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# Further Comments on A General Explanation for the Compensation Effect: Reply to Galwey

I appreciate an opportunity to respond to the comments of Galwey (*1*) and to clarify my position on the general explanation for the Compensation Effect which I recently proposed in this Journal (*2*). I am convinced that compensation is a general and may be an expected phenomenon in kinetics. I would recall the following characteristics.

**Compensation is not unique to catalysis.** A Compensation Effect has been found for many homogeneous as well as heterogeneous reactions. Leffler has reviewed over 70 reactions in organic chemistry where compensation has been found (*3*). None of these were heterogeneously catalyzed by a surface. Explanations unique to heterogeneous catalysis are not applicable.

**The explanation does not depend on the method of analysis.** Though statistical thermodynamics and transition state theory were used to express mathematically the relationship between activation enthalpy and activation entropy, the explanation does not depend on either of these models. However, even for bond fission, the change in transition entropy can be estimated (*4*), though Galwey (*1*) implies that for dissociative adsorption this may be too complex. A relationship between the energy levels where one state changes to another and the degeneracy of the modes of energy that can transform within that level is independent of the method by which it is expressed. Nor does the explanation depend on a specific form of statistical energy distribution (Maxwell–Boltzmann). One can use any form of temperature-dependent distribution of energy.

**The specific mechanism may not be needed.** The establishment of a proper mechanism prior to an analysis of the energetics of a transformation between one state and another does not seem necessary. Indeed, if the relationship between energy levels and their degeneracy had to wait for the detailed proper mechanism, the application of kinetic analysis to heterogeneous catalysis would be severely constrained. If there is no change in mechanism over the temperature range of interest, an activation energy, relating the temperature dependence of the reaction rate, and a preexponential factor (the temperature-independent component) are meaningful. A linear relationship between ln(rate) and $1/T$ suggests a single mechanism is in effect over the region of interest (but not necessarily a single rate-controlling step).

**Temperature of onset of reaction.** Most studies that have been used to demonstrate compensating behavior have involved the intersections of straight lines on an Arrhenius plot. For a common mechanistic step to become effective within the same *small* temperature interval implies that the mechanism is changing from below to above the temperature interval. It would be most unusual that a straight line could be drawn through the interval of interest. Some form of discontinuity should exist, yet none is evident in any of the studies cited (*5*). The theory that a common reaction step gives rise to the onset of reaction focuses on isokinetic behavior and not a more general relationship that may exist between the reaction energy and entropy.

**Theory of heterogeneous kinetics.** I agree with Galwey (*1*) that the current theory of catalytic kinetics needs to be reappraised. The approach discussed in my article (*2*) is a step in that direction. Reaction state space is multidimensional. One of the crucial dimensions is the availability of energy levels that may connect one state to another. As an example, in three dimensions a reaction profile can be expressed with inter-

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nal energy (or enthalpy) and entropy as two of the dimensions and a reaction coordinate (separation between thermodynamic states) as the other. We are working on such a model for catalytic reactions. Kinetically it is not necessary to identify the exact nature of each state. It may only be necessary to establish the sequence of reactant interactions to gain insight into the nature of the reaction kinetics. This approach is particularly useful in complex reactions (such as oxyhydrochlorination (*6*)).

**Restatement of a "General Explanation for the Compensation Effect."** A thermodynamic state is determined by a local minimum in free energy. The state contains a series of quantized energy levels. Within an energy level the energy may be distributed in a variety of modes of internal energy (vibrational, rotational, etc.). The levels are degenerate and the degeneracy increases with level. Access to higher levels depends on temperature. For a single system an overlap (crossover) of the higher energy levels may exist between two states. Within a level not all modes of energy are involved in the overlap (certain "selection" rules apply). Reaction (conversion between the states) is dictated by access to the levels where crossover occurs (temperature dependence) and the probability that the energy is in the convertible (overlapping) distribution of energy modes. In a different system the crossover may involve lower (or higher) energy levels. The degeneracy (number of energetic modes of overlap) may decrease if lower energy levels are involved. Higher levels are more closely spaced and the individual degeneracies are greater; the probability of crossover increases with energy level. The result is a compensation between a lowering in the level of overlap and in the probability that within the level the specific modes of crossover are involved. Thus "energetic funneling" could be expected.

To sum up, I agree with Galwey (*1*) that a variety of phenomena may give rise to compensation. The concept presented (*2*) depends on a fundamental relationship between the energy levels of overlap between thermodynamic states and the probability (selection rules) of the crossover. Specific phenomena may result in the same behavior. This does not exclude the fundamental explanations presented.

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## REFERENCES

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