

values of $E \pm \delta E$ and $\log A \pm \delta \log A$ are related by a compensation effect with $T_s = T$. But the uncertainty in $\log k$ of $\delta \log k$ has an associated uncertainty in $\log A$ of identical magnitude independent of E . In a plot of experimentally observed values of $\log A$ and E for a particular reaction, therefore, the experimental temperature determines the slope and the uncertainty in $\log k$ determines the scatter. The fit to the compensation effect plot is independent of the uncertainty in E , as was found by Banks, Damjanovic and Vernon¹, but the spread of activation energies covered by it is only $2\delta E$. Because it is k which is measured experimentally and $\delta \log k$ which is responsible for the scatter, compensation effect plots of this kind would usually appear to be obeyed very well.

I now consider the experimentally observed compensation effect for a series of reactions in which E and A are intrinsically related by equation (2). Taking δE and $\delta \log k$ as the uncertainties in E and $\log k$ as before,

$$\log A \pm \delta \log A = \frac{E}{RT_s} \pm \frac{\delta E}{RT} + \log k_0 \pm \delta \log k \quad (5)$$

This represents an area in the compensation effect plot bounded by the envelope of all of the compensation effects due to errors in E and $\log k$ for all the individual reactions. The shape depends on the relative magnitudes of T and T_s in equation (5) and on the relation between δE and E . In Fig. 1 I show the case where δE is proportional to E . Clearly as T approaches T_s , the fit to equation (2) improves, and when $T \neq T_s$ the magnitude of δE becomes important.

I conclude that if the range of an experimentally obtained compensation effect exceeds twice the uncertainty in the activation energy then there probably exists an intrinsic relation between A and E . In the absence of large systematic errors the parameter T_s is obtained from the slope of the compensation effect plot. Only the quality of the plot is dependent on the magnitudes of the errors and it is the uncertainty in E which assumes greatest importance at temperatures much different from T_s .

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¹ Banks, B. E. C., Damjanovic, V., and Vernon, C. A., *Nature*, **240**, 147 (1972).

² Bond, G. C., *Catalysis by Metals* (Academic Press, London, 1962).

³ Cremer, E., *Adv. Catalysis*, **7**, 75 (1956).

REPLY to Boon and to Harris: We are well aware that the so-called compensation law behaviour has been observed in the case of the electrical behaviour of semiconductors, and as we indicated, may not be wholly artefactual in some cases in physical organic chemistry. We were merely concerned to show that the experimental data on the denaturation of proteins and the thermal death of viruses and microorganisms cannot be used to adduce compensation law behaviour in these cases. The linearity of the plot of ΔH^\ddagger against ΔS^\ddagger arises wholly from the near constancy of the left hand side of the equation used in calculating ΔS^\ddagger from values of ΔH^\ddagger which vary between 10 and 200 kcalorie mol⁻¹. It is unlikely that the uncertainty in the experimentally determined activation energies for protein denaturation is greater than half the range over which compensation law behaviour is observed so the analysis put forward by Harris does not seem to cover all cases where compensation law behaviour is artefactual.

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Compensation Effect in Heterogeneous Catalytic Reactions including Hydrocarbon Formation on Clays

A SERIES of comparable reactions is said to exhibit compensation behaviour when the Arrhenius plots show systematic variations of the activation energy (E) and the pre-exponential factor (A) according to the expression

$$\log A = bE + c \quad (1)$$

Many examples of such behaviour have been reported for diverse reaction systems, but hitherto no explanation of the effect has been generally accepted. Indeed, it has been suggested¹⁻³ that obedience of data from a sequence of reactions to equation (1) may arise through the method of analysis of the kinetic measurements or it may be an artefact. But before compensation behaviour is dismissed as a phenomenon of little theoretical significance, we suggest that in at least one field, heterogeneous catalysis, obedience to equation (1) may be considered to result from a useful mechanistic model. Many examples of compensation behaviour among reactions catalysed by solids have been reported and Bond⁴ has discussed the theoretical implications. The present preliminary report describes a further sequence of surface rate processes which exhibit the compensation effect and proposes a model to explain these observations.

Alcohols and hydrocarbons react⁵ on montmorillonite surfaces to yield a characteristic mixture of hydrocarbon products in which *iso* and *anteiso* alkanes predominate. The mechanism of these reactions, proceeding under conditions of possible primary product and water vapour readsorption⁵, includes polymerization, cracking, isomerization and hydrogen transfer steps. We have now completed a study of the reactions of *n*-dodecanol and of stearic acid on the clay minerals illite, kaolinite and montmorillonite. These reactions yielded product hydrocarbon mixtures similar to those referred to above⁵ and will be described elsewhere. The present report is restricted to the consideration of two particular observations for the six reactant mixtures studied: (1) The A and E values exhibit compensation behaviour (Fig. 1); (2) kinetic data, measured for comparable reaction rates, were obtained at similar temperatures (within the approximate range 420–550 K).

From comparison of the product mixtures, we conclude that the reactions to which Fig. 1 refers proceeded by comparable mechanisms involving⁵ the rearrangement of similar mixtures of hydrocarbon fragments bonded to the clay surfaces. In spite of crystallographic differences between the three mineral phases, the catalytic properties of the active surfaces, composed of somewhat different arrays of oxide and hydroxide ions⁶, were closely similar. Significantly, these similarities include the appearance of detectable catalytic activity at temperatures slightly below the range of onset of bulk dehydroxylation. Accordingly, we associate the participation of clays in reactions of organic compounds with the reactivity and mobility of active constituents of the mineral surface. Such surface species undoubtedly include protons and hydroxyl groups which are involved in the dehydration reaction; water loss, in common with many reactions of solids, probably proceeds preferentially at crystal surfaces. The same groups