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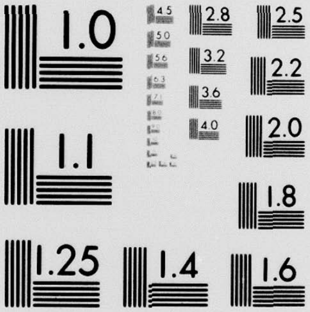

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by

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TRANSITION STATE THEORY AND THE COMPENSATION EFFECT IN CHEMICAL KINETICS

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ABSTRACT

Detailed balancing is applied to transition state theory with the result that the necessity of a compensation law relating the pre-exponential factor and the energy in chemical kinetics is clearly established. It is pointed out that the correct compensation behavior is achieved if the volume change that enters into the Clapeyron equation is taken to mean the volume change in phase space.

1. INTRODUCTION

In a recently published letter, Menzel et al. use a very simple transition state model to describe their kinetic results for the chemisorption of CO on Ru(001).(1) The close agreement of their model with the observed pre-exponential kinetic factors, obtained by several independent methods, argues convincingly in favor of their general model for the desorption mechanism. Another interesting experimental feature in this study is the pronounced "compensation" behavior exhibited by the measured isosteric heat of adsorption versus coverage. In fact, the variation in E_{iso} exactly compensates, within experimental accuracy, the concomitant change in the pre-exponential factor versus coverage which was observed to vary almost six orders of magnitude from $\theta = 0$ to $\theta > 0.5$. The explanation for this compensation behavior is actually quite simple, but further consideration of this simple case gives important insight into the reason for the existence of a more general compensation law. Although previous attempts to derive an explicit compensation law from basic thermodynamic arguments have been largely unsuccessful,(2) many intuitively appealing qualitative explanations have been proposed in the past to explain this effect.(3) We will now consider this problem again in the light of Menzel's results and, hopefully, clarify some issues relative to the compensation law, transition state theory, and the use of Arrhenius plots in chemical kinetics.

2. THE COMPENSATION EFFECT IN ADSORPTION/DESORPTION KINETICS

The necessity of a compensation effect for the cases such as that studied by Menzel et al. can be illustrated by considering a heterogeneous chemisorption system at thermodynamic equilibrium with the gas phase. Since the introduction of an intermediate precursor or transition state can in no way affect the equilibrium gas phase pressure, then an increased pre-exponential factor for desorption that results from the insertion of a high entropy state into the reaction path must be compensated by a concomitant increase in either the sticking coefficient and/or the heat of adsorption. (We assume for the moment that we have simple first order kinetics and that the adsorption is not activated.) While it is reasonable that the sticking probability S would tend to increase if a precursor adsorption state is introduced, the maximum value for S is, of course, unity so that only a limited amount of compensation can be attributed to changes in S. Certainly not the many orders of magnitude change required by transition state theory. Conceptually, we can always pick the transition state partition function F^* to have sufficient degrees of freedom (i.e., entropy) such that $S \approx 1$ so that a further increase in F^* then requires strict compensation behavior in $\Delta H_{iso}(\theta)$. Consequently, we have established, at least for this simple example, the necessity of a compensation effect although we have yet to identify the mechanism by which the introduction of a transition state into the reaction path would change the measured $\Delta H_{iso}(\theta)$ in precisely the right fashion.

3. TRANSITION STATE THEORY

In order to look for the link between the pre-exponential and exponential factors in chemical kinetics, first consider the idea of a transition state. This is visualized in n-dimensional phase space as the dividing surface between reactant and product and the area of this surface controls the probability of transitions, both ways, across the boundary. By analogy, this can be compared with the rate of evaporation of a water droplet in equilibrium with its vapor. As we increase the geometrical surface area (i.e., transition state) of the droplet, both the rates of evaporation and condensation are increased by the same geometrical factor. However, if we increase the evaporation rate by increasing only the entropy of the surface layer or transition state we no longer have a corresponding increase in the rate of condensation since the geometrical surface area in real space is constant, so again either the sticking probability (i.e., transmission factor) or the heat of vaporization must then increase. Increasing the entropy of the transition state might be visualized as analogous to packing together more compactly or miniaturizing the molecules at the physical dividing surface. Of course, for homogeneous processes, every molecule is at the physical dividing surface, but in this case another non-physical surface in phase space could be constructed which is a subset analogous to a physical surface so that the rate of the reverse reaction is again limited by the rate of arrival at that surface. For example, we might consider that some particular vibrational state of a molecule is part of the transition state for dissociation. We could consider increasing the transition probability by creating more and more rotational states at that particular vibration. But the rate of recombination at equilibrium is still kinetically limited by the frequency of physical collisions, so although we could conceptually increase the rate of dissociation without limit by increasing the number of rotational sublevels, the rate of recombination eventually reaches a maximum rate equal to the collision frequency. Thus, it is clear that a compensation effect is needed for this very general case and is not peculiar to heterogeneous processes. Discussions of transition state theory have traditionally avoided the foregoing line of reasoning by considering only reactions in the forward direction which are, of course, all that one is usually concerned with.(4) But there is often a great deal of additional insight to be gained by considering a particular process at thermodynamic equilibrium and then applying detailed balancing.

4. ISOSTERIC HEATS AND THE CLAPEYRON EQUATION

We have shown that increasing the entropy of the transition state must, eventually at least, lead to a strict compensation relationship between the entropy of the transition state and enthalpy of reaction. Previous attempts to derive this relationship from thermodynamic considerations have not been very convincing,(2) so it would appear that further efforts in this direction are perhaps ill advised. However, it may be important to at least point out that there are two assumptions in the derivation of the Clausius-Clapeyron equation from the more general Clapeyron equation for a change of state that may not be valid for cases similar to CO chemisorption on Ru(001). First, the assumption is made that the gas phase obeys the ideal gas law and, second, that the specific volume of the condensed phase is negligible compared with the specific volume of gas. For an adsorbed layer like CO on Ru(001) which is better described as a two-dimensional gas, this is probably a very bad assumption. An Arrhenius plot, in this case, of the equilibrium pressure versus T^{-1} at constant coverage may still give a reasonably straight line, but the slope will no longer be equal to the isosteric heat of adsorption. As a matter of fact, the slope will be increased by the factor $(K_3-K_2)^{-1}$ where K_3 and K_2 are the compressibilities of the three dimensional and two dimensional gases, respectively. It appears likely that for the case of CO on Ru(001), the increase in the measured $\Delta H_{iso}(\theta)$ that accompanies the highly mobile transition state can be attributed to K_2 becoming significant compared with K_3. A slightly different way of looking at this would be to consider the entropy of the transition state as a measure of the "volume" of the state not only in physical space but in phase space as well. Whereas the change in volume in the Clapeyron equation $\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$ has always been taken to mean physical volume, if we expand its sense to include phase space then we have a much more general explanation for the compensation effect since increasing the entropy of the transition state will increase the total volume difference in phase space. Whether it will prove effective to use this interpretation of the Clapeyron equation in general, of course, remains to be seen.

5. SUMMARY

Arguments have been made which, it is hoped, will persuade the reader to consider the so-called "compensation effect" a likely result of changing the entropy of a transition state and absolutely necessary if the change exceeds what can be compensated by a change in the sticking probability or transmission factor for the reverse process. While a rigorous derivation of a "Compensation Law" from basic thermodynamic or other arguments is not obvious, some ideas in that direction have been considered. Certainly we must not assume that an Arrhenius plot gives a straightforward isosteric heat unless the specific volume of the reactant can be assumed to be negligible. Finally, it has been suggested that it may be helpful to expand the meaning of the Clapeyron equation to include the change in volume in phase space. We then achieve a very general compensation law with, at least qualitatively, the right dependence on the entropy of the transition state. From this expanded viewpoint then, we only expect a transition state to affect the overall rate of a process when the specific volume of the reactant in phase space, including the transition state, is small compared with the phase space specific volume of the product.

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