

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.

Cracking and reforming

Many of the small organic molecules used in the preparation of all kinds of chemical products come from oil. These small building blocks of polymers, perfumes, and petrochemicals in general, are usually cut from the long-chain hydrocarbons drawn from the Earth as petroleum. The catalytically induced fragmentation of the long-chain hydrocarbons is called **cracking**, and is often brought about on silica-alumina catalysts. These catalysts act by forming unstable carbocations, which dissociate and rearrange to more highly branched isomers. These branched isomers burn more smoothly and efficiently in internal combustion engines, and are used to produce higher octane fuels.

Catalytic **reforming** uses a dual-function catalyst, such as a dispersion of platinum and acidic alumina. The platinum provides the metal function, and brings about dehydrogenation and hydrogenation. The alumina provides the acidic function, being able to form carbocations from alkenes. The sequence of events in catalytic reforming shows up very clearly the complications that must be unravelled if a reaction as important as this is to be understood and improved. The first step is the attachment of the long-chain hydrocarbon by chemisorption to the platinum. In this process first one and then a second H atom is lost, and an alkene is formed. The alkene migrates to a Brønsted acid site, where it accepts a proton and attaches to the surface as a carbocation. This carbocation can undergo several different reactions. It can break into two, isomerize into a more highly branched form, or undergo varieties of ring-closure. Then it loses a proton, escapes from the surface, and migrates (possibly through the gas) as an alkene to a metal part of the catalyst where it is hydrogenated. We end up with a rich selection of smaller molecules that can be withdrawn, fractionated, and then used as raw materials for other products.

CHECK LIST OF KEY IDEAS

- 1 The concept of **surface tension** (Section 28.1).
- 2 The **Laplace equation** (eqn 3) for the difference in pressure across a curved surface and the **Kelvin equation** (eqn 4) for the effect of curvature on the vapour pressure of a substance.
- 3 The role of **nucleation** in the formation of condensed phases (Section 28.2).
- 4 The phenomenon of **capillary action** (Section 28.3) and the height to which a liquid can rise in a capillary tube (eqn 6), including the role of the **contact angle** (eqn 7).
- 5 The definition of **surface excess** (eqn 8) and the **Gibbs surface-tension equation** (eqn 9) between the change in surface tension and the surface excess.
- 6 The experimental study of surface films in terms

of **Langmuir-Blodgett films** and the use of a **surface film balance** (Section 28.5) to determine **surface pressure**.

- 7 The classification and preparation of **colloids** (Section 28.6) and the origin of their stabilities in terms of the **electric double layer** (Section 28.7).
- 8 The formation of **micelles** (Section 28.7).
- 9 The **DVLO theory** of the stability of lyophobic dispersions (Section 28.7, eqns 11-13).
- 10 The role of **defects** in the growth of surfaces and the self-propagating property of a **screw dislocation** (Section 28.8).
- 11 The importance of **high-vacuum techniques** when studying surfaces (Section 28.9).
- 12 The study of surface composition using **photo-emission spectroscopy**, **electron energy-loss spectroscopy**, and **Auger electron spectroscopy** (Section 28.9).
- 13 The composition of surfaces from **low-energy electron diffraction**, **field emission microscopy**, and **field ionization microscopy** (Section 28.9).
- 14 The use of **scanning-tunnelling microscopy** to show details of surface structure (Section 28.9).
- 15 The definition of **fractional coverage** (eqn 15) and its determination.
- 16 The processes of **physisorption** and **chemisorption** and the experimental distinctions between them (Section 28.10).
- 17 The derivation of the **Langmuir isotherm** (eqn 16) and its modification when the adsorbate dissociates (eqn 17).
- 18 The determination of the **isosteric enthalpy of adsorption** from the adsorption isotherm (eqn 18 and Example 28.4).
- 19 The **Brunauer-Emmett-Teller isotherm** when multilayer adsorption may occur (eqn 19).
- 20 The **Temkin isotherm** (eqn 22) and the **Freundlich isotherm** (eqn 23).
- 21 The **rate of adsorption** in terms of the **sticking probability** (Section 28.12 and eqn 24).
- 22 The **rate of desorption** in terms of the **desorption activation energy** (eqn 25) and the technique of **flash desorption spectroscopy** (Section 28.12).
- 23 The **mobility** of adsorbates on surfaces (Section 28.12).
- 24 The **Eley-Rideal mechanism** and the **Langmuir-Hinshelwood mechanism** of heterogeneous catalysis (Section 28.13).
- 25 The significance of a **volcano curve** and examples of catalysis (Section 28.14).

EXERCISES

- 28.1. The surface tensions of aqueous salt solutions are normally greater than that of water itself. Does the salt accumulate at the surface?
- 28.2. How many molecules of cetanol (of cross-sectional area $2.58 \times 10^{-19} \text{ m}^2$) can be adsorbed on the surface of a spherical drop of dodecane of radius 17.8 nm?
- 28.3. Calculate the vapour pressure of a spherical droplet of water of radius 10 nm at 20°C. The vapour pressure of bulk water at that temperature is 2.3 kPa and its density is 0.9982 g cm^{-3} .
- 28.4. The contact angle for water on clean glass is close to zero. Calculate the surface tension of water at 20°C given that at that temperature water climbs to a height of 4.96 cm in a clean glass capillary tube of internal radius 0.300 mm. The density of water at 20°C is 998.2 kg m^{-3} .
- 28.5. Calculate the pressure differential of water across the surface of a spherical droplet of radius 200 nm at 20°C.
- 28.6. The values of γ_{ig} and γ_{iw} are 27.5 and 8.5 mN m^{-1} , respectively, for octanol (l) and water (w) at 20°C; g denotes air. Will octanol spread on a water surface?
- 28.7. Calculate the surface excess of l-aminobutanoic acid in a 0.10 M aqueous solution at 20°C given that $d\gamma/d(\ln c) = -40 \mu\text{N m}^{-1}$. Convert the answer to the number of molecules per square metre, and calculate the area occupied by a molecule.
- 28.8. Calculate the change in Gibbs energy when a

spherical droplet of mercury of diameter 1.0 mm is distorted to an oblate spheroid of double the surface area at 20°C.

28.9. Calculate the frequency of molecular collision per square centimetre of surface in a vessel containing (a) hydrogen, (b) propane at 25°C when the pressure is (i) 100 Pa, (ii) 0.10 μ Torr.

28.10. What pressure of argon gas is required to produce a collision rate of $4.5 \times 10^{20} \text{ s}^{-1}$ at 425 K on a circular surface of diameter 1.5 mm?

28.11. Calculate the average rate at which He atoms strike a Cu atom in a surface formed by exposing a (100) plane in metallic copper to helium gas at 80 K and a pressure of 35 Pa. Crystals of copper are face-centred cubic with a cell edge of 361 pm.

28.12. A monolayer of N_2 molecules is adsorbed on the surface of 1.00 g of an Fe/Al₂O₃ catalyst at 77 K, the boiling point of liquid nitrogen. Upon warming, the nitrogen occupies 2.86 cm³ at 0°C and 760 Torr. What is the surface area of the catalyst? The effective area of an N_2 molecule is 0.167 nm².

28.13. The volume of oxygen gas at 0°C and 101 kPa adsorbed on the surface of 1.00 g of a sample of silica at 0°C was 0.284 cm³ at 142.4 Torr and 1.430 cm³ at 760 Torr O₂. What is the value of V_{mon} ?

28.14. The enthalpy of adsorption of CO on a surface is found to be -120 kJ mol^{-1} . Is the adsorption physisorption or chemisorption? Estimate the mean lifetime of a CO molecule on the surface at 400 K.

28.15. The half-life for which an oxygen atom remains adsorbed to a tungsten surface is 0.36 s at 2548 K and 3.49 s at 2362 K. Find the activation energy for desorption. What is the pre-exponential factor for these tightly chemisorbed atoms?

28.16. The chemisorption of hydrogen on manganese is activated, but only weakly so. Careful measurements have shown that it proceeds 35 per cent faster at 1000 K than at 600 K. What is the activation energy for chemisorption?

28.17. The adsorption of a gas is described by the Langmuir isotherm with $K = 0.85 \text{ kPa}^{-1}$ at 25°C. Calculate the pressure at which the fractional surface coverage is (a) 0.15, (b) 0.95.

28.18. A certain solid sample adsorbs 0.44 mg of CO when the pressure of the gas is 26.0 kPa and the temperature is 300 K. The mass of gas adsorbed when the pressure is 3.0 kPa and the temperature is 300 K is 0.19 mg. The Langmuir isotherm is known to describe the adsorption. Find the fractional coverage of the surface at the two pressures.

28.19. What half-life would an H atom have on a surface at 298 K if its desorption activation energy were (a) 15 kJ mol⁻¹, (b) 150 kJ mol⁻¹? Take $\tau_0 = 0.10 \text{ ps}$. For how long on average would the same atoms remain at 1000 K?

28.20. A solid in contact with a gas at 12 kPa and 25°C adsorbs 2.5 mg of the gas and obeys the Langmuir isotherm. The enthalpy change when 1.00 mmol of the adsorbed gas is desorbed is +10.2 J. What is the equilibrium pressure for the adsorption of 2.5 mg of gas at 40°C?

28.21. Hydrogen iodide is very strongly adsorbed on gold but only slightly adsorbed on platinum. Assume the adsorption follows the Langmuir isotherm and predict the order of the HI decomposition reaction $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$ on each of the two metal surfaces.

28.22. Suppose it is known that ozone adsorbs on a particular surface in accord with a Langmuir isotherm. How could you use the pressure dependence of the fractional coverage to distinguish between adsorption (a) without dissociation, (b) with dissociation into O + O₂, (c) with dissociation into O + O + O?

28.23. Nitrogen gas adsorbed on charcoal to the extent of 0.921 cm³ g⁻¹ at 490 kPa and 190 K, but at 250 K the same amount of adsorption was achieved only when the pressure was increased to 3.2 MPa. What is the molar enthalpy of adsorption of nitrogen on charcoal?

28.24. In an experiment on the adsorption of oxygen on tungsten it was found that the same volume of oxygen was desorbed in 27 min at 1856 K, 2 min at 1978 K, and 0.3 min at 2070 K. What is the activation energy of desorption? How long would it take for the same amount to desorb at (a) 298 K, (b) 3000 K?

28.25. Ammonia was introduced into a bulb at a pressure of 27 kPa. At 856°C it was found that a tungsten catalyst brought about a pressure change of 8 kPa in 500 s, and 15 kPa in 1000 s. What is the order of the catalysed decomposition? Account for the result.

surfactant were measured at 20°C, with the following results:

$[A]/(\text{mol L}^{-1})$	0	0.10	0.20	0.30	0.40	0.50
$\gamma/(\text{mN m}^{-1})$	72.8	70.2	67.7	65.1	62.8	59.8

PROBLEMS

Numerical problems

28.1. The surface pressure can be expressed as $\pi\sigma = n(\sigma)RT$, where σ is the area of the surface. The surface tensions of a series of aqueous solutions of a

Calculate the surface excess concentration and the surface pressure exerted by the surfactant, and investigate whether the equation quoted is satisfied.

28.2. The surface tensions of solutions of salts in water at molar concentration c can be expressed in the form $\gamma = \gamma^* + (c/\text{mol L}^{-1})\Delta\gamma$. The values of $\Delta\gamma$ at 20°C and near $c = 1 \text{ mol L}^{-1}$ are as follows: $\Delta\gamma/(\text{mN m}^{-1}) = 1.4$ (KCl), 1.64 (NaCl), 2.7 (Na₂CO₃). Calculate the surface excess concentrations when the bulk concentrations are 1.0 mol L⁻¹.

28.3. The concentration and corresponding surface tensions of aqueous solution of butanol were measured at 20°C with the following results:

$c/(\text{mol L}^{-1})$	0.0264	0.0536	0.1050	0.2110	0.4330
$\gamma/(\text{mN m}^{-1})$	68.00	63.14	56.31	48.08	38.87

Determine the area occupied per molecule.

28.4. The surface tensions of aqueous solution of NH₄NO₃ have been measured at 20°C and have been found to fit the equation $\gamma/(\text{mN m}^{-1}) = 72.75 + c/(\text{mol L}^{-1})$. Calculate the surface excess for a solution of concentration 1.00 mol L⁻¹.

28.5. Nickel is face-centred cubic with a unit cell of side 352 pm. What is the number of atoms per square centimetre exposed on a surface formed by (a) (100), (b) (110), (c) (111) planes? Calculate the frequency of molecular collisions per surface atom in a vessel containing (1) hydrogen, (2) propane at 25°C when the pressure is (i) 100 Pa, (ii) 0.10 μ Torr.

28.6. The data below are for the chemisorption of hydrogen on copper powder at 25°C. Confirm that they fit the Langmuir isotherm at low coverages. Then find the value of K for the adsorption equilibrium and the adsorption volume corresponding to complete coverage.

p/Torr	0.19	0.97	1.90	4.05	7.50	11.95
V/cm^3	0.042	0.163	0.221	0.321	0.411	0.471

28.7. The data for the adsorption of ammonia on barium fluoride are reported below. Confirm that they fit a BET isotherm and find values of c and V_{mon} .
(a) $\theta = 0^\circ\text{C}$, $p^* = 3222 \text{ Torr}$:

p/Torr	105	282	492	594	620	755	798
V/cm^3	11.1	13.5	14.9	16.0	15.5	17.3	16.5

(b) $\theta = 18.6^\circ\text{C}$, $p^* = 6148 \text{ Torr}$:

p/Torr	39.5	62.7	108	219	466	555	601	765
V/cm^3	9.2	9.8	10.3	11.3	12.9	13.1	13.4	14.1

28.8. Carbon monoxide adsorbs on mica, and the data for 90 K are given below. Decide whether the Langmuir or the Freundlich isotherm is a better representation of the system. What is the value of K ? Given that the total

sample area is $6.2 \times 10^3 \text{ cm}^2$, calculate the area occupied by each adsorbed molecule.

p/Torr	100	200	300	400	500	600
V/cm^3	0.130	0.130	0.162	0.166	0.173	0.180

What volume of carbon monoxide would be adsorbed by the mica 90 K when the pressure is 1.00 atm?

28.9. The following data have been obtained for the adsorption of H₂ on the surface of 1.00 g of copper at 0°C. The volume of H₂ below is the volume that the gas would occupy at STP (0°C and 1 atm).

p/atm	0.050	0.100	0.150	0.200	0.250
V/mL	1.22	1.33	1.31	1.36	1.40

Determine the volume of H₂ necessary to form a monolayer and estimate the surface area of the copper sample. The density of liquid hydrogen is 0.0708 g cm⁻³.

28.10. The designers of a new industrial plant wanted to use a catalyst code-named CR-1 in a step involving the fluorination of butadiene. As a first step in the investigation they determined the form of the adsorption isotherm. The volume of butadiene adsorbed per gram of CR-1 at 15°C varied with pressure as given below. Is the Langmuir isotherm suitable over this pressure range?

p/Torr	100	200	300	400	500	600
V/cm^3	17.9	33.0	47.0	60.8	75.3	91.3

Investigate whether the BET isotherm gives a better description of the adsorption of butadiene on CR-1. At 15°C, p^* (butadiene) = 200 kPa. Find V_{mon} and c .

28.11. The adsorption of solutes on solids from liquids often follows a Freundlich isotherm. Check the applicability of this isotherm to the following data for the adsorption of acetic acid on charcoal at 25°C and find the value of the parameters c_1 and c_2 .

$[\text{acid}]/(\text{mol L}^{-1})$	0.05	0.10	0.50	1.0	1.5
w_s/g	0.04	0.06	0.12	0.16	0.19

w_s is the mass adsorbed per unit mass of charcoal.

28.12. In some catalytic reactions the products may adsorb more strongly than the reacting gas. This is the case, for instance, in the catalytic decomposition of ammonia on platinum at 1000°C. As a first step in examining the kinetics of this type of process, show that the rate of ammonia decomposition should follow

$$\frac{dp(\text{NH}_3)}{dt} = -k_c \frac{p(\text{NH}_3)}{p(\text{H}_2)}$$

in the limit of very strong adsorption of hydrogen. Start by showing that when a gas J adsorbs very strongly, and its pressure is $p(\text{J})$, that the fraction of uncovered sites is approximately $1/Kp(\text{J})$. Solve the rate equation for the

catalytic decomposition of NH_3 on platinum and show that a plot of $F(t) = (1/t) \ln(p/p_0)$ against $G(t) = (p - p_0)/t$, where p is the pressure of ammonia, should give a straight line from which k_c can be determined. Check the rate law on the basis of the data below, and find k_c for the reaction.

t/s	0	30	60	100	160	200	250
p/Torr	100	88	84	80	77	74	72

Theoretical problems

28.13. The deposition of atoms and ions on a surface depends on their ability to stick, and therefore on the energy changes that occur. As an illustration, consider a two-dimensional square lattice of univalent positive and negative ions separated by 200 pm, and consider a cation approaching the upper terrace of this array from the top of the page. Calculate, by direct summation, its Coulombic interaction when it is in an empty lattice point directly above an anion. Now consider a high cliff-like step in the same lattice, and let the approaching ion go into the corner formed by the step and the terrace. Calculate the Coulombic energy for this position, and decide on the likely settling point for a deposited cation.

28.14. Although the attractive van der Waals interaction between individual molecules varies as R^{-6} , the interaction of a molecule with a nearby solid (a homogeneous collection of molecules) varies as R^{-3} , where R is its vertical distance above the surface. Confirm this assertion.

Calculate the interaction energy between an Ar atom and the surface of solid argon on the basis of a Lennard-Jones (6, 12)-potential. Estimate the equilibrium distance of an atom above the surface.

28.15. Show from the Gibbs surface tension equation that, if the surface excess is proportional to the concentration, then the surface phase satisfies the equation of state of a two-dimensional perfect gas.

28.16. Use the Gibbs adsorption isotherm (another name for eqn 9), to show that the volume adsorbed per unit area of solid, V_a/σ , is related to the pressure of the gas by $V_a = -(\sigma/RT)(d\mu/d \ln p)$, where μ is the chemical potential of the adsorbed gas.

28.17. If the dependence of the chemical potential of the gas on the extent of surface coverage is known, the Gibbs adsorption isotherm, eqn 9, can be integrated to give a relation between V_a and p , as in a normal adsorption isotherm. For instance, suppose that the change in the chemical potential of a gas when it adsorbs is of the form $d\mu = -c_2(RT/\sigma) dV_a$, where c_2 is a constant of proportionality: show that the Gibbs isotherm leads to the Freundlich isotherm in this case.

28.18. Finally we come full circle and return to the Langmuir isotherm. Find the form of $d\mu$ that, when inserted in the Gibbs adsorption isotherm, leads to the Langmuir isotherm.

Dynamic electrochemistry

Processes at electrodes

- 29.1 The electrical double layer
- 29.2 The rate of charge transfer
- 29.3 Polarization

Electrochemical processes

- 29.4 Electrolysis
- 29.5 The characteristics of working cells
- 29.6 Fuel cells and secondary cells

Corrosion

- 29.7 The rate of corrosion
- 29.8 The inhibition of corrosion

Check list of key ideas

Exercises

Problems

In this final chapter of the text we examine one more example of chemical change, that of the transfer of electrons at electrodes. The approach we adopt is largely phenomenological and draws on the thermodynamic language inspired by activated complex theory. First, a model of a solution-electrode interface is constructed, and that model is used to derive a relation, the Butler-Volmer equation, between the current density at the electrode and the overpotential. The latter is the difference between the electrode potential when a current is flowing and when it is not. We shall see that there is a characteristic relation between the current and the overpotential at an electrode, which can be used to identify the species in solution. Moreover, the variation of current with overpotential can be used to infer details of the electron-transfer mechanism responsible for the redox process at the electrode. The Butler-Volmer equation can also be used to analyse the behaviour of working cells and to demonstrate how their potentials differ from the zero-current value when they are in use. Finally, the same approach can be used to analyse the kinetics of reactions that are responsible for corrosion, and point the way to methods of decreasing its rate.

The economic consequences of electrochemistry are almost incalculable. Most of the modern methods of generating electricity are inefficient, and the development of fuel cells could revolutionize our production and deployment of energy. Today we produce energy inefficiently to produce goods that then decay by corrosion. Each step of this wasteful sequence could be improved by discovering more about the kinetics of electrochemical processes. Similarly, the emerging techniques of organic and inorganic electrosynthesis, where an electrode is an active component of an industrial process, depend on a detailed knowledge of the factors affecting their rates. One example is from nylon production, in which adiponitrile is synthesized commercially by the electrolytic reductive coupling (hydrodimerization) of acrylonitrile.