SOLUTIONS MANUAL

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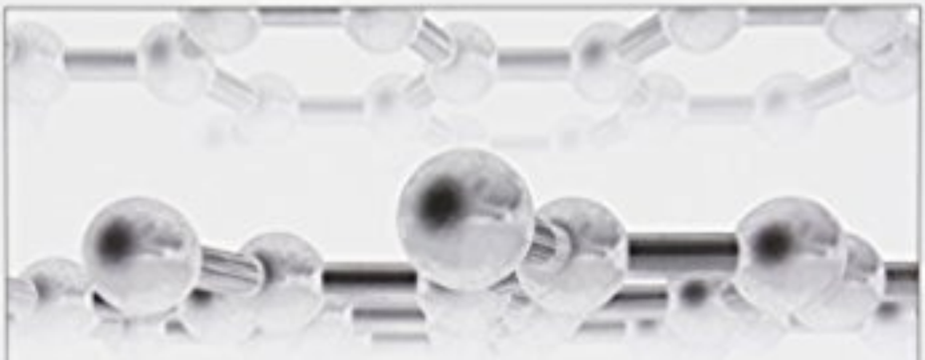


CHEMISTRY

Structure and Properties

NIVALDO J. TRO

Student Guide to Using This Solutions Manual

The vision behind this solutions manual is to provide guidance that is useful for both the struggling student and the advanced student.

An important feature of this solutions manual is that answers for the review questions are given. This will help in the review of the major concepts in the chapter.

The format of the solutions follows the format in the textbook very closely. Each mathematical problem includes **Given, Find, Conceptual Plan, Solution**, and **Check** sections.

Given and Find: Many students struggle with taking the written problem, parsing the information into categories, and determining the goal of the problem. It is also important to know which pieces of information in the problem are not necessary to solve the problem and if additional information needs to be gathered from sources such as tables in the textbook.

Conceptual Plan: The conceptual plan shows a step-by-step method to solve the problem. In many cases, the given quantities need to be converted to a different unit. Under each of the arrows is the equation, constant, or conversion factor needed to complete this portion of the problem. In the "Problems by Topic" section of the end-of-chapter exercises, the odd-numbered and even-numbered problems are paired. This allows you to use a conceptual plan from an odd-numbered problem in this manual as a starting point to solve the following even-numbered problem. Students should keep in mind that the examples shown are one way to solve the problems. Other mathematically equivalent solutions may be possible.

11.45 **Given:** $m\,(CO_2) = 28.8$ g, $P = 742$ mmHg, and $T = 22\,°C$ **Find:** V

Conceptual Plan: °C → K and mmHg → atm and g → mol then $n, P, T \rightarrow V$

$$K = °C + 273.15 \qquad \frac{1\ \text{atm}}{760\ \text{mmHg}} \qquad \frac{1\ \text{mol}}{44.01\ \text{g}} \qquad PV = nRT$$

Solution: $T_1 = 22\,°C + 273.15 = 295$ K, $P = 742\ \cancel{\text{mmHg}} \times \frac{1\ \text{atm}}{760\ \cancel{\text{mmHg}}} = 0.97\underline{6}316$ atm

$n = 28.8\ \cancel{g} \times \frac{1\ \text{mol}}{44.01\ \cancel{g}} = 0.65\underline{4}397$ mol $PV = nRT$ Rearrange to solve for V.

$$V = \frac{nRT}{P} = \frac{0.65\underline{4}397\ \cancel{\text{mol}} \times 0.08206\ \frac{\text{L} \cdot \cancel{\text{atm}}}{\cancel{\text{mol}} \cdot \cancel{\text{K}}} \times 295\ \cancel{\text{K}}}{0.97\underline{6}316\ \cancel{\text{atm}}} = 16.2\ \text{L}$$

Check: The units (L) are correct. The magnitude of the answer (16 L) makes sense because one mole of an ideal gas under standard conditions (273 K and 1 atm) occupies 22.4 L. Although these are not standard conditions, they are close enough for a ballpark check of the answer. Because this gas sample contains 0.65 mole, a volume of 16 L is reasonable.

Solution: The Solution section walks you through solving the problem after the conceptual plan. Equations are rearranged to solve for the appropriate quantity. Intermediate results are shown with additional digits to minimize round-off error. The units are canceled in each appropriate step.

Check: The Check section confirms that the units in the answer are correct. This section also challenges the student to think about whether the magnitude of the answer makes sense. Thinking about what is a reasonable answer can help uncover errors such as calculation errors.

1 Atoms

Review Questions

1.1 "The properties of the substances around us depend on the atoms, ions, or molecules that compose them" means that the specific types of atoms and molecules that compose something tell us a great deal about which properties to expect from a substance. A material composed of only sodium and chloride ions will have the properties of table salt. A material composed of molecules with one carbon atom and two oxygen atoms will have the properties of the gas carbon dioxide. If the atoms and molecules change, so do the properties that we expect the material to have.

1.2 The main goal of chemistry is to seek to understand the behavior of matter by studying the behavior of atoms and molecules.

1.3 Matter can be classified according to its state—solid, liquid, or gas—and according to its composition.

1.4 In solid matter, atoms or molecules pack close to each other in fixed locations. Although the atoms and molecules in a solid vibrate, they do not move around or past each other. Consequently, a solid has a fixed volume and rigid shape.

In liquid matter, atoms or molecules pack about as closely as they do in solid matter, but they are free to move relative to each other, giving liquids a fixed volume but not a fixed shape. Liquids assume the shape of their container.

In gaseous matter, atoms or molecules have a lot of space between them and are free to move relative to one another, making gases compressible. Gases always assume the shape and volume of their container.

1.5 A pure substance is composed of only one type of atom or molecule. In contrast, a mixture is a substance composed of two or more different types of atoms or molecules that can be combined in variable proportions.

1.6 An element is a pure substance that cannot be decomposed into simpler substances. A compound is composed of two or more elements in fixed proportions.

1.7 A homogeneous mixture has the same composition throughout, while a heterogeneous mixture has different compositions in different regions.

1.8 The scientific approach to knowledge is based on observation and experiment. Scientists observe and perform experiments on the physical world to learn about it. Observations often lead scientists to formulate a hypothesis, a tentative interpretation or explanation of their observations. Hypotheses are tested by experiments, highly controlled procedures designed to generate such observations. The results of an experiment may support a hypothesis or prove it wrong—in which case the hypothesis must be modified or discarded. A series of similar observations can lead to the development of scientific law, a brief statement that summarizes past observations and predicts future ones. One or more well-established hypotheses may form the basis for a scientific theory. A scientific theory is a model for the way nature is and tries to explain not merely what nature does, but why.

4.129 **Given:** Ra, $Z = 88$ **Find:** Z for next two alkaline earth metals
Solution: The next element would lie in period 8, column 2A. The largest currently known element is 116 in period 7, column 6A. To reach period 8 column 2A, you need to add four protons and would have $Z = 120$.

The alkaline earth metal following 120 would lie in period 9, column 2A. To reach this column, you need to add 18 g-block element protons, 10 d-block element protons, 14 f-block element protons, 6 p-block element protons, and 2 s-block element protons. This would give $Z = 170$.

4.130 **Given:** Pd = $[Kr]4d^{10}$ **Find:** electron configuration of first two excited states
Solution: The first excited state of Pd would move an electron from a $4d$ to a $5s$ orbital. The second excited state would move the electron from a $4d$ to the $5p$ orbital.
First excited state: $[Kr]4d^9 5s^1$
Second excited state: $[Kr]4d^9 5p^1$

Conceptual Problems

4.131 If six electrons rather than eight electrons led to a stable configuration, the electron configuration of the stable configuration would be ns^2np^4.

(a) A noble gas would have the electron configuration ns^2np^4. This could correspond to the O atom.
(b) A reactive nonmetal would have one less electron than the stable configuration. This would have the electron configuration ns^2np^3. This could correspond to the N atom.
(c) A reactive metal would have one more electron than the stable configuration. This would have the electron configuration of ns^1. This could correspond to the Li atom.

4.132 Atom B would have the higher first ionization energy. Even though the effective nuclear charge is less, the outermost electron is closer to the nucleus and the potential energy becomes more negative with decreasing distance, making it harder to remove and requiring a larger ionization energy.

4.133 (a) True: An electron in a $3s$ orbital is more shielded than an electron in a $2s$ orbital. This is true because there are more core electrons below a $3s$ orbital.
(b) True: An electron in a $3s$ orbital penetrates the region occupied by the core electrons more than electrons in a $3p$ orbital. Examine Figure 4.8, the radial distribution functions for the $3s$, $3p$, and $3d$ orbitals. You will see that the $3s$ electrons penetrate more deeply than the $3p$ electrons and more than the $3d$ electrons.
(c) False: An electron in an orbital that penetrates closer to the nucleus will experience *less* shielding than an electron in an orbital that does not penetrate as far.
(d) True: An electron in an orbital that penetrates close to the nucleus will tend to experience a higher effective nuclear charge than one that does not. Because the orbital penetrates closer to the nucleus, the electron will experience less shielding and therefore a higher effective nuclear charge.

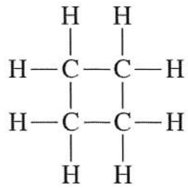
4.134 An electron in a $5p$ orbital could have any one of the following combinations of quantum numbers:
$(5, 1, -1, +1/2)$ $(5, 1, -1, -1/2)$ $(5, 1, 0, +1/2)$ $(5, 1, 0, -1/2)$ $(5, 1, 1, +1/2)$ $(5, 1, 1, -1/2)$
An electron in a $6d$ orbital could have any one of the following combinations of quantum numbers:
$(6, 2, -2, +1/2)$ $(6, 2, -2, -1/2)$ $(6, 2, -1, +1/2)$ $(6, 2, -1, -1/2)$ $(6, 2, 0, +1/2)$ $(6, 2, 0, -1/2)$
$(6, 2, 1, +1/2)$ $(6, 2, 1, -1/2)$ $(6, 2, 2, +1/2)$ $(6, 2, 2, -1/2)$

4.135 The $4s$ electrons in calcium have relatively low ionization energies ($IE_1 = 590$ kJ/mol; $IE_2 = 1145$ kJ/mol) because they are valence electrons. The energetic cost for calcium to lose a third electron is extraordinarily high because the next electron to be lost is a core electron. Similarly, the electron affinity of fluorine to gain one electron (-328 kJ/mol) is highly exothermic because the added electron completes fluoride's valence shell. The gain of a second electron by the negatively charged fluoride anion would not be favorable. Therefore, we would expect calcium and fluoride to combine in a 1:2 ratio.

Finally, write the Lewis structure in brackets with the charge of the ion in the upper right-hand corner.

$$Sr^{2+}\ 2\left[:C{\equiv}N:\right]^{-}$$

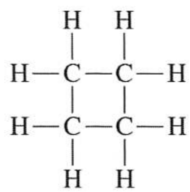
6.77 (a) C_4H_8: Write the correct skeletal structure for the molecule.



Calculate the total number of electrons for the Lewis structure by summing the number of valence electrons of each atom in the molecule.

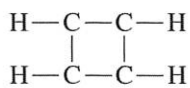
$$4(\text{number of valence e}^- \text{ for C}) + 8(\text{number of valence e}^- \text{ for H}) = 4(4) + 8(1) = 24$$

Distribute the electrons among the atoms, giving octets (or duets for H) to as many atoms as possible.



All atoms have octets or duets for H.

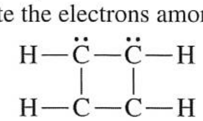
(b) C_4H_4: Write the correct skeletal structure for the molecule.



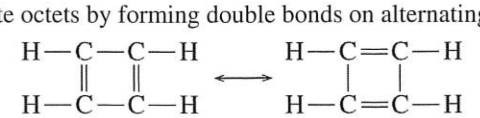
Calculate the total number of electrons for the Lewis structure by summing the number of valence electrons of each atom in the molecule.

$$4(\text{number of valence e}^- \text{ for C}) + 4(\text{number of valence e}^- \text{ for H}) = 4(4) + 4(1) = 20$$

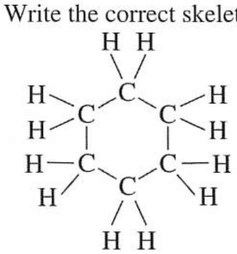
Distribute the electrons among the atoms, giving octets (or duets for H) to as many atoms as possible.



Complete octets by forming double bonds on alternating carbons; draw resonance structures.



(c) C_6H_{12}: Write the correct skeletal structure for the molecule.



Calculate the total number of electrons for the Lewis structure by summing the valence electrons of each atom in the molecule.

$$6(\text{number of valence e}^- \text{ for C}) + 12(\text{number of valence e}^- \text{ for H}) = 6(4) + 12(1) = 36$$

Distribute the electrons among the atoms, giving octets (or duets for H) to as many atoms as possible. Begin with the bonding.

$$\text{fraction remaining} = \frac{[C_5H_{12}]_t}{[C_5H_{12}]_0} = \frac{8.8808 \times 10^{16}\,\frac{\text{molecules}}{\text{cm}^2}}{8.9 \times 10^{16}\,\frac{\text{molecules}}{\text{cm}^2}} = 0.99784 = 1.0\text{; so within experimental error,}$$

all are remaining on the surface.

Check: The units (s and none) are correct. The half-life is reasonable considering the size of the rate constant. The fraction at 10 s is reasonable given the fact that the time is very, very small compared to the half-life.

15.99 (a) **Given:** table of rate constant versus T **Find:** E_a and A

Conceptual Plan: First, convert temperature data into kelvin (°C + 273.15 = K). Because

$\ln k = \frac{-E_a}{R}\left(\frac{1}{T}\right) + \ln A$, a plot of ln k versus 1/T will have a *slope* $= -E_a/R$ and an *intercept* $= \ln A$.

Solution: The slope can be determined by measuring $\Delta y/\Delta x$ on the plot or by using functions such as "add trendline" in Excel. Because the *slope* $= -10759\ K = -E_a/R$,

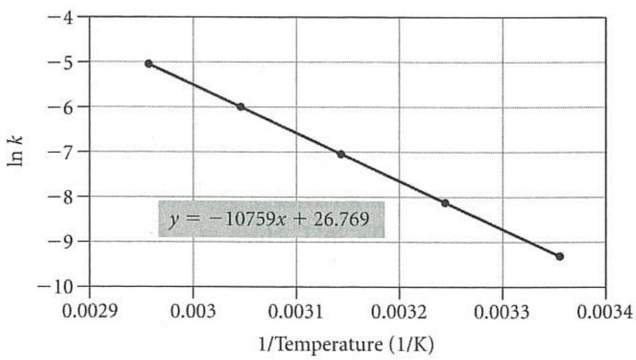
$E_a = -(slope)R$

$= -(-10759\,\text{K})\left(8.314\frac{\text{J}}{\text{K}\cdot\text{mol}}\right)\left(\frac{1\text{ kJ}}{1000\text{ J}}\right)$

$= 89.5\,\frac{\text{kJ}}{\text{mol}}$

and *intercept* $= 26.769 = \ln A$ then

$A = e^{intercept} = e^{26.769} = 4.22 \times 10^{11}\ \text{s}^{-1}$



Check: The units (kJ/mol and s^{-1}) are correct. The plot was linear, confirming Arrhenius behavior. The activation and frequency factor are typical for many reactions.

(b) **Given:** part (a) results **Find:** k at 15 °C

Conceptual Plan: °C → K then T, E_a, $A \rightarrow k$

°C + 273.15 = K $\qquad \ln k = \frac{-E_a}{R}\left(\frac{1}{T}\right) + \ln A$

Solution: 15 °C + 273.15 = 288 K then

$$\ln k = \frac{-E_a}{R}\left(\frac{1}{T}\right) + \ln A = \frac{-89.5\frac{\text{kJ}}{\text{mol}} \times \frac{1000\text{ J}}{1\text{ kJ}}}{8.314\frac{\text{J}}{\text{K}\cdot\text{mol}}}\left(\frac{1}{288\text{ K}}\right) + \ln(4.22 \times 10^{11}\ \text{s}^{-1}) = -10.610 \rightarrow$$

$k = e^{-10.610} = 2.5 \times 10^{-5}\ \text{M}^{-1}\cdot\text{s}^{-1}$

Check: The units ($\text{M}^{-1}\cdot\text{s}^{-1}$) are correct. The value of the rate constant is less than the value at 25 °C.

(c) **Given:** part (a) results, 0.155 M C_2H_5Br and 0.250 M OH^- at 75 °C **Find:** initial reaction rate

Conceptual Plan: °C → K then T, E_a, $A \rightarrow k$ then k, $[C_2H_5Br]$, $[OH^-]$ → initial reaction rate

°C + 273.15 = K $\qquad \ln k = \frac{-E_a}{R}\left(\frac{1}{T}\right) + A \qquad$ Rate $= k[C_2H_5Br][OH^-]$

Solution: 75 °C + 273.15 = 348 K then

$$\ln k = \frac{-E_a}{R}\left(\frac{1}{T}\right) + \ln A = \frac{-89.5\frac{\text{kJ}}{\text{mol}} \times \frac{1000\text{ J}}{1\text{ kJ}}}{8.314\frac{\text{J}}{\text{K}\cdot\text{mol}}}\left(\frac{1}{348\text{ K}}\right) + \ln(4.22 \times 10^{11}\ \text{s}^{-1}) = -4.1656 \rightarrow$$

$k = e^{-4.1656} = 1.5521 \times 10^{-2}\ \text{M}^{-1}\cdot\text{s}^{-1}$

Rate $= k[C_2H_5Br][OH^-] = (1.5521 \times 10^{-2}\ \text{M}^{-1}\cdot\text{s}^{-1})(0.155\ \text{M})(0.250\ \text{M}) = 6.0 \times 10^{-4}\ \text{M}\cdot\text{s}^{-1}$

The Kinetics of Radioactive Decay and Radiometric Dating

21.45 **Given:** U-235, $t_{1/2}$ for radioactive decay = 703 million years **Find:** t to 10.0% of initial amount
Conceptual Plan: Radioactive decay implies first-order kinetics, $t_{1/2} \rightarrow k$ then

$$t_{1/2} = \frac{0.693}{k}$$

$m_{\text{U-235 } 0}, m_{\text{U-235 } t}, k \rightarrow t$

$$\ln N_t = -kt + \ln N_0$$

Solution: $t_{1/2} = \dfrac{0.693}{k}$ Rearrange to solve for k. $k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{703 \times 10^6 \text{ yr}} = 9.8\underline{5}7752 \times 10^{-10} \text{ yr}^{-1}$

Because $\ln m_{\text{U-235 } t} = -kt + \ln m_{\text{U-235 } 0}$, rearrange to solve for t.

$$t = -\frac{1}{k} \ln \frac{m_{\text{U-235 } t}}{m_{\text{U-235 } 0}} = -\frac{1}{9.8\underline{5}7752 \times 10^{-10} \text{ yr}^{-1}} \ln \frac{10.0\cancel{\%}}{100.0\cancel{\%}} = 2.34 \times 10^9 \text{ yr}$$

Check: The units (yr) are correct. The time is just over three half-lives, when 1/8 of the original amount will be left.

21.46 **Given:** initially, 0.050 mg Tc-99m, $t_{1/2}$ for radioactive decay = 6.0 h **Find:** t to 6.3×10^{-3} mg
Conceptual Plan: Radioactive decay implies first-order kinetics, $t_{1/2} \rightarrow k$ then

$$t_{1/2} = \frac{0.693}{k}$$

$m_{\text{Tc-99 m } 0}, m_{\text{Tc-99 m } t}, k \rightarrow t.$

$$\ln N_t = -kt + \ln N_0$$

Solution: $t_{1/2} = \dfrac{0.693}{k}$ Rearrange to solve for k. $k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{6.0 \text{ h}} = 0.1\underline{1}55 \text{ h}^{-1}$

Because $\ln m_{\text{Tc-99 m } t} = -kt + \ln m_{\text{Tc-99 m } 0}$, rearrange to solve for t.

$$t = -\frac{1}{k} \ln \frac{m_{\text{Tc-99 m } t}}{m_{\text{Tc-99 m } 0}} = -\frac{1}{0.1\underline{1}55 \text{ h}^{-1}} \ln \frac{6.3 \times 10^{-3} \cancel{\text{mg}}}{0.050 \cancel{\text{mg}}} = 18 \text{ h}$$

Check: The units (h) are correct. The time is about three half-lives, and the amount is about 1/8, or $1/2^3$, of the original amount.

21.47 **Given:** $t_{1/2}$ for isotope decay = 3.8 days; 1.55 g isotope initially **Find:** mass of isotope after 5.5 days
Conceptual Plan: Radioactive decay implies first-order kinetics, $t_{1/2} \rightarrow k$ then

$$t_{1/2} = \frac{0.693}{k}$$

$m_{\text{isotope } 0}, t, k \rightarrow m_{\text{isotope } t}.$

$$\ln N_t = -kt + \ln N_0$$

Solution: $t_{1/2} = \dfrac{0.693}{k}$ Rearrange to solve for k. $k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{3.8 \text{ days}} = 0.1\underline{8}237 \text{ day}^{-1}$ Because $\ln N_t = -kt + \ln N_0 = -(0.1\underline{8}237 \cancel{\text{day}^{-1}})(5.5 \cancel{\text{day}}) + \ln(1.55 \text{ g}) = -0.5\underline{6}478 \rightarrow N_t = e^{-0.5\underline{6}478} = 0.57 \text{ g}.$

Check: The units (g) are correct. The amount is consistent with a time between one and two half-lives.

21.48 **Given:** $t_{1/2}$ for I-131 = 8 days; 58 mg dose at 8 a.m. **Find:** mass of I-131 at 5 p.m. next day
Conceptual Plan: Radioactive decay implies first-order kinetics, $t_{1/2} \rightarrow k$ and determine days since dose

$$t_{1/2} = \frac{0.693}{k}$$

then $m_{\text{I-131 } 0}, t, k \rightarrow m_{\text{I-131 } t}.$

$$\ln N_t = -kt + \ln N_0$$

Solution: $t_{1/2} = \dfrac{0.693}{k}$ Rearrange to solve for k. $k = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{8 \text{ days}} = 0.0\underline{8}6625 \text{ day}^{-1}$ The time since the dose is one day plus 9 hours, or $(1 + 9/24)$ days = 1.375 days. Because $\ln m_{\text{I-131 } t} = -kt + \ln m_{\text{I-131 } 0} = -(0.0\underline{8}6625 \cancel{\text{day}^{-1}})(1.375 \cancel{\text{day}}) + \ln(58 \text{ mg}) = 3.\underline{9}413 \rightarrow m = e^{3.\underline{9}413} = 51 \text{ mg}$

Check: The units (mg) are correct. The amount is consistent with a time less than one half-life.