LETTERS TO THE EDITORS

Comments on the Theoretical Explanation
of Compensation Behavior

In a recent article (*1*), Conner provides "a possible general explanation" for the compensation effect. Since my own contributions to this subject (*2, 3*) are generously cited in the introduction to the theory developed, I consider it appropriate and timely to comment on general aspects of the applications of the transition state theory to the kinetics of heterogeneous reactions. At present it is widely accepted that, if a surface reaction obeys the Arrhenius equation, then its rate is controlled by a single rate limiting step of the type fashioned during development of the absolute reaction rate model. I believe that this representation oversimplifies the mechanistic variability possible in gas–solid reactions.

Without wishing to detract from Conner's elegant and specific treatment of compensation in the catalyzed *ortho–para* hydrogen conversion, I would like to query the suggestion that this argument can be generalized. This suggestion appears to be implicit in the second section (Background) of his article (*1*). The system selected for his statistical mechanical treatment is particularly simple and, indeed, apparently does not involve bond rupture. Unusually, therefore, for a heterogeneous catalytic reaction, the transition complex can be identified and considered quantitatively with some confidence. However, application of the same statistical mechanical approach to the consideration of heterogeneous reactions involving dissociatively adsorbed intermediates is not necessarily straightforward. Identification of the active surface participants in heterogeneous rate processes is not, at present, easily achieved and this is a necessary prerequisite to the

quantitative consideration of bond structures of intermediates and of the transition state bond rupture step. Moreover, various other factors, some of which are mentioned below, may exert greater effects on kinetic behavior than the enthalpy–entropy relationship of the transition state.

The objective of this article is to stimulate a reappraisal of the theory of heterogeneous reaction kinetics by making two general points. (i) The results of statistical mechanical analyses can be meaningful only *after* the mechanism of the reaction considered has been properly established. The properties of the bonds involved can only be discussed profitably following identification of the controlling step with some precision. (ii) The magnitudes of the activation energy, E, and the frequency factor, A, calculated using the Arrhenius relation, do not necessarily have the same significance for a surface reaction as they do for a homogeneous reaction. The distribution of energy in adsorbed surface species is not necessarily expressed by the Maxwell–Boltzmann relation. (Aspects of this problem have been eloquently discussed by Garn (*4*).)

Several relevant fundamental problems underlying and concerning the kinetics of surface reactions in general, and of compensation behavior in particular, are rephrased and reappraised below. More comprehensive background material has already been given (*2*) and the present article restates important points that remain in conflict with widely accepted theory. It appears that the resolution of these inconsistencies may require a new approach to the interpretation of heterogeneous kinetic

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observations. Such a change of attitudes must now surely be overdue since the early promise of the kinetic approach to the elucidation of surface reaction mechanisms cannot be regarded as having been fulfilled.

Kinetics of heterogeneous rate processes. Fundamental respects by which the kinetic control of reactions on surfaces may be expected to differ from those proceeding in a homogeneous phase are discussed under the various headings below.

Energetics. The energy distribution within freely moving, loosely adsorbed molecules at a surface may approximately conform to a modified two-dimensional version of the Maxwell–Boltzmann equation. Strongly held, chemisorbed species may be regarded as components of or extensions of the structure of the solid, for which different factors control energetics. Some surface reactions may involve the collision of a gaseous molecule with an adsorbed reactant. As a consequence of these differences in properties, which do not necessarily involve the same energy distribution function as that applied to homogeneous rate processes, it is at present difficult to justify the single general theoretical conclusion that the magnitude of E is to be identified with the activation of one particular bond. Moreover, it seems that the possible contribution from entropy changes in modification of E are usually much too small [perhaps a few kJ mol^{-1} (1)] to be capable of explaining the very large variations in apparent values of E that have been reported [often >100 kJ mol^{-1} (2)].

Surface concentrations. Unlike homogeneous systems, the effective availability (concentrations) of adsorbed precursors in heterogeneous systems may vary considerably with temperature changes, due to systematic displacement of adsorption and dissociation equilibria particularly when more than a single gas is present. This effect is quite capable of explaining compensation phenomena (2).

Three-body collisions. While three-body collisions represent an insignificant contri-

bution in homogeneous reactions, these may be important on surfaces, particularly when coverages are high and site residence times are long. A two-dimensional cage (fence) effect may operate and crystallographic factors may introduce a pattern into site occupancy by the various surface-retained species. Moreover, stabilization and immobilization of intermediates introduce the possibility that reactions may proceed through sequences of successive interdependent steps. Such mechanisms are not possible during the more random encounters experienced in homogeneous rate processes, though in certain circumstances there may be a resemblance to chain reactions. The theoretical implications of these considerations do not appear to have been explored in heterogeneous kinetic analyses.

System selection. Compensation behavior is invariably described for a *selected group* of reactions, involving one or more common features. The identification and delimitation of such a group are necessarily selective and it is difficult to apply objective criteria to the collection of data. Thus experimental errors may contribute toward the appearance of an isokinetic effect and this tendency may be enhanced by the collective consideration of related rate processes.

Threshold temperature of onset of reactivity. At the present state of development of the subject, the most convincing explanation of compensation behavior appears to me to be as follows. *Related* reactions within the selected group proceed with rate control involving a necessary *common mechanistic step* and for these reactions this step becomes effective within the same characteristic small temperature interval. This threshold temperature determines the similarity of surface reactivity that is implicit in isokinetic behavior and this leads to compensation between log A and E. The significant common step for reactions within a selected group may be the rupture of a particular bond (or closely similar linkages), involvement of the same intermedi-

ate, onset of surface mobility of a chemisorbed participant, movement of constituents of the solid resulting in turmoil of the chemisorbed layer and the active crystal components, etc.

It is important that we characterize the chemistry of the reactions in some detail before we attempt to apply statistical mechanical models to the interpretation of compensation phenomena.

REFERENCES

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