

(ii) A series of r_{0i} obtained at different initial partial pressures (P_{0i}) and constant reaction temperature (T) are fitted to a kinetic rate expression, and kinetic rate constants (K) are obtained.

(iii) Steps (i) and (ii) are repeated for different reaction temperatures, and a series of K_i , T_i values are produced. They are fitted to the Arrhenius equation, and from this the parameters A and E_a are determined.

(iv) The Arrhenius parameters calculated for a set of related systems may be adequately fitted to Eq. [1], and the compensation parameters (a , b) can be calculated.

This sequential analysis can be summarized in the following way:



Since kinetic measurements are subject to experimental errors, before establishing that a compensation effect may or may not exist, it is necessary to specify the criteria to be used in order to decide if the adequate correlation exists.

Galwey, in a very valuable review (1), suggested that the most widely used method for identification of a compensation effect in the literature comes from the observation that a good linear correlation exists between E_a and $\ln(A)$. Thus, it would appear that the criteria as to whether the compensation relation given by Eq. [1] is obeyed could be subjective, since it could depend on the limits of the variation of data. Such an analysis should also properly consider the minimum number of data points required to enable the correlation to be meaningfully recognized.

The application of statistical methods to the recognition of a linear relationship between values of E_a and $\ln(A)$ has been given by Exner and co-workers (2, 5–7). Although their discussions are primarily concerned with homogeneous reactions, the treatment of data and concepts they developed could also be applied to heterogeneous catalyzed reactions and thus provide a useful starting point for the meaningful recognition of the compensation effect. In their approach, rate constants and reaction temperatures are used to determine the isokinetic temperature, if the linear relationship between E_a and $\ln(A)$ can be written in the form

$$\ln A_i = \ln K_{\text{iso}} + \frac{E_{ai}}{RT_{\text{iso}}}.$$

This, when transformed in the Arrhenius form, gives a family of straight lines of the form

$$\ln K_i = \ln K_{\text{iso}} - E_{ai}/R (1/T - 1/T_{\text{iso}}).$$

They will intersect in one point where the ordinate and the abscissa will give $\ln K_{\text{iso}}$ and $1/T_{\text{iso}}$, respectively. Exner has suggested that this single point of intersection could be used for a sound statistical test, since $\ln(K)$ and T are statistically independent. This is the base of the isokinetic relationship (IKR) (8). It is evident that for a set of experimental data one may infer from such a point of intersection the linearity between $\ln A_i$ and E_{a_i} , but the reverse is not necessarily true.

Exner (8) and Linert and Jameson (9) have reexamined a large number of kinetic and equilibrium data published over many years, and they have concluded that isosolvent and isocatalytic relationships are rarely statistically sound. In our work, correlation coefficients were always given to show the goodness of the fit. It was seen, as stated by Exner and Linert, that in some cases they were not statistically sound. However, the approach described by Exner cannot be directly applied to many of the reported data for heterogeneous catalytic reactions, since values of $\log(K)$ and $1/T$ are not usually recorded. Also, and more significantly, one cannot regard the values of T for many of the catalytic reactions carried out at high temperatures, especially for systems with a relatively large heat of reaction, as being statistically free of error. Therefore, we believe that the quantitative recognition of a compensation behavior in heterogeneous catalytic reactions requires the development of an appropriate statistical analysis (10, 11).

Nevertheless, and being aware of this, we have avoided speaking about an isokinetic relationship, and we have considered only a compensation effect in the classical mode, just as suggested by Galwey (1), in which we discuss the constant correlation parameters a , b , c , and d (3).

We have also considered that while the Arrhenius equation is generally obeyed and it is generally found that A and E_a do not change very much with temperature (12), there is still the possibility that a nonlinear relationship between $\log(K)$ and $1/T$ exists in large temperature ranges (13). Thus, we stated (3) that in our studies all the values of the d parameter (which has been related by others to the isokinetic temperature) are greater than 1000 K, while all the reactions were studied at temperatures lower than 600 K. We said that since the extrapolation was substantial "one might question the significance of any isokinetic temperature that is above the temperatures where the catalysts would be stable or the reactions would even proceed as they are measured." We thought that from

this it appeared clearly that, at least for these reactions, the term " T_{iso} " is artificial at best. Thus we used parameters c and d to reflect the compensation between activation energy and activation entropy. The terms compensation effect and isokinetic temperature are not equivalent. The compensation effect is evident from these data, but an isokinetic temperature has little meaning for them (14, 15), as has been found by other authors (16–21).

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