Material properties controlling adsorption kinetics and temperature programmed desorption spectra

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Abstract

When statistical rate theory (SRT) is applied to obtain the expression for the gas adsorption rate on a solid surface, it is predicted that the unidirectional adsorption and desorption rates depend on the chemical potentials in the gas and the adsorbed phase. This prediction is in contrast to that obtained from transition state theory which claims the unidirectional desorption rate only depends on the chemical potential in the adsorbed phase, and in order for the theory to be consistent, imposes a condition on the chemical potential in the low pressure limit. If the coverage dependence of the chemical potential function is explicitly known this consistency condition can be evaluated. A previously proposed chemical potential expression that is explicitly expressed in terms of the coverage dependent material properties is reviewed. These material properties can be evaluated from the measured equilibrium adsorption isotherms and the electron-energy-loss spectrum of a well-defined gas–solid system. When this chemical potential is used with SRT, the coverage during beam-dosing adsorption kinetics can be calculated and pressure spectra during temperature programmed desorption (TPD) can be predicted and compared with experiments reported by others. Close agreement is found in both cases, giving substantial support to the expression for the chemical potential. When this same chemical potential function is used to examine transition state theory of adsorption kinetics and the expressions for the “coverage dependent reaction rate constants” inconsistencies are found.

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1. Introduction

When adsorption at a gas–solid interface occurs, there is molecular transport from one macroscopic phase to another. Using the statistical rate theory (SRT) approach [1–7], one may obtain an expression for the net molecular flux between the phases that is in terms of the molecular and material properties and the thermodynamic (local equilibrium) properties in each phase. SRT has been examined in a number of circumstances [1–31]. It has proven possible to express the phase change rate of water in terms of its molecular and material properties and the interfacial temperature and pressure existing in each phase. When the experimental results for evaporation and for condensation [4–7] were compared with the predictions from SRT, excellent agreement was found. Since there are no fitting constants in the calculations,
SRT receives important experimental support from these cases.

For gas adsorption the material properties that are predicted to control the rate are those appearing in the expression for the chemical potential. An expression for this function, denoted as $\mu^G$, has been previously proposed and the material properties for the CO–Ni(1 1 1) system determined from the measured equilibrium adsorption isotherms and the electron-energy-loss spectrum [8]. This expression for the chemical potential has been used with SRT to examine beam-dosing adsorption, isothermal desorption kinetics [9], and TPD kinetics [10]. In the case of TPD kinetics, several spectra are predicted without the aid of any fitting constants. A comparison of the predictions with the measurements shows good agreement. Previous analyses of isothermal adsorption kinetic data had used the sticking coefficient approach and found it necessary to propose a precursor state. An earlier analysis of the TPD spectra had used a coverage-dependent model of the activation energy. The SRT approach does not indicate the need for either a precursor state or the assumption of a coverage-dependent function to obtain agreement between the measurements and the predictions.

We emphasize that the SRT calculations are based on the chemical potential expression and the material properties that were determined from the equilibrium adsorption isotherms. Thus, the expression for that function has significant experimental support. We use it to examine one of the assumptions in transition state theory. We find that the expression for the "coverage dependent rate constants" of that theory are not consistent with the expression for $\mu^G$.

2. Kinetics of gas adsorption of well-defined solid surfaces

Consider a single-crystal solid surface that is exposed to a gas phase of diatomic molecules. Suppose there are $M$ adsorption sites on the solid surface per unit area, $M_0$ substrate atoms per unit area and that the total surface area is $A$. We will approximate the (nonvolatile, nonabsorbing) solid substrate as a thermal reservoir, and suppose the gas, the surface and the solid substrate form an isolated system. If it is assumed that (i) the rate of transition between quantum states is the same for all states available to the isolated system; (ii) the Boltzmann definition of entropy is valid; and (iii) within each phase a state of local equilibrium exists, but disequilibrium exists between the phases, then from the transition probability concept of quantum mechanics, the instantaneous unidirectional adsorption flux may be written [2–7]

$$\tau_{G\sigma} = \frac{A_0|V_{ve}|^2\xi_{AE}}{\hbar} \left( \exp \left[ \frac{\Delta s_{G\sigma}}{k} \right] \right)$$

(1)

where $|V_{ve}|^2$ is the matrix element corresponding to a transition between quantum mechanical (QM) states of different molecular distributions, $\xi_{AE}$ the QM state density which has been assumed uniform over the range of quantum states that are within the energy uncertainty of the isolated system, and $A_0$ is the value of the integral:

$$A_0 = \int_{-\pi/2}^{\pi/2} \frac{\sin(y)}{y} dy$$

Note that according to the assumptions made, $|V_{ve}|^2\xi_{AE}$ is a constant for the isolated system that we consider. The term $\Delta s_{G\sigma}$ is the change in entropy that results from one molecule transferring from the gas to the solid surface. For an isothermal system, it may be expressed [4,7]:

$$\Delta s_{G\sigma} = \left( \frac{\mu^G}{T^G} - \frac{\mu^\sigma}{T^\sigma} \right)$$

(2)

where $\mu^G$, $\mu^\sigma$, $T$ are the chemical potentials in the gas phase at the surface and in the adsorbed phase and $T$ is the temperature. A property of the gas or adsorbed phase is denoted by superscript G or $\sigma$. Similarly, the unidirectional desorption flux may be expressed

$$\tau_{\sigma G} = \frac{A_0|V_{ve}|^2\xi_{AE}}{\hbar} \left( \exp \left[ -\frac{\Delta s_{G\sigma}}{k} \right] \right)$$

(3)

Since $|V_{ve}|^2\xi_{AE}$ has been approximated as constant for all quantum states within the energy uncertainty of the isolated system, the net molecular flux from the liquid to the vapor phase, $j_{G\sigma}$ is the difference between $\tau_{G\sigma}$ and $\tau_{\sigma G}$:

$$J_{G\sigma} = 2 \frac{A_0|V_{ve}|^2\xi_{AE}}{\hbar} \sinh \left[ \frac{\Delta s_{G\sigma}}{k} \right]$$

(4)

Note that a molecular flux at the interface in both directions is predicted, but the direction of the net molecular flux is determined by the sign of $\Delta s_{G\sigma}$. If the
entropy increases when a molecule transfers from the
gas to the solid surface (i.e. $\Delta S_{G,G}$ is positive) the
prediction is that the net flux would be from the gas
phase to the solid surface, and if $\Delta S_{G,G}$ is negative the
net molecular flux is from the surface to the gas phase
[7].

Under equilibrium conditions in the isolated system,$\Delta S_{G,G}$ is equal to zero. Note from Eqs. (3) and (4) that in this limit, the unidirectional molecular trans-
port rates are equal

$$
\tau_{G,G} = \tau_{eG} = \frac{A_0[V_m]^2 \zeta}{h}
$$

Thus since in the isolated system $(A_0[V_m]^2 \zeta)/h$ has
been assumed constant, we interpret it as the equili-
brum exchange rate between the phases.

To determine the expression for the equilibrium exchange rate, we shall suppose that a molecular collision with a vacant site results in the adsorption
of a molecule. If the number of molecules adsorbed
under equilibrium conditions is $N_e^0$, and the equilib-
rium pressure is $P_e$, then the equilibrium adsorption
flux would be

$$
\frac{A_0[V_m]^2 \zeta}{h} = \frac{P_e(AM - N_e^0)}{AM \sqrt{2\pi mkT_e}}
$$

where $m$ is the molecular mass and $T_e$ is the equili-
brum temperature. There would be an equal flux in the
opposite direction. Eqs. (2), (4) and (6) constitute a
closed system of equations obtained from the SRT
procedure for the net adsorption flux when the process
takes place in an isolated system.

2.1. Material properties controlling gas adsorption kinetics

To make use of the SRT expression for the adsorp-
tion rate, an expression for the chemical potential must
be used [8,18]. If the equilibrium coverage, $\theta_e$ is
defined as $(N_e^0/AM_0)$, and $\theta_M$ as the ratio $Mf/M_0$, then the chemical potential may be written

$$
\mu^e = kT_e \ln \left[ \frac{\theta_e}{(\theta_M - \theta_e)q} \right]
$$

where the partition function for the adsorbed diatomic
molecule is denoted as $q$. We allow the zero-point
energy of an adsorbed molecule to depend on the

number of molecules in the adsorbed phase. Thus, the
QM energy levels are of the form

$$
e_{ijklm} = E_{0j}^0 + (i + \frac{1}{2})\hbar \omega_1 + (j + \frac{1}{2})\hbar \omega_2 + \cdots
$$

where $\omega_i$ are vibrational frequencies for the adsorbed
molecule. Suppose that certain of the frequencies (say
$l < 6$) have been measured spectroscopically. Then we
define the function $\psi$

$$
\psi = \prod_{j=1}^{l} \frac{\exp(\hbar \omega_j/2kT)}{\exp(\hbar \omega_j/kT) - 1}
$$

and write the molecular partition function in the form

$$
q = \psi \exp \left( \frac{b(T) - \beta(0)}{kT} \right)
$$

Since $E_{0j}^0$ depends on coverage, $q$ depends on both $T_e$
and the coverage; however, it has been shown that the
coverage and the temperature dependence of $q(T_e, \theta_e)$
may be separated [8]:

$$
\beta(0) = c_0 + c_1 \theta + c_2 \theta^2 + c_3 \theta^3
$$

$$
b(T) = b_0 + b_1 T + b_2 T^2 + b_3 T^3
$$

We note that the expression for the chemical potential is
of the same form as the familiar Langmuir expression,
but the expression given by Eqs. (7)–(9) is more
general, because it allows the adsorbate–adsorbate and
the adsorbate–substrate interactions to be taken into
account. These enter through the energy $E_{0j}^0(\theta)$.

The chemical potential of a diatomic molecule in the
gas phase is well known and may be expressed

$$
\mu^G = kT_e \ln(P_e \phi)
$$

where $\phi$ is a known function of temperature $T_e$ and
molecular properties [32].

Under equilibrium conditions, the chemical poten-
tial in the gas phase must be equal to that of the
adsorbed phase. After equating these expressions for
the chemical potentials and solving for $P_e$, one finds

$$
P_e = \frac{N_e^0}{(AM - N_e^0)q\phi}
$$

This is the expression for the equilibrium adsorption
isotherm. Note from Eq. (9) that $q$ depends on cov-
erage as a result of the adsorbate–adsorbate and ad-
orbate–substrate interactions. The pressure in the gas
phase may also be written in terms of the total number of molecules in the isolated system \((N^G + N^o)\) and the number adsorbed under equilibrium conditions. After making use of Eq. (13) and the ideal gas equation of state:

\[
\frac{N^o}{(AM - N^o)q\phi} = \frac{kT_e}{V^G} (N^G + N^o - N^o)
\]

To define the isolated system, the volume of the gas phase, \(V^G\), \(T_e\), \(A\), and \(N^G + N^o\) would be specified. Thus, once the material properties appearing in \(q\) and \(\phi\) have been determined, Eq. (14) may be solved (numerically) to determine the value \(N^o\), and once its value has been determined, it may be used in Eq. (13) to determine \(P_e\). Then the value of the equilibrium exchange rate may be determined from Eq. (6).

If the adsorption process may be approximated as isothermal, the expression for the chemical potential may be used with Eqs. (2) and (4) to obtain the expression for the net adsorption rate in terms of the material and molecular properties of the adsorbed phase.

### 2.2. Determination of the properties of CO adsorbed on Ni(1 1 1)

For a “well-defined” gas–solid system, it should be possible for the system to be created in different laboratories and for the systems to have the same material properties. We have previously shown that CO–Ni(1 1 1) satisfies this condition [8].

The values of \(\omega_1\), \(\omega_2\) were measured by Erley et al. [33], and equilibrium adsorption isotherms were measured by both Christmann et al. [34] and by Gijzeman et al. [35]. The gas phase properties of CO appearing in \(\phi\) are well known [32]. The measured values of \(\omega_1\), \(\omega_2\) and the equilibrium adsorption isotherms are sufficient to permit the determination of \(c_j\), \(b_j\). The values obtained are given in Table 1. Although their values were determined by fitting the measured equilibrium isotherms, they may be used to determine the coverage dependence of the partition function, \(q(T, \theta)\). We then view the partition function as a material property. This view has been examined in three different ways.

Firstly, \(q(T, \theta)\) was used to predict the coverage dependence of the heat of adsorption of CO adsorbing on Ni(1 1 1), and the predictions were compared with the measurements reported by Stuckless et al. [36].

There were no fitting constants in the predictions of the coverage dependence of the adsorption heat and there was no measured disagreement between the predictions and the measurements over a range of coverage.

### 2.3. Beam-dosing adsorption kinetics

Secondly, \(q(T, \theta)\) was used in the chemical potential function to obtain the adsorption rate expression, and this expression was used to calculate the coverage as a function of time. For isothermal kinetics, one finds from Eqs. (2), (4), (6) and (7)

\[
\frac{dN^o}{dt} = \frac{P_e(AM - N^o)}{M\sqrt{2(\pi)\pi kT_e}} \left[ \frac{N^o P\phi}{(AM - N^o)q(T, \theta)} - \frac{(AM - N^o)q(T, \theta)}{N^o P\phi} \right]
\]

This is the expression for the adsorption rate in an isolated system. To apply this expression to an open system, we suppose that if at one instant \(N^o\), \(T\), \(P\), and the material properties are the same in an open and in an isolated system, then at that instant the adsorption rate would be the same. The future in the two systems could be very different. The isolated system would evolve to equilibrium, but the open system would not necessarily. Also, we suppose that knowledge of the conditions existing in the open system at one instant would be sufficient to determine the conditions in an isolated system once it had evolved to the final equilibrium state.

### Table 1

Properties of CO adsorbed on Ni(1 1 1) [8] for 296 K ≤ \(T\) ≤ 508 K, 10⁻¹³ ≤ \(P\)/Torr ≤ 10⁻³

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>(M_o) (at./m²)</td>
<td>186 × 10¹⁹</td>
<td>Geometry</td>
</tr>
<tr>
<td>(M) (sites/m²)</td>
<td>0.57M₀</td>
<td>[37]</td>
</tr>
<tr>
<td>(\omega_1) (rad/2π)</td>
<td>1.23 × 10¹³</td>
<td>[37]</td>
</tr>
<tr>
<td>(\omega_2) (rad/2π)</td>
<td>5.57 × 10¹³</td>
<td>[37]</td>
</tr>
<tr>
<td>(b_0 - c_0) (J/molecule)</td>
<td>1.4921 × 10⁻¹⁸</td>
<td>[8]</td>
</tr>
<tr>
<td>(b_1) (J/molecule K)</td>
<td>1.3627 × 10⁻²¹</td>
<td>[8]</td>
</tr>
<tr>
<td>(b_2) (J/molecule K²)</td>
<td>-2.5408 × 10⁻²⁴</td>
<td>[8]</td>
</tr>
<tr>
<td>(b_3) (J/molecule K³)</td>
<td>1.7016 × 10⁻²⁷</td>
<td>[8]</td>
</tr>
<tr>
<td>(c_1) (J/molecule)</td>
<td>5.6821 × 10⁻²⁰</td>
<td>[8]</td>
</tr>
<tr>
<td>(c_2) (J/molecule)</td>
<td>-2.2721 × 10⁻¹⁹</td>
<td>[8]</td>
</tr>
<tr>
<td>(c_3) (J/molecule)</td>
<td>4.8990 × 10⁻¹⁹</td>
<td>[8]</td>
</tr>
</tbody>
</table>
In the analysis of each beam-dosing experiment, two fitting constants had to be introduced because not all of the apparatus constants were specified. For example, in the case of Froitzheim and Köhler [37], and Surnev et al. [38], two constants were introduced. One related to the size of the system $AM_d k T / V^G$ and one related to the pumping speed. Using one value of each constant at a particular temperature gave excellent agreement between the calculated coverage as a function of time and the measurements [9]. We note that in [37,38], a coverage dependent sticking coefficient and precursor state were used to analyze their kinetic data. The SRT analysis does not indicate the need to introduce any ad-hoc, coverage dependent functions in order to obtain good agreement between the calculations and the measurements.

2.4. Thermal desorption of CO from Ni(1 1 1)

Thirdly, the TPD spectra for the CO–Ni(1 1 1) system were used [10]. Since the values of the apparatus constants had to be assigned for each of the beam-dosing experiments, SRT could only be said to be consistent with the measurements. However, in the TPD experiments of Miller et al. [39], an initial coverage was established; afterwards the substrate was heated at a constant rate and the pressure measured as a function of time. The initial coverage was then set at a different value, and the heating process repeated. Thus, in these experiments, the apparatus constants would be unchanged. Also, in the experiments reported by Miller et al. [39], the area of the Ni(1 1 1) crystal used during the thermal desorption of CO was reported, as was the base pressure of the pumping system, but neither the pumping rate, $R^P$ nor the volume, $V^G$ were reported.

In the SRT analysis only one spectrum was used to determine the values of $R^P$ and $V^G$. Once the values of the apparatus constants $R^P$ and $V^G$ had been determined, the information provided by Miller et al. was used with Eq. (15) to “predict” the other eight spectra; thus these spectra were critically compared with the spectra measured. The results indicate close agreement throughout the range of temperatures and initial coverages [10].

The analysis of the TPD spectra using SRT stands in strong contrast to that performed using the Polanyi–Wigner equation [40]. When the latter was used, it was necessary to propose a model for the coverage dependent activation energy, $E_d$ [39]. The SRT procedure appears to give explicitly the coverage dependence of the TPD kinetic equations. The coverage dependence obtained from the SRT procedure comes from the form of the equations and the expression for the chemical potential. The latter depends on coverage through the material properties (Table 1).

3. Transition state approach to adsorption kinetics

Since an expression for the chemical potential has been developed and the explicit coverage dependence of this function for CO–Ni(1 1 1) has been obtained, the chemical potential function may be used to examine one of the tenets of transition state theory. A summary of the transition state approach to adsorption kinetics was presented recently [41]. In that approach, it is claimed that the net rate of adsorption is “phenomenologically” described by

$$\frac{1}{AM} \frac{d}{dt} N^\sigma = k_d - k_d \left( \frac{N^\sigma}{AM} \right)$$

(16)

but $k_d$ and $k_a$ are defined as “coverage dependent rate constants”. If $k_d$ and $k_a$ depend on coverage, the basis for Eq. (16) is not clear. The coverage dependent rate constants $k_d$ and $k_a$, are then written in terms of other rate constants, $k_0^d, k_0^a$, that are supposed to be valid in the “low coverage limit”

$$k_d = k_0^d \left( 1 - N^\sigma / AM \right) \sum_i P_{0,i} \exp \left( -\frac{e_i^d}{kT} \right)$$

(17)

$$k_a = k_0^a \left( 1 - N^\sigma / AM \right) \exp \left( \frac{\mu_a}{kT} \right) \sum_i P_{0,i} \exp \left( -\frac{e_i^d}{kT} \right)$$

(18)

where $P_{0,i}$ is the probability that a vacant site has the environment denoted by the index $i$, and $e_i^d$ is the lateral adsorbate–adsorbate interactions in the ‘activated’ state [41]. The expression for $\mu_a$, the chemical potential of the adsorbed molecules is not given, but it has been correctly pointed out that if Eq. (16) is to be valid, then at adsorption equilibrium

$$k_a P = k_d \left( \frac{N^\sigma}{AM} \right)$$

(19)
Eq. (19) is used to argue that transition state theory satisfies the principle of detailed balance (i.e. at adsorption equilibrium $\mu_a = \mu_g$). From the expressions for $k_a$ and $k_d$, Eq. (19) gives

$$P_k^0 = k_d^0 \exp \left( \frac{\mu_a}{kT} \right)$$

(20)

In transition state theory, it is recognized that in order for Eqs. (19) and (20) to be satisfied in the low coverage limit, the form of the chemical potential must be such that

$$\lim_{\theta \to 0} \mu_a = kT \ln \left( \frac{N^\theta}{AM} \right)$$

(21)

We note that Eq. (21) is a very severe restriction on the expression for the chemical potential. For example, the expression for the chemical potential given in Eq. (7) would not satisfy this condition. It reduces to

$$\lim_{N^\theta \to 0} \mu_a = kT \ln \left( \psi \exp \left[ \left( -c_0 + \sum_{j=0}^3 b_j T^j \right) / kT \right] \right)$$

(22)

Thus, in order for the condition stipulated in Eq. (21) to be met

$$\psi \exp \left[ \left( -c_0 + \sum_{j=0}^3 b_j T^j \right) / kT \right] \to 1$$

The values of $(b_0 - c_0), b_j (j = 1, 2, 3)$, for the CO–Ni(1 1 1) system are listed in Table 1. The calculated values of this function are shown in Fig. 1. As may be seen in that figure, there is no temperature at which this condition is met.

Ideally, transition state theory would be applied to predict the coverage as a function of time, and the predictions compared with the measurements. But to have an expression for the coverage dependence of $k_d$ an expression for $\mu_a$ must be available (see Eq. (18)). The expression for a chemical potential that is in agreement with the measured isotherms ($\mu^\theta$, Eq. (7)) does not satisfy Eq. (21). Thus, until an expression for the chemical potential is found that is both in agreement with the measurements and satisfies Eq. (21), it does not seem that transition state theory can be logically applied. It is not clear that an expression for the chemical potential that satisfies both of these conditions can be found.

4. Summary and conclusion

An expression for the chemical potential has been developed for the CO–Ni(1 1 1) system that gives an explicit expression for the coverage dependence of the chemical potential. When that expression was examined by using it to predict the coverage dependence of the heat of adsorption [8], it gave results that supported the validity of the expression. The expression for the chemical potential has also been used with SRT to calculate the coverage as a function of time during beam-dosing adsorption kinetics [9]. The results were compared with measurements made in three laboratories. However, in each case there were apparatus constants that had to be assigned. The agreements between the calculations and the measurements in each case were very close. This indicates that the coverage dependence of the rate expression was given explicitly. This contention was examined further by applying the SRT expression for adsorption kinetics to examine measurements of the TPD spectra of the CO–Ni(1 1 1) system [10,39]. This has the advantage of repeating the measurement procedure with only the initial coverage changed, and permits the apparatus constants to be determined from one TPD spectrum. The other spectra could then be predicted and compared critically with measurements. The agreement strongly suggests that the explicit coverage and temperature dependence were obtained when the expression for the chemical potential given by Eqs. (7) and (9) was used in the SRT approach to obtain Eq. (15).

The availability of this expression for the chemical potential allows certain of the assumptions of transition state theory to be examined. It is shown that the expressions for the “coverage dependent reaction rate constants” do not satisfy the condition imposed by detailed balance in the low coverage limit.

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