

28 Processes at solid surfaces

Solutions to exercises

Discussion questions

- E28.1(b)** The motion of one section of a crystal past another (a dislocation) results in steps and terraces. See Figures 28.2 and 28.3 of the text. A special kind of dislocation is the screw dislocation shown in Fig. 28.3. Imagine a cut in the crystal, with the atoms to the left of the cut pushed up through a distance of one unit cell. The surface defect formed by a screw dislocation is a step, possibly with kinks, where growth can occur. The incoming particles lie in ranks on the ramp, and successive ranks reform the step at an angle to its initial position. As deposition continues the step rotates around the screw axis, and is not eliminated. Growth may therefore continue indefinitely. Several layers of deposition may occur, and the edges of the spirals might be cliffs several atoms high (Fig. 28.4).

Propagating spiral edges can also give rise to flat terraces (Fig. 28.5). Terraces are formed if growth occurs simultaneously at neighbouring left- and right-handed screw dislocations (Fig. 28.6). Successive tables of atoms may form as counter-rotating defects collide on successive circuits, and the terraces formed may then fill up by further deposition at their edges to give flat crystal planes.

- E28.2(b)** Consult the appropriate sections of the textbook (listed below) for the advantages and limitations of each technique.

AFM: 28.2(h) and Box 28.1; FIM: 28.5(c); LEED: 28.2(g); MBRS: 28.6(c); MBS: 28.2(i); SAM: 28.2(e); SEM: 28.2(h); and STM: 28.2(h).

- E28.3(b)** In the Langmuir–Hinshelwood mechanism of surface catalysed reactions, the reaction takes place by encounters between molecular fragments and atoms already adsorbed on the surface. We therefore expect the rate law to be second-order in the extent of surface coverage:



Insertion of the appropriate isotherms for A and B then gives the reaction rate in terms of the partial pressures of the reactants. For example, if A and B follow Langmuir isotherms (eqn 28.5), and adsorb without dissociation, then it follows that the rate law is

$$v = \frac{kK_A K_B p_A p_B}{(1 + K_A p_A + K_B p_B)^2}$$

The parameters K in the isotherms and the rate constant k are all temperature dependent, so the overall temperature dependence of the rate may be strongly non-Arrhenius (in the sense that the reaction rate is unlikely to be proportional to $\exp(-E_a/RT)$).

In the Eley-Rideal mechanism (ER mechanism) of a surface-catalysed reaction, a gas-phase molecule collides with another molecule already adsorbed on the surface. The rate of formation of product is expected to be proportional to the partial pressure, p_B of the non-adsorbed gas B and the extent of surface coverage, θ_A , of the adsorbed gas A. It follows that the rate law should be



The rate constant, k , might be much larger than for the uncatalysed gas-phase reaction because the reaction on the surface has a low activation energy and the adsorption itself is often not activated.

If we know the adsorption isotherm for A, we can express the rate law in terms of its partial pressure, p_A . For example, if the adsorption of A follows a Langmuir isotherm in the pressure range

of interest, then the rate law would be

$$v = \frac{kKp_A p_B}{1 + Kp_A}$$

If A were a diatomic molecule that adsorbed as atoms, we would substitute the isotherm given in eqn 28.8 instead.

According to eqn 28.24, when the partial pressure of A is high (in the sense $Kp_A \gg 1$, there is almost complete surface coverage, and the rate is equal to kp_B . Now the rate-determining step is the collision of B with the adsorbed fragments. When the pressure of A is low ($Kp_A \ll 1$), perhaps because of its reaction, the rate is equal to $kKp_A p_B$; and now the extent of surface coverage is important in the determination of the rate.

In the Mars van Krevelen mechanism of catalytic oxidation, for example in the partial oxidation of propene to propenal, the first stage is the adsorption of the propene molecule with loss of a hydrogen to form the allyl radical, $\text{CH}_2=\text{CHCH}_2$. An O atom in the surface can now transfer to this radical, leading to the formation of acrolein (propenal, $\text{CH}_2=\text{CHCHO}$) and its desorption from the surface. The H atom also escapes with a surface O atom, and goes on to form H_2O , which leaves the surface. The surface is left with vacancies and metal ions in lower oxidation states. These vacancies are attacked by O_2 molecules in the overlying gas, which then chemisorb as O_2^- ions, so reforming the catalyst. This sequence of events involves great upheavals of the surface, and some materials break up under the stress.

E28.4(b) Zeolites are microporous aluminosilicates, in which the surface effectively extends deep inside the solid. M^{n+} cations and H_2O molecules can bind inside the cavities, or pores, of the Al–O–Si framework (see Fig. 28.31 of the text). Small neutral molecules, such as CO_2 , NH_3 , and hydrocarbons (including aromatic compounds), can also adsorb to the internal surfaces and this partially accounts for the utility of zeolites as catalysts.

Like enzymes, a zeolite catalyst with a specific composition and structure is very selective toward certain reactants and products because only molecules of certain sizes can enter and exit the pores in which catalysis occurs. It is also possible that zeolites derive their selectivity from the ability to bind to stabilize only transition states that fit properly in the pores.

Numerical exercises

E28.5(b) The number collisions of gas molecules per unit surface area is

$$Z_W = \frac{N_A p}{(2\pi MRT)^{1/2}}$$

(a) For N_2

$$\begin{aligned} \text{(i)} \quad Z_W &= \frac{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (10.0 \text{ Pa})}{(2\pi \times (28.013 \times 10^{-3} \text{ kg mol}^{-1}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}))^{1/2}} \\ &= 2.88 \times 10^{23} \text{ m}^{-2} \text{ s}^{-1} \\ &= \boxed{2.88 \times 10^{19} \text{ cm}^{-2} \text{ s}^{-1}} \end{aligned}$$

$$\begin{aligned} \text{(ii)} \quad Z_W &= \frac{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (0.150 \times 10^{-6} \text{ Torr}) \times (1.01 \times 10^5 \text{ Pa}/760 \text{ Torr})}{(2\pi \times (28.013 \times 10^{-3} \text{ kg mol}^{-1}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}))^{1/2}} \\ &= 5.75 \times 10^{17} \text{ m}^{-2} \text{ s}^{-1} \\ &= \boxed{5.75 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}} \end{aligned}$$

(b) For methane

$$\begin{aligned} \text{(i)} \quad Z_W &= \frac{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (10.0 \text{ Pa})}{(2\pi \times (16.04 \times 10^{-3} \text{ kg mol}^{-1}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}))^{1/2}} \\ &= 3.81 \times 10^{24} \text{ m}^{-2} \text{ s}^{-1} \\ &= \boxed{3.81 \times 10^{20} \text{ cm}^{-2} \text{ s}^{-1}} \end{aligned}$$

$$\begin{aligned} \text{(ii)} \quad Z_W &= \frac{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (0.150 \times 10^{-6} \text{ Torr}) \times (1.01 \times 10^5 \text{ Pa}/760 \text{ Torr})}{(2\pi \times (16.04 \times 10^{-3} \text{ kg mol}^{-1}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}))^{1/2}} \\ &= 7.60 \times 10^{17} \text{ m}^{-2} \text{ s}^{-1} \\ &= \boxed{7.60 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}} \end{aligned}$$

E28.6(b) The number of collisions of gas molecules per unit surface area is

$$\begin{aligned} Z_W &= \frac{N_A p}{(2\pi MRT)^{1/2}} \quad \text{so} \quad p = \frac{Z_W A (2\pi MRT)^{1/2}}{N_A A} \\ p &= \frac{(5.00 \times 10^{19} \text{ s}^{-1})}{(6.022 \times 10^{23} \text{ mol}^{-1}) \times \pi \times (1/2 \times 2.0 \times 10^{-3} \text{ m})^2} \\ &\quad \times (2\pi \times (28.013 \times 10^{-3} \text{ kg mol}^{-1}) \times (8.3145 \text{ J mol}^{-1} \text{ K}^{-1}) \times (525 \text{ K}))^{1/2} \\ &= \boxed{7.3 \times 10^2 \text{ Pa}} \end{aligned}$$

E28.7(b) The number of collisions of gas molecules per unit surface area is

$$Z_W = \frac{N_A p}{(2\pi MRT)^{1/2}}$$

so the rate of collision per Fe atom will be $Z_W A$ where A is the area per Fe atom. The exposed surface consists of faces of the bcc unit cell, with one atom per face. So the area per Fe is

$$A = c^2 \quad \text{and} \quad \text{rate} = Z_W A = \frac{N_A p c^2}{(2\pi MRT)^{1/2}}$$

where c is the length of the unit cell. So

$$\begin{aligned} \text{rate} &= \frac{(6.022 \times 10^{23} \text{ mol}^{-1}) \times (24 \text{ Pa}) \times (145 \times 10^{-12} \text{ m})^2}{(2\pi \times (4.003 \times 10^{-3} \text{ kg mol}^{-1}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (100 \text{ K}))^{1/2}} \\ &= \boxed{6.6 \times 10^4 \text{ s}^{-1}} \end{aligned}$$

E28.8(b) The number of CO molecules adsorbed on the catalyst is

$$\begin{aligned} N = nN_A &= \frac{pVN_A}{RT} = \frac{(1.00 \text{ atm}) \times (4.25 \times 10^{-3} \text{ L}) \times (6.022 \times 10^{23} \text{ mol}^{-1})}{(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (273 \text{ K})} \\ &= 1.14 \times 10^{20} \end{aligned}$$

The area of the surface must be the same as that of the molecules spread into a monolayer, namely, the number of molecules times each one's effective area

$$A = Na = (1.14 \times 10^{20}) \times (0.165 \times 10^{-18} \text{ m}^2) = \boxed{18.8 \text{ m}^2}$$

E28.9(b) If the adsorption follows the Langmuir isotherm, then

$$\theta = \frac{Kp}{1 + Kp} \quad \text{so} \quad K = \frac{\theta}{p(1 - \theta)} = \frac{V/V_{\text{mon}}}{p(1 - V/V_{\text{mon}})}$$

Setting this expression at one pressure equal to that at another pressure allows solution for V_{mon}

$$\frac{V_1/V_{\text{mon}}}{p_1(1 - V_1/V_{\text{mon}})} = \frac{V_2/V_{\text{mon}}}{p_2(1 - V_2/V_{\text{mon}})} \quad \text{so} \quad \frac{p_1(V_{\text{mon}} - V_1)}{V_1} = \frac{p_2(V_{\text{mon}} - V_2)}{V_2}$$

$$V_{\text{mon}} = \frac{p_1 - p_2}{p_1/V_1 - p_2/V_2} = \frac{(52.4 - 104) \text{ kPa}}{(52.4/1.60 - 104/2.73) \text{ kPa cm}^{-3}} = \boxed{9.7 \text{ cm}^3}$$

E28.10(b) The mean lifetime of a chemisorbed molecule is comparable to its half life:

$$t_{1/2} = \tau_0 \exp\left(\frac{E_d}{RT}\right) \approx (10^{-14} \text{ s}) \exp\left(\frac{155 \times 10^3 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (500 \text{ K})}\right) = \boxed{200 \text{ s}}$$

E28.11(b) The desorption rate constant is related to the mean lifetime (half-life) by

$$t = (\ln 2)/k_d \quad \text{so} \quad k_d = (\ln 2)/t$$

The desorption rate constant is related to its Arrhenius parameters by

$$k_d = A \exp\left(\frac{-E_d}{RT}\right) \quad \text{so} \quad \ln k_d = \ln A - \frac{E_d}{RT}$$

$$\text{and } E_d = \frac{(\ln k_1 - \ln k_2)R}{T_2^{-1} - T_1^{-1}} = \frac{(\ln 1.35 - \ln 0) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1})}{(600 \text{ K})^{-1} - (1000 \text{ K})^{-1}}$$

$$E_d = \boxed{3.7 \times 10^3 \text{ J mol}^{-1}}$$

E28.12(b) The Langmuir isotherm is

$$\theta = \frac{Kp}{1 + Kp} \quad \text{so} \quad p = \frac{\theta}{K(1 - \theta)}$$

$$\text{(a)} \quad p = \frac{0.20}{(0.777 \text{ kPa}^{-1}) \times (1 - 0.20)} = \boxed{0.32 \text{ kPa}}$$

$$\text{(b)} \quad p = \frac{0.75}{(0.777 \text{ kPa}^{-1}) \times (1 - 0.75)} = \boxed{3.9 \text{ kPa}}$$

E28.13(b) The Langmuir isotherm is

$$\theta = \frac{Kp}{1 + Kp}$$

We are looking for θ , so we must first find K or m_{mon}

$$K = \frac{\theta}{p(1 - \theta)} = \frac{m/m_{\text{mon}}}{p(1 - m/m_{\text{mon}})}$$

Setting this expression at one pressure equal to that at another pressure allows solution for m_{mon}

$$\frac{m_1/m_{\text{mon}}}{p_1(1 - m_1/m_{\text{mon}})} = \frac{m_2/m_{\text{mon}}}{p_2(1 - m_2/m_{\text{mon}})} \quad \text{so} \quad \frac{p_1(m_{\text{mon}} - m_1)}{m_1} = \frac{p_2(m_{\text{mon}} - m_2)}{m_2}$$

$$m_{\text{mon}} = \frac{p_1 - p_2}{p_1/m_1 - p_2/m_2} = \frac{(36.0 - 4.0) \text{ kPa}}{(36.0/0.63 - 4.0/0.21) \text{ kPa mg}^{-1}} = 0.84 \text{ mg}$$

$$\text{So } \theta_1 = 0.63/0.84 = \boxed{0.75} \quad \text{and} \quad \theta_2 = 0.21/0.84 = \boxed{0.25}$$

E28.14(b) The mean lifetime of a chemisorbed molecule is comparable to its half-life

$$t_{1/2} = \tau_0 \exp\left(\frac{E_d}{RT}\right)$$

$$\begin{aligned} \text{(a) At 400 K: } t_{1/2} &= (0.12 \times 10^{-12} \text{ s}) \exp\left(\frac{20 \times 10^3 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (400 \text{ K})}\right) \\ &= \boxed{4.9 \times 10^{-11} \text{ s}} \end{aligned}$$

$$\begin{aligned} \text{At 800 K: } t_{1/2} &= (0.12 \times 10^{-12} \text{ s}) \exp\left(\frac{20 \times 10^3 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (800 \text{ K})}\right) \\ &= \boxed{2.4 \times 10^{-12} \text{ s}} \end{aligned}$$

$$\begin{aligned} \text{(b) At 400 K: } t_{1/2} &= (0.12 \times 10^{-12} \text{ s}) \exp\left(\frac{200 \times 10^3 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (400 \text{ K})}\right) \\ &= \boxed{1.6 \times 10^{13} \text{ s}} \end{aligned}$$

$$\begin{aligned} \text{At 800 K: } t_{1/2} &= (0.12 \times 10^{-12} \text{ s}) \exp\left(\frac{200 \times 10^3 \text{ J mol}^{-1}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (800 \text{ K})}\right) \\ &= \boxed{1.4 \text{ s}} \end{aligned}$$

E28.15(b) The Langmuir isotherm is

$$\theta = \frac{Kp}{1 + Kp} \quad \text{so} \quad p = \frac{\theta}{K(1 - \theta)}$$

For constant fractional adsorption

$$pK = \text{constant} \quad \text{so} \quad p_1 K_1 = p_2 K_2 \quad \text{and} \quad p_2 = p_1 \frac{K_1}{K_2}$$

$$\text{But } K \propto \exp\left(\frac{-\Delta_{\text{ad}}H^\ominus}{RT}\right) \quad \text{so} \quad \frac{K_1}{K_2} = \exp\left(\frac{-\Delta_{\text{ad}}H^\ominus}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right)$$

$$\begin{aligned} p_2 &= p_1 \exp\left(\frac{-\Delta_{\text{ad}}H^\ominus}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right) \\ &= (8.86 \text{ kPa}) \times \exp\left(\left(\frac{-12.2 \times 10^3 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}\right) \times \left(\frac{1}{298 \text{ K}} - \frac{1}{318 \text{ K}}\right)\right) = \boxed{6.50 \text{ kPa}} \end{aligned}$$

E28.16(b) The Langmuir isotherm would be

$$\text{(a)} \quad \theta = \frac{Kp}{1 + Kp}$$

$$\text{(b)} \quad \theta = \frac{(Kp)^{1/2}}{1 + (Kp)^{1/2}}$$

$$\text{(c)} \quad \theta = \frac{(Kp)^{1/3}}{1 + (Kp)^{1/3}}$$

A plot of θ versus p at low pressures (where the denominator is approximately 1) would show progressively weaker dependence on p for dissociation into two or three fragments.

E28.17(b) The Langmuir isotherm is

$$\theta = \frac{Kp}{1 + Kp} \quad \text{so} \quad p = \frac{\theta}{K(1 - \theta)}$$

For constant fractional adsorption

$$pK = \text{constant} \quad \text{so} \quad p_1 K_1 = p_2 K_2 \quad \text{and} \quad \frac{p_2}{p_1} = \frac{K_1}{K_2}$$

$$\text{But } K \propto \exp\left(\frac{-\Delta_{\text{ad}}H^\ominus}{RT}\right) \quad \text{so} \quad \frac{p_2}{p_1} = \exp\left(\frac{-\Delta_{\text{ad}}H^\ominus}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right)$$

$$\text{and } \Delta_{\text{ad}}H^\ominus = R\left(\frac{1}{T_1} - \frac{1}{T_2}\right)^{-1} \ln \frac{p_1}{p_2},$$

$$\begin{aligned} \Delta_{\text{ad}}H^\ominus &= (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times \left(\frac{1}{180 \text{ K}} - \frac{1}{240 \text{ K}}\right)^{-1} \times \left(\ln \frac{350 \text{ kPa}}{1.02 \times 10^3 \text{ kPa}}\right) \\ &= -6.40 \times 10^4 \text{ J mol}^{-1} = \boxed{-6.40 \text{ kJ mol}^{-1}} \end{aligned}$$

E28.18(b) The time required for a given quantity of gas to desorb is related to the activation energy for desorption by

$$t \propto \exp\left(\frac{E_{\text{d}}}{RT}\right) \quad \text{so} \quad \frac{t_1}{t_2} = \exp\left(\frac{E_{\text{d}}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right)$$

$$\text{and } E_{\text{d}} = R\left(\frac{1}{T_1} - \frac{1}{T_2}\right)^{-1} \ln \frac{t_1}{t_2}$$

$$\begin{aligned} E_{\text{d}} &= (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times \left(\frac{1}{873 \text{ K}} - \frac{1}{1012 \text{ K}}\right)^{-1} \times \left(\ln \frac{1856 \text{ s}}{8.44 \text{ s}}\right) \\ &= \boxed{2.85 \times 10^5 \text{ J mol}^{-1}} \end{aligned}$$

(a) The same desorption at 298 K would take

$$t = (1856 \text{ s}) \times \exp\left(\left(\frac{2.85 \times 10^5 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}\right) \times \left(\frac{1}{298 \text{ K}} - \frac{1}{873 \text{ K}}\right)\right) = \boxed{1.48 \times 10^{36} \text{ s}}$$

(b) The same desorption at 1500 K would take

$$\begin{aligned} t &= (8.44 \text{ s}) \times \exp\left(\left(\frac{2.85 \times 10^5 \text{ J mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}\right) \times \left(\frac{1}{1500 \text{ K}} - \frac{1}{1012 \text{ K}}\right)\right) \\ &= \boxed{1.38 \times 10^{-4} \text{ s}} \end{aligned}$$

Solutions to problems

Solutions to numerical problems

P28.2 Refer to Fig. 28.1.

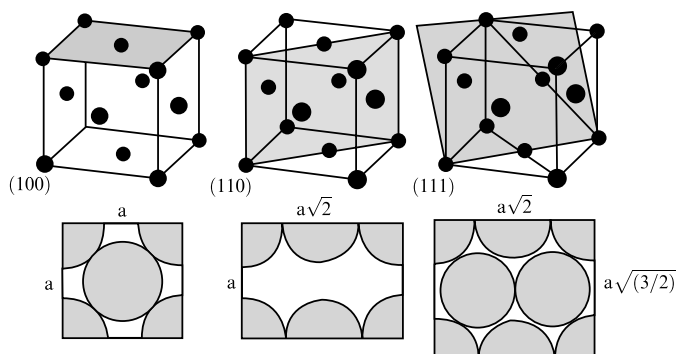


Figure 28.1

The (100) and (110) faces each expose two atoms, and the (111) face exposes four. The areas of the faces of each cell are (a) $(352 \text{ pm})^2 = 1.24 \times 10^{-15} \text{ cm}^2$, (b) $\sqrt{2} \times (352 \text{ pm})^2 = 1.75 \times 10^{-15} \text{ cm}^2$, and (c) $\sqrt{3} \times (352 \text{ pm})^2 = 2.15 \times 10^{-15} \text{ cm}^2$. The numbers of atoms exposed per square centimetre are therefore

$$(a) \quad \frac{2}{1.24 \times 10^{-15} \text{ cm}^2} = \boxed{1.61 \times 10^{15} \text{ cm}^{-2}}$$

$$(b) \quad \frac{2}{1.75 \times 10^{-15} \text{ cm}^2} = \boxed{1.14 \times 10^{15} \text{ cm}^{-2}}$$

$$(c) \quad \frac{4}{2.15 \times 10^{-15} \text{ cm}^2} = \boxed{1.86 \times 10^{15} \text{ cm}^{-2}}$$

For the collision frequencies calculated in Exercise 28.5(a), the frequency of collision per atom is calculated by dividing the values given there by the number densities just calculated. We can therefore draw up the following table

$Z/(\text{atom}^{-1} \text{ s}^{-1})$	Hydrogen		Propane	
	100 Pa	10^{-7} Torr	100 Pa	10^{-7} Torr
(100)	6.8×10^5	8.7×10^{-2}	1.4×10^5	1.9×10^{-2}
(110)	9.6×10^5	1.2×10^{-1}	2.0×10^5	2.7×10^{-2}
(111)	5.9×10^5	7.5×10^{-2}	1.2×10^5	1.7×10^{-2}

P28.4

$$\frac{V}{V_{\text{mon}}} = \frac{cz}{(1-z)\{1-(1-c)z\}} \left[28.10, \text{ BET isotherm, } z = \frac{p}{p^*} \right]$$

This rearranges to

$$\frac{z}{(1-z)V} = \frac{1}{cV_{\text{mon}}} + \frac{(c-1)z}{cV_{\text{mon}}}$$

Therefore a plot of the left-hand side against z should result in a straight line if the data obeys the

BET isotherm. We draw up the following tables

(a) 0°C, $p^* = 3222$ Torr

p/Torr	105	282	492	594	620	755	798
$10^3 z$	32.6	87.5	152.7	184.4	192.4	234.3	247.7
$\frac{10^3 z}{(1-z)(V/\text{cm}^3)}$	3.04	7.10	12.1	14.1	15.4	17.7	20.0

(b) 18°C, $p^* = 6148$ Torr

p/Torr	39.5	62.7	108	219	466	555	601	765
$10^3 z$	6.4	10.2	17.6	35.6	75.8	90.3	97.8	124.4
$\frac{10^3 z}{(1-z)(V/\text{cm}^3)}$	0.70	1.05	1.74	3.27	6.36	7.58	8.09	10.08

The points are plotted in Fig. 28.2, but we analyse the data by a least-squares procedure. The intercepts are at (a) 0.466 and (b) 0.303. Hence

$$\frac{1}{cV_{\text{mon}}} = \text{(a)} 0.466 \times 10^{-3} \text{ cm}^{-3}, \text{ (b)} 0.303 \times 10^{-3} \text{ cm}^{-3}$$

The slopes of the lines are (a) 76.10 and (b) 79.54. Hence

$$\frac{c-1}{cV_{\text{mon}}} = \text{(a)} 76.10 \times 10^{-3} \text{ cm}^{-3}, \text{ (b)} 79.54 \times 10^{-3} \text{ cm}^{-3}$$

Solving the equations gives

$$c-1 = \text{(a)} 163.\bar{3}, \text{ (b)} 262.\bar{5}$$

and hence

$$c = \text{(a)} \boxed{164}, \text{ (b)} \boxed{264} \quad V_{\text{mon}} = \text{(a)} \boxed{13.1 \text{ cm}^3}, \text{ (b)} \boxed{12.5 \text{ cm}^3}$$

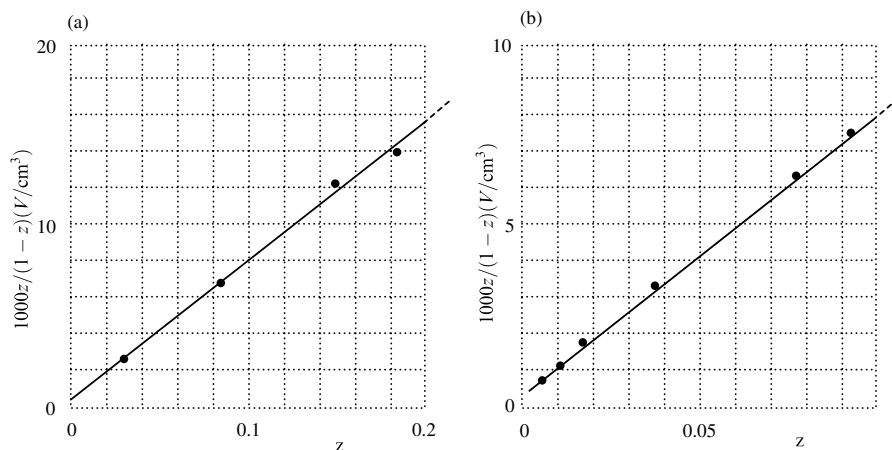


Figure 28.2

P28.7 We assume that the Langmuir isotherm applies.

$$\theta = \frac{Kp}{1 + Kp} [28.5] \quad \text{and} \quad 1 - \theta = \frac{1}{1 + Kp}$$

For a strongly adsorbed species, $Kp \gg 1$ and $1 - \theta = \frac{1}{Kp}$. Since the reaction rate is proportional to the pressure of ammonia and the fraction of sites left uncovered by the strongly adsorbed hydrogen product, we can write

$$\frac{d p_{\text{NH}_3}}{dt} = -k_c p_{\text{NH}_3} (1 - \theta) \approx -\frac{k_c p_{\text{NH}_3}}{K p_{\text{H}_2}}$$

To solve the rate law, we write

$$p_{\text{H}_2} = \frac{3}{2} \{p_{0\text{NH}_3} - p_{\text{NH}_3}\} \quad [\text{NH}_3 \rightarrow \frac{1}{2}\text{N}_2 + \frac{3}{2}\text{H}_2]$$

from which it follows that, with $p = p_{\text{NH}_3}$

$$\frac{-dp}{dt} = \frac{kp}{p_0 - p}, \quad k = \frac{2k_c}{3K}$$

This equation integrates as follows

$$\int_{p_0}^p \left(1 - \frac{p_0}{p}\right) dp = k \int_0^t dt$$

$$\text{or } \frac{p - p_0}{t} = k + \frac{p_0}{t} \ln \frac{p}{p_0}$$

$$\text{We write } F' = \frac{p_0}{t} \ln \frac{p}{p_0}, \quad G = \frac{p - p_0}{t}$$

$$\text{and obtain } G = k + F' = p_0 F$$

Hence, a plot of G against F' should give a straight line with intercept k at $F' = 0$. Alternatively, the difference $G - F'$ should be a constant, k . We draw up the following table

t/s	0	30	60	100	160	200	250
p/Torr	100	88	84	80	77	74	72
$G/(\text{Torr s}^{-1})$		-0.40	-0.27	-0.20	-0.14	-0.13	-0.11
$F'/(\text{Torr s}^{-1})$		-0.43	-0.29	-0.22	-0.16	-0.15	-0.13
$(G - F')/(\text{Torr s}^{-1})$		0.03	0.02	0.02	0.02	0.02	0.02

Thus, the data fit the rate law, and we find $k = 0.02 \text{ Torr s}^{-1}$.

P28.9 Taking the log of the isotherm gives

$$\ln c_{\text{ads}} = \ln K + (\ln c_{\text{sol}})/n$$

so a plot of $\ln c_{\text{ads}}$ versus $\ln c_{\text{sol}}$ would have a slope of $1/n_\infty$ and a y-intercept of $\ln K$. The transformed data and plot are shown in Fig. 28.3.

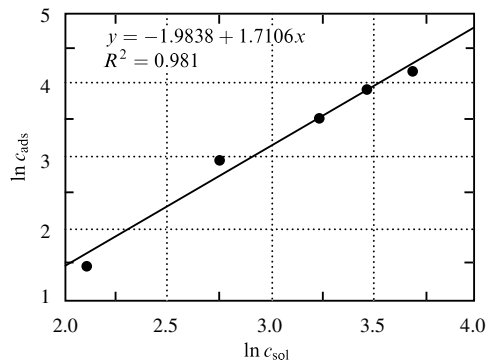


Figure 28.3

$c_{sol}/(\text{mg g}^{-1})$	8.26	15.65	25.43	31.74	40.00
$c_{ads}/(\text{mg g}^{-1})$	4.4	19.2	35.2	52.0	67.2
$\ln c_{sol}$	2.11	2.75	3.24	3.46	3.69
$\ln c_{ads}$	1.48	2.95	3.56	3.95	4.21

$$K = e^{-1.9838} \text{ mg g}^{-1} = \boxed{0.138 \text{ mg g}^{-1}} \quad \text{and} \quad n = 1/1.71 = \boxed{0.58}$$

In order to express this information in terms of fractional coverage, the amount of adsorbate corresponding to monolayer coverage must be known. This saturation point, however, has no special significance in the Freundlich isotherm (i.e. it does not correspond to any limiting case).

P28.11 The Langmuir isotherm is

$$\theta = \frac{Kp}{1 + Kp} = \frac{n}{n_{\infty}} \quad \text{so} \quad n(1 + Kp) = n_{\infty}Kp \quad \text{and} \quad \frac{p}{n} = \frac{p}{n_{\infty}} + \frac{1}{Kn_{\infty}}$$

So a plot of p/n against p should be a straight line with slope $1/n_{\infty}$ and y -intercept $1/Kn_{\infty}$. The transformed data and plot (Fig. 28.4) follow

p/kPa	31.00	38.22	53.03	76.38	101.97	130.47	165.06	182.41	205.75	219.91
$n/(\text{mol kg}^{-1})$	1.00	1.17	1.54	2.04	2.49	2.90	3.22	3.30	3.35	3.36
$\frac{p/n}{\text{kPa mol}^{-1} \text{ kg}}$	31.00	32.67	34.44	37.44	40.95	44.99	51.26	55.28	61.42	65.45

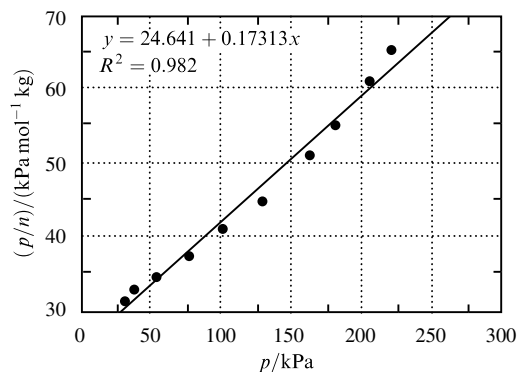


Figure 28.4

$$n_{\infty} = \frac{1}{0.17313 \text{ mol}^{-1} \text{ kg}} = \boxed{5.78 \text{ mol kg}^{-1}}$$

The y-intercept is

$$b = \frac{1}{Kn_{\infty}} \quad \text{so} \quad K = \frac{1}{bn_{\infty}} = \frac{1}{(24.641 \text{ kPa mol}^{-1} \text{ kg}) \times (5.78 \text{ mol kg}^{-1})}$$

$$K = 7.02 \times 10^{-3} \text{ kPa}^{-1} = \boxed{7.02 \text{ Pa}^{-1}}$$

P28.12 For the Langmuir adsorption isotherm we must alter eqn 5 so that it describes adsorption from solution. This can be done with the transforms

$p \rightarrow$ concentration, c

$V \rightarrow$ amount adsorbed per gram adsorbent, s

Langmuir isotherm and regression analysis

$$\frac{c}{s} = \frac{c}{s_{\infty}} + \frac{1}{Ks_{\infty}}$$

$$\frac{1}{s_{\infty}} = 0.163 \text{ g mmol}^{-1}, \quad \text{standard deviation} = 0.017 \text{ g mmol}^{-1}$$

$$\frac{1}{Ks_{\infty}} = 35.6 \text{ (mmol L}^{-1}) \times (\text{g mmol}^{-1}), \quad \text{standard deviation} = 5.9 \text{ (mmol L}^{-1}) \times (\text{g mmol}^{-1})$$

$$\boxed{R \text{ (Langmuir)} = 0.973}$$

$$K = \frac{0.163 \text{ g mmol}^{-1}}{35.6 \text{ (mmol L}^{-1}) \times (\text{g mmol}^{-1})} = 0.0046 \text{ L mmol}^{-1}$$

Freundlich isotherm and regression analysis

$$s = c_1 c^{1/c_2}$$

$$c_1 = 0.139, \quad \text{standard deviation} = 0.012$$

$$\frac{1}{c_2} = 0.539, \quad \text{standard deviation} = 0.003$$

$$\boxed{R \text{ (Freundlich)} = 0.99994}$$

Temkin isotherm and regression analysis

$$s = c_1 \ln(c_2 c)$$

$$c_1 = 1.08, \quad \text{standard deviation} = 0.14$$

$$c_2 = 0.074, \quad \text{standard deviation} = 0.023$$

$$\boxed{R \text{ (Temkin)} = 0.9590}$$

The correlation coefficients and standard deviations indicate that the $\boxed{\text{Freundlich isotherm}}$ provides the best fit of the data.

Solutions to theoretical problems

P28.17

$$\theta = \frac{Kp}{1 + Kp}, \quad \theta = \frac{V}{V_\infty}$$

$$p = \frac{\theta}{K(1 - \theta)} = \frac{V}{K(V_\infty - V)}$$

$$\frac{dp}{dV} = \frac{1}{K(V_\infty - V)} + \frac{V}{K(V_\infty - V)^2} = \frac{V_\infty}{K(V_\infty - V)^2}$$

$$\begin{aligned} d\mu' &= -\left(\frac{RT}{\sigma}\right) V d \ln p = \frac{-RT}{p\sigma} V dp \\ &= -\left(\frac{RT}{\sigma}\right) \left(\frac{K(V_\infty - V)}{V}\right) V \left(\frac{V_\infty}{K(V_\infty - V)^2}\right) dV \\ &= -\left(\frac{RT}{\sigma}\right) \left(\frac{V_\infty dV}{V_\infty - V}\right) \end{aligned}$$

Therefore, we can adopt any of several forms,

$$d\mu' = -\left(\frac{RT}{\sigma}\right) \frac{V_\infty}{V_\infty - V} dV = -\left(\frac{RT}{\sigma}\right) \frac{1}{1 - \theta} dV = -\left(\frac{RTV_\infty}{\sigma}\right) \frac{1}{1 - \theta} d\theta = \boxed{\frac{RTV_\infty}{\sigma} d \ln(1 - \theta)}$$

P28.18

For the Langmuir and BET isotherm tests we draw up the following table (using $p^* = 200 \text{ kPa} = 1500 \text{ Torr}$) [Examples 28.1 and 28.3]

p/Torr	100	200	300	400	500	600
$\frac{p}{V}/(\text{Torr cm}^{-3})$	5.59	6.06	6.38	6.58	6.64	6.57
$10^3 z$	67	133	200	267	333	400
$\frac{10^3 z}{(1 - z)(V/\text{cm}^3)}$	4.01	4.66	5.32	5.98	6.64	7.30

$\frac{p}{V}$ is plotted against p in Fig. 28.5(a), and $\frac{10^3 z}{(1 - z)V}$ is plotted against z in Fig. 28.5(b).

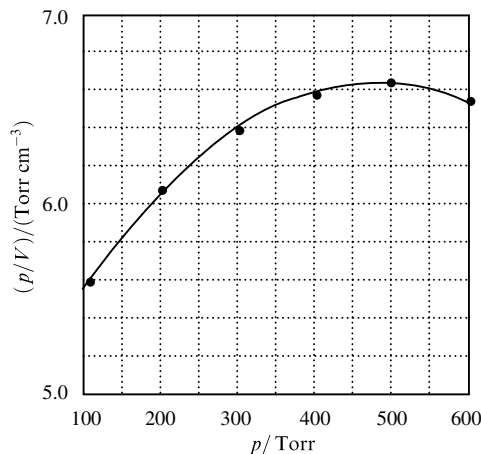


Figure 28.5(a)

We see that the BET isotherm is a much better representation of the data than the Langmuir isotherm. The intercept in Fig. 28.5(b) is at 3.33×10^{-3} , and so $\frac{1}{cV_{\text{mon}}} = 3.33 \times 10^{-3} \text{ cm}^{-3}$. The slope of the graph is 9.93, and so

$$\frac{c-1}{cV_{\text{mon}}} = 9.93 \times 10^{-3} \text{ cm}^{-3}$$

Therefore, $c-1 = 2.98$, and hence $c = 3.98$, $V_{\text{mon}} = 75.4 \text{ cm}^3$

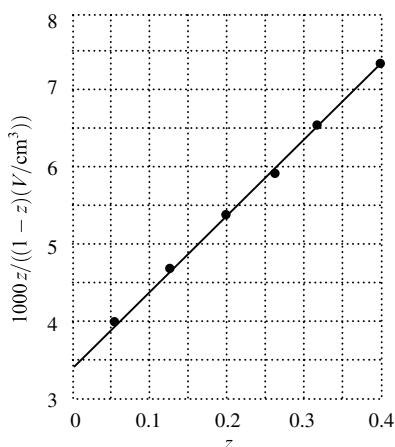


Figure 28.5(b)

P28.22 (a) K unit: $(\text{g}_R \text{ L}^{-1})^{-1}$ [g_R = mass (grams) of rubber]

$$K_F \text{ unit: } (\text{mg})^{(1-1/n)} \text{g}_R^{-1} \text{ L}^{-1/n}$$

$$K_L \text{ unit: } (\text{mg L}^{-1})^{-1}$$

$$M \text{ unit: } (\text{mg g}_R^{-1})$$

(b) Linear sorption isotherm

$$q = K c_{\text{eq}}$$

$K = \frac{q}{c_{\text{eq}}}$ so K is best determined as an average of all q/c_{eq} data pairs.

$$\boxed{K_{\text{av}} = 0.126(\text{g}_R \text{ L}^{-1})^{-1}}, \quad \text{standard deviation} = 0.041(\text{g}_R \text{ L}^{-1})^{-1}$$

$$95 \text{ per cent confidence limit: } (0.083 - 0.169)(\text{g}_R \text{ L}^{-1})^{-1}$$

If this is done as a linear regression, the result is significantly different.

$$K (\text{linear}) = 0.0813(\text{g}_R \text{ L}^{-1})^{-1}, \quad \text{standard deviation} = 0.0092(\text{g}_R \text{ L}^{-1})^{-1}$$

$$\boxed{R (\text{linear}) = 0.9612}$$

Freundlich sorption isotherm: $q = K_F c_{\text{eq}}^{1/n}$, using a power regression analysis, we find that

$$\boxed{K_F = 0.164}, \quad \text{standard deviation} = 0.317$$

$$\frac{1}{n} = 0.877, \quad \text{standard deviation} = 0.113; \quad n = 1.14$$

$$R (\text{Freundlich}) = 0.9682$$

Langmuir sorption isotherm

$$q = \frac{K_L M c_{\text{eq}}}{1 + K_L c_{\text{eq}}}$$

$$\frac{1}{q} = \left(\frac{1}{K_L M} \right) \left(\frac{1}{c_{\text{eq}}} \right) + \frac{1}{M}$$

$$\frac{1}{K_L M} = 8.089 \text{ g}_R \text{ L}^{-1}, \quad \text{standard deviation} = 1.031; \quad K_L = -0.00053(\text{g}_R \text{ L}^{-1})^{-1}$$

$$\frac{1}{M} = -0.0043 \text{ g}_R \text{ mg}^{-1}, \quad \text{standard deviation} = 0.1985; \quad M = -233 \text{ mg g}_R^{-1}$$

$$R (\text{Langmuir}) = 0.9690$$

All regression fits have nearly the same correlation coefficient so that cannot be used to determine which is the best fit. However, the Langmuir isotherm give a negative value for K_L . If K_L is to represent an equilibrium constant, which must be positive, the Langmuir description must be rejected. The standard deviation of the slope of the Freundlich isotherm is twice as large as the slope itself. This would seem to be unfavourable. Thus, the linear description seems to be the best, but not excellent choice. However, the Freundlich isotherm is usually preferred for this kind of system, even though that choice is not supported by the data in this case.

$$(c) \quad \frac{q_{\text{rubber}}}{q_{\text{charcoal}}} = \frac{0.164 c_{\text{eq}}^{1.14}}{c_{\text{eq}}^{1.6}} = 0.164 c_{\text{eq}}^{-0.46}$$

The sorption efficiency of ground rubber is much less than that of activated charcoal and drops significantly with increasing concentration. The only advantage of the ground rubber is its exceedingly low cost relative to activated charcoal, which might convert to a lower cost per gram of contaminant adsorbed.