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Desorption of Hydrogen from Iron—Influence of the Activity Coefficient of Adsorbed Hydrogen

E. CHORNET* AND R. W. COUGHLIN

Center for Surface and Coatings Research and Chemical Engineering Department, Lehigh University, Bethlehem, Pennsylvania 18015

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Within the framework of absolute reaction rate theory as applied to surface reactions, the chemical activities of the adsorbed species can be formulated in terms of thermodynamic activity coefficients. This leads directly to the prediction that the Arrhenius parameters of activation energy and preexponential factor also depend on the thermodynamic activity coefficients of the adsorbed species. This development also produces a simple algebraic relationship between activation energy and preexponential factor which not only provides a thermodynamic rationale for the compensation effect but also permits calculation of thermodynamic activity coefficients from experimentally observed compensatory behavior of the Arrhenius kinetic parameters. The development is carried out for the case of desorption of hydrogen from iron, which involves the chemical combination of adsorbed hydrogen atoms to hydrogen molecules as the rate-limiting step. Activity coefficients and entropies of activation are also thereby computed from measured rates of desorption of hydrogen from assiduously cleaned iron wire which provides a homogeneous, smooth surface. In this case, the compensation effect involves variation of activation energy and preexponential factor depending on surface coverage, and this information is used to compute the thermodynamic activity coefficient of adsorbed hydrogen atoms as a function of surface coverage. The results can be interpreted as a departure from two-dimensional, adsorbed-phase, ideal-gas behavior as surface coverage increases. The results also demonstrate that the intrinsic relationship between activation energy and preexponential factor can be explained in terms of variation of thermodynamic activity coefficients of adsorbed reactants.

I. INTRODUCTION

Previous work has demonstrated the compensation effect for the desorption of carbon monoxide from nickel, molybdenum, and tungsten. In the following we explain this effect, as observed for the desorption of hydrogen from iron, in terms of a smooth and homogeneous surface (our experimental approach employed ultrahigh vacuum techniques and preparation of the surface was carried out by hydrogen reduction, argon ion bombardment, and annealing) upon which a mobile adsorbent (hydrogen atoms in this study) is present. The adsorbed phase behaves as an ideal, two-dimensional gas at low coverages, but with increasing adsorbed amounts, deviations from ideality occur due to lateral interactions resulting in changes in the thermodynamic activity of the adsorbed species. These changes are accounted for by introducing activity coefficients in the usual thermodynamic way.

Desorption reactions of gases from solid surfaces, like other reactions, are commonly analyzed by the Arrhenius equation,

$$-dn/dt = An^{\alpha} \exp(-E_d/RT), \qquad (1)$$

where n = the amount adsorbed per unit surface; A = the frequency factor; E_d =

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* Present address: Faculté des Sciences Appliquées, Université de Sherbrooke, Sherbrooke, P. Q., Canada.

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the activation energy for desorption; α = reaction order; T = temperature, °K; t = time; R = gas constant.

Using this equation, desorption studies have shown that the frequency factor, A, can be correlated with the activation energy, E_d, according to the compensation law. Such desorption investigations have included studies of the following systems: carbon monoxide (*1*) from nickel and molybdenum; nitrogen from tungsten and molybdenum (*2, 3*); carbon monoxide, hydrogen, nitrogen, and oxygen from tungsten (*4*); and hydrogen from nickel (*5*).

Although early studies (*6, 7*) had attributed the compensation law to surface heterogeneity, Armand and Lapujoulade (*8*) in a theoretical treatment of first-order desorption reactions concluded that the former hypothesis was an unsatisfactory explanation for desorption from metals.

In a recent study of hydrogen chemisorption on iron (*9*), we have also found a compensation effect when analyzing the desorption reaction. Our equilibrium data suggest both a mobile adsorbate and a smooth and homogeneous surface. In the present work we explain the observed effect as caused by deviations from the initial ideality of the two-dimensional adsorbate.

II. Experimental Methods

The following precautions must be taken in the investigation of gas desorption reactions from a metal surface. First, in order to avoid interferences from the residual gases present in the experimental chamber, their partial pressures must be sufficiently low that competition during adsorption and desorption as well as possible poisoning of the surface are minimized if not entirely eliminated; second, the surface of the metal should be prepared in such a way that neither oxides nor carbon, sulfur, or other impurities are present. Furthermore, the metals should be well annealed so that surface roughness is reduced to a minimum. These conditions can be satisfied using ultrahigh vacuum techniques (UHV). Since iron was our specimen, the conventional methods of surface preparation, i.e., extensive annealing in UHV and prolonged hydrogen reduction, did not suffice in obtaining a reproducible surface, a difficulty that can be attributed to the thermodynamic stability of the surface oxides. To circumvent this problem we used argon-ion bombardment of the specimen for surface preparation, a method which resulted in a uniform reproducible surface. Details of the procedure and experimental arrangement can be found elsewhere (*11*).

The desorption reaction was studied using the flash filament method (*12, 13*). The technique can be summarized as follows: after a controlled adsorption interval ($t_a - t_o$) at a chosen pressure, p, and temperature, T_a, the specimen (a thin ribbon or wire) is brought to a preselected maximum temperature T_d within the few seconds duration of the flash. During this heating period desorption of the adsorbate takes place at a rate dictated by the kinetics of the process. When both the temperature of the filament and partial pressures of sorbate (by mass spectrometry) are followed in time, the reaction rate law can be determined according to Eq. (1), including the temperature dependence.

A material balance of the experimental cell permits determination of the desorption rate as a function of time:

$$-dn/dt = (V/akT)[dp/dt + (S/V)(p - p_{ss})], \quad (2)$$

where a = sample surface area, V = volume of the cell, S = pumping speed of the system during the desorption interval, p_{ss} = steady-state pressure, k = Boltzmann constant, and n, t, p, and T have the definitions given for Eq. (1).

Integration of (2) will provide n, at any time t.

Assuming that desorption follows the Arrhenius law, Eq. (1), a plot of log $(-(1/n^\alpha)(dn/dt))$ vs $1/T$ will determine A and E_d with α chosen to provide the best fit of the data to the rate equation.

Since T was found to be a complex function of t in these experiments, it was necessary to carry out a numerical solution using a CDC 6400 computer.

III. Results

Because a second-order desorption reaction was always found to hold in the range of coverages investigated (*9, 11*), it can be assumed that the adsorbed species are hydrogen atoms at 298 K. The energy of activation for desorption as a function of adsorbed amount is shown in Fig. 1. The shape of this curve agrees qualitatively with the general relationship of the bonding energy of an adsorbed layer when nearest-neighbor interactions are important (*14*).

The derived data of Fig. 2 show the preexponential factor correlated with the activation energy for desorption, displaying the usual compensation law relationship.

IV. Discussion

According to Eyring's theory of reaction rates (*15*) or Horiuti's formulation (*16*), the desorption rate is given by:

$$v = (kT/h) \cdot n_\ddagger, \qquad (3)$$

where kT/h is the universal frequency of decomposition of the activated complex into products (gas molecules) and $n_\ddagger$ stands for the concentration of activated complex per unit surface area. The essential assumption of the absolute rate theory is that equilibrium between reactants and activated complex is rapidly established according to the reaction:

$$H_{adsorbed} + H_{adsorbed} \overset{K_\ddagger}{\rightleftarrows} (H\cdots H)^\ddagger \xrightarrow{kT/h} H_2(g). \qquad (4)$$

Accordingly, it is possible to apply the usual steady-state assumption for the activated complex and use the equilibrium expression:

$$K_\ddagger = a_\ddagger/a_H a_H = (n_\ddagger/n_H \cdot n_H) \cdot (\gamma_\ddagger/\gamma_H \cdot \gamma_H), \qquad (5)$$

to eliminate $n_\ddagger$ from Eq. (3):

$$v_d = (kT/h) \cdot K_\ddagger \cdot (\gamma_H^2/\gamma_\ddagger) \cdot n_H^2, \qquad (6)$$

where $a_\ddagger$, a_H, $\gamma_\ddagger$, and γ_H stand for the thermodynamic activities and activity coefficients of adsorbed hydrogen atoms (subscript H) and activated complex (subscript ‡). The surface concentration of adsorbed hydrogen atoms per unit area is designated by n_H in Eq. (6) but the subscript H is discarded in the development which follows. A physical view that pictures the activated complex as situated above the layer of adsorbed hydrogen atoms and thus possessing a chemical potential not influenced by hydrogen atoms

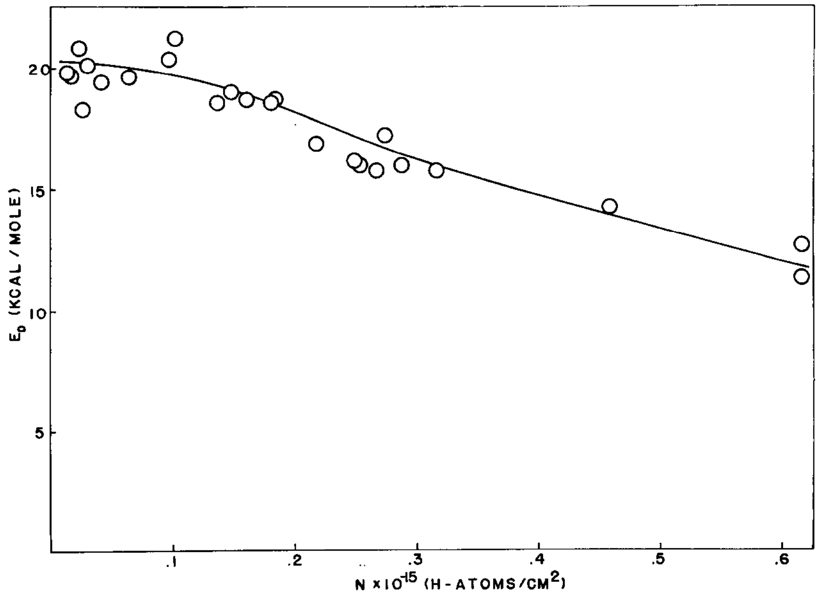

Fig. 1. Energy of activation for desorption of hydrogen from iron as a function of amount adsorbed.

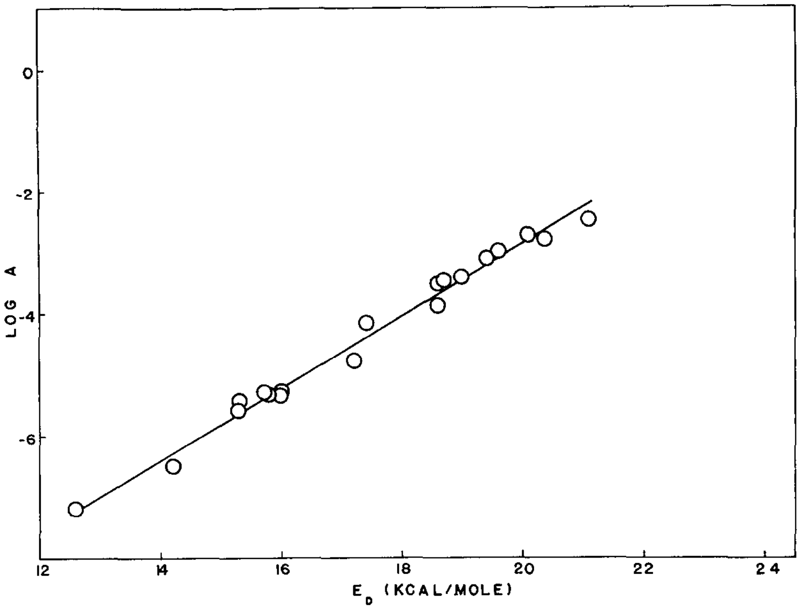

FIG. 2. Log of the mean preexponential factor plotted against mean activation energy of desorption of hydrogen from iron.

in the adsorbed layer is consistent with the interpretations of observed sticking coefficient for the adsorption of hydrogen on iron (*9*) and resembles a model that has been elucidated for CO on Ni (*10*). Based on this model, $\gamma_\ddagger$ may be taken as unity whereupon Eq. (6) becomes

$$v_d = (kT/h) \cdot \mathrm{K}_\ddagger(\gamma_{\mathrm{H}} n_{\mathrm{H}})^2 = (kT/h) \cdot \mathrm{K}_\ddagger \cdot a_{\mathrm{H}}^2, \tag{7}$$

a form that is identical to a formulation of absolute rate theory based on thermodynamic chemical activity rather than concentration (*10, 16*) and which implies a standard state for activated complex of $n_\ddagger = 1$. The activity coefficient γ_{H} accounts for deviations from ideal behavior of adsorbed hydrogen atoms arising from lateral adsorbate–adsorbate interactions primarily, but it may also include adsorbent–adsorbate interactions as well. Identifying Eq. (7) with Arrhenius' law, Eq. (1), which has been assumed to hold experimentally, we arrive at

$$\begin{aligned} A &= (kT/h)\mathrm{K}_\ddagger\gamma_{\mathrm{H}}^2 \exp(E_d/RT) \\ &= (kT/h)\exp(-\Delta\mathrm{F}^\circ{}_\ddagger/RT)\gamma_{\mathrm{H}}^2 \exp(E_d/RT). \end{aligned} \tag{8}$$

$\Delta\mathrm{F}^\circ{}_\ddagger$, the standard Gibbs free energy of the reaction in which the reactants form the activated complex, has a definite value once the standard states have been specified. A further step in the formulation of an expression for the frequency factor, A, is obtained by considering the direct relationship between the standard free energy $\Delta F^\circ{}_\ddagger$ and the energy of activation E_d. The latter quantity is determined experimentally from the slope of log $[-(1/n^2)(dn/dt)]$ vs $1/T$, and can thus be defined as:

$$d \ln k_s/d(1/T) = -E_d/R, \tag{9}$$

where $k_s = -(1/n^2)\ (dn/dt)$. The specific rate constant, k_s, is also expressed by Eq. (7) as:

$$\begin{aligned} k_s = v_d/n^2 &= (kT/h)\mathrm{K}_\ddagger\gamma_{\mathrm{H}}^2 \\ &= (kT/h)\exp(-\Delta\mathrm{F}^\circ{}_\ddagger/RT)\gamma_{\mathrm{H}}^2. \end{aligned} \tag{10}$$

Equation (9) assumes that neither the frequency factor, A, nor the activation energy, E_d, depend upon T. In fact, and following Armand and Lapujoulade (*8*), A may depend weakly on T. However, its dependence should not exceed a variation of an order of magnitude in the interval of temperatures considered in order for Eq. (9) to provide a usefully accurate representation of activation energy of desorption. The data plotted in Fig. 3 clearly show that the sensitivity of A to temperature is sufficiently small in the present case.

Substituting (10) into (9) and performing the differentiation gives:

$$E_d = RT + \Delta F^\circ_\ddagger + (1/T)[d\Delta F^\circ_\ddagger/d(1/T)] - R[d \ln \gamma_H^2/d(1/T)]. \quad (11)$$

Using the thermodynamic relationships,

$$\Delta F = \Delta H - T\Delta S \text{ and } (1/T)(\partial \Delta H/\partial T)_p = (\partial \Delta S/\partial T)_p, \quad (12)$$

Eq. (11) reduces to:

$$E_d = RT + \Delta H^\circ_\ddagger + RT^2(d \ln \gamma_H^2/dT). \quad (13)$$

Because the reacting species are within a sorbed phase the thermodynamic entities in the formulations are, in fact, partial molar quantities (*18*).

Combining Eqs. (8) and (13), results in

$$A = (kT/h)\gamma_H^2 \exp[(\Delta S^\circ_\ddagger/R) + 1] \times \exp[T(d \ln \gamma_H^2/dT)]. \quad (14)$$

At very low coverage where n is small,

$$\gamma_H = 1 \quad \text{and} \quad E_d = E_{d,0}. \quad (15)$$

We can define

$$A_0 = (kT/h) \exp[(\Delta S^\circ_\ddagger/R) + 1]. \quad (16)$$

Then

$$A = A_0\gamma_H^2 \exp[T(d \ln \gamma_H^2/dT)]. \quad (17)$$

The equations which have now been developed relate the variations of the activity coefficients of the adsorbed species to the desorption activation energy [Eq. (13)] and to the preexponential factor of the desorption rate constant [Eqs. (14) and (17)].

Determination of Activity Coefficients of the Adsorbed Phase

It is possible to continue the foregoing general development to compute values of activity coefficient for adsorbed hydrogen at different coverages using experimental data for desorption. Such desorption experiments are carried out over the range

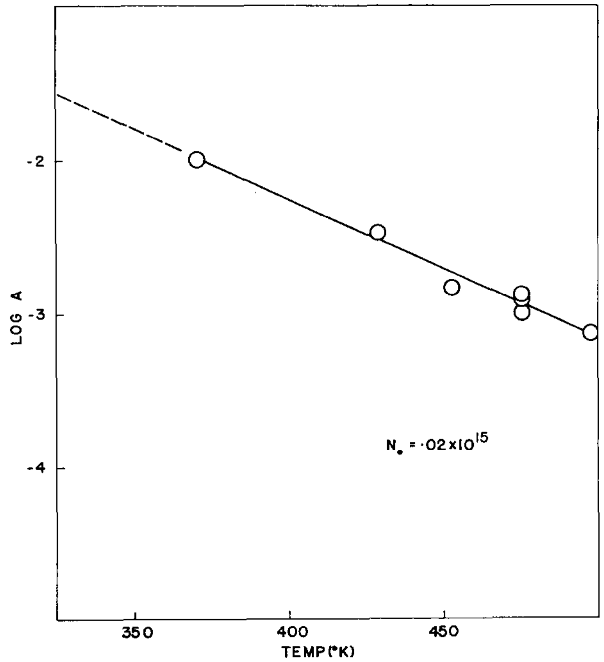

FIG. 3. Log of the preexponential factor for the desorption of hydrogen from iron as a function of temperature.

of temperature and coverage beginning with T_2 and n before desorption and ending with T_1 and $n \approx 0$, when n is small and desorption is complete. Recalling the assumption implicit in Eqs. (9)–(11) that E_d is independent of T [the effect of the RT term in Eq. (13) is small compared to $\Delta H^{\circ\ddagger}$] and recognizing that only the last term in Eq. (12) is coverage dependent we write:

$$E_d = E_{d,0} + RT^2(d \ln \gamma_{\mathrm{H}}^2/dT), \tag{18}$$

where $E_{d,0}$ is the activation at small or zero n where $\gamma_{\mathrm{H}} \simeq 1$. Eliminating the temperature derivative of $\ln \gamma_{\mathrm{H}}^2$ between Eqs. (17) and (18) we obtain:

$$E_d = E_{d,0} + RT \ln (A/A_0) - RT \ln \gamma_{\mathrm{H}}^2,$$

or

$$\ln \gamma_{\mathrm{H}} = [(E_{d,0} - E_d)/2RT] + \tfrac{1}{2} \ln (A/A_0). \tag{19}$$

It should be emphasized that each of the terms γ_{H}, E_d, and A in (19) refer to the same extent of coverage, and, therefore, they may be regarded as functions of n. As mentioned previously, our experimental values for activation energy and preexponential factor were obtained over a range of coverage from an initial value of n up to small $n \approx 0$. Such experimental values may, therefore, be regarded as integral values or averages, $\overline{E_d}(n)$, $\bar{A}(n)$ and can be expressed in terms of the point values, E_d and A, to a first approximation, using the equations:

$$\bar{A}(n) = \frac{1}{n} \int_0^n A\,dn \quad \text{and}$$

$$\overline{E_d}(n) = \frac{1}{n} \int_0^n E_d dn. \tag{20}$$

Differentiating these equations:

$$\begin{aligned} A &= \bar{A}(n) + n[d\bar{A}(n)/dn], \\ E_d &= \overline{E_d}(n) + n\,[d\overline{E_d}(n)/dn]. \end{aligned} \tag{21}$$

Equations (21) have been used to compute point values of A and E_d from the average experimental values, $\bar{A}(n)$ and $\overline{E_d}(n)$; such point values have been used to compute $\log \gamma_{\mathrm{H}}$ as a function of coverage via Eq. (19). It should be recognized that the values of $\log \gamma_{\mathrm{H}}$ so obtained may be regarded as somewhat approximate as a result of the error introduced by differentiating experimental data according to Eqs. (21). The values of E_d, A, $\bar{A}(n)$, and $\overline{E_d}(n)$ are recorded in Table 1 and $\log \gamma_{\mathrm{H}}$ is plotted vs n in Fig. 4. The activity coefficient γ_{H} increases exponentially from a value of unity at low coverages.

Equation (19), of course, is a statement of the usual compensation effect if A_0 and $E_{d,0}$ are taken as constant. Moreover, it is clear from Fig. 2 that $\bar{E}(n)$ and $\bar{A}(n)$ also show a distinct compensation effect, and, it is evident from Table 1 that the changes in $\ln \gamma_{\mathrm{H}}$ are small compared to changes in $\bar{E}(n)$ and $\bar{A}(n)$; nevertheless,

TABLE 1

Integral Values of the Activation Energy for Desorption, Preexponential Factor, Activity Coefficient and Entropy as Functions of Adsorbed Amount at Room Temperature

$n \times 10^{-15}$ (H-atoms × cm^{-2})	E_d (kcal/mole)	$\log_{10} A$	$\log_{10} \gamma_{\mathrm{H}}$	$-\Delta S\ddagger/R$ (cal/deg)
0.1	20.3	−2.66	1.000	37.03
0.11	20.0	−2.85	1.036	37.46
0.175	19.0	−3.40	1.270	38.73
0.215	18.0	−4.03	1.428	40.19
0.250	17.0	−4.63	1.657	41.58
0.290	16.0	−5.22	1.947	42.93
0.325	15.0	−5.81	2.281	44.28
0.480	14.0	−6.40	2.681	45.64
0.600	13.0	−6.99	3.150	47.01

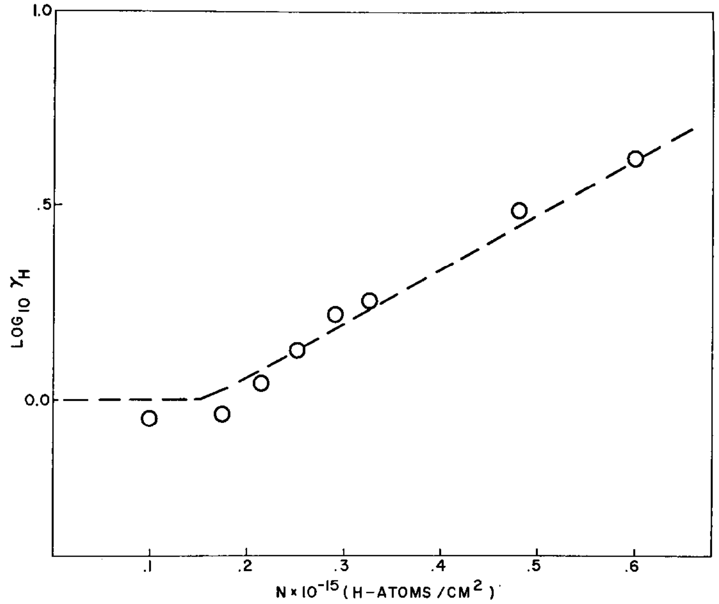

FIG. 4. Log of the activity coefficient of adsorbed hydrogen atoms plotted against amount adsorbed.

γ_H increases monotonically with surface coverage.

Also tabulated in Table 1 are computed values of the integral entropy change, $\Delta S_\ddagger$, of the reaction between hydrogen atoms to form the activated complex. These entropy values have been computed from Eq. (10) written (*15*) in the form:

$$k_s = (kT/h)\exp\{[\Delta S_\ddagger(n)/R] + 1\} \times \exp[-\bar{E}_d(n)/RT]. \quad (25)$$

It is clear from the values of ΔS in Table 1 that the mobility of the activated complex approaches that of the adsorbed hydrogen atoms as the coverage decreases. Since $\Delta S_\ddagger$ is negative for each coverage, it is also clear that the activated complex is in general less mobile than the adsorbed hydrogen atoms.

Measurements of isobars and isotherms for the same system (*9, 11*) have shown through calculation of the molar entropy of the adsorbed species, that the adsorbate behaves initially as a mobile two-dimensional gas, thus justifying the present treatment, which has also assumed a two-dimensional adsorbed gas with strong lateral interactions.

V. CONCLUSIONS

The results reported here show, in a general way, that when a mobile adsorbate is present, strong lateral interactions among the adsorbed species can influence both the activation energy for desorption and the preexponential factor. From the thermodynamic standpoint, these entities are uniquely related to the thermodynamic activity coefficients of the adsorbed phase. These activity coefficients have been calculated from the experimental data in the present work, thereby showing a strong dependence of thermodynamic activity upon adsorbed amount.

The observed compensation effect is thus explained herein in terms of a departure from thermodynamic ideality due to lateral interactions between adsorbed species in the surface phase on homogeneous surface. This relationship between the activation energy for desorption and the preexponential factor has been developed through the well-known parameter of the activity coefficient. Entropy calculations indicate that the activated complex for the desorption of hydrogen from iron is less mobile than the adsorbed hydrogen atoms which behave as a two-dimensional gas.

It is evident that the rationale for the compensation effect developed herein for flash desorption reactions can be extended to the general surface reactions of heterogeneous catalysis. Thus, for the compensation effect observed over a range of experimental conditions for the same catalyst, the explanation can take the form of variation of thermodynamic activity coefficients with variation in coverage, for example due to interactions of dislocations (*18*), which in turn depends on experimental conditions. For compensatory behavior observed at identical experimental conditions but over a suite of different catalysts, the explanation can be in terms of variation of thermodynamic activity coefficients of the adsorbed reactants from catalyst to catalyst, which variations arise not only from lateral interactions (adsorbate–adsorbate interactions) but also from interactions between adsorbate and catalyst.

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