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Statistical rate theory description of beam-dosing adsorption kinetics

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Absolute rate theory and the sticking probability approach have been previously examined as possible means of predicting the rate of adsorption. However, when applied to examine adsorption kinetics, they have been found not to contain the coverage and pressure dependence required for several important systems including CO–Ni(111). Statistical rate theory (SRT) is being developed with the objective of predicting the rate of molecular (or atomic) transport across the interface between macroscopic phases in terms of experimentally controllable variables and material properties of the two phases. Previous applications of SRT to adsorption have been limited to systems for which both the gas phase pressure and the temperature could be assumed to be constant. Herein, the SRT approach is extended to systems in which the number of molecules in the system (and hence the gas phase pressure) is not constant. To examine this extension, SRT is used to formulate the equations governing the rate of adsorption in isothermal, beam-dosing experiments. These equations are then combined with the values of certain material properties that have previously been established and a hypothesis that the value of the equilibrium adsorption cross section is given by the area of an adsorption site. The kinetic data for CO adsorbing on Ni(111) data reported by three different laboratories are then examined. For each set of experimental data, constants had to be inferred that were related to the experimental apparatus used and as such they were not expected to have any coverage or pressure dependence. The good agreement found between the predicted and measured adsorption kinetics indicates that all of the necessary coverage and pressure dependence was explicitly predicted from the SRT approach. © 1997 American Institute of Physics. [S0021-9606(97)01112-4]

I. INTRODUCTION

A theory that could be used to predict the rate of molecular (or atomic) transport across the interface between macroscopic phases in terms of experimentally controllable variables and material properties of the phases would have a number of important applications. In the case of adsorption, this would mean that the rate would be written in terms of the molecular properties of the gas and properties of the gas–solid interface that could be established at equilibrium. By definition, the material properties would be independent of the nonequilibrium variable(s). This would eliminate the absolute rate theory approach, since it has been shown not to predict the coverage dependence found in the adsorption rate.¹ This would also eliminate from the theoretical approach such concepts as the “sticking probability” or “sticking coefficient,”^{2,3} since for a number of adsorption systems, the sticking coefficient has been found to depend on the instantaneous coverage.^{2,4}

Statistical rate theory is being developed with the objective of filling this need.^{5–16} In this approach, a thermodynamically isolated system is considered and the transition probability concept is used to construct the expression for the rate of molecular transport. If this approach is successful, the material properties of a particular pair of macroscopic phases

could be tabulated and used in the governing equations for predicting the rate of molecular transport across the interface in any circumstance. The SRT approach shows promise of being successful, but it has not been fully tested previously. Since it was first proposed in an elementary form in 1977,⁵ it has been placed on firmer theoretical grounds^{6,7} and applied to examine the rates of gas absorption at a liquid–gas interface,^{8–10} hydrogen absorption by metals,¹¹ electron exchange between ionic isotopes in solution,^{6,12} permeation of ionic channels in biological membranes,¹³ and both nondissociative^{12,14,15} and dissociative^{14,16} adsorption kinetics in isothermal, isobaric systems. In each case, the SRT approach led to improvements in the theoretical description of the rate process. However, application of the theoretical approach to adsorption kinetics has been limited to systems for which both the gas phase pressure and the temperature could be assumed to be constant during the adsorption process.^{12,14–16} These assumptions unnecessarily limit the theory, and since important kinetic data are available for systems in which there is a variation in pressure during the adsorption process, the SRT approach is extended herein to systems that are not of constant pressure.

To examine this extension, we consider isothermal, beam-dosing experiments. SRT is used to formulate the expression for the rate of adsorption in terms of a set of material properties. All of these, except one, can be determined from equilibrium measurements. The exception is the “adsorption cross section” that has been previously defined.^{12,14,15} In an isolated system, SRT leads to the pre-

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diction that this cross section is constant throughout the adsorption process, and in previous studies of systems that could be approximated as isolated, a constant value of this cross section has been found to be in agreement with the observations. The question arises of whether this cross section is constant for a well defined interface, such as CO–Ni(111), or does it depend on the temperature or, for the nonisolated systems considered herein, the time-dependent pressure. We examine the possibility that this cross section is simply the geometrical area of an adsorption site. A similar hypothesis has been used with success in describing gas absorption by a liquid.^{5,9,10}

The CO–Ni(111) system is one in which adsorption occurs nondissociatively (at moderate temperatures) and in which there is predominately one type of bonding (bridge). The molecular properties of CO in a gas phase are already known, and with the hypothesis regarding the adsorption cross section, the additional material properties controlling the rate of CO adsorption on Ni(111) have been determined entirely from the equilibrium measurements. Thus, their determination is independent of any kinetic experiment, and this hypothesis can be evaluated by determining if SRT can be used to predict the measured rate of CO adsorption on Ni(111) in beam-dosing experiments.

II. ADSORPTION RATE IN AN ISOLATED SYSTEM

Consider an isolated system consisting of a diatomic gas phase that is adsorbing under sub-monolayer conditions on a well defined single crystal surface with one type of localized bond. If the solid is large enough that the adsorption takes place isothermally, SRT may be used to formulate the expression for the instantaneous rate of adsorption, J . In this case, one finds^{7,12,14,15}

$$J = K_e \left[\exp\left(\frac{\mu^g - \mu^\sigma}{kT}\right) - \exp\left(\frac{\mu^\sigma - \mu^g}{kT}\right) \right], \quad (1)$$

where K_e is the exchange rate between the gas phase and the solid surface once the isolated system has reached the condition of thermodynamic equilibrium, k is Boltzmann's constant, T is the temperature and μ^g and μ^σ are the chemical potentials of the molecules in the gas phase and in the adsorbed phase respectively.

Using the Born–Oppenheimer approximation, the chemical potential per molecule of an ideal, asymmetric, diatomic gas can be found from the partition function¹⁷ to be

$$\mu^g = kT \ln(P\phi), \quad (2)$$

where P is the pressure in the gas phase and ϕ is given by

$$\phi = \frac{\left[1 - \exp\left(\frac{\hbar\omega_g}{kT}\right)\right] \exp\left(-\frac{D_0}{kT}\right) \hbar^5 (2\pi)^{3/2}}{(kT)^{7/2} 2m_1 m_2 r_e^2 (m_1 + m_2)^{1/2}}, \quad (3)$$

where ω_g is the characteristic vibration frequency of a gas molecule, D_0 is its dissociation energy, r_e is the separation distance of the two component atoms and m_1 and m_2 are their atomic masses. The values of the gas phase properties for CO are given in Table I.

TABLE I. Gas phase properties of carbon monoxide (Ref. 17).

ω_g (rad)/ 2π	r_e (nm)	D_0 (J/molecule)
6.394×10^{13}	0.1128	1.464×10^{-18}

An expression for the chemical potential of the adsorbed molecules has been found by modeling the adsorbed molecules as quantum mechanical, double harmonic oscillators with a coverage-dependent potential energy.^{18,19} If A is the area of the interphase, M is the number of adsorption sites per unit area and N^σ is the number of adsorbed molecules, then the chemical potential may be written

$$\mu^\sigma(T, N^\sigma) = kT \ln \left[\frac{N^\sigma}{(AM - N^\sigma) \psi \exp\left(\frac{b - \beta'}{kT}\right)} \right], \quad (4)$$

where

$$\psi(T) = \prod_{j=1}^2 \frac{\exp\left(\frac{\hbar\omega_j}{2kT}\right)}{\exp\left(\frac{\hbar\omega_j}{kT}\right) - 1}, \quad (5)$$

$$b(T) = b_0 + b_1 T + b_2 T^2 + b_3 T^3, \quad (6)$$

and

$$\beta'(\theta) = c_0 + c_1 \theta + c_2 \theta^2 + c_3 \theta^3. \quad (7)$$

Note that ω_1 and ω_2 are the two characteristic vibration frequencies of an adsorbed molecule that have been experimentally resolved.²⁰ The function b is related¹⁹ to the four unknown vibration frequencies and depends on temperature. The function β' is related¹⁹ to the potential energy of an adsorbed molecule and is a function of coverage. The coverage, θ is defined as

$$\theta = \frac{N^\sigma}{AM_0}, \quad (8)$$

where M_0 is the number of surface substrate atoms per unit area. The coefficients appearing in Eqs. (6) and (7) have been found¹⁹ from measured equilibrium adsorption isotherms for CO adsorbed on Ni(111) and are given in Table II along with other properties for CO–Ni(111).

To complete the expression for the adsorption rate, an expression for the equilibrium exchange rate, K_e must be given. We follow earlier studies and use^{14,15}

$$K_e = \nu A_{\text{eff}}, \quad (9)$$

where ν is the collision frequency which at equilibrium may be found from the Maxwell–Boltzmann distribution and A_{eff} is the effective area available for adsorption. Thus, K_e may be written

$$K_e = \frac{P_e}{\sqrt{2\pi m kT}} (AM - N_e^\sigma) \sigma_e, \quad (10)$$

TABLE II. Properties of carbon monoxide adsorbed on Ni(111).

Property	Value	Source
$M_0(\text{atoms/m}^2)$	1.86×10^{19}	geometry
$M(\text{sites/m}^2)$	$0.57M_0$	Refs. 22 and 19
$\omega_1(\text{rad})/2\pi$	1.23×10^{13}	EELS (Ref. 20)
$\omega_2(\text{rad})/2\pi$	5.57×10^{13}	EELS (Ref. 20)
$b_0 - c_0(\text{J/molecule})$	1.4921×10^{-18}	Ref. 19, obtained by fitting the measured data of Refs. 4 and 27 with the procedure presented in Ref. 12
$b_1(\text{J/molecule K})$	1.3627×10^{-21}	
$b_2(\text{J/molecule K}^2)$	-2.5408×10^{-24}	
$b_3(\text{J/molecule K}^3)$	1.7016×10^{-27}	
$c_1(\text{J/molecule})$	5.6821×10^{-20}	
$c_2(\text{J/molecule})$	-2.2721×10^{-19}	
$c_3(\text{J/molecule})$	4.8990×10^{-19}	

where σ_e is the equilibrium adsorption cross section and m is the mass of the diatomic molecule. The subscript e on a property indicates that the property is to be evaluated in the equilibrium circumstance. Previously, the equilibrium adsorption cross section was taken to be the cross sectional area of a site multiplied by a probability.^{12,14,15} We suppose it to be simply the geometrical area of an adsorption site

$$\sigma_e = \frac{1}{M}, \quad (11)$$

and then evaluate this supposition by comparing the predictions that follow with three independent sets of measurements.

Substituting the expression for the equilibrium exchange rate, Eq. (10), and the expressions for the chemical potentials, Eqs. (2) and (4), into Eq. (1) the net rate of change of surface coverage may now be written

$$\frac{d\theta}{dt} = \frac{P_e(\theta_M - \theta_e)\sigma_e}{\sqrt{2\pi mkT}} \left[\frac{(\theta_M - \theta)P\phi\psi \exp\left(\frac{b - \beta'}{kT}\right)}{\theta} - \frac{\theta}{(\theta_M - \theta)P\phi\psi \exp\left(\frac{b - \beta'}{kT}\right)} \right], \quad (12)$$

where

$$\theta_M \equiv \frac{M}{M_0}. \quad (13)$$

The application of Eq. (12) to predict the adsorption kinetics in an isolated, isothermal system that may be approximated as having constant mass (or that may be approximated as isobaric) is straight forward.^{12,14,15} Once the constraints (either total energy, total number of molecules of each species, and total volume; or temperature, total number of molecules of each species, and pressure) of the isolated system have been specified, the equilibrium pressure and coverage can be found from the equilibrium isotherm for the system.

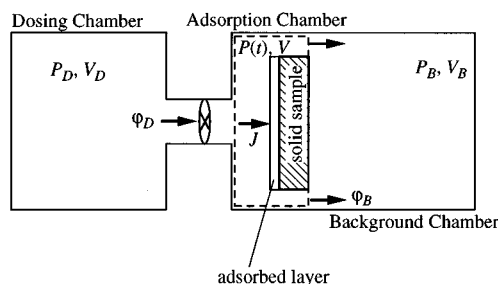


FIG. 1. Schematic diagram of the model system for beam-dosing experiments. The statistical rate theory equation is applied to the isolated system shown within the dotted line and consisting of the solid, adsorbed, and gas phases. The diagram is not to scale.

These quantities may then be used in Eq. (12) together with the known material properties. However, for beam-dosing adsorption, the number of molecules in the system is not constant and hence such a system can not be treated as isolated.

III. ISOTHERMAL, BEAM-DOSING ADSORPTION KINETICS

A common arrangement for low pressure kinetic adsorption experiments is an isothermal, beam-dosing experiment in which a solid sample is placed very close to the beam nozzle and within a large vacuum chamber. When the beam is on, a relatively small amount of gas is needed to cause a pressure rise in the small volume between the sample and the nozzle. The large vacuum chamber remains at the low background pressure. This arrangement results in low gas loading on the system so that the adsorption system can be brought quickly back down to the background pressure and multiple experiments can be performed efficiently.

A beam-dosing arrangement is shown schematically in Fig. 1. Properties of the dosing chamber are denoted with the subscript D . Properties of the adsorption chamber are not subscripted. The subscript B identifies properties of the large vacuum chamber which is assumed to be maintained at a “background pressure,” P_B , by a pump and to behave as a constant pressure sink for gas molecules. It is assumed that the dosing chamber is maintained at a high pressure, P_D , by a dosing system and behaves as a constant pressure source of gas molecules.

At the start of an experiment, the valve between the dosing chamber and the adsorption chamber is opened and there is a flow rate, ϕ_D , of molecules from the dosing chamber into the adsorption chamber. As the pressure in the adsorption chamber rises, there is a pressure differential between the adsorption chamber and the background chamber causing a rate, ϕ_B , of molecular transport into the background chamber. In addition, when the pressure in the adsorption chamber rises, molecules will adsorb onto the surface at the rate J . The pressure in the adsorption chamber, P , will be a function of time, and will be determined by the relative magnitude of these three flow rates.

Coupled equations must be solved for the pressure and surface coverage in the adsorption chamber. The SRT equation for the surface coverage was derived for an isolated system. In order to use it here, the system will be “stepped” through a series of states. In each state, the adsorption chamber is considered to be isolated with a fixed volume, V . At the end of each step, molecules are added or removed from the adsorption chamber according to a second equation describing the interaction of the “isolated” adsorption chamber with its surroundings (which would be the dosing and background chambers).

The total number of gas molecules, N , in the volume V is divided between the gas phase (denoted by the superscript g) and the adsorbed phase (denoted by the superscript σ).

$$N = N^g + N^\sigma. \quad (14)$$

The change in the number of molecules in the gas phase will be determined by the three flow rates

$$\frac{dN^g}{dt} = \varphi_D - J - \varphi_B. \quad (15)$$

The rates φ_D and φ_B will be assumed to have a functional form that is consistent with the classical kinetic theory of gases in free molecular flow²¹

$$\varphi_D = \frac{C_D}{\sqrt{mkT}} (P_D - P) \quad (16)$$

and

$$\varphi_B = \frac{C_B}{\sqrt{mkT}} (P - P_B), \quad (17)$$

where C_D and C_B are constants related to the two apertures (and associated volumes) through which the flow occurs. If, for example, the “valve” connecting volumes V_D and V were simply a hole of area A , then C_D would be given by $A/(\sqrt{2\pi})$.

Combining Eqs. (15), (16), and (17) yields

$$\frac{dN^g}{dt} = \frac{C_D}{\sqrt{mkT}} (P_D - P) - J - \frac{C_B}{\sqrt{mkT}} (P - P_B). \quad (18)$$

Usually, it is not the pressure in the dosing system, P_D , that is given, but rather the pressure that occurs at the sample surface when the system is in steady state, P_{ss} . Evaluating Eq. (18), at steady state and rearranging the result, one finds

$$P_{ss} = \frac{C_D P_D + C_B P_B}{C_D + C_B}. \quad (19)$$

Equation (18) may then be written

$$\frac{dN^g}{dt} = \frac{C}{\sqrt{mkT}} (P_{ss} - P) - J, \quad (20)$$

where

$$C \equiv C_D + C_B. \quad (21)$$

Note that the pressures, P_D and P_B , have been removed and replaced by P_{ss} , and the two constants, C_D and C_B , have been replaced by a single constant, C .

Equation (20) can also be applied to desorption experiments performed in the system shown in Fig. 1 by noting that during the desorption experiments, the valve from the dosing system is closed so that $C_D = 0$. Using Eqs. (19) and (21), this implies

$$P_{ss|des} = P_B \quad (22)$$

and

$$C|_{des} = C_B. \quad (23)$$

Using the ideal gas equation and the definition of coverage in Eq. (8), one may write Eq. (20) in a pressure and coverage format

$$\frac{dP}{dt} = \frac{1}{\tau} (P_{ss} - P) - \alpha \frac{d\theta}{dt}, \quad (24)$$

where

$$\tau \equiv \frac{V}{C} \sqrt{\frac{m}{kT}} \quad (25)$$

and

$$\alpha \equiv \frac{AM_0 kT}{V}. \quad (26)$$

The constant τ has units of time and physically it represents the time constant of the net flow into the adsorption chamber. The constant α has units of pressure and physically the product $\alpha\theta$ is the pressure that the adsorbed molecules would have if they alone occupied the volume of the adsorption chamber, V . Thus, the number of adsorbed molecules is small compared to the number of molecules in the gas phase if $\alpha\theta/P \ll 1$.

Equation (24) is the final form of the differential equation for P that will be solved simultaneously with the SRT equation for coverage, Eq. (12). Statistical rate theory must now be applied to the subsystem shown in Fig. 1 within the dashed line which consists of the solid substrate, a gas phase, and an adsorbed phase. This subsystem is not isolated in that gas molecules are being added to the system from the dosing chamber and removed from the system into the background chamber. Thus, the equilibrium exchange rate, K_e , in Eq. (1) is not constant, as it is for an isolated system.

To take the variation of K_e into account, the number of gas molecules in the isolated system will be “stepped” in time. In other words, one considers the system to be isolated at a given instant in time with a fixed number of gas molecules, N , and then allowed to evolve for a short period of time, say until t_1 . The solid phase will be assumed to be large enough that the temperature in the isolated system does not change. The value of K_e during the time period will be the value that the equilibrium exchange rate would have if the system were isolated for an arbitrary long period of time and allowed to come to equilibrium. At the end of the time period, molecules are added or removed from the volume V

according to Eq. (24), and the isolated subsystem (with a new value of N) is again allowed to evolve for another short time period. As the time periods become infinitesimal, Eqs. (12) and (24), may be integrated to find both coverage and pressure as functions of time.

In order to find the equilibrium pressure and coverage at each time step, we will make use of the isotherm relation¹⁹

$$P_e(T, \theta_e) = \frac{\theta_e}{(\theta_M - \theta_e) \phi \psi \exp\left(\frac{b - \beta'}{kT}\right)}. \quad (27)$$

In addition, the ideal gas law also applies at equilibrium which may be written in terms of coverage

$$P_e = (\Theta - \theta_e) \alpha, \quad (28)$$

where Θ is the total number of molecules (in both the gas and adsorbed phases) present at a given time per number of adsorption sites

$$\Theta \equiv \frac{N}{AM_0}. \quad (29)$$

The two equations for the equilibrium pressure, Eqs. (27) and (28), may be equated to give an equation to be solved numerically for the equilibrium amount adsorbed, θ_e , as a function of Θ

$$\frac{\theta_e}{(\theta_M - \theta_e) \phi \psi \exp\left(\frac{b - \beta'(\theta_e)}{kT}\right)} = (\Theta - \theta_e) \alpha. \quad (30)$$

Once θ_e is known, P_e can be evaluated from Eq. (28). Since the problem is being formulated with pressure and coverage as the independent variables, the ideal gas equation is used to write Θ in terms of the instantaneous pressure

$$\Theta = \frac{P}{\alpha} + \theta. \quad (31)$$

The set of equations consisting of Eqs. (12), (24), (28), (30), and (31) form a complete set, and when combined with the initial pressure, $P(0)$, and the initial coverage, $\theta(0)$, may be solved simultaneously for the variables θ , P , P_e , θ_e , and Θ as functions of time. The procedure would be to solve Eq. (30) numerically for $\theta_e(\Theta)$ which may be represented as a numerical function. This solution is then substituted into Eq. (12) along with Eqs. (28) and (31). The differential equation obtained from Eq. (12) is then solved simultaneously with Eq. (24) to get $\theta(t)$ and $P(t)$. The full solution can lead to a variety of shapes for coverage and pressure as functions of time. There are two important limits to the full equations in which simplified equations may be solved.

A. Solution when the pressure change is volume dominated

First, consider the limit in which the adsorption has a negligible effect on both the instantaneous pressure and the

equilibrium pressure. From Eq. (24) one can see that the condition on the instantaneous pressure requires, for all t , that

$$\alpha \frac{d\theta}{dt} \ll \frac{1}{\tau} (P_{ss} - P). \quad (32)$$

The condition on the equilibrium pressure requires that if the isolated system were to come to equilibrium, the change in the number of adsorbed molecules multiplied by α be small compared to the gas phase pressure. Thus, for all t ,

$$|(\theta - \theta_e) \alpha| \ll P. \quad (33)$$

If the conditions in Eqs. (32) and (33) are both met, then one can consider the equations in the limit of

$$\alpha \Rightarrow 0. \quad (34)$$

When α approaches zero, Eq. (24) yields

$$\frac{dP}{dt} = \frac{1}{\tau} (P_{ss} - P), \quad (35)$$

which has the solution

$$P(t) = P_{ss} - (P_{ss} - P(0)) \exp\left(\frac{-t}{\tau}\right), \quad (36)$$

where the requirement that $P \Rightarrow P_{ss}$ as $t \Rightarrow \infty$ has been imposed. After combining Eqs. (28) and (31) and taking the limit indicated in Eq. (34), one finds

$$P_e = P. \quad (37)$$

Note that this implies that the equilibrium pressure is a function of time. When Eq. (28) is combined with Eqs. (30) and (37) substituted, one obtains

$$\frac{\theta_e}{(\theta_M - \theta_e) \phi \psi \exp\left(\frac{b - \beta'(\theta_e)}{kT}\right)} = P(t). \quad (38)$$

Thus, the SRT equation for the coverage, Eq. (12), becomes

$$\frac{d\theta}{dt} = \frac{P(\theta_M - \theta_e(P)) \sigma_e}{\sqrt{2\pi m k T}} \left[\frac{(\theta_M - \theta) P \phi \psi \exp\left(\frac{b - \beta'}{kT}\right)}{\theta} - \frac{\theta}{(\theta_M - \theta) P \phi \psi \exp\left(\frac{b - \beta'}{kT}\right)} \right]. \quad (39)$$

The solution procedure for this regime is as follows. The pressure P as a function of time is found from Eq. (36). The equilibrium coverage, θ_e , as a function of P (or equivalently time) is found numerically from Eq. (38). Finally, the coverage as a function of time is found numerically from Eq. (39). In this regime there is an exponential rise in pressure. The smaller the value of τ , the steeper the rise. In a coverage versus time plot, there exists a point of inflection and the initial slope is less than that for the isobaric solution (see Sec. III B below). These two features are characteristic of the solution in this regime.

B. Solution in the isobaric limit

If, in addition to the limit given in Eq. (34), the flow through the dosing valve is very fast compared to other processes, then τ can also be considered to approach zero.

When both α and τ approach zero, Eq. (35) yields

$$\frac{dP}{dt} = [P_{ss} - P(0_-)]\delta(t), \quad (40)$$

where δ is the Dirac delta-function. The solution to Eq. (40) is a step function from the initial value, $P(0_-)$, at time t equal zero to P_{ss} for $t > 0$. Thus for t greater than zero, one finds from Eq. (37) that

$$P_e = P_{ss}, \quad (41)$$

and for $t > 0$, Eq. (41) may be substituted into Eq. (38) to obtain

$$\frac{\theta_e}{(\theta_M - \theta_e)\phi\psi \exp\left(\frac{b - \beta'(\theta_e)}{kT}\right)} = P_{ss}. \quad (42)$$

Hence, the SRT equation for the coverage, Eq. (39), becomes

$$\begin{aligned} \frac{d\theta}{dt} = & \frac{P_{ss}(\theta_M - \theta_e(P_{ss}))\sigma_e}{\sqrt{2\pi mkT}} \\ & \times \left[\frac{(\theta_M - \theta)P_{ss}\phi\psi \exp\left(\frac{b - \beta'}{kT}\right)}{\theta} \right. \\ & \left. - \frac{\theta}{(\theta_M - \theta)P_{ss}\phi\psi \exp\left(\frac{b - \beta'}{kT}\right)} \right]. \quad (43) \end{aligned}$$

Equations (42) and (43) can be solved numerically to get coverage as a function of time. A large initial slope of the coverage versus time plot is characteristic of this regime. Equations (42) and (43) are the same as those obtained when the isobaric assumption is made from the outset and these were the equations that were used previously to predict kinetic adsorption data.^{12,14}

IV. EXAMINATION OF CO-Ni(111) MEASUREMENTS

The predictions in Sec. III will now be compared with data obtained from beam-dosing experiments that have been previously reported for CO adsorbed on Ni(111). All of the properties appearing in the SRT expression for the adsorption rate, Eq. (12), have been tabulated for CO-Ni(111) and are listed in Tables I and II.

Ideally, details of the experimental apparatus would be specified so that τ and α could be calculated from Eqs. (25) and (26) and a true prediction made with the equations developed herein. However, in the experimental literature being used to evaluate the theory, the information needed to calculate τ and α is not specified and thus, for the analysis

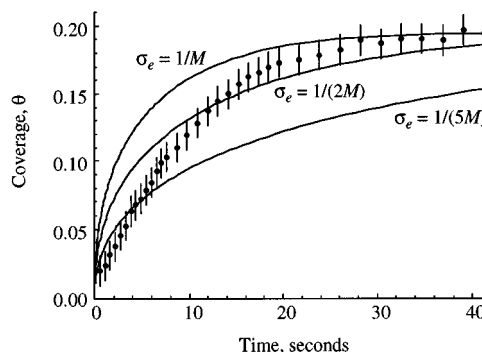


FIG. 2. Isobaric statistical rate theory predictions shown with the kinetic adsorption measurements of Froitzheim and Köhler. Even with various values for the equilibrium adsorption cross section, the isobaric equations are not in agreement with the measurements.

presented here, the apparatus constants τ and α will be selected as those for which the sum of the squared errors between the predictions and experimental data points is minimized.

A. Kinetic measurements for CO-Ni(111) reported by Froitzheim and Köhler

High resolution electron energy loss spectroscopy (HREELS) was used by Froitzheim and Köhler²² to measure an adsorption-desorption cycle at 408 K in a beam-dosing apparatus. They state that the beam was on for a period of 42 s and that the beam pressure was 10^{-8} Torr. The nominal²³ background pressure was 10^{-10} mbar.

Since the analytical expression for the equilibrium adsorption isotherms, Eq. (27), is now known,¹⁹ it allows us to obtain more accurate values for the pressures than the nominal values stated above. Thus, we may use as the value of P_{ss} during adsorption, $P_{ss|ads}$, the value of pressure that corresponds on the isotherm to the maximum coverage measured when the beam was on. Similarly, we may use as $P_{ss|des}$ the value of pressure corresponding on the isotherm to the minimum coverage measured when the beam was off. The values so obtained were, $P_{ss|ads} = 4.2 \times 10^{-8}$ Torr and $P_{ss|des} = 2.4 \times 10^{-10}$ mbar which agree with the nominal orders of magnitude given by Froitzheim and Köhler. The initial pressure in the adsorption case was assumed to be $P_{ss|des}$ and the initial pressure in the desorption case was taken to be $P_{ss|ads}$. In both cases it was assumed that before the start of the experiment the surface coverage had equilibrated with the pressure.

In earlier studies,^{12,14} the equilibrium adsorption cross section was used as a fitting parameter in order to have better agreement between experiment and the isobaric theory. However, there exist experimental data for which the shape of the coverage curve is in disagreement with the shape predicted by the isobaric equation, regardless of the value of the cross section used. The data obtained by Froitzheim and Köhler²² are of this type. In Fig. 2, their data are shown along with predictions using the isobaric equation, Eq. (43), with various values for the equilibrium adsorption cross sec-

tion. As can be seen in the figure, the shape predicted by Eq. (43) is not satisfactory no matter what value of σ_e is used. The desorption data could not be satisfactorily explained with the isobaric equations either.

These same data were analyzed using the full equations developed herein and the assumption that the adsorption cross section is simply given by Eq. (11). Using the previously tabulated properties of CO–Ni(111), the listed temperature and pressures and the full solution procedure, calculations were made for both the adsorption and the desorption portion of the data and values of the apparatus constants τ and α were inferred. The results are shown in Figs. 3 and 4.

For the adsorption data (Fig. 3), the inferred values were $\tau=4.5$ s and $\alpha=0$. (For $\alpha \leq 10^{-7}$ mbar the change in the sum of the squared errors is negligible.) The same time constant was obtained by neglecting α at the outset and using the solution procedure in Sec. III A. In either case, the predicted shape in Fig. 3 is in much better agreement with the data than that predicted by the isobaric equation and shown in Fig. 2.

For the desorption data (Fig. 4), the inferred values of the apparatus constants were $\alpha=2 \times 10^{-6}$ mbar and $\tau=0.29$ s. The agreement is equally good for this case. The question now arises as to whether or not it is physically reasonable to have different values of τ and α for the adsorption and desorption experiments.

Since V is defined by the assumptions in SRT rather than some portion of the apparatus, the value of V may not be the same for adsorption and desorption in the same system. During adsorption (when the dosing valve is open) V may contain some portion of the dosing chamber. This means that V would be larger for the adsorption case than for the desorption case which in turn would imply that α would be smaller for adsorption than for desorption which was what was found. For this same reason and the fact that $C|_{\text{ads}}$ is not equal to $C|_{\text{des}}$, the time constant, τ , would also be expected to have different values during adsorption and desorption.

B. Examination of the CO–Ni(111) measurements reported by Surnev, Xu, and Yates

Temperature programmed desorption spectroscopy was used by Surnev *et al.*²⁴ to measure adsorption kinetics occurring at a pressure of 1×10^{-8} mbar. The temperature during

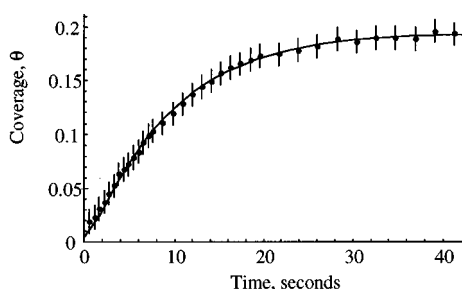


FIG. 3. Comparison of the statistical rate theory prediction with the kinetic adsorption measurements of Froitzheim and Köhler. The apparatus constants used for the prediction were $\tau=4.5$ s and $\alpha=0$.

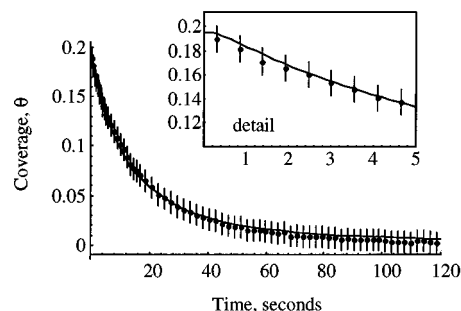


FIG. 4. Comparison of the statistical rate theory prediction with the kinetic desorption measurements of Froitzheim and Köhler. The apparatus constants used for the prediction were $\tau=0.29$ s and $\alpha=2 \times 10^{-6}$ mbar. The initial 5 s of data have been expanded in the inset labeled "detail."

the experiment was 288 K. At this low temperature, the nickel surface will be almost completely covered with CO even at very low pressures.^{4,19} Thus, before the start of each CO exposure, it was necessary to carefully clean the nickel surface by Ar^+ sputtering and annealing cycles. After the cleaning procedure, the carbon impurity in the Auger sampling depth was found to be below 0.15 atomic%. Although the stated base pressure of the apparatus is 4×10^{-11} mbar, the partial pressure of CO may be less than this. We will assume that the system is initially in equilibrium with a coverage of 0.0015. The initial pressure will be taken to be the partial pressure of CO corresponding to a coverage of 0.0015 which is found from the equilibrium adsorption isotherm to be 1.65×10^{-16} mbar. (The solution is not very sensitive to this small initial coverage. In fact, doubling the assumed initial coverage does not affect the predictions.)

In order to calibrate the coverages obtained, Surnev *et al.* assumed that the saturation coverage was 0.5. However, using our detailed description of the adsorption isotherms indicates that, at a pressure of 1×10^{-8} mbar and a temperature of 288 K, the equilibrium coverage is 0.524. For this reason, the coverage values given in Ref. 24 have been multiplied by a factor of 0.524/0.5.

Using the tabulated properties of CO–Ni(111), the listed temperature and pressures and the full solution procedure, predictions were made for the adsorption kinetics and values of the apparatus constants τ and α inferred. In Fig. 5, the prediction is shown with the experimental data. The values

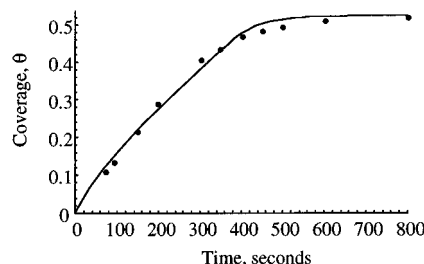


FIG. 5. Comparison of the statistical rate theory prediction with the kinetic adsorption measurements of Surnev, Xu, and Yates. The apparatus constants used for the prediction were $\tau=4.8$ s and $\alpha=3 \times 10^{-7}$ mbar.

inferred for the apparatus constants were $\alpha=3\times 10^{-7}$ mbar and $\tau=4.8$ s. The agreement is not as good as those in Figs. 3 and 4, but it should be noted that in this case the function representing the equilibrium adsorption isotherm had to be extrapolated from 296 to 288 K. As with the data of Froitzheim and Köhler, the shape of the experimental curve could not be explained using the isobaric equations.

C. Examination of the CO–Ni(111) measurements reported by Rubloff

Ultraviolet photoelectron spectroscopy was used by Rubloff¹ to measure adsorption–desorption cycles occurring isothermally at several different temperatures. Nine of the experiments were carried out at temperatures that were within the temperature range for which the parameters have been established.¹⁹ In Rubloff's experiments, a fast-acting valve and nozzle were used to suddenly expose the sample to a high pressure, $P_{\text{samp}}^{\text{on}}$, so that adsorption took place isothermally. At a nominal time of 250 ms after the start of an experiment, the valve was closed, the pressure fell to a low pressure of $P_{\text{samp}}^{\text{off}}$ and isothermal desorption took place. The adsorption portions of the curves recorded by Rubloff occurred too quickly to accurately analyze so that only the desorption portions will be analyzed here. In previous analyses of Rubloff's experiments,^{12,14} the equilibrium cross section was left as an adjustable parameter. However, since the pressure at which Rubloff's experiments occurred was not recorded, the data are not sufficient to determine the value of the equilibrium adsorption cross section. Hence, we will again investigate the possibility that this cross section has the value given by Eq. (11).

Although the pressures at which the experiments were performed were not recorded, Rubloff states that the ratio of $P_{\text{samp}}^{\text{on}}$ to $P_{\text{samp}}^{\text{off}}$ is 10^3 and that $P_{\text{samp}}^{\text{on}} \leq 5 \times 10^{-3}$ Torr. This indicates that Rubloff's experiments may well be occurring at pressures outside of the free molecular flow regime, since the mean free path for CO at a pressure of 5×10^{-3} Torr and a temperature of 395 K is 1.3 cm. Without using the free molecular flow prediction for the pressure, one can still analyze Rubloff's data in keeping with the idea that the pressure does not change instantaneously after the valve is closed. We will assume that after the valve is closed, the pressure falls in the adsorption chamber in some unknown way with time. After a time, Δt , the pressure will have reached the value $P_{\text{samp}}^{\text{off}}$. Thus, one may examine Rubloff's data using the isobaric equations by assuming that the starting time is Δt after the nominal starting time and that the initial coverage is the experimental coverage at the time Δt . In other words, one examines only the data which were recorded after the pressure has reached a constant value. In this way, for each of the nine temperatures, best fit values of $P_{\text{samp}}^{\text{on}}$ and Δt were inferred.

It is necessary to mention two points about this analysis. Firstly, Rubloff's data are presented as fractional coverage. That is, the coverage at the high pressure is assigned a value of unity and the coverage at the low pressure is assigned a value of zero. Once a value of $P_{\text{samp}}^{\text{on}}$ is chosen, it is thus

TABLE III. Parameters inferred from Rubloff's experiments.

Temperature (K)	Pressure, $P_{\text{samp}}^{\text{on}}$ (Torr)	Time delay, Δt (s)
395	3.0×10^{-5}	0.45
408	5.1×10^{-5}	0.56
422	7.5×10^{-5}	0.20
435	1.1×10^{-4}	0.26
448	2.7×10^{-4}	0.14
461	8.4×10^{-4}	0.11
474	8.5×10^{-4}	0.081
487	3.2×10^{-4}	0.023
500	2.1×10^{-4}	0.031

necessary to use the isotherm relation,¹⁹ Eq. (27), to convert the data to absolute coverages.^{12,14} The second point is that rather than using the sum of the squared errors as a means for determining the best fit values, it is necessary to use the standard deviation since the number of points in the analysis will be changing as Δt changes (because data points recorded at times less than Δt will not be used). The standard deviation was found using the following equation:

$$SD = \sqrt{\frac{\sum_{i=1}^n (\theta_{mi} - \theta_{ci})^2}{n-d}}, \quad (44)$$

where n is the number of data points used, θ_{mi} is the i th measured coverage, θ_{ci} is the coverage calculated at the same time that the i th data point was measured and d is the number of parameters being inferred.

In Table III, the inferred values of $P_{\text{samp}}^{\text{on}}$ and Δt are listed. Note that all of the pressures are below 5×10^{-3} Torr as required. The delay times, Δt , are small compared to the length of time for which the desorption was recorded. In Figs. 6 and 7 the data from two of the desorption experiments are shown along with the predictions from SRT. As can be seen in those figures, the agreement with statistical rate theory is very good. The agreement in the other cases that were analyzed was equally as good. In a previous analysis of Rubloff's data¹² it was also found that the measurements could not be satisfactorily explained without including a delay time, Δt , although at that time the implications of this delay were not fully understood.

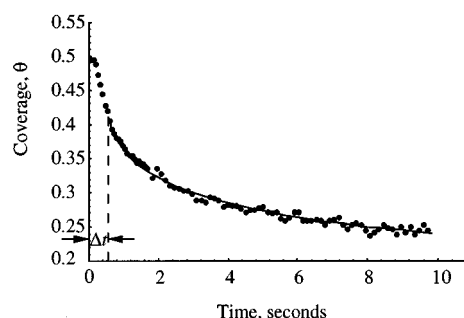


FIG. 6. Comparison of the statistical rate theory prediction with the kinetic desorption measurement made by Rubloff at 408 K. The apparatus constants used for the prediction were $P_{\text{samp}}^{\text{on}} = 5.1 \times 10^{-5}$ Torr and $\Delta t = 0.56$ s.

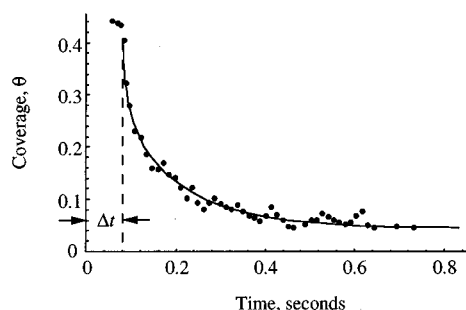


FIG. 7. Comparison of the statistical rate theory prediction with the kinetic desorption measurement made by Rubloff at 474 K. The apparatus constants used for the prediction were $P_{\text{on}}^{\text{on}} = 8.5 \times 10^{-4}$ Torr and $\Delta t = 0.081$ s.

Previously, when SRT was used to treat the adsorption of CO on Ni(111) in an isolated system, the equilibrium adsorption cross section was found to be constant and an attempt was made to infer its value from experiments. Here we have investigated the possibility that the cross section is simply the geometrical area of an adsorption site and that it is, therefore, a material property of this interface. This assumption has led to the conclusion that Rubloff's experiments would have to have been performed at different pressures. (Pressure was not a controlled variable in Rubloff's experiment). This suggests one further check on the consistency of this assumption. Some of the pressures inferred from Rubloff's measurements were low enough that the assumption of free molecular flow could be valid. For these experiments, then, the data should be adequately explained using the free molecular flow equation for the change of pressure with time. For the assumption of free molecular flow to be valid, the mean free path must be large compared with the experimental dimensions. For the temperatures and pressures indicated in Table III, the mean free path was calculated. Also for these temperatures and pressures, the data were analyzed a second time using the equations in Sec. III A. As expected, only when the mean free path is large does the assumption of free molecular flow lead to reasonable agreement. These results support the assumption that the equilibrium adsorption cross section is a constant.

V. DISCUSSION AND CONCLUSIONS

The SRT approach has been expanded to include systems for which the number of molecules within the system (and hence the pressure) is changing with time and the theoretical approach has been used to examine experimental results in the literature for beam-dosing adsorption kinetics of CO on Ni(111). In this approach, the system was treated as though it were isolated for an element of time. In order to isolate the system, it was thought of as though it were contained within a volume, V , that was defined such that SRT was valid. This allowed the adsorption kinetics to be predicted in terms of known material properties and a set of apparatus constants such as V that were independent of coverage and of pressure. This calculation contains the equilibrium exchange rate that is written in terms of equilibrium

properties which may be calculated from the isotherm relation, the material properties and the volume, V . The calculation also includes the chemical potential relations for both the gas phase and adsorbed molecules. The adsorbed molecules were treated as quantum mechanical, double harmonic oscillators with a coverage-dependent potential energy in order to account for adsorbate-adsorbate interactions.¹⁹ It is not possible to assess separately the validity of each of these aspects of the calculation. Thus, we go ahead and make the calculations and determine whether the complete approach gives a good description of the physical phenomenon by comparing the predictions with measurements reported from three different laboratories.

In comparing the data of Froitzheim and Köhler and the data of Surnev *et al.* with the SRT predictions, values of τ and α had to be inferred. In comparing Rubloff's data with the SRT predictions, values of the pressure and the delay time, Δt , had to be inferred. In each case, the constants inferred were physical quantities related to the experimental apparatus that were expected to have constant values (i.e., no coverage or pressure dependence) during the experiment. The good agreement, then, in each of the cases (see Figs. 3–7), indicates that all of the necessary coverage and pressure dependence was entirely predicted by SRT. This is in contrast to the use of absolute rate theory²⁵ in describing this same system.^{1,12} When absolute rate theory is used, additional coverage dependence must be added empirically to the equations. The same is true of the sticking probability approach.^{2,4}

All of the material properties except one (the equilibrium adsorption cross section) needed to make a kinetic prediction are given explicitly in Tables I and II. Herein, the cross section was taken to be equal to $1/M$. When a similar assumption was used in treating gas absorption by a liquid with SRT,⁵ a value of the diffusion coefficient was inferred that was in agreement with the diffusion coefficient measured by other methods. Due to the fact that in each case, when SRT was compared with the experimental beam-dosing adsorption results, at least one apparatus constant had to be inferred, it is not possible to establish error bounds on the determination of the cross section. However, the agreement between the theoretical predictions and the measurements of Froitzheim and Köhler,²² Surnev *et al.*²⁴ and Rubloff,¹ indicates that the cross section is independent of coverage and pressure. The indication that the cross section has a constant value implies that all of the material properties needed to describe the kinetics of CO–Ni(111) adsorption have been identified. This is an important conclusion that will impact the interpretation of temperature programmed desorption spectra using SRT.²⁶

In previous SRT studies, the treatment was limited to isolated systems that could be approximated as isothermal and isobaric. Herein, these limitations have been removed and SRT has been applied to systems of variable mass for which the pressure was changing with time. In each of the isothermal, beam-dosing experiments studied, the use of the current approach led to better agreement with the experimental data than could be obtained previously. These results lend

support to the SRT approach which includes, as a fundamental assumption, the interpretation of the equilibrium exchange rate.

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