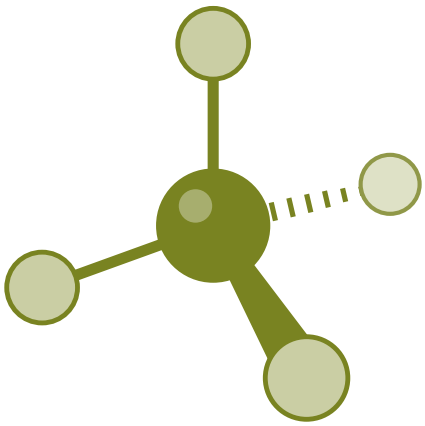
GENERAL CHEMISTRY

PROBLEM BOOK

SAMPLE PAGES

16 chapters · 188 problems · step-by-step solutions



Ertan Sinan Şahin

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How to use this book

- Each chapter opens with a reminder box summarizing the definitions and formulas the problems rely on.
- Difficulty: ★☆☆ basic ★★☆ intermediate ★★★ advanced. Each chapter has a few multiple-choice concept questions; its last problem is an exam-style mixed problem combining several topics.
- The dotted area below each problem is for your own work. Solve first; if stuck, go back to the reminder box and the lecture notes, and look at the solution last.
- All solutions are at the end of the book. The Solution → link next to a problem takes you to its solution, and ← Problem takes you back. Short answers are in the **ANSWER** box.
- **Data:** Atomic weights, constants, and other data are in the appendices; data not there are given in the problem.
- **Chemistry I and Chemistry II:** General chemistry is a one-semester course in most departments, but its scope varies from school to school. Chapters 1–11 are marked **Chemistry I** and Chapters 12–16 **Chemistry II**. If your course covers only the Chemistry I topics, the first eleven chapters are enough; if it extends to equilibrium, acids and bases, or electrochemistry, study the relevant Chemistry II chapters as well. For a two-semester sequence, the book covers both courses.
- **Midterm and final:** Choose the chapters according to your own syllabus. Schools that teach thermochemistry after atomic structure can study Chapter 5 after Chapter 7.

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Page numbers refer to the full book. Chapters in color are in this sample; click to go there.

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CHAPTER 4

GASES

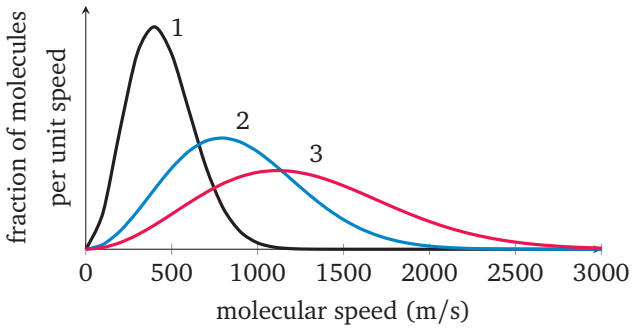
ideal gas equation	$PV = nRT$	root-mean-square speed	$u_{\text{rms}} = \sqrt{\dfrac{3RT}{M}}$
combined gas law	$\dfrac{P_1V_1}{n_1T_1} = \dfrac{P_2V_2}{n_2T_2}$	most probable speed	$u_{\text{mp}} = \sqrt{\dfrac{2RT}{M}}$
density	$d = \dfrac{PM}{RT}$	Graham's law	$\dfrac{r_1}{r_2} = \sqrt{\dfrac{M_2}{M_1}}$
Dalton's law	$P_{\text{tot}} = \sum P_i, \quad P_i = x_i P_{\text{tot}}$	van der Waals	$\left(P + \dfrac{an^2}{V^2}\right)(V - nb) = nRT$

In the gas laws the temperature is always in kelvins: $T = t + 273.15$. In the speed relations $R = 8.314\ \text{J/(mol·K)}$ and M is in kg/mol. The average translational kinetic energy of one mole of gas is $\frac{3}{2}RT$; it depends only on the temperature. Pressure units: 1 atm = 760 mmHg = 101.325 kPa, 1 bar = 100 kPa; $R = 0.08206\ \text{L·atm/(mol·K)} = 0.08314\ \text{L·bar/(mol·K)}$.

Kinetic-molecular theory, effusion, and real gases

4.11 ★★☆ Solution →

The figure shows the molecular speed distributions of three gas samples: O_2 at 300 K, O_2 at 1200 K, and He at 300 K. The areas under the curves are equal.



To which samples do curves 1, 2, and 3 belong, respectively?

A) He (300 K); O_2 (1200 K); O_2 (300 K)

B) O_2 (300 K); He (300 K); O_2 (1200 K)

C) O_2 (300 K); O_2 (1200 K); He (300 K)

D) O_2 (1200 K); O_2 (300 K); He (300 K)

E) He (300 K); O_2 (300 K); O_2 (1200 K)

Mixed problems

4.14 ★★★ Solution →

A rigid 4.00 L container holds a mixture of hydrogen and ethylene (C_2H_4) at 25 °C; the total pressure is 1.200 atm. On the catalyst in the container the reaction

$$C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$$

proceeds until the limiting reactant is used up; when the temperature returns to 25 °C, the pressure is measured as 0.750 atm.

a. Show that the pressure drop equals the initial partial pressure of the limiting reactant. Find the two possible compositions (partial pressures) of the initial mixture.

b. The density of the initial mixture is 0.578 g/L. Which composition is correct? Find the initial mole fractions.

c. Find the partial pressures of the gases in the container after the reaction and the mass of ethane formed.

d. Find the ratio of the root-mean-square speeds of the H_2 and C_2H_6 molecules in the final mixture.

CHAPTER 8

CHEMICAL BONDING I: LEWIS STRUCTURES AND MOLECULAR GEOMETRY

total valence electrons	$N_e = \sum V - q$	percent ionic character	$100\left(1 - e^{-(\Delta\chi)^2/4}\right)$
formal charge	$\mathrm{FC} = V - L - \frac{1}{2}B$	debye	$1\ \mathrm{D} = 3.336 \times 10^{-30}\ \mathrm{C{\cdot}m}$
sum of formal charges	$\sum \mathrm{FC} = q$	polar molecule	$\sum \vec{\mu}_{\mathrm{bond}} \neq 0$
electronegativity difference	$\Delta\chi = \lvert\chi_A - \chi_B\rvert$	bond order	single 1, double 2, triple 3
dipole moment	$\mu = Q\,r$	from bond enthalpies	$\Delta H \approx \sum D_{\mathrm{broken}} - \sum D_{\mathrm{formed}}$
bond type (approximate limits)	$\Delta\chi \lesssim 0.4$: nonpolar covalent; 0.4–1.7: polar covalent; $\gtrsim 1.7$: ionic		

Groups	Electron-group geometry	Ideal angle	Molecular geometry
2	linear	180°	AX_2 linear
3	trigonal planar	120°	AX_3 trigonal planar; AX_2E bent (angular)
4	tetrahedral	109.5°	AX_4 tetrahedral; AX_3E trigonal pyramidal; AX_2E_2 bent
5	trigonal bipyramidal	90°, 120°	AX_5 trigonal bipyramidal; AX_4E seesaw; AX_3E_2 T-shaped; AX_2E_3 linear
6	octahedral	90°	AX_6 octahedral; AX_5E square pyramidal; AX_4E_2 square planar

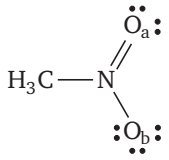
Electronegativity (Pauling): H 2.20, Li 0.98, B 2.04, C 2.55, N 3.04, O 3.44, F 3.98, Na 0.93, Mg 1.31, Al 1.61, Si 1.90, P 2.19, S 2.58, Cl 3.16, K 0.82, Ca 1.00, As 2.18, Br 2.96, Kr 3.00, I 2.66

In the formal charge, V is the number of valence electrons of the atom, L the number of nonbonding (lone-pair) electrons, and B the number of bonding electrons; q is the charge of the species (0 for a molecule). In valence-shell electron-pair repulsion (VSEPR) theory (AX_mE_n), A is the central atom, X an atom bonded to the central atom, and E a lone pair on the central atom; a double or triple bond counts as one electron group. Lone pairs take up more space than bonding pairs and make the bond angles smaller than the ideal values; in structures with five electron groups the lone pairs occupy equatorial positions. In geometry drawings a wedged bond points out of the page toward the reader and a dashed bond points behind the page; lone pairs on terminal atoms are not shown in geometry drawings. Dipole arrows use the chemistry convention: the crossed tail is at the partially positive (δ^+) end and the arrowhead at the partially negative (δ^-) end. Bond enthalpies (bond energies) are average values for species in the gas phase and are given in the problem.

Lewis structures and formal charge

8.3 ★☆☆ Solution →

Nitromethane (CH_3NO_2) is used as a fuel in racing engines. A Lewis structure of the molecule is given in the figure (formal charges are not shown).



What are the formal charges of the N, O_a, and O_b atoms, respectively?

A) 0, 0, 0 **B)** +1, 0, −1 **C)** +3, −2, −2 **D)** −3, −2, −2 **E)** +1, +2, +2

VSEPR theory and molecular geometry

8.9 ★★☆ Solution →

Four gases used in semiconductor manufacturing are phosphine PH_3 for n-type doping of silicon, H_2Se for selenization of thin-film solar cells, dichlorosilane SiH_2Cl_2 (central atom Si) for epitaxial silicon growth, and WF_6 (W in group 6, with 6 valence electrons) for tungsten deposition.

a. Find the total number of valence electrons of each molecule, draw its Lewis structure, and classify its central atom with the AX_mE_n notation.

b. Name the electron-group geometry and the molecular geometry of each molecule; draw the three-dimensional geometries with wedges and dashes.

c. Write the ideal values of the H–P–H, H–Se–H, and adjacent F–W–F bond angles. Which of them deviate from the ideal value, in which direction, and why? In which is the larger deviation expected? Why are the bond angles in the SiH_2Cl_2 molecule not exactly 109.5° even though there is no lone pair?

CHAPTER 16

ELECTROCHEMISTRY

cell potential $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$

free energy $\Delta G = -nFE, \quad \Delta G^\circ = -nFE^\circ_{\text{cell}}$

equilibrium constant $\ln K = \dfrac{nFE^\circ_{\text{cell}}}{RT}$

at 25 °C $\log K = \dfrac{nE^\circ_{\text{cell}}}{0.05916\,\text{V}}$

Nernst (Q: reaction quotient) $E = E^\circ - \dfrac{RT}{nF}\ln Q$

Nernst (25 °C) $E = E^\circ - \dfrac{0.05916\,\text{V}}{n}\log Q$

charge Q and moles of electrons

$Q = It, \quad n_e = Q/F$

electrical energy

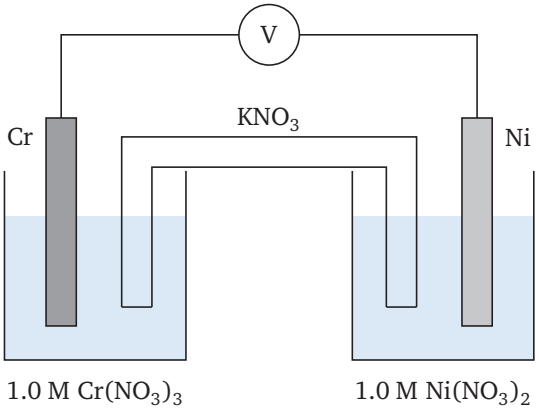
$W = QE$; 1 kWh = 3.6 MJ; 1 Ah = 3600 C

Oxidation occurs at the anode and reduction at the cathode. In a galvanic cell the anode is the negative and the cathode the positive terminal; in electrolysis the external source pushes electrons into the cathode. In a cell diagram the anode is written on the left; | denotes a phase boundary and || a salt bridge. When a half-reaction is multiplied by a number, E° does not change (intensive property), while ΔG° is multiplied by the same number. The potentials are from the table of standard reduction potentials in the Appendix (25 °C).

Galvanic cells and cell diagrams

16.2 ★☆☆ Solution →

In the galvanic cell in the figure, a chromium electrode is immersed in 1.0 M $Cr(NO_3)_3$ solution and a nickel electrode in 1.0 M $Ni(NO_3)_2$ solution; the two compartments are connected by a KNO_3 salt bridge. The temperature is 25 °C. Use the data in the Appendix.



a. Identify the anode and the cathode. Write the half-reactions and the balanced cell reaction; how many electrons (n) are transferred in the reaction?

b. State the direction of electron flow in the external circuit and the direction of migration of the K^+ and NO_3^- ions in the salt bridge. As the cell operates, which electrode gains mass?

c. Write the cell diagram and calculate E°_{cell}.

Electrolysis and Faraday's laws

16.7 ★★★ Solution →

Aluminum is produced by electrolysis of Al_2O_3 dissolved in molten cryolite. At the cathode Al^{3+} ions are reduced to liquid aluminum; at the carbon anode oxide ions form CO_2 with carbon, and the anode is consumed. Use the data in the Appendix.

a. Write the cathode and anode half-reactions and the overall reaction. How many moles of electrons are transferred in the overall reaction?

b. Calculate ΔG° of the overall reaction with the 298 K data and find the minimum voltage required for the electrolysis.

c. A cell operates at a current of 300 000 A with a current efficiency of 94.0% (94.0% of the current goes to aluminum production). Find the mass of aluminum produced by the cell in one day.

d. If the cell voltage is 4.10 V, how many kWh of electrical energy are used per 1 kg of aluminum? How many kg of carbon anode are theoretically consumed per 1 kg of aluminum?

SOLUTIONS

4 GASES

4.11

← Problem

The peak of the distribution is at the most probable speed: $u_{\text{mp}} = \sqrt{2RT/M}$; so as the ratio T/M increases, the peak shifts to the right and the curve spreads out and becomes lower. $M(\text{O}_2) = 31.998$ g/mol, $M(\text{He}) = 4.0026$ g/mol:

$$\text{O}_2\ (300\ \text{K}):\ T/M = 9.38,\ u_{\text{mp}} = 395\ \text{m/s}$$
$$\text{O}_2\ (1200\ \text{K}):\ T/M = 37.5,\ u_{\text{mp}} = 790\ \text{m/s}$$
$$\text{He}\ (300\ \text{K}):\ T/M = 75.0,\ u_{\text{mp}} = 1116\ \text{m/s}$$

$$u_{\text{mp}}(\text{O}_2, 300\ \text{K}) = \sqrt{\frac{2(8.314)(300)}{0.031998}} = 395\ \text{m/s}$$

Curve 1 is O_2 at 300 K, curve 2 is O_2 at 1200 K, and curve 3 is the He sample. **C** is correct.

- (A) and (E): Heavier molecules are assumed to be faster; at the same temperature the light He atoms are much faster.
- (B): The effect of temperature is assumed to be larger than that of molar mass. Quadrupling the temperature only doubles the speed; reducing the molar mass to one-eighth increases it by $\sqrt{8} = 2.83$ times.
- (D): The curve of the hot gas is assumed to be narrower and taller than that of the cold gas; as the temperature increases, the distribution broadens.

ANSWER C

4.14

← Problem

a. At constant V and T the pressures are proportional to the numbers of moles; stoichiometry can be done with partial pressures instead of moles. In the reaction two moles of gas become one mole: x atm of C_2H_4 and x atm of H_2 are used up and x atm of C_2H_6 forms; the net drop is x. Since the reaction stops when the limiting reactant is gone, x is its initial partial pressure:

$$x = 1.200 - 0.750 = 0.450\ \text{atm}$$

Possibility 1: H_2 limiting, $P_{\text{H}_2} = 0.450$ atm, $P_{\text{C}_2\text{H}_4} = 0.750$ atm. Possibility 2: C_2H_4 limiting, $P_{\text{C}_2\text{H}_4} = 0.450$ atm, $P_{\text{H}_2} = 0.750$ atm.

b. The average molar mass is $\bar{M} = \sum x_i M_i$ and $d = P\bar{M}/(RT)$, with $RT = (0.08206)(298.15) = 24.466$:

$$1:\ \bar{M} = \frac{0.450(2.016)+0.750(28.054)}{1.200} = 18.29\ \text{g/mol},\quad d = \frac{(1.200)(18.29)}{24.466} = 0.897\ \text{g/L}$$
$$2:\ \bar{M} = \frac{0.750(2.016)+0.450(28.054)}{1.200} = 11.78\ \text{g/mol},\quad d = \frac{(1.200)(11.78)}{24.466} = 0.578\ \text{g/L}$$

The measured density matches possibility 2: C_2H_4 is limiting. $x_{\text{H}_2} = 0.750/1.200 = 0.625$, $x_{\text{C}_2\text{H}_4} = 0.450/1.200 = 0.375$.

c. $P_{\text{C}_2\text{H}_6} = 0.450$ atm, $P_{\text{H}_2} = 0.750 - 0.450 = 0.300$ atm, $P_{\text{C}_2\text{H}_4} = 0$. **Check:** $0.450 + 0.300 = 0.750$ atm.

$$n(\text{C}_2\text{H}_6) = \frac{(0.450)(4.00)}{24.466} = 0.07357\ \text{mol}$$
$$m = (0.07357)(30.070) = 2.21\ \text{g}$$

d. At the same temperature $u_{\text{rms}} \propto 1/\sqrt{M}$:

$$\frac{u_{\text{rms}}(\text{H}_2)}{u_{\text{rms}}(\text{C}_2\text{H}_6)} = \sqrt{\frac{30.070}{2.016}} = 3.86$$

ANSWER a. $x = 0.450$ atm; (H_2 0.450, C_2H_4 0.750 atm) or (H_2 0.750, C_2H_4 0.450 atm) b. the second; $x_{\text{H}_2} = 0.625$, $x_{\text{C}_2\text{H}_4} = 0.375$ c. C_2H_6 0.450 atm, H_2 0.300 atm; 2.21 g d. 3.86

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8 CHEMICAL BONDING I: LEWIS STRUCTURES AND MOLECULAR GEOMETRY

8.3

← Problem

The formal charge is $\mathrm{FC} = V - L - \frac{1}{2}B$: V is the number of valence electrons, L the number of lone-pair electrons, and B the number of bonding electrons.

$$\mathrm{N}: \ 5 - 0 - \tfrac{1}{2}(8) = +1,$$
$$\mathrm{O_a}: \ 6 - 4 - \tfrac{1}{2}(4) = 0,$$
$$\mathrm{O_b}: \ 6 - 6 - \tfrac{1}{2}(2) = -1.$$

The formal charges of the C and H atoms are zero. **Check:** $+1 + 0 - 1 = 0$; the molecule is neutral. **B** is correct.

- (A): A neutral molecule only requires the *sum* of the formal charges to be zero; individual atoms can be charged.
- (C): These are the oxidation states: all bonding electrons are assigned to the more electronegative atom. In the formal charge, bonding electrons are shared equally.
- (D): All bonding electrons are counted for the atom instead of half: for N, $5 - 0 - 8 = -3$.
- (E): The number of lone pairs is subtracted instead of the number of lone-pair electrons: for $\mathrm{O_a}$, $6 - 2 - 2 = +2$. The sum is +5, which contradicts a neutral molecule.

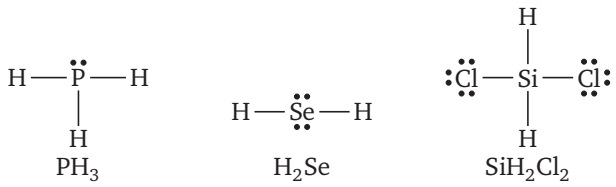
ANSWER B

8.9

← Problem

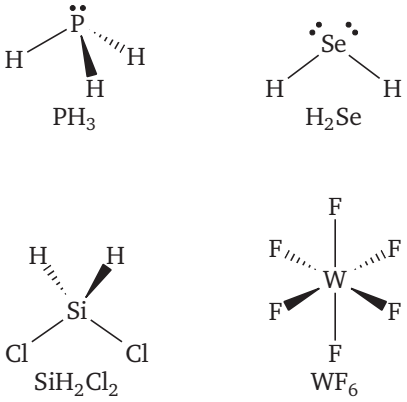
a. The terminal atoms are bonded by single bonds; H is completed with two electrons, Cl and F with eight (one bond and three lone pairs each). The remaining electrons go to the central atom:

- PH_3: $5 + 3(1) = 8$; after 6 bonding electrons, one lone pair on P: AX_3E.
- H_2Se: $2(1) + 6 = 8$; after 4 bonding electrons, two lone pairs on Se: AX_2E_2.
- SiH_2Cl_2: $4 + 2(1) + 2(7) = 20$; 8 (bonds) + 12 (lone pairs on Cl) = 20, no lone pair on Si: AX_4.
- WF_6: $6 + 6(7) = 48$; 12 (bonds) + 36 (lone pairs on F) = 48, no lone pair on W: AX_6. There are 12 electrons around W (expanded valence shell); $\mathrm{FC(W)} = 6 - 0 - 6 = 0$.



The Lewis structure of the WF_6 molecule is obtained by adding three lone pairs to each F atom in the drawing in part b.

b. PH_3: four groups, tetrahedral / trigonal pyramidal. H_2Se: four groups, tetrahedral / bent. SiH_2Cl_2: four groups, tetrahedral / tetrahedral. WF_6: six groups, octahedral / octahedral.



c. Ideal angles: H–P–H and H–Se–H 109.5°, adjacent F–W–F 90°. In the WF_6 molecule all six groups are identical bonds; the angles are exactly 90°. A lone pair takes up more space than a bonding pair and pushes the bonds together: the H–P–H and H–Se–H angles are smaller than 109.5°. Since the H_2Se molecule has two lone pairs, the larger deviation is expected there (the measured angles are about 93° and 91°; for heavy atoms the deviation is even larger than VSEPR predicts). The SiH_2Cl_2 molecule has no lone pair, but its four bonds are not identical: since the electron groups of the Si–Cl and Si–H bonds differ in size, the angles take slightly different values around 109.5°.

ANSWER a. 8, 8, 20, 48 electrons; AX_3E, AX_2E_2, AX_4, AX_6 b. tetrahedral / trigonal pyramidal; tetrahedral / bent; tetrahedral / tetrahedral; octahedral / octahedral c. 109.5°, 109.5°, 90°; H–P–H and H–Se–H become smaller, H–Se–H the most (two lone pairs); SiH_2Cl_2: the bonds are not identical

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16 ELECTROCHEMISTRY

16.2

← Problem

a. $E°(Ni^{2+}/Ni) = -0.26$ V and $E°(Cr^{3+}/Cr) = -0.74$ V. Ni^{2+}, with the larger reduction potential, is reduced: nickel is the cathode and chromium is the anode.

$$\text{Anode: } Cr(s) \longrightarrow Cr^{3+}(aq) + 3\,e^-$$

$$\text{Cathode: } Ni^{2+}(aq) + 2\,e^- \longrightarrow Ni(s)$$

To equalize the numbers of electrons, the anode reaction is multiplied by 2 and the cathode reaction by 3:

$$2\,Cr(s) + 3\,Ni^{2+}(aq) \longrightarrow 2\,Cr^{3+}(aq) + 3\,Ni(s), \quad n = 6.$$

b. Electrons flow in the external circuit from the chromium electrode to the nickel electrode. Positive charge (Cr^{3+}) builds up in the anode compartment and positive charge (Ni^{2+}) decreases in the cathode compartment: NO_3^- ions migrate into the chromium compartment and K^+ ions into the nickel compartment. Metal is deposited on the nickel cathode; the electrode that gains mass is nickel, and the chromium electrode wears away.

c. Cell notation:

$$Cr(s)\,|\,Cr^{3+}(aq, 1.0\,M)\,||\,Ni^{2+}(aq, 1.0\,M)\,|\,Ni(s)$$

$$E°_{cell} = -0.26 - (-0.74) = 0.48\text{ V}$$

Multiplying the half-reactions by 2 and 3 does not change the $E°$ values.

ANSWER a. anode Cr, cathode Ni; $2\,Cr(s) + 3\,Ni^{2+}(aq) \longrightarrow 2\,Cr^{3+}(aq) + 3\,Ni(s)$, $n = 6$ b. electrons from Cr to Ni; NO_3^- into the chromium compartment, K^+ into the nickel compartment; the nickel electrode gains mass c. $E°_{cell} = 0.48$ V

16.7

← Problem

a. The Al^{3+} and O^{2-} ions are in the molten cryolite; in the thermodynamic calculation Al_2O_3 is taken with the data of its solid state.

$$\text{Cathode: } Al^{3+} + 3\,e^- \longrightarrow Al(l) \quad (\times 4)$$

$$\text{Anode: } C(s) + 2\,O^{2-} \longrightarrow CO_2(g) + 4\,e^- \quad (\times 3)$$

$$\text{Overall: } 2\,Al_2O_3(s) + 3\,C(s) \longrightarrow 4\,Al(l) + 3\,CO_2(g)$$

Electrons transferred: $4 \times 3 = 3 \times 4 = 12$ mol.

b. With the $\Delta G_f°$ values in the Appendix (solid and gas states, 298 K):

$$\Delta G° = 3(-394.4) - 2(-1582.3)$$
$$= -1183.2 + 3164.6 = +1981.4\text{ kJ}$$

$$E_{min} = \frac{\Delta G°}{nF} = \frac{1\,981\,400}{(12)(96\,485)} = 1.71\text{ V}$$

Since the burning of carbon contributes energy to the overall reaction, this value is smaller than what the decomposition of Al_2O_3 alone would require. A real cell operates at a much higher voltage because of resistance and electrode losses.

c. Charge and amount of electrons:

$$Q = (300\,000)(86\,400) = 2.592 \times 10^{10}\text{ C}$$

$$n_e = \frac{2.592 \times 10^{10}}{96\,485} = 2.686 \times 10^5\text{ mol}$$

$$n_{Al} = \frac{(0.940)(2.686 \times 10^5)}{3} = 8.417 \times 10^4\text{ mol}$$

$$m_{Al} = (8.417 \times 10^4)(26.982) = 2271\text{ kg}$$

d. The energy for one day:

$$W = QE = (2.592 \times 10^{10})(4.10)$$
$$= 1.063 \times 10^{11}\text{ J} = 29\,520\text{ kWh}$$

$$\frac{29\,520\text{ kWh}}{2271\text{ kg}} = 13.0\text{ kWh (per kg)}$$

Carbon: 3 mol of C per 4 mol of Al in the overall reaction:

$$\frac{3(12.011)}{4(26.982)} = 0.334\text{ kg C (per kg of Al)}$$

(At 100% efficiency and a voltage of 1.71 V, the energy would be 5.10 kWh per kg; more than half of the energy used turns into heat and keeps the electrolyte molten.)

ANSWER a. $Al^{3+} + 3\,e^- \longrightarrow Al(l)$; $C(s) + 2\,O^{2-} \longrightarrow CO_2(g) + 4\,e^-$; $2\,Al_2O_3(s) + 3\,C(s) \longrightarrow 4\,Al(l) + 3\,CO_2(g)$; 12 mol of electrons b. $\Delta G° = +1981.4$ kJ; $E_{min} = 1.71$ V c. 2271 kg d. 13.0 kWh per kg; 0.334 kg of C

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IN THE FULL BOOK

- 16 chapters and 188 problems, all with step-by-step solutions.
- A reminder box at the start of each chapter, summarizing the relations the problems rely on.
- Basic, intermediate and advanced problems, each with a dotted area for your own work.
- One-click links from each problem to its solution and back.
- An 11-page Appendix of our own at the end of the book: the periodic table, thermodynamic data for 114 substances, acid-base and solubility constants, standard reduction potentials, constants, and the properties of water.



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