Instructor Solutions Manual for
Mathematics for Physical Chemistry

Instructor Solutions Manual for *Mathematics for Physical Chemistry*

Fourth Edition

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Contents

Preface

This instructor's solutions manual provides solutions to nearly all of the exercises and problems in *Mathematics for Physical Chemistry*, Fourth Edition, by Robert G. Mortimer. This edition is a revision of the third edition, published by Elsevier/Academic Press in 2005. Some of the exercises and problems have been carried over from the third edition. Others have been modified, and a number of new ones have been added.

I am pleased to acknowledge the cooperation and help of Linda Versteeg-Buschman, Beth Campbell, Jill Cetel, and their collaborators at Elsevier. It is also a pleasure to acknowledge the assistance of all those who helped with all editions of the book for which this is the solutions manual, and especially to thank my wife, Ann, for her patience, love, and forbearance.

There are inevitably errors in the solutions in this manual, and I would appreciate learning of them through the publisher.

Robert G. Mortimer

Chapter 1

Problem Solving and Numerical Mathematics

EXERCISES

Exercise 1.1. Take a few fractions, such as $\frac{2}{3}, \frac{4}{9}$ or $\frac{3}{7}$ and represent them as decimal numbers, finding either all of the nonzero digits or the repeating pattern of digits.

$$\frac{2}{3} = 0.66666666\cdots$$
$$\frac{4}{9} = 0.4444444\cdots$$
$$\frac{3}{7} = 0.428571428571\cdots$$

Exercise 1.2. Express the following in terms of SI base units. The electron volt (eV), a unit of energy, equals 1.6022×10^{-18} J.

a. $(13.6 \text{ eV})\left(\frac{1.6022 \times 10^{-19} \text{ J}}{1 \text{ eV}}\right) = 2.17896 \times 10^{-19} \text{ J}$
$\approx 2.18 \times 10^{-18}$ J

b. $(24.17 \text{ mi})\left(\frac{5280 \text{ ft}}{1 \text{ mi}}\right)\left(\frac{12 \text{ in}}{1 \text{ ft}}\right)\left(\frac{0.0254m}{1 \text{ in}}\right)$
$= 3.890 \times 10^4$ m

c. $(55 \text{ mi h}^{-1})\left(\frac{5280 \text{ ft}}{1 \text{ mi}}\right)\left(\frac{12 \text{ in}}{1 \text{ ft}}\right)\left(\frac{0.0254 \text{ m}}{1 \text{ in}}\right)$
$\left(\frac{1 \text{ h}}{3600 \text{ s}}\right) = 24.59 \text{ m s}^{-1} \approx 25 \text{ m s}^{-1}$

d. $(7.53 \text{ nm ps}^{-1})\left(\frac{1 \text{ m}}{10^9 \text{ nm}}\right)\left(\frac{10^{12} \text{ ps}}{1 \text{ s}}\right)$
$= 7.53 \times 10^3 \text{ m s}^{-1}$

Exercise 1.3. Convert the following numbers to scientific notation:

a. $0.00000234 = 2{,}34 \times 10^{-6}$
b. $32.150 = 3.2150 \times 10^1$

Exercise 1.4. Round the following numbers to three significant digits

a. $123456789123 \approx 123{,}000{,}000{,}000$
b. $46.45 \approx 46.4$

Exercise 1.5. Find the pressure P of a gas obeying the ideal gas equation

$$PV = nRT$$

if the volume V is 0.200 m^3, the temperature T is 298.15 K and the amount of gas n is 1.000 mol. Take the smallest and largest value of each variable and verify your number of significant digits. Note that since you are dividing by V the smallest value of the quotient will correspond to the largest value of V.

$$\begin{aligned}
P &= \frac{nRT}{V} \\
&= \frac{(1.000 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{0.200 \text{ m}^3} \\
&= 12395 \text{ J m}^{-3} = 12395 \text{ N m}^{-2} \approx 1.24 \times 10^4 \text{ Pa} \\
P_{\max} &= \frac{nRT}{V} \\
&= \frac{(1.0005 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.155 \text{ K})}{0.1995 \text{ m}^3} \\
&= 1.243 \times 10^4 \text{ Pa} \\
P_{\min} &= \frac{nRT}{V} \\
&= \frac{(0.9995 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.145 \text{ K})}{0.2005 \text{ m}^3} \\
&= 1.236 \times 10^4 \text{ Pa}
\end{aligned}$$

Mathematics for Physical Chemistry. http://dx.doi.org/10.1016/B978-0-12-415809-2.00025-2

Exercise 1.6. Calculate the following to the proper numbers of significant digits.

a. $17.13 + 14.6751 + 3.123 + 7.654 - 8.123 = 34.359 \approx 34.36$

b. $\ln(0.000123)$

$$\ln(0.0001235) = -8.99927$$
$$\ln(0.0001225) = -9.00740$$

The answer should have three significant digits:

$$\ln(0.000123) = -9.00$$

PROBLEMS

1. Find the number of inches in 1.000 meter.

$$(1.000\ \text{m})\left(\frac{1\ \text{in}}{0.0254\ \text{m}}\right) = 39.37\ \text{in}$$

2. Find the number of meters in 1.000 mile and the number of miles in 1.000 km, using the definition of the inch.

$$(1.000\ \text{mi})\left(\frac{5280\ \text{ft}}{1\ \text{mi}}\right)\left(\frac{12\ \text{in}}{1\ \text{ft}}\right)\left(\frac{0.0254\ \text{m}}{1\ \text{in}}\right) = 1609\ \text{m}$$

$$(1.000\ \text{km})\left(\frac{1000\ \text{m}}{1\ \text{km}}\right)\left(\frac{1\ \text{in}}{0.0254\ \text{m}}\right)\left(\frac{1\ \text{ft}}{12\ \text{in}}\right) \times \left(\frac{1\ \text{mi}}{5280\ \text{ft}}\right) = 0.6214$$

3. Find the speed of light in miles per second.

$$(299792458\ \text{m s}^{-1})\left(\frac{1\ \text{in}}{0.0254\ \text{m}}\right)\left(\frac{1\ \text{ft}}{12\ \text{in}}\right) \times \left(\frac{1\ \text{mi}}{5280\ \text{ft}}\right) = 186282.397\ \text{mi s}^{-1}$$

4. Find the speed of light in miles per hour.

$$(299792458\ \text{m s}^{-1})\left(\frac{1\ \text{in}}{0.0254\ \text{m}}\right)\left(\frac{1\ \text{ft}}{12\ \text{in}}\right) \times \left(\frac{1\ \text{mi}}{5280\ \text{ft}}\right)\left(\frac{3600\ \text{s}}{1\ \text{h}}\right) = 670616629\ \text{mi h}^{-1}$$

5. A furlong is exactly one-eighth of a mile and a fortnight is exactly 2 weeks. Find the speed of light in furlongs per fortnight, using the correct number of significant digits.

$$(299792458\ \text{m s}^{-1})\left(\frac{1\ \text{in}}{0.0254\ \text{m}}\right)\left(\frac{1\ \text{ft}}{12\ \text{in}}\right) \times \left(\frac{1\ \text{mi}}{5280\ \text{ft}}\right)\left(\frac{8\ \text{furlongs}}{1\ \text{mi}}\right) \times \left(\frac{3600\ \text{s}}{1\ \text{h}}\right)\left(\frac{24\ \text{h}}{1\ \text{d}}\right)\left(\frac{14\ \text{d}}{1\ \text{fortnight}}\right) = 1.80261750 \times 10^{12}\ \text{furlongs fortnight}^{-1}$$

6. The distance by road from Memphis, Tennessee to Nashville, Tennessee is 206 miles. Express this distance in meters and in kilometers.

$$(206\ \text{mi})\left(\frac{5380\ \text{ft}}{1\ \text{mi}}\right)\left(\frac{12\ \text{in}}{1\ \text{ft}}\right)\left(\frac{0.0254\ \text{m}}{1\ \text{in}}\right) = 3.32 \times 10^5\ \text{m} = 332\ \text{km}$$

7. A U. S. gallon is defined as 231.00 cubic inches.

a. Find the number of liters in 1.000 gallon.

$$(1\ \text{gal})\left(\frac{231.00\ \text{in}^3}{1\ \text{gal}}\right)\left(\frac{0.0254\ \text{m}}{1\ \text{in}}\right)^3\left(\frac{1000\ \text{l}}{1\ \text{m}^3}\right) = 3.785\ \text{l}$$

b. The volume of 1.0000 mol of an ideal gas at 0.00 °C (273.15 K) and 1.000 atm is 22.414 liters. Express this volume in gallons and in cubic feet.

$$(22.414\ \text{l})\left(\frac{1\ \text{m}^3}{1000\ \text{l}}\right)\left(\frac{1\ \text{in}}{0.0254\ \text{m}^3}\right)^3 \times \left(\frac{1\ \text{gal}}{231.00\ \text{in}^3}\right) = 5.9212\ \text{gal}$$

$$(22.414\ \text{l})\left(\frac{1\ \text{m}^3}{1000\ \text{l}}\right)\left(\frac{1\ \text{in}}{0.0254\ \text{m}^3}\right)^3 \times \left(\frac{1\ \text{ft}}{12\ \text{in}}\right)^3 = 0.79154\ \text{ft}^3$$

8. In the USA, footraces were once measured in yards and at one time, a time of 10.00 seconds for this distance was thought to be unattainable. The best runners now run 100 m in 10 seconds or less. Express 100.0 m in yards. If a runner runs 100.0 m in 10.00 s, find his time for 100 yards, assuming a constant speed.

$$(100.0\ \text{m})\left(\frac{1\ \text{in}}{0.0254\ \text{m}}\right)\left(\frac{1\ \text{yd}}{36\ \text{in}}\right) = 109.4\ \text{m}$$

$$(10.00\ \text{s})\left(\frac{100.0\ \text{yd}}{109.4\ \text{m}}\right) = 9.144\ \text{s}$$

9. Find the average length of a century in seconds and in minutes. Use the rule that a year ending in 00 is not a leap year unless the year is divisible by 400, in which case it is a leap year. Therefore, in four centuries there will be 97 leap years. Find the number of minutes in a microcentury.

Number of days in 400 years

$$= (365\ \text{d})(400\ \text{y}) + 97\ \text{d} = 146097\ \text{d}$$

Average number of days in a century

$$= \frac{146097\ \text{d}}{4} = 36524.25\ \text{d}$$

$$1\ \text{century} = (36524.25\ \text{d})\left(\frac{24\ \text{h}}{1\ \text{d}}\right)\left(\frac{60\ \text{min}}{1\ \text{h}}\right)$$

$$= 5.259492 \times 10^7\ \text{min}$$

$$(5.259492 \times 10^7\ \text{min})\left(\frac{1\ \text{century}}{1 \times 10^6\ \text{microcenturies}}\right)$$

$$= 52.59492\ \text{min}$$

$$(52.59492\ \text{min})\left(\frac{60\ \text{s}}{1\ \text{min}}\right) = 3155.695\ \text{s}$$

10. A light year is the distance traveled by light in one year.

a. Express this distance in meters and in kilometers. Use the average length of a year as described in the previous problem. How many significant digits can be given?

$$(299792458\ \text{m s}^{-1})\left(\frac{60\ \text{s}}{1\ \text{min}}\right)$$

$$\times(5.259492 \times 10^5\ \text{min})$$

$$= (9.46055060 \times 10^{15}\ \text{m})$$

$$(9.46055060 \times 10^{15}\ \text{m})\left(\frac{1\ \text{km}}{1000\ \text{m}}\right)$$

$$= 9.4605506 \times 10^{12}\ \text{km}$$

$$\approx 9.460551 \times 10^{12}\ \text{km}$$

Since the number of significant digits in the number of days in an average century is seven, we round to seven significant digits.

b. Express a light year in miles.

$$(9.460551 \times 10^{15}\ \text{m})\left(\frac{1\ \text{in}}{0.0254\ \text{m}}\right)\left(\frac{1\ \text{ft}}{12\ \text{in}}\right)$$

$$\times\left(\frac{1\ \text{mi}}{5280\ \text{ft}}\right) = 5.878514 \times 10^{12}\ \text{mi}$$

11. The Rankine temperature scale is defined so that the Rankine degree is the same size as the Fahrenheit degree, and absolute zero is 0 °R, the same as 0 K.

a. Find the Rankine temperature at 0.00 °C.

$$0.00\ ^\circ\text{C} \leftrightarrow (273.15\ \text{K})\left(\frac{9\ ^\circ\text{F}}{5\ \text{K}}\right) = 491.67\ ^\circ\text{R}$$

b. Find the Rankine temperature at 0.00 °F.

$$273.15\ \text{K} - 18.00\ \text{K} = 255.15\ \text{K}$$

$$(255.15\ \text{K})\left(\frac{9\ ^\circ\text{F}}{5\ \text{K}}\right) = 459.27\ ^\circ\text{R}$$

12. The volume of a sphere is given by

$$V = \frac{4}{3}\pi r^3$$

where V is the volume and r is the radius. If a certain sphere has a radius given as 0.005250 m, find its volume, specifying it with the correct number of digits. Calculate the smallest and largest volumes that the sphere might have with the given information and check your first answer for the volume.

$$\begin{aligned}
V &= \frac{4}{3}\pi r^3 = V = \frac{4}{3}\pi(0.005250\ \text{m})^3 \\
&= 6.061 \times 10^{-7}\ \text{m}^3 \\
V_{\text{min}} &= \frac{4}{3}\pi(0.005245\ \text{m})^3 = 6.044 \times 10^{-7}\ \text{m}^3 \\
V_{\text{max}} &= \frac{4}{3}\pi(0.005255\ \text{m})^3 = 6.079 \times 10^{-7}\ \text{m}^3 \\
V &= 6.06 \times 10^{-7}\ \text{m}^3
\end{aligned}$$

The rule of thumb gives four significant digits, but the calculation shows that only three significant digits can be specified and that the last digit can be wrong by one.

13. The volume of a right circular cylinder is given by

$$V = \pi r^2 h,$$

where r is the radius and h is the height. If a right circular cylinder has a radius given as 0.134 m and a height given as 0.318 m, find its volume, specifying it with the correct number of digits. Calculate the smallest and largest volumes that the cylinder might have with the given information and check your first answer for the volume.

$$\begin{aligned}
V &= \pi(0.134\ \text{m})^2(0.318\ \text{m}) = 0.0179\ \text{m}^3 \\
V_{\text{min}} &= \pi(0.1335\ \text{m})^2(0.3175\ \text{m}) = 0.01778\ \text{m}^3 \\
V_{\text{max}} &= \pi(0.1345\ \text{m})^2(0.3185\ \text{m}) = 0.0181\ \text{m}^3
\end{aligned}$$

14. The value of an angle is given as 31°. Find the measure of the angle in radians. Find the smallest and largest values that its sine and cosine might have and specify the sine and cosine to the appropriate number of digits.

$$
\begin{aligned}
(31^\circ)\left(\frac{2\pi \text{ rad}}{360^\circ}\right) &= 0.54 \text{ rad}\\
\sin(30.5^\circ) &= 0.5075\\
\sin(31.5^\circ) &= 0.5225\\
\sin(31^\circ) &= 0.51\\
\cos(30.5^\circ) &= 0.86163\\
\cos(31.5^\circ) &= 0.85264\\
\cos(31^\circ) &= 0.86
\end{aligned}
$$

15. Some elementary chemistry textbooks give the value of R, the ideal gas constant, as $0.0821 \text{ l atm K}^{-1} \text{ mol}^{-1}$.

a. Using the SI value, $8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$, obtain the value in $\text{l atm K}^{-1} \text{ mol}^{-1}$ to five significant digits.

$$
(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})\left(\frac{1 \text{ Pa m}^3}{1 \text{ J}}\right)\left(\frac{1 \text{ atm}}{101325 \text{ Pa}}\right) \times \left(\frac{1000 \text{ l}}{1 \text{ m}^3}\right) = 0.082058 \text{ l atm K}^{-1} \text{ mol}^{-1}
$$

b. Calculate the pressure in atmospheres and in N m^{-2} (Pa) of a sample of an ideal gas with $n = 0.13678$ mol, $V = 10.000$ l and $T = 298.15$ K.

$$
\begin{aligned}
P &= \frac{nRT}{V}\\
&= \frac{(0.13678 \text{ mol})(0.082058 \text{ l atm K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{1.000 \text{ l}}\\
&= 0.33464 \text{ atm}\\
P &= \frac{nRT}{V}\\
&= \frac{(0.13678 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{10.000 \times 10^{-3} \text{ m}^3}\\
&= 3.3907 \times 10^4 \text{ J m}^{-3} = 3.3907 \times 10^4 \text{ N m}^{-2}\\
&= 3.3907 \times 10^4 \text{ Pa}
\end{aligned}
$$

16. The van der Waals equation of state gives better accuracy than the ideal gas equation of state. It is

$$
\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT
$$

where a and b are parameters that have different values for different gases and where $V_m = V/n$, the molar volume. For carbon dioxide, $a = 0.3640 \text{ Pa m}^6 \text{ mol}^{-2}$, $b = 4.267 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$. Calculate the pressure of carbon dioxide in pascals, assuming that $n = 0.13678$ mol, $V = 10.00$ l, and $T = 298.15$ K. Convert your answer to atmospheres and torr.

$$
\begin{aligned}
P &= \frac{RT}{V_m - b} - \frac{a}{V_m^2}\\
&= \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{7.3110 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1} - 4.267 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}}\\
&\quad - \frac{0.3640 \text{ Pa m}^6 \text{ mol}^{-2}}{(7.3110 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1})^2}\\
P &= \frac{RT}{V_m - b} - \frac{a}{V_m^2}\\
&= \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{7.3110 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1} - 4.267 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}}\\
&\quad - \frac{0.3640 \text{ Pa m}^6 \text{ mol}^{-2}}{(7.3110 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1})^2}\\
&= 3.3927 \times 10^4 \text{ J m}^{-3} - 68.1 \text{ Pa}\\
&= 3.3927 \times 10^4 \text{ Pa} - 68.1 \text{ Pa} = 3.386 \text{ Pa}\\
&\quad (3.3859 \text{ Pa})\left(\frac{1 \text{ atm}}{101325 \text{ Pa}}\right) = 0.33416 \text{ atm}
\end{aligned}
$$

The prediction of the ideal gas equation is

$$
\begin{aligned}
P &= \frac{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{7.3110 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1}}\\
&= 3.3907 \times 10^4 \text{ J m}^{-3} = 3.3907 \times 10^4 \text{ Pa}
\end{aligned}
$$

17. The specific heat capacity (specific heat) of a substance is crudely defined as the amount of heat required to raise the temperature of unit mass of the substance by 1 degree Celsius (1 °C). The specific heat capacity of water is $4.18 \text{ J °C}^{-1} \text{ g}^{-1}$. Find the rise in temperature if 100.0 J of heat is transferred to 1.000 kg of water.

$$
\begin{aligned}
\Delta T &= \frac{100.0 \text{ J}}{(4.18 \text{ J °C}^{-1} \text{ g}^{-1})(1.000 \text{ kg})}\left(\frac{1 \text{ kg}}{1000 \text{ g}}\right)\\
&= 0.0239 \text{ °C}
\end{aligned}
$$

18. The volume of a cone is given by

$$
V = \frac{1}{3}\pi r^2 h
$$

where h is the height of the cone and r is the radius of its base. Find the volume of a cone if its radius is given as 0.443 m and its height is given as 0.542 m.

$$
V = \frac{1}{3}\pi r^3 h = \frac{1}{3}\pi (0.443 \text{ m})^2 (0.542 \text{ m}) = 0.111 \text{ m}^3
$$

19. The volume of a sphere is equal to $\frac{4}{3}\pi r^3$ where r is the radius of the sphere. Assume that the earth is spherical with a radius of 3958.89 miles. (This is the radius of a sphere with the same volume as the earth, which is flattened at the poles by about 30 miles.) Find the volume of the earth in cubic miles and in cubic meters. Use a value of π with at least six digits and give the correct number of significant digits in your answer.

$$\begin{aligned} V &= \frac{4}{3}\pi r^3 = \frac{4}{3}\pi(3958.89 \text{ mi})^3 \\ &= 2.59508 \times 10^{11} \text{ mi}^3 \end{aligned}$$

$$(2.59508 \times 10^{11} \text{ mi}^3)\left(\frac{5280 \text{ ft}}{1 \text{ mi}}\right)^3\left(\frac{12 \text{ in}}{1 \text{ ft}}\right)^3$$

$$\times\left(\frac{0.0254 \text{ m}}{1 \text{ in}}\right)^3 = 1.08168 \times 10^{21} \text{ m}^3$$

20. Using the radius of the earth in the previous problem and the fact that the surface of the earth is about 70% covered by water, estimate the area of all of the bodies of water on the earth. The area of a sphere is equal to four times the area of a great circle, or $4\pi r^2$, where r is the radius of the sphere.

$$\begin{aligned} A &\approx (0.7)4\pi r^2 = (0.7)4\pi(3958.89 \text{ mi})^2 \\ &= 1.4 \times 10^8 \text{ mi}^2 \end{aligned}$$

We give two significant digits since the use of 1 as a single digit would specify a possible error of about 50%. It is a fairly common practice to give an extra digit when the last significant digit is 1.

21. The hectare is a unit of land area defined to equal exactly 10,000 square meters, and the acre is a unit of land area defined so that 640 acres equals exactly one square mile. Find the number of square meters in 1.000 acre, and find the number of acres equivalent to 1.000 hectare.

$$\begin{aligned} 1.000 \text{ acre} &= \left(\frac{(5280 \text{ ft})^2}{640}\right)\left(\frac{12 \text{ in}}{1 \text{ ft}}\right)^2 \\ &\quad \times\left(\frac{0.0254 \text{ m}}{1 \text{ in}}\right)^2 = 4047 \text{ m}^2 \\ 1.000 \text{ hectare} &= (1.000 \text{ hectare})\left(\frac{10000 \text{ m}^2}{1 \text{ hectare}}\right) \\ &\quad \times\left(\frac{1 \text{ acre}}{4047 \text{ m}^2}\right) = 2.471 \text{ acre} \end{aligned}$$