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ON THE INTERPRETATION OF ADSORPTION AND
DESORPTION KINETICS EXPERIMENTS

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On The Interpretation of Adsorption and Desorption Kinetics Experiments

Experimental results on adsorption and desorption kinetics are frequently interpreted in terms of some reaction mechanism and approximate solutions to the rate equations associated with that mechanism. It is the purpose of this note to present numerically accurate solutions to a particular set of rate equations in order to assess the validity of approximations usually made. Aside from providing new insight into the kinetics that may be observed experimentally, these calculations will clarify an apparent contradiction between isothermal\(^1,2\) and flash desorption experiments\(^3,4\) on the H\(_2\)/Ni system. The results presented below will also have implications for the interpretation of surface catalytic reactions.

The reaction mechanism considered describes dissociative chemisorption via an immobile precursor state and can be depicted schematically as follows:

\[
X_2(g) \xrightleftharpoons[k_d]{k_a} X^*_2(s) \xrightarrow[k_2]{k_1} 2X(s)
\]  

(1)

The rate equations associated with this mechanism are given as

\[
\frac{d\theta^*}{dt} = p_{X_2} k_a (1 - \theta^*) - k_d \theta^* - \frac{1}{2} \frac{d\theta}{dt}
\]

\[
\frac{1}{2} \frac{d\theta}{dt} = k_1 \theta^*(1 - \theta)^2 - k_2 (1 - \theta^*) \theta^2
\]

(2)

\(\theta^*\) and \(\theta\) denote the coverages in the precursor and chemisorbed states, respectively, \(p_{X_2}\) is the gas pressure, and \(k_a\) is proportional to \(s^* (2\pi m k_B T_g)^{-\frac{1}{2}}\) with \(s^*\) being the sticking coefficient into the precursor state. Rate equations of the form of Eq.(2) have been used frequently.\(^5,6\)
In typical adsorption experiments $k_2 = 0$. The assumption of a steady state for the precursor state, (i.e. $d\theta*/dt = 0$, or equivalently, $\theta* \ll \theta$), then leads to the following expression for the rate of adsorption $r_a$:

$$r_a = \frac{1}{2} \frac{d\theta}{dt} = p_{X_2} k_a \left( 1 + \frac{k_d + p_{X_2} k_a}{k_1 (1 - \theta)^2} \right)^{-1}.$$  

(3)

It is not usually recognized that one can easily integrate Eq. (3) in order to obtain an approximate expression for $\theta$ as a function of $t$. With $\theta(0) = 0$, $\theta(t)$ is found to be the solution of the equation

$$\theta \left( 1 + \frac{k_d + p_{X_2} k_a}{k_1 (1 - \theta)} \right) = 2 p_{X_2} k_a t.$$  

(4)

Equivalently, experimental results are often discussed in terms of the coverage-dependent sticking coefficient $s(\theta)$:

$$s(\theta) = \left( p_{X_2} k_a \right)^{-1} s^* r_a = s^* \left( 1 + \frac{k_d + p_{X_2} k_a}{k_1 (1 - \theta)^2} \right)^{-1}.$$  

(5)

(If the precursor state were mobile, the term $p_{X_2} k_a$ in the brackets in Eqs. (3) to (5) would be absent. Cf. also Ref. 6). In typical desorption experiments $p_{X_2} k_a = 0$. If, during desorption, equilibrium is obtained between the precursor and the chemisorbed state, the rate of desorption $r_d$ is given by

$$r_d = k_d \theta* = k_d k_2 \theta^2 (k_1 (1 - \theta)^2 + k_2 \theta^2)^{-1}.$$  

(6)

(With a mobile precursor state, the term $k_2 \theta^2$ in the brackets in Eq. (6) would be missing).
In order to obtain physically significant solutions to Eq. (2), one must know the relative magnitudes of the rate constants $k_j$ under the experimental conditions in question. The values of the $k_j$ depend on the pre-exponential factors $A_j$, the activation energies $E_j$, and the surface temperature $T_S$. Although there are no systems for which all of these parameters are known, one can guess reasonable values for the $k_j$ by combining some experimental information with representative figures for the $A_j$ and $E_j$. The precursor state should be much more loosely bound than the chemisorbed state (hence $A_d \ll A_2$), and adsorption is generally non-activated (hence $E_1 < E_d$). For example, for H$_2$ on Ni, $A_d = A_1 \approx 10^8$ sec$^{-1}$, $A_2 \approx 10^{13}$ sec$^{-1}$; $E_d \approx E_1 \approx 8$ kcal/mole, $E_2 \approx 20$ kcal/mole (cf. refs. 2 to 5). A further point of comparison with experiments is provided by the desorption times predicted from a set of rate parameters at a given surface temperature.

In discussing the exact solutions of Eq. (2), a brief comment on adsorption kinetics seems worthwhile. In a typical adsorption experiment, $p_X \ll 10^{-7}$ torr so that at room temperature $p_X k_a/k_d < 10^{-2}$. Also, from experiments, $k_d/k_1 \approx 0.1$. The exact solutions of Eq. (2) then show that the steady state assumption for the precursor state is indeed very good at all coverages. In general $\theta* < 10^{-2} \theta$, and the approximate $\theta(t)$ and $s(\theta)$ are both accurate to within 1%. (Under these conditions, the cases of a mobile and an immobile precursor state are indistinguishable because $1 - \theta* \approx 1$ in Eq. (2)). In order to determine $k_d/k_1$ from experimental data, it may well be advantageous to evaluate data for $\theta(t)$ directly using Eq. (4) rather than to obtain $s(\theta)$ by differentiating $\theta(t)$ and then fit $s(\theta)$ by an expression such as Eq. (5).
The desorption kinetics predicted by Eq. (2) are illustrated in Figs. 1 to 4. The rate parameters chosen, particularly in Figs. 3 and 4, are representative of H₂ on Ni. It is remarkable that under certain conditions, $-\log \theta$ may be, after a brief initial period, very nearly a linear function of $t$. In fact, the linear portions of the curves for $T_S = 450$ K in Figs. 1 and 3 extend over at least twice the range shown in the figures. This may be interpreted as first-order desorption kinetics, although chemisorption was assumed to be dissociative. Such behavior has been observed in some isothermal desorption experiments of H₂ on Ni.¹,² However, the explanation of this behavior offered previously by Shanabarger⁵ does not hold. Linearization of a system of nonlinear equations such as Eq. (2) always lead to exponentially decaying solutions, but such a procedure is only valid for very short and not for physically significant time intervals. For the rate parameters used in Figs. 1 and 3, the exact solutions of Eq. (2) also show that after a time of the order of $10^{-2}$ to $10^{-3}$ times $(k_d k_2 / k_1)^{-1}$, the rate of desorption is given to within ~2% by the approximate expression (6) assuming equilibrium between the precursor and the chemisorbed state.

As regards the order of desorption, it should be pointed out that the desorption rate is usually assumed to be proportional to some power of the total amount of gas adsorbed.⁶ Hence, one can obtain an effective order of desorption by plotting $\log r_d$ as a function of $\log (\theta^* + \frac{1}{2} \theta)$, as is shown in Figs. 2 and 4. However, the effective order of desorption itself depends on the coverage, since $\log r_d$ is not exactly a linear function of $\log (\theta^* + \frac{1}{2} \theta)$ over the entire range of coverage (cf. Figs. 2 and 4). This can also be seen by noting that if $k_1 >> k_2$, then $\theta^* << \frac{k_2}{k_1}$ so that
Thus, if $k_1 \gg k_2$, then at low $\theta$ the two-step process (1) resembles a one-step second-order desorption process with an activation energy of $E_d - E_1 + E_2$. ($E_d - E_1 + E_2$ corresponds to the potential energy difference between the gas phase and the chemisorbed state). It should also be mentioned that the shapes of the curves in Figs. 1 and 3 and the effective orders of desorption as illustrated in Figs. 2 and 4 do not depend on the initial coverage within reasonable limits.

It remains to be discussed to what extent the above results are dependent on the values chosen for the rate parameters and on the particular form of the chemisorption mechanism. Fortunately, the kinetics turn out to be relatively insensitive to certain changes in the values of the rate parameters. An increase of $A_1$ (and $A_d$) by a factor 10 decreases a typical desorption time by about 20%. The shapes of the curves in Figs. 1 and 3 are left virtually unchanged, and the effective orders of desorption are changed slightly, by changes of 3 kcal/mole in the activation energies $E_j$ as long as $E_d - E_1 + E_2$ remains constant. On the other hand, changing $E_d - E_1 + E_2$ affects the kinetics markedly, as is evident from a comparison of the time scale and effective orders in Figs. 1 and 2 with those in Figs. 3 and 4.

In interpreting adsorption experiments in terms of a precursor mechanism, it is often found difficult to ascertain the precise form of that mechanism, a major question being whether chemisorption is dissociative or non-dissociative. For the case of non-dissociative chemisorption, the rate equations (2) would have to be modified by replacing the factors $\theta^2$ and $(1 - \theta)^2$ by $\theta$ and $(1 - \theta)$. The resulting desorption kinetics then differ from those shown in Figs. 1
to 4 in two respects. With the same rate parameters as used in Figs. 1 to 4, all the curves of $-\log S$ vs. $t$ are, after a brief initial period, linear over a wide range of coverage, and the effective orders are reduced by about 1.

In summary, the exact solutions of the rate equations (2) have clarified some assumptions frequently made in analyzing adsorption and desorption rate data. They have revealed similarities and differences between one-step and two-step chemisorption mechanisms. They have also shown no evidence that isothermal and flash desorption experiments should yield conflicting information.

Experimental results produced by the two techniques have generally been in agreement with each other for a number of gas-surface systems including H$_2$ on Ni. The two examples where isothermal desorption experiments on the H$_2$/Ni system yielded differing results are probably due to experimental artifacts. It is less than straightforward to determine amounts of gas adsorbed on a metal film by measuring its resistance change because of fundamental difficulties in the physical basis of interpretation and because the resistance change is a nonlinear function of the coverage even at quite low coverages.

Furthermore, recent experiments on single-crystal surfaces have clearly shown that adsorption and desorption kinetics depend on the detailed structure of the surface and may differ markedly between different crystal planes of the same material. In the one instance of first-order desorption of H$_2$ from a Ni(100) surface, the substrate was probably covered by an oxide. (Note the very high surface temperature, ~750 K, required to effect appreciable desorption in that experiment).

Finally, the results presented here also have implications for catalytic reactions and may provide a partial explanation for the contradictory
observations on H₂-D₂ exchange on platinum reported recently.¹⁷,¹⁸ Whereas Bernasek et al., in a molecular beam experiment, found the exchange reaction to occur only on a stepped surface but not on the (111) surface, Lu and Rye observed exchange to occur readily on the (111) surface in an experiment involving adsorption from a homogeneous background. If the precursor state in the reaction mechanism (1) is interpreted as the transition state in the exchange reaction, then the curves in Figs. 1 and 3 show that equilibration of the adsorbed reactants may require a fairly long time. In a modulated-molecular-beam experiment, however, only products with a short time lag with respect to the beam signal are detected. Hence, equilibrium is probably not established at all, and a considerably smaller rate of reaction will thus be measured. The qualitative conclusions reached above on desorption kinetics also indicate that the kinetics of catalytic reactions may depend sensitively on the surface concentrations of the reactants maintained under given experimental conditions.

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References


7. C. Kohrt and R. Gomer, Surf. Sci. 24 (1971) 77. For CO on W(110), the pre-exponential of the virgin state, which can convert into the chemisorbed $\beta$ state, is much smaller than the pre-exponential of the $\beta$ state.


Ref. contd.


Figure Captions

Fig. 1. Isothermal desorption kinetics for H₂ on Ni predicted from Eq.(2):
plots of -logθ vs. t. Initial conditions: θ* = 0 and θ = 0.7.
Rate parameters: A₀ = A₁ = 10⁷ sec⁻¹, A₂ = 10¹³ sec⁻¹, E₀ = 9 kcal/mole,
E₁ = 6 kcal/mole, E₂ = 18 kcal/mole. At T₀ = 350 K, k₀/k₁ = 0.014,
k₂/k₁ = 0.035, and (k₀k₂/k₁)⁻¹ = 1.1 sec. At T₀ = 400 K,
k₀/k₁ = 0.024, k₂/k₁ = 0.32, and (k₀k₂/k₁)⁻¹ = 0.03 sec. At
T₀ = 450 K, k₀/k₁ = 0.036, k₂/k₁ = 1.6, and (k₀k₂/k₁)⁻¹ = 0.0016 sec.

Fig. 2. Plots of -log r₀ vs. -log(θ* + ½θ) calculated from Eq.(2) with the
same rate parameters as in Fig. 1. Slopes of curves represent
effective orders of desorption.

Fig. 3. Isothermal desorption kinetics for H₂ on Ni predicted from Eq.(2):
plots of -logθ vs. t. Initial conditions: θ* = 0 and θ = 0.7.
Same rate parameters as in Fig. 1 except E₂ = 20 kcal/mole. At
T₀ = 350 K, k₀/k₁ = 0.014, k₂/k₁ = 0.002, and (k₀k₂/k₁)⁻¹ = 20 sec.
At T₀ = 400 K, k₀/k₁ = 0.024, k₂/k₁ = 0.025, and (k₀k₂/k₁)⁻¹ = 0.3 sec.
At T₀ = 450 K, k₀/k₁ = 0.036, k₂/k₁ = 0.18 and (k₀k₂/k₁)⁻¹ = 0.012 sec.

Fig. 4. Plots of -log r₀ vs. -log(θ* + ½θ) calculated from Eq.(2) with the
same rate parameters as in Fig. 3. Slopes of curves represent
effective orders of desorption.
Fig. 1.

T_s = 350°K, 400, 450

\(-\log \theta\)

t\left(\frac{k_d k_2}{k_1}\right)^{-1}\)
Fig. 2. XBL 754-6225

-\log r_d

-\log (\theta^* + \frac{1}{2} \theta)

effective order

T_s = 350^\circ K

400

450

2.7

2.0

1.4

XBL 754-6225
\[ T_s = 350^\circ K \]

Fig. 3. XBL 754-6226
Fig. 4. XBL754-6227
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