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NOTES

Compensation Parameters in Heterogeneous Catalysis

In many reports of kinetic and mechanistic studies of heterogeneous catalytic reactions it is stated that the group of rate processes considered exhibits compensation behavior. This is most usually (*1*) described as obedience to the equation

$$\log A = B + eE, \qquad (1)$$

where the Arrhenius parameters, A and E, are referred to (by analogy with the terminology used in homogeneous reactions) as the "frequency factor" and the "activation energy," respectively, and B and e are constants, the "compensation parameters." While several theoretical explanations for the occurrence of compensation behavior have been advanced (*1*), most of these are not amenable to direct experimental test. Moreover, obedience of data to Eq. (1) has not provided a method for the quantitative prediction of kinetic characteristics in hitherto untested systems. Thus, the appearance of this relation is frequently accepted as an empirical observation and many authors give no evidence of attempts to provide a theoretical basis for this experimental result. Such studies have not, therefore, advanced understanding of those factors which control kinetic properties of the surfaces concerned.

A recent survey (*1*) of the literature relating to compensation behavior in heterogeneous catalysis has provided a semiquantitative comparison of available data and tabulated all relevant information obtained in a search of appropriate sources (up to mid-1976). It was not possible to apply a rigorous statistical approach in this comparative analysis, since the published reports upon which it was based often simply do not contain the necessary detailed information and quantitative assessments of accuracy. The survey was concerned with available data giving A and E values for groups of related heterogeneous process, in which due account was taken of catalyst area. Comparisons were made across as wide a spectrum of systems as was practicable, within limitations imposed by the precision and scope of the reported results.

The identification and characterization of a compensation effect is the outcome of a sequence of three distinct computational steps during the analysis of data. (1) Yield-time ($\alpha - t$) measurements for isothermal reaction, when fitted to a kinetic expression, gives a rate coefficient (k); (2) a series of isothermal experiments, extending across an appropriate temperature interval (k, T), are used to obtain Arrhenius parameters (A, E); (3) Arrhenius parameters for reactions in a group of related systems may give a linear compensation relation with compensation parameters (B, e). This analysis may be summarized as

$$(\alpha, t) \xrightarrow{(1)} (k, T) \xrightarrow{(2)} (A, E) \xrightarrow{(3)} (B, e).$$

The present note is intended to comment upon some properties of the compensation parameters available (*1*) and to discuss the significance of experimental errors on analyses of the above type, since no statistical basis has been developed for the

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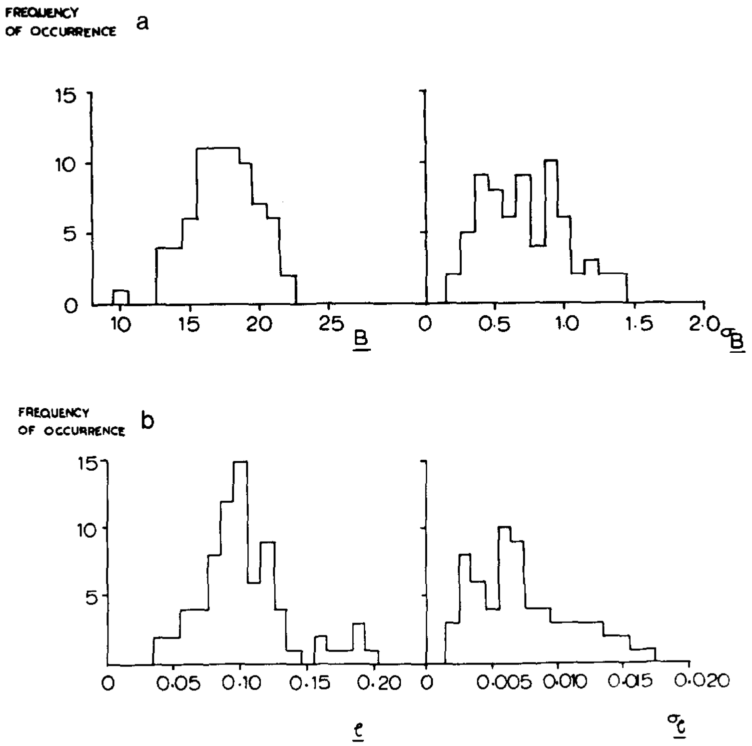

FIG. 1. Histograms showing frequency of occurrence of values of B and σ_B, e, and σ_e in Tables I–V of Ref. (*1*).

quantitative consideration of the magnitude of uncertainties in calculated B and e values.

Distribution curves for the frequency of occurrence of different magnitudes of all values of B and e listed in Tables I–V of Ref. (*1*) are shown in Fig. 1. The accuracies with which these compensation relationships were obeyed, as measured by their standard deviations, σ_B and σ_e, showed a significant spread: These frequency distribution curves have also been included in Fig. 1. Values of σ_B and σ_e tended to increase together, but there was less correlation between the magnitude of each parameter and its standard deviation (i.e., B with σ_B and e with σ_e).

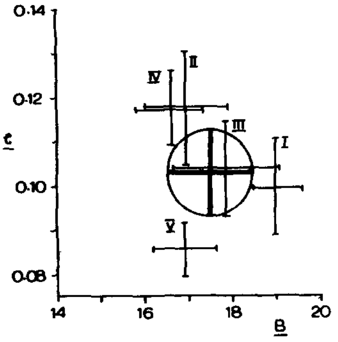

FIG. 2. Mean magnitudes of B and e from results in Tables I–V in Ref. (*1*), as labeled, and overall mean (circle). Lengths of lines refer to mean values of σ_B and σ_e.

Figure 2 records arithmetic mean values of B and e for data from each Table (I–V) in Ref. (*1*) and the overall mean value (the circle): The size of each cross represents ± (mean standard deviation). With the exception of the group of reactions on oxides (Table V), it is found that the range of *mean* compensation parameters, referring to somewhat different groups of data, are within the rather narrow limits:

$$16.6 < B < 19.0 \quad \text{and} \quad 0.099 < e < 0.118$$

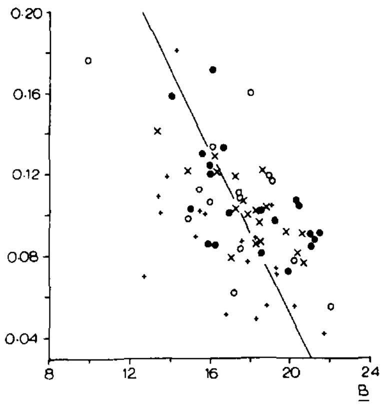

FIG. 3. A "supercompensation" plot of values of slope (*e*) against intercept (*B*) for compensation parameters reported in Ref. (1). Points from Table 1, ●; II, ○; III, ×; IV, ● and V, +. Mean regression line calculated for all data.

and

$$0.1 < \sigma_B < 1.4 \quad \text{and} \quad 0.002 < \sigma_e < 0.018.$$

Uncertainties in the magnitudes of B and e, arising as a consequence of errors in measured α, t, and T values, cannot be rigorously determined since neither data nor statistical procedures are available. An approximate analysis of the significance of errors can, however, be provided using the methods developed (*2*) to estimate the uncertainties in slope and intercept for lines drawn through two points, each containing stated uncertainties. With due regard to the considerations discussed by Benson (*3*), and, assuming the error in t values to be negligible and that temperature control ($\Delta T/T$) = 0.002 can be maintained, calculation of the propagation of error across the three stages of computation indicated that the ratios (σ_B/B) and (σ_e/e) are approximately 0.05. These calculations do not include (*inter alia*) due allowance for the larger number of experimental points on plots of data, the possibility of systematic curvature of Arrhenius or compensation plot (*4*) or the arbitrary nature of the selection of systems to be included in any group of related reactions (*1*). However, the above calculation is entirely consistent with the observation that the ratios of maximum values in Fig. 1 have comparable magnitudes, $\sigma_{B\max}/B_{\max} = 0.9/18 = 0.05$ and $\sigma_{e\max}/e_{\max} = 0.006/0.10 = 0.06$. It is apparent, therefore, that the uncertainties in (B, e) values are about those anticipated for the most reliable kinetic data.

Taking all the data in Tables I–V of Ref. (*1*), and extending the sequence of correlation plots one step further, we obtain what might be termed a "supercompensation plot" (Fig. 3) for values of B and e and the calculated regression line ($B = me + c$) with slope -50 ± 8 and intercept 22.6 ± 0.8. No systematic trend is apparent and the large scatter of data makes it inappropriate to consider possible alternative mathematical relationships between B and e. Extension of the uncertainty calculation, as outlined above, to this step estimates *minimum* errors of 16% in slope and 24% in intercept. In consequence, the realistic identification of any functional relation at this level is seen to be impracticable.

The reason for the numerous reported instances of compensation behavior would appear, therefore, to be that most of the available data refer to catalysts of broadly similar activities, studied over comparable temperature intervals. Isokinetic temperatures (*5*) (β) corresponding to the most frequently observed values of e are often 450 to 550°K, a temperature range widely used in experimental kinetic studies of catalysis so that changes in rate attributable to variation of one Arrhenius parameter are completely (or largely) offset by changes in the other. This relative ease of recognition, together with the understandable preoccupation of interest in the most active catalysts (studied < 600°K) and exclusion of inactive systems, readily accounts for the maximum in the distribution curve at $e \sim 0.1$ (Fig. 1). Consequently, this general observation specifically refers to the rather homogeneous pattern of kinetic behavior described in the literature, wherein the compensation effect appears as a unifying parameter. Such behavior does not, unfortunately, permit distinctions to be made as to which of the several mechanistic explanations proposed (*1*) may be operative in particular groups of reactions.

We believe, therefore, that the conclusive demonstration that compensation behavior provides information concerning the fundamental kinetic controls of catalysis requires either more precise kinetic measurements (α, t, T) than are usually obtained, or a more rigorous method of statistical treatment of results. At present the effect can be accepted as a consequence of kinetic studies concerned with processes proceeding at comparable rates within similar temperature intervals. The occurrence of isokinetic behavior for any group of related reactions may be indicative of the participation of common surface intermediates or a rate-controlling step involving similar surface bond redistribution steps.

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ANDREW K. GALWEY

Chemistry Department
Queen's University
Belfast BT9 5AG, Northern Ireland

MICHAEL E. BROWN

Chemistry Department
Rhodes University
Grahamstown, 6140, South Africa

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