**31–46.** The enthalpy of adsorption for H_2 adsorbed on a surface of copper is $-54.4 \text{ kJ} \cdot \text{mol}^{-1}$. The activation energy for going from the physisorbed state to the chemisorbed state is $31.3 \text{ kJ} \cdot \text{mol}^{-1}$, and the curve crossing between these two potentials occurs at $V(z) \approx 21 \text{ kJ} \cdot \text{mol}^{-1}$. Draw a schematic representation similar to that in Figure 31.20 for the case of H_2 interacting with copper.
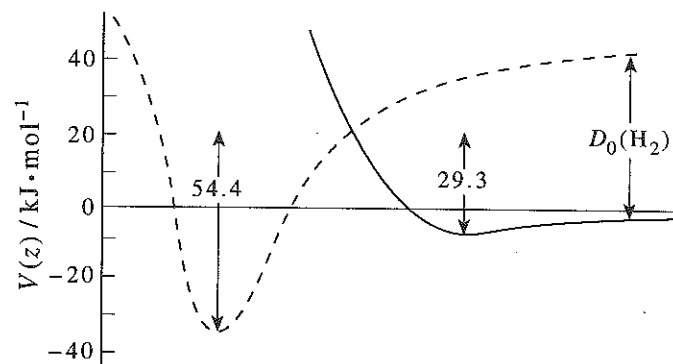
31–47. In Section 27–4, we showed that the collision frequency per unit area is (Equation 27.48)

$$z_{coll} = \frac{\rho \langle u \rangle}{4} \tag{1}$$

Use Equation 1 and the ideal-gas law to show that J_N, the number of molecules striking a surface of unit area (1 m^2) in one second, is

$$J_N = \frac{P N_A}{(2\pi M R T)^{1/2}}$$

where M is the molar mass of the molecule, P is the pressure of the gas, and T is the temperature. How many nitrogen molecules will strike a 1.00-cm^2 surface in 1.00 s at 298.1 K and a gas pressure of 1.05×10^{-6} Pa?

The average speed is given by

$$\langle u \rangle = \left(\frac{8RT}{\pi M} \right)^{1/2} \tag{27.42}$$

Using the ideal gas law, we find that $\rho = N_A/V = P N_A/RT$, so

$$z_{coll} = \frac{\rho \langle u \rangle}{4} = \frac{\rho}{4} \left(\frac{8RT}{\pi M} \right)^{1/2} = \frac{N_A P}{4RT} \left(\frac{8RT}{\pi M} \right)^{1/2} = \frac{N_A P}{(2\pi M R T)^{1/2}} = J_N$$

Under the conditions given,

$$J_N = \frac{N_A P}{(2\pi M R T)^{1/2}}$$
$$= \frac{(6.022 \times 10^{23} \text{ mol}^{-1})(1.05 \times 10^{-6} \text{ Pa})}{[2\pi (0.02802 \text{ kg} \cdot \text{mol}^{-1})(8.315 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298.15 \text{ K})]^{1/2}}$$
$$= \frac{6.323 \times 10^{17} \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2}}{20.89 \text{ kg} \cdot \text{m} \cdot \text{s}^{-1}}$$
$$= 3.03 \times 10^{16} \text{ s}^{-1} \cdot \text{m}^{-2} = 3.03 \times 10^{12} \text{ cm}^{-2} \cdot \text{s}^{-1}$$

so 3.03×10^{12} molecules will collide with the 1.00-cm^2 surface in one second.

31–48. One *langmuir* corresponds to an exposure of a surface to a gas at a pressure of 1.00×10^{-6} torr for 1 second at 298.15 K. Define one langmuir in units of pascals instead of torr. How many nitrogen molecules will strike a surface of area 1.00 cm^2 when exposed to 1.00 langmuir? (See Problem 31–47.)

$$1.00 \times 10^{-6} \text{ torr} \left(\frac{1.01325 \times 10^5 \text{ Pa}}{760 \text{ torr}} \right) = 1.33 \times 10^{-4} \text{ Pa}$$

A langmuir thus corresponds to an exposure of a surface to a gas at a pressure of 1.33×10^{-4} Pa for one second at 298.15 K. Using these conditions, we can substitute into our expression for J_N from the previous problem:

$$J_N = \frac{N_A P}{(2\pi M R T)^{1/2}}$$
$$= \frac{(6.022 \times 10^{23} \text{ mol}^{-1})(1.33 \times 10^{-4} \text{ Pa})}{[2\pi (0.02802 \text{ kg} \cdot \text{mol}^{-1})(8.315 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298.15 \text{ K})]^{1/2}}$$
$$= \frac{8.029 \times 10^{19} \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2}}{20.89 \text{ kg} \cdot \text{m} \cdot \text{s}^{-1}}$$
$$= 3.83 \times 10^{18} \text{ s}^{-1} \cdot \text{m}^{-2} = 3.83 \times 10^{14} \text{ cm}^{-2} \cdot \text{s}^{-1}$$

A total of 3.83×10^{14} nitrogen molecules will strike the 1.00-cm^2 surface in one second.

31–49. If the density of surface sites is $2.40 \times 10^{14} \text{ cm}^{-2}$ and every molecule that strikes the surface adsorbs to one of these sites, determine the fraction of a monolayer created by the exposure of a 1.00-cm^2 surface to 1.00×10^{-4} langmuir of $N_2(g)$ at 298.15 K.

In the previous problem, we found that the exposure of a 1.00-cm^2 surface to one langmuir resulted in 3.83×10^{14} molecules colliding with the surface. Then exposure of the same surface to 1.00×10^{-4} L would result in 3.83×10^{10} collisions. Assuming that all these molecules are adsorbed,

$$\frac{3.83 \times 10^{10}}{2.40 \times 10^{14}} = 0.016\%$$

of the surface will be covered. This is the fraction of monolayer created.

31–50. For conducting surface experiments it is important to maintain a clean surface. Suppose that a 1.50-cm^2 surface is placed inside a high-vacuum chamber at 298.15 K and the pressure inside the chamber is 1.00×10^{-12} torr. If the density of the surface sites is $1.30 \times 10^{16} \text{ cm}^{-2}$ and we assume that the only gas in the chamber is H_2O and that each of the H_2O molecules that strike the surface adsorb to one surface site, how long will it be until 1.00% of the surface sites are occupied by water?

The pressure inside the chamber in Pa is

$$1 \times 10^{-12} \text{ torr} \left(\frac{1.01325 \times 10^5 \text{ Pa}}{760 \text{ torr}} \right) = 1.33 \times 10^{-10} \text{ Pa}$$

The rate of collision per unit of surface area is given by J_N from Problem 31–47 is

$$J_N = \frac{N_A P}{(2\pi M R T)^{1/2}}$$

$$= \frac{(6.022 \times 10^{23}\ \text{mol}^{-1})(1.33 \times 10^{-10}\ \text{Pa})}{[2\pi(0.01801\ \text{kg·mol}^{-1})(8.315\ \text{J·K}^{-1}\text{·mol}^{-1})(298.15\ \text{K})]^{1/2}}$$

$$= \frac{8.029 \times 10^{13}\ \text{kg·m}^{-1}\text{·s}^{-2}}{16.79\ \text{kg·m·s}^{-1}}$$

$$= 4.79 \times 10^{12}\ \text{s}^{-1}\text{·m}^{-2} = 4.79 \times 10^{8}\ \text{cm}^{-2}\text{·s}^{-1}$$

Now if 1.00% of the surface sites are occupied, the density of occupied surface sites will be $1.30 \times 10^{14}\ \text{cm}^{-2}$. Then

$$(4.79 \times 10^{8}\ \text{cm}^{-2}\text{·s}^{-1})t = 1.30 \times 10^{14}\ \text{cm}^{-2}$$

$$t = 2.71 \times 10^{5}\ \text{s}$$

31–51. Use the results of Example 31–12 to determine the rate of desorption of CO from palladium at 300 K and 500 K.

Because $k_d = 1/\tau$, at 300 K $k_d = 3.8 \times 10^{-14}\ \text{s}^{-1}$ and at 500 K $k_d = 5.6 \times 10^{-4}\ \text{s}^{-1}$.


31–52. The following data were obtained for the adsorption of $N_2(g)$ to a piece of solid graphite at 197 K. The tabulated volumes are the volumes that the adsorbed gas would occupy at 0.00°C and one bar

P/bar	3.54	10.13	16.92	26.04	29.94
$V/10^{-4}\ \text{m}^3$	328	456	497	527	536

Determine the values of V_m and b using the Langmuir adsorption isotherm. The total mass of the carbon solid is 1325 g. Determine the fraction of the carbon atoms that are accessible as binding sites if you assume that each surface atom can adsorb one N_2 molecule.

Use the equation from Example 31–10 to fit the above data:

$$\frac{1}{V} = \frac{1}{PbV_m} + \frac{1}{V_m}$$
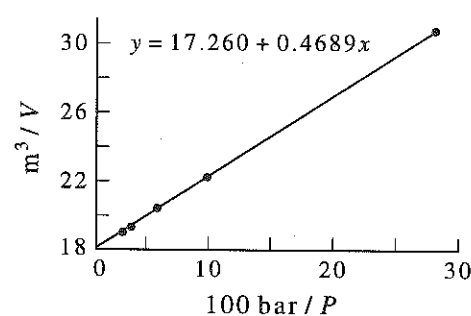
Comparing the line of best fit to the equation above, we see that

$$\frac{1}{V_m} = 17.260\ \text{m}^{-3}$$

and

$$V_m = 5.79 \times 10^{-2}\ \text{m}^3$$

Likewise,

$$\frac{1}{bV_m} = 46.89\ \text{bar·m}^{-3}$$

and

$$b = \frac{1}{46.89 V_m} = 0.368\ \text{bar}$$

At 0.00° C and one bar, one mole of gas occupies about $22.4 \times 10^{-3}\ \text{m}^3$. The number of moles of gas in V_m is then

$$\frac{5.59 \times 10^{-2}\ \text{m}^3}{22.4 \times 10^{-3}\ \text{m}^3\text{·mol}^{-1}} = 2.58\ \text{mol}$$

If each surface atom adsorbs one N_2 molecule, then 2.58 mol of carbon atoms on the surface are accessible to $N_2(g)$. The total number of moles of carbon is 1325 g/12.01 g·mol^{-1} = 110 mol, and so the fraction of carbon atoms accessible is 0.023, or 2.3%.

31–53. The first-order surface reaction

$$A(g) \Longrightarrow A(\text{ads}) \Longrightarrow B(g)$$
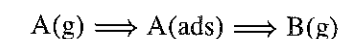
has a rate of $1.8 \times 10^{-4}\ \text{mol·dm}^{-3}\text{·s}^{-1}$. The surface has a dimension of 1.00 cm by 3.50 cm. Calculate the rate of reaction if the dimensions of the two sides of the surface were each doubled. [Assume that A(g) is in excess.]

Because A(g) is in excess, the second step is the rate-determining step and

$$v = k_d \theta \sigma_0$$

If the dimensions of each side of the surface are doubled, the surface area will increase by a factor of 4. The quantity σ_0 will therefore increase by a factor of 4, and the the reaction rate on the larger reaction surface will be $v = 7.2 \times 10^{-4}\ \text{mol·dm}^{-3}\text{·s}^{-1}$.

31–54. Consider the reaction scheme

$$A(g) + S \xrightarrow{k_1} A\text{–S} \xrightarrow{k_2} P(g)$$
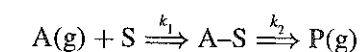
for which the rate law is

$$v = k_2 \theta_A$$

where θ_A is the fraction of surface sites occupied by A molecules. Use the Langmuir adsorption isotherm (Equation 31.35) to obtain an expression for the reaction rate in terms of K_c and [A]. Under what conditions will the reaction be first order in the concentration of A?

Begin with the Langmuir adsorption isotherm (Equation 31.35) and solve for θ_A:

$$\frac{1}{\theta_A} = 1 + \frac{1}{K_c[A]}$$

$$\theta_A = \frac{K_c[A]}{K_c[A] + 1}$$
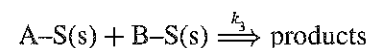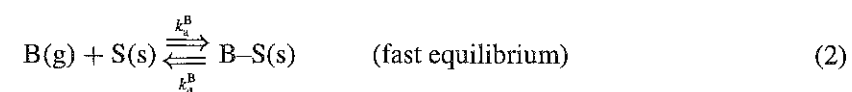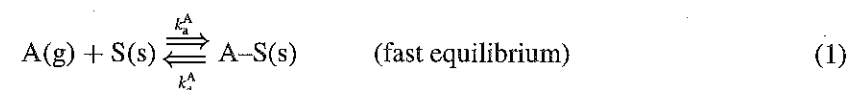
Substituting this result into the given rate law gives

$$v = \frac{K_c k_2[A]}{K_c[A] + 1}$$

The reaction will be first order in [A] if $K_c[A] \ll 1$, in which case the expression above reduces to $v = k_2 K_c[A]$.

31–55. Consider a surface-catalyzed bimolecular reaction between molecules A and B that has a rate law of the form

$$v = k_3 \theta_A \theta_B$$

where θ_A is the fraction of surface sites occupied by reactant A and θ_B is the fraction of surface sites occupied by reactant B. A mechanism consistent with this reaction is as follows:

$$A(g) + S(s) \underset{k_d^A}{\overset{k_a^A}{\rightleftharpoons}} A\text{–}S(s) \qquad \text{(fast equilibrium)} \qquad (1)$$

$$B(g) + S(s) \underset{k_d^B}{\overset{k_a^B}{\rightleftharpoons}} B\text{–}S(s) \qquad \text{(fast equilibrium)} \qquad (2)$$

$$A\text{–}S(s) + B\text{–}S(s) \overset{k_3}{\Longrightarrow} \text{products}$$

Take K_A and K_B to be the equilibrium constants for Equations 1 and 2, respectively. Derive expressions for θ_A and θ_B in terms of [A], [B], K_A, and K_B. Use your results to show that the rate law can be written as

$$v = \frac{k_3 K_A K_B[A][B]}{(1 + K_A[A] + K_B[B])^2}$$

At any given time, the fraction of available surface sites is $1 - \theta_A - \theta_B$.

From Equation 1, we have the equations (analogous to Equations 31.33 and 31.34)

$$v_d^A = k_d^A \theta_A \sigma_0$$
$$v_a^A = k_a^A[A](1 - \theta_A - \theta_B)\sigma_0$$

Likewise, for reactant B,

$$v_d^B = k_d^B \theta_B \sigma_0$$
$$v_a^B = k_a^B[B](1 - \theta_A - \theta_B)\sigma_0$$

At equilibrium,

$$k_d^A \theta_A = k_a^A[A](1 - \theta_A - \theta_B)$$

$$\frac{\theta_A}{1 - \theta_A - \theta_B} = K_A[A] \qquad (3)$$

and

$$k_d^B \theta_B = k_a^B[B](1 - \theta_A - \theta_B)$$

$$\frac{\theta_B}{1 - \theta_A - \theta_B} = K_B[B] \qquad (4)$$

We can solve Equations 3 and 4 simultaneously to obtain

$$\theta_A = \frac{K_A[A]}{1 + K_A[A] + K_B[B]}$$

$$\theta_B = \frac{K_B[B]}{1 + K_A[A] + K_B[B]}$$

Substituting these expressions for θ_A and θ_B into the rate law gives

$$v = \frac{k_3 K_A K_B[A][B]}{(1 + K_A[A] + K_B[B])^2}$$

31–56. Reconsider the surface-catalyzed bimolecular reaction in Problem 31–55. If A(g) and B(g) do not compete for surface sites, but instead each molecule uniquely binds to a different type of surface site, show that the rate law is given by

$$v = \frac{k_3 K_A K_B[A][B]}{(1 + K_A[A])(1 + K_B[B])}$$

If A and B do not compete for surface sites, the fraction of surface sites available for A is $1 - \theta_A$ and the fraction available for B is $1 - \theta_B$. Then, at equilibrium,

$$k_a^A[A](1 - \theta_A) = k_d^A \theta_A$$
$$k_a^B[B](1 - \theta_B) = k_d^B \theta_B$$

Solving for θ_A and θ_B gives

$$\theta_A = \frac{K_A[A]}{1 + K_A[A]}$$

$$\theta_B = \frac{K_B[B]}{1 + K_B[B]}$$

and substituting these expressions into the rate law gives

$$v = k_3 \theta_A \theta_B = \frac{k_3 K_A K_B[A][B]}{(1 + K_A[A])(1 + K_B[B])}$$

31–57. In this problem we derive Equation 31.45, the rate law for the oxidation reaction $2\,CO(g) + O_2(g) \longrightarrow 2\,CO_2(g)$ assuming that the reaction occurs by the Langmuir-Hinshelwood mechanism. The overall rate law for this mechanism is

$$v = k_3 \theta_{CO} \theta_{O_2}$$

Show that

$$\theta_{O_2} = \frac{(K_{O_2}[O_2])^{1/2}}{1 + (K_{O_2}[O_2])^{1/2} + K_{CO}[CO]}$$

and

$$\theta_{CO} = \frac{K_{CO}[CO]}{1 + (K_{O_2}[O_2])^{1/2} + K_{CO}[CO]}$$

Use these expressions and the relationship $b = K_c/k_B T$ to obtain the rate law given by Equation 31.45. (Assume ideal-gas behavior.)

For CO, as in Problem 31–55,

$$k_a^{CO}[CO](1 - \theta_{CO} - \theta_{O_2}) = k_d^{CO}\theta_{CO}$$

Because the second reaction of the mechanism produces 2 O atoms,

$$k_a^{O_2}[O_2](1 - \theta_{CO} - \theta_{O_2})^2\sigma_0^2 = k_d\theta_{O_2}^2\sigma_0^2$$

or

$$k_a^{O_2}[O_2](1 - \theta_{CO} - \theta_{O_2})^2 = k_d\theta_{O_2}^2$$

Taking the square root of both sides of this equation gives

$$\left(k_a^{O_2}[O_2]\right)^{1/2}(1 - \theta_{CO} - \theta_{O_2}) = \left(k_d^{O_2}\right)^{1/2}\theta_{O_2}$$

We can substitute K_{CO} and K_{O_2} for the adsorption and desorption constants in the above expression and find

$$\left(K_{O_2}[O_2]\right)^{1/2} = \frac{\theta_{O_2}}{1 - \theta_{CO} - \theta_{O_2}}$$

and

$$K_{CO}[CO] = \frac{\theta_{CO}}{1 - \theta_{CO} - \theta_{O_2}}$$

Solving these two equations simultaneously gives

$$\theta_{O_2} = \frac{\left(K_{O_2}[O_2]\right)^{1/2}}{1 + \left(K_{O_2}[O_2]\right)^{1/2} + K_{CO}[CO]}$$

$$\theta_{CO} = \frac{K_{CO}[CO]}{1 + \left(K_{O_2}[O_2]\right)^{1/2} + K_{CO}[CO]}$$

Substituting these results into the overall rate law, we find that

$$v = k_3\theta_{CO}\theta_{O_2} = \frac{k_3 K_{CO}[CO]K_{O_2}^{1/2}[O_2]^{1/2}}{(1 + K_{O_2}^{1/2}[O_2]^{1/2} + K_{CO}[CO])^2}$$

Assuming ideal behavior, $[O_2] = P_{O_2}/k_B T$ and $[CO] = P_{CO}/k_B T$, and from the text $b_{CO} = K_{CO}/k_B T$ and $b_{O_2} = K_{O_2}/k_B T$. Substituting these expressions into the rate law above gives

$$v = \frac{k_3 b_{O_2}^{1/2} P_{O_2}^{1/2} b_{CO} P_{CO}}{(1 + b_{O_2}^{1/2} P_{O_2}^{1/2} + b_{CO} P_{CO})^2} \qquad (31.45)$$

31–58. In this problem we derive Equation 31.46, the rate law for the oxidation reaction $2\,CO(g) + O_2(g) \longrightarrow 2\,CO_2(g)$ assuming that the reaction occurs by the Eley-Rideal mechanism. The overall rate law for this mechanism is

$$v = k_3\theta_{O_2}[CO]$$

Assuming that both CO(g) and O_2(g) compete for adsorption sites, show that

$$v = \frac{k_3 K_{O_2}^{1/2}[O_2]^{1/2}[CO]}{1 + K_{O_2}^{1/2}[O_2]^{1/2} + K_{CO}[CO]}$$

Use the relationship between K_c and b and the ideal-gas law to show that this equation is equivalent to Equation 31.46.

The step of the mechanism for the absorption of O_2 is the same as that discussed in the previous problem for O_2, so θ_{O_2} is

$$\theta_{O_2} = \frac{\left(K_{O_2}[O_2]\right)^{1/2}}{1 + \left(K_{O_2}[O_2]\right)^{1/2} + K_{CO}[CO]}$$

Substituting into the overall rate law,

$$v = k_3\theta_{O_2}[CO] = \frac{k_3 K_{O_2}^{1/2}[O_2]^{1/2}[CO]}{1 + K_{O_2}^{1/2}[O_2]^{1/2} + K_{CO}[CO]}$$

Assuming ideal behavior, $[O_2] = P_{O_2}/k_B T$ and $[CO] = P_{CO}/k_B T$, and from the text $b_{CO} = K_{CO}/k_B T$ and $b_{O_2} = K_{O_2}/k_B T$. Substituting these expressions into the above rate law gives

$$v = \frac{k_3 b_{O_2}^{1/2} P_{O_2}^{1/2} b_{CO} P_{CO}}{1 + b_{O_2}^{1/2} P_{O_2}^{1/2} + b_{CO} P_{CO}} \qquad (31.46)$$

31–59. The hydrogenation of ethene on copper obeys the rate law

$$v = \frac{k[H_2]^{1/2}[C_2H_4]}{(1 + K[C_2H_4])^2}$$

where k and K are constants. Mechanistic studies show that the reaction occurs by the Langmuir-Hinshelwood mechanism. How are k and K related to the rate constants for the individual steps of the reaction mechanism? What can you conclude about the relative adsorption of H_2(g) and C_2H_4(g) to the copper surface from the form of the observed rate law?
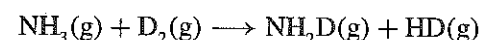

The rate law for the Langmuir-Hinshelwood mechanism is (Problem 31–57)

$$v = k_3\theta_{C_2H_4}\theta_{H_2} = \frac{k_3 K_{C_2H_4}[C_2H_4]K_{H_2}^{1/2}[H_2]^{1/2}}{(1 + K_{H_2}^{1/2}[H_2]^{1/2} + K_{C_2H_4}[C_2H_4])^2}$$

The $K_{H_2}^{1/2}[H_2]^{1/2}$ term does not appear in the denominator of the rate law provided in the problem, so $1 + K_{C_2H_4}[C_2H_4] \gg K_{H_2}^{1/2}[H_2]^{1/2}$. This means that C_2H_4 must adsorb much more extensively than

H_2. Comparing the given rate law and the above expression for v, we find that $k = k_3 K_{H_2}^{1/2} K_{C_2H_4}$ and $K = K_{C_2H_4}$.

31–60. The iron-catalyzed exchange reaction

$$NH_3(g) + D_2(g) \longrightarrow NH_2D(g) + HD(g)$$

obeys the rate law

$$v = \frac{k[D_2]^{1/2}[NH_3]}{(1 + K[NH_3])^2}$$

Is this rate law consistent with either the Eley-Rideal or Langmuir-Hinshelwood mechanisms? How are k and K related to the rate constants of the individual steps of the mechanism you chose? What does the rate law tell you about the relative adsorption of $D_2(g)$ and $NH_3(g)$ to the iron surface?

This rate law is consistent with the Langmuir-Hinshelwood mechanism (Problem 31–57). The total rate law for the mechanism would be

$$v = \frac{k_3 K_{NH_3}[NH_3] K_{D_2}^{1/2}[D_2]^{1/2}}{(1 + K_{D_2}^{1/2}[D_2]^{1/2} + K_{NH_3}[NH_3])^2}$$

If $K_{D_2}^{1/2}[D_2]^{1/2} \ll 1 + K_{NH_3}[NH_3]$, this reduces to the rate law given in the problem, in which case $K = K_{NH_3}$ and $k = k_3 K_{NH_3} K_{D_2}^{1/2}$. The above inequality tells us that NH_3 adsorbs to the surface much more extensively than D_2.

31–61. Consider the surface-catalyzed exchange reaction

$$H_2(g) + D_2(g) \longrightarrow 2\,HD(g)$$
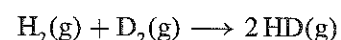
Experimental studies show that this reaction occurs by the Langmuir-Hinshelwood mechanism by which both $H_2(g)$ and $D_2(g)$ first dissociatively chemisorb to the surface. The rate-determining step is the reaction between the adsorbed H and D atoms. Derive an expression for the rate law for this reaction in terms of the gas-phase pressures of $H_2(g)$ and $D_2(g)$. (Assume ideal-gas behavior.)

Because both reactions produce two atoms, we can write (as in Problem 31–57)

$$k_a^{D_2}[D_2](1 - \theta_{H_2} - \theta_{D_2})^2 = k_d \theta_{D_2}^2$$

Taking the square root of both sides gives

$$\left(k_a^{D_2}[D_2]\right)^{1/2}(1 - \theta_{H_2} - \theta_{D_2}) = \left(k_d^{D_2}\right)^{1/2}\theta_{D_2}$$

or

$$K_{D_2}^{1/2}[D_2]^{1/2} = \frac{\theta_{D_2}}{1 - \theta_{H_2} - \theta_{D_2}}$$

with an equivalent expression in K_{H_2}. Solving for θ_{D_2} and θ_{H_2} gives

$$\theta_{D_2} = \frac{K_{D_2}^{1/2}[D_2]^{1/2}}{1 + K_{D_2}^{1/2}[O_2]^{1/2} + K_{H_2}^{1/2}[H_2]^{1/2}}$$

$$\theta_{H_2} = \frac{K_{H_2}^{1/2}[H_2]^{1/2}}{1 + K_{D_2}^{1/2}[O_2]^{1/2} + K_{H_2}^{1/2}[H_2]^{1/2}}$$

Finally,

$$v = k_3 \theta_{D_2}\theta_{H_2} = \frac{k_3 K_{D_2}^{1/2} K_{H_2}^{1/2}[D_2]^{1/2}[H_2]^{1/2}}{(1 + K_{D_2}^{1/2}[O_2]^{1/2} + K_{H_2}^{1/2}[H_2]^{1/2})^2} = \frac{(k_3 b_{D_2} b_{H_2} P_{D_2} P_{H_2})^{1/2}}{(1 + b_{D_2}^{1/2} P_{D_2}^{1/2} + b_{H_2}^{1/2} P_{H_2}^{1/2})^2}$$

31–62. LEED spectroscopy records the intensities and locations of electrons that are diffracted from a surface. For an electron to diffract, its de Broglie wavelength must be less than twice the distance between the atomic planes in the solid (see Section 31–9). Show that the de Broglie wavelength of an electron accelerated through a potential difference of ϕ volts is given by

$$\lambda/pm = \left(\frac{1.504 \times 10^6 \text{ V}}{\phi}\right)^{1/2}$$

The de Broglie equation is $\lambda = h/p$ (Equation 1.12). Because $E = p^2/2m$, and the energy of an electron accelerated through a potential difference of ϕ volts is $e\phi$,

$$\lambda = \frac{h}{(2mE)^{1/2}} = \left(\frac{h^2}{2me\phi}\right)^{1/2}$$

$$= \left[\frac{(6.626 \times 10^{-34} \text{ J·s})^2}{2(9.109 \times 10^{-31} \text{ kg})(1.602 \times 10^{-19} \text{ C})\phi}\right]^{1/2}$$

$$\lambda = \left(\frac{1.504 \times 10^{-18} \text{ V·m}^2}{\phi}\right)^{1/2}$$

$$\lambda/pm = \left[\frac{(1.504 \times 10^{-18} \text{ V·m}^2)(10^{12} \text{ pm·m}^{-1})^2}{\phi}\right]^{1/2} = \left(\frac{1.504 \times 10^6 \text{ V}}{\phi}\right)^{1/2}$$

31–63. The distance between the 100 planes of a nickel substrate, whose surface is a 100 plane, is 351.8 pm. Calculate the minimum accelerating potential so that electrons can diffract from the crystal. Calculate the kinetic energy of these electrons. (*Hint*: See Problem 31–62.)

From Problem 31–62, we know that the de Broglie wavelength must be less than twice the distance between the atomic planes. Therefore, the minimum accelerating potential so that electrons can diffract from the crystal is

$$2(351.8) = \left(\frac{1.504 \times 10^6 \text{ V}}{\phi_{min}}\right)^{1/2}$$

$$\phi_{min} = \frac{1.504 \times 10^6 \text{ V}}{(703.6)^2} = 3.04 \text{ V}$$

and the kinetic energy of the diffracted electrons is

$$E = e\phi = 4.87 \times 10^{-19} \text{ J} = 293 \text{ kJ·mol}^{-1}$$

31–64. The distance between the 111 surface of silver and the second layer of atoms is 235 pm, the same as in the bulk. If electrons with a kinetic energy of 8.77 eV strike the surface, will an electron diffraction pattern be observed? (*Hint*: See Problem 31–62.)