

## Compensation Effects?

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### ABSTRACT

Several terms have been employed essentially interchangeably to describe sympathetic relationships between the apparent activation energies and the preexponential factors for a series of catalytic reactions. These include: “Kinetic Compensation”, “Compensation Effect”, “Isokinetic Temperature”, and the “Theta Rule”. Numerous series of catalytic studies have inferred that there is a Compensation Effect and have estimated a specific Isokinetic Temperature for individual series. Many theoretical analyses have offered explanations for these phenomena; although, the majority have focussed on interpreting any isokinetic temperature that is evident or determining if compensation exists. However, there is no commonly accepted explanation for either kinetic compensation, a compensation effect or an isokinetic temperature. My analyses suggests that that there are several actual forms of kinetic compensation that may be evident in catalysis depending on the nature of the series that are being compared; further, the terms are not interchangeable.

### BACKGROUND

Any time kinetic measurements are made for a series of catalysts, series of Arrhenius plots, between  $\ln(\text{rate})$  and  $1/T$ , are constructed to express the dependence of the observed rates on temperature. The apparent activation energies are estimated from slopes these constructions and the preexponential factors,  $A$ , from the “effective” intercepts of the lines. If the activation energies are different for the series being studied, these linear relationships will intersect at a given set of temperatures. Below the temperatures of intersection there is kinetic compensation where the  $A$  factors are lower for the members of the series with the higher activation energies. Most studies which claim a compensation effect estimate the point of intersection significantly above the temperature where kinetic data is available. This is often expressed as a theta rule,  $E_a = \square \ln A + b$ , where  $\square$  is the “isokinetic temperature”. Any two studies which exhibit differences in activation energy will intersect and a single temperature of intersection might be estimated for any three or more studies with data significantly below the temperatures where the intersections would occur. Again, many theoretical analyses have offered interpretations for this value or have questioned whether a series of more than two different catalysts with three or more lines intersect at a single temperature. Few studies have suggested that these effects may have several explanations depending of the series being analyzed.

The series of catalysts that have been compared and where compensation has been inferred include:

- i.* Variations in catalyst composition (promoters, supports or metal loading) for the same reaction
- ii.* Modifications to a single catalyst (pretreatments) for the same reaction
- iii.* Series of related reactions (e.g., oxidations) over the same catalyst

*iv.* Even broader combinations of catalyst or reaction variables.

## **RESULTS AND DISCUSSION**

First analyses of kinetic relationships should be confined to series of reactions where the rate controlling and mechanistic processes are the same. It would appear pointless to search for kinetic relationships for series of reactions or series of catalysts where the mechanism or rate controlling steps in the process differ within the series. This does not necessarily restrict these analyses to reactions that are only surface reaction controlled since transport, adsorption or desorption could be common rate controlling processes within a series being analyzed. Indeed, kinetic compensation has been found in many series of diffusion processes which do not involve reaction, for example. However, the explanation for kinetic compensation will probably not be the same for dissimilar rate controlling steps. This concern is crucial in series such as *iii*, above.

Similarly, there might be different reasons why kinetic compensation and/or an isokinetic temperature exists when the catalysts differ, as in *i*. above. Changes in catalyst composition by changes in the loading of the catalytic component should differ from those employing different promoters or different metals. The first question is whether the comparisons of rates are normalized to the number of active sites, for example by comparing turn over frequencies. Otherwise, the calculated preexponential factors will naturally include the density of active sites.

This paper will also discuss whether the terms “Kinetic Compensation”, “Compensation Effect”, “Isokinetic Temperature”, and the “Theta Rule” should be used interchangeably. I will argue that these terms are related but are not mutually inclusive. Kinetic compensation should be found for many series of catalytic reactions. The result might be a Compensation Effect which might (or might not) exhibit a Theta Rule. The Theta Rule might reflect an Isokinetic Temperature which has physical/mechanistic significance. The several classes of catalytic reactions where kinetic compensation has been inferred will be identified and the potential explanations for a “Compensation Effect” as they relate to the different classes. The several other areas out side of catalysis where kinetic compensation has been found will noted. Hopefully, this analysis will lead to an understanding of the significance and interpretations for kinetic compensation in its various forms. I will, however, suggest that some common elements in the explanations may be universal.