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Kinetics of a Surface Reaction with a Logarithmic Adsorption Isotherm

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Starting with the expression for the activity coefficient of the activated complex obtained earlier on the basis of the Brønsted relation, an equation has been derived for the rate of reaction involving an arbitrary number of adsorbed species, obeying a logarithmic adsorption isotherm. It has been shown that, under certain conditions when the logarithmic isotherm holds, the rate of reaction is not an exponential function of the degree of coverage.

The usual derivation of kinetic equations for reactions involving adsorbed substances, obeying a logarithmic adsorption isotherm, is based on the Brønsted relation¹. Since the logarithmic adsorption isotherm arises from a linear relation between the heat of adsorption and the degree of surface coverage θ , and since according to the Brønsted relation the change in activation energy constitutes a fraction α of the change in the heat of reaction, the activation energy is linearly related to θ . The aim of the present paper was to obtain similar kinetic relations by another procedure, also ultimately based on the Brønsted relation. The rate of reaction is $v = kTc^\ddagger/h$, where $c^\ddagger = L\theta^\ddagger$ is the surface concentration of activated complexes expressed in terms of the number of species per cm^2 , and the remaining symbols have the usual significance. Within the framework of the activated complex treatment, $\theta^\ddagger$ may be found from the condition of equilibrium with the initial reactants; $\theta^\ddagger = (\Pi a_i/\gamma^\ddagger) \exp(-\Delta G^\ddagger/RT)$. Here $\gamma^\ddagger$ is the activity coefficient of the transition state ($\gamma^\ddagger = a^\ddagger/\theta^\ddagger$), a are the activities, and $\Delta G^\ddagger$ is the standard free energy of activation (a quantity which is independent of the concentrations of all the components). The following expression can be written for the chemical potentials of adsorbed substances:

$$\mu_i - \mu_i^0 = RT \ln a_i = RT \ln \frac{\theta_i}{1 - \sum_j \theta_j} + \sum_j r_{ij} \theta_j,$$

where r_{ij} is a constant characterising the effect of adsorption of substance j on the adsorption energy of substance i . With the standard state adopted, we have

$$\gamma_i = \frac{1}{1 - \sum_j \theta_j} \exp \left(\sum_j r_{ij} \theta_j / RT \right).$$

It was shown earlier², on the basis of the Brønsted relation applied to the free energies of activation for the fundamental reaction step, that the activity coefficient of

the activated complex $\gamma^\ddagger$ may be expressed in terms of the activity coefficients of the initial reactants γ_i and reaction products γ_k :

$$\gamma^\ddagger = \prod_i \gamma_i^\beta \prod_k \gamma_k^\alpha,$$

where $\beta = 1 - \alpha$. On substituting the above expressions in the basic equation of the theory of absolute reaction rates, we obtain finally

$$v = \frac{kT}{h} L \prod_i \theta_i \prod_j \left(1 - \sum_j \theta_j \right)^{-\alpha} \prod_k \left(1 - \sum_j \theta_j \right)^\alpha \times \\ \times \exp \left[-\frac{1}{RT} \left(\Delta G^\ddagger - \alpha \sum_i \sum_j r_{ij} \theta_j + \alpha \sum_k \sum_j r_{kj} \theta_j \right) \right].$$

Here $\sum_i$ denotes summation with respect to the initial species only, $\sum_k$ summation with respect to products, and $\sum_j$ summation with respect to all the adsorbed substances.

As usual, in the case of a logarithmic adsorption isotherm the reaction rate proves to be in general an exponential function of the degree of coverage. However, there is one interesting exception. If the number of adsorbed substances and reaction products is the same ($i = k$) and if each adsorbed substance has the same effect on the adsorption energies of all the remaining substances (this conclusion follows from the model of the interaction of adsorbed atoms via a surface electron gas³), or more precisely if the pairs of equalities $r_{ij} = r_{kj}$ hold, then all the terms in the exponential function depending on θ cancel. Under these conditions, the reaction rate changes slowly with coverage, despite marked changes in the chemical potentials of the adsorbed substances.

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The Effect of Adsorbed Water Molecules on the Electrical Parameters of the Real Surface of Germanium

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It has been shown that water molecules adsorbed at low coverages on the germanium oxide film form donor-acceptor bonds with coordination-unsaturated surface germanium atoms. The local fields of the effective dipoles generated alter the potential of the surface and neutralise the surface recombination centres. A mechanism is proposed which explains the changes in the principal electrical parameters of the germanium surface when the latter is heated in a vacuum and hydrated.