INFLUENCE OF THE ENTROPY FACTOR ON THE EQUILIBRIUM AND KINETICS OF CHEMISORPTION

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A correction to the model of uniform heterogeneous surface has been introduced. This correction extends the limits of application to processes with entropy changes of the adsorbent. On the basis of the model thus corrected a kinetic equation has been deduced, which takes into account the role of the entropy factor. The presence of a "compensation effect" in chemisorption kinetics is supported theoretically.

According to the theory of processes proceeding on heterogeneous surfaces, the surface of a solid is formed of a specified number of sites, whose abilities for adsorption are different, and it is characterized by a certain standard free energy value. A change in the standard free energy of the given chemisorption process is related to the adsorption equilibrium constant

\[ K_\theta = \exp \left( - \Delta F_\theta / RT \right) = A_\theta \exp \left( q_\theta / RT \right) \]  

(1)

where

\[ A_\theta = \exp \left( \Delta S_\theta / R \right) \]  

(2)

is the entropy factor.
According to the model of a uniformly heterogeneous surface/1/, \( \Delta F_0 \) increases linearly with increasing surface coverage \( \theta \)

\[
\Delta F_0 = \Delta F_0 + C \theta
\]  

Such a model conforms to a linear decrease in the adsorption heat \( q_0 \) and a linear increase in the activation energy \( E_0 \) with increasing \( \theta \)

\[
q_0 = q_0 - C \theta \quad (4)
\]
\[
E_0 = E_0 + B \theta \quad (5)
\]

Constants \( C \) and \( B \) are related to the linearity factor \( \alpha \) of the Brønsted, Polanyi, Temkin relationship/2/

\[
\Delta E_0 = -z q_0 \theta \quad ; \quad z = B/C
\]  

The dependence of the equilibrium constant on the surface coverage for a uniformly heterogeneous surface is expressed in the following way

\[
K_\theta = K_0 \exp \left[ -f \theta \right] \quad (7)
\]

where \( K_\theta \) is the equilibrium constant at a specified \( \theta \), and \( K_0 \) is that at \( \theta \to 0 \). The factor \( f \) is determined from eqs. \( (4) \) and \( (7) \)

\[
f = C/RT
\]  

The model of the uniformly heterogeneous surface is based on the assumption that the preexponential factors of equilibrium and rate constants retain the same values for different sites on the surface. The relationships corresponding to this model can be obtained if the adsorption process takes place without changes in the entropy of the adsorbent and only changes in the entropy of the adsorbed substance are taken into account. In this form the model of a uniformly