# 2.16: Problems

1. If $A$ is an ideal gas in a mixture of ideal gases, prove that its partial pressure, $P_A$, is given by $P_A = x_A P_{mixture}$ .
2. If $A$ is an ideal gas in a mixture of ideal gases, prove that its partial volume, $V_A$, is given by $V_A = x_A V_{mixture}$ .
3. A sample of hydrogen chloride gas, $HCl$, occupies 0.932 L at a pressure of 1.44 bar and a temperature of 50 C. The sample is dissolved in 1 L of water. What is the resulting hydronium ion, $H_3O^+$, concentration?
4. Ammonia gas, $NH_3$, also dissolves quantitatively in water. If it is measured at 0.720 bar and 50 C, what volume of $NH_3$ gas is required to neutralize the solution prepared in problem 3? For present purposes, assume that the neutralization reaction occurs quantitatively.
5. Two pressure vessels are separated by a closed valve. One contains 10.0 moles of helium, $He$, at 5.00 bar. The other contains 5.00 moles of neon, $Ne$, at 20.0 bar. Both vessels are at the same temperature. The valve is opened and the gases are allowed to mix. The temperature remains constant. What is the final pressure?
6. What is the average velocity of a molecule of nitrogen, $N_2$, at 300 K? Of a molecule of hydrogen, $H_2$, at the same temperature?
7. The Homestake gold mine near Lead, South Dakota, is excavated to 8000 feet below the surface. Lead is nearly a mile high; the bottom of the Homestake is about 900 m below sea level. Nearby Custer Peak is about 2100 m above sea level. What is the ratio of the barometric pressure on top of Custer Peak to the barometric pressure at the bottom of the Homestake? Assume that the entire atmosphere is at 300 K and that it behaves as a single ideal gas whose molar mass is 29.
8. On the sidewalk in front of a tall building, the barometric pressure is 740 torr and the temperature is 25 C. On the roof of this building, the barometric pressure is 732 torr. Assuming that the entire atmosphere behaves as an ideal gas of molecular weight 29 at 25 C, estimate the height of the building. Comment on the likely accuracy of this estimate.
9. At 1 bar, the boiling point of water is 372.78 K. At this temperature and pressure, the density of liquid water is 958.66 kg m$^{--3}$ and that of gaseous water is 0.59021 kg m$^{--3}$. What are the molar volumes, in $\mathrm{m^3\ mol^{-1}}$, of liquid and gaseous water at this temperature and pressure? In $\mathrm{L\ mol^{-1}}$?
10. Refer to your results in Problem 9. Assuming that a water molecule excludes other water molecules from a cubic region centered on itself, estimate the average distance between nearest-neighbor water molecules in the liquid and in the gas.
11. Calculate the molar volume of gaseous water at 1 bar and 372.78 K from the ideal gas equation. What is the error, expressed as a percentage of the value you calculated in Problem 9?
12. At 372.78 K, the virial coefficient B* for water is $-1.487 \times 10^{-7}\ \mathrm{Pa^{-1}}$. Calculate the molar volume of gaseous water at 1 bar and 372.78 K from the virial equation: $Z = P\overline{V}/RT = 1 + B^*P$ . What is the error, expressed as a percentage of the value you calculated in Problem 9?
13. Calculate the molar volume of gaseous water at 1 bar and 372.78 K from van der Waals' equation. The van der Waals' parameters for water are $a = 5.537\ \mathrm{bar\ L^2\ mol^{-1}}$ and $b = 0.0305\ \mathrm{L\ mol^{-1}}$. What is the error, expressed as a percentage of the value you calculated in Problem 9?
14. Comment on the results in Problems 11 – 13. At this temperature, would you expect the accuracy to increase or decrease at lower pressures?
15. The critical temperature for water is 647.1 K. At $10^3$bar and 700 K, the density of supercritical water is 651.37 kg $\mathrm{m^3}$. Note that this is about 68% of the value for liquid water at the boiling point at 1 bar. What is the molar volume, in $\mathrm{m^3\ mol^{-1}}$, of water at this temperature and pressure? In $\mathrm{L\ mol^{-1}}$?
16. Refer to your results in Problem 15. Assuming that a water molecule excludes other water molecules from a cubic region centered on itself, estimate the average distance between nearest-neighbor water molecules in supercritical water at $10^3$ bar and 700 K.
17. Calculate the molar volume of supercritical water at $10^3$ bar and 700 K from the ideal gas equation. What is the error, expressed as a percentage of the value you calculated in Problem 15?
18. At 700 K, the virial coefficient B* for water is $-1.1512 \times 10^{-8}\ \mathrm{Pa^{-1}}$ Calculate the molar volume of supercritical water at $10^3$ bar and 700 K from the virial equation. (See Problem 12.) What is the error, expressed as a percentage of the value you calculated in Problem 15?
19. Calculate the molar volume of supercritical water at $10^3$ bar and 700 K from van der Waals' equation. (See Problem 13.) What is the error, expressed as a percentage of the value you calculated in Problem 15?
20. Comment on the results in Problems 16 – 19.
21. Comment on the results in Problems 10 – 13 *versus* the results in Problems 16 – 19.
22. A 1.000 L combustion bomb is filled with natural gas at 2.00 bar and 300 K. Pure oxygen is then pressured into the bomb until the pressure reaches 7.00 bar, at 300 K. Combustion is initiated. When reaction is complete, the bomb is thermostatted at 500 K,

and the pressure is measured to be 12.08 bar. Thereafter, the bomb is cooled to 260 K, so that all of the water freezes. The pressure is then found to be 2.812 bar. The natural gas is a mixture of helium, methane, and ethane. How many moles of each gas are in the original sample?

23. An unknown liquid compound boils at 124 C. A classical method is used to find the approximate molecular weight of this compound. This method uses a glass bulb whose only opening is a long thin capillary tube, so that a gas sample inside the bulb can mix with the air outside only slowly. Filled with water, the bulb weighs 102.7535 grams. Empty, it weighs 50.0230 grams. A quantity of the unknown liquid is put into the bulb, and the body of the bulb is immersed in an oil bath at 150 C. The end of the capillary tube extends out of the oil bath. The liquid vaporizes filling the bulb with its gas. The total amount of vapor generated is large compared to the volume of the bulb, so the escaping vapor effectively sweeps all of the air out of the bulb, leaving the bulb filled with just the vapor of the unknown compound. When the last drop of liquid has just vaporized, the bulb is filled with the vapor of the unknown substance at the ambient atmosphere pressure, which is 0.980 bar, and a temperature of 150 C. The bulb is then removed from the oil bath and allowed to cool quickly so that the vapor condenses to a liquid film on the inside of the bulb. The oil is cleaned from the outside of the bulb, and the bulb is reweighed. The bulb and the liquid inside weigh 50.1879 grams. What is the approximate molecular weight of the liquid?
24. From the data below, calculate the molar volume, in liters, of each substance. For each substance, divide van der Waals' $b$ by the molar volume you calculate. Comment.

| Compound | Mol Mass, $\mathrm{g\ mol^{-1}}$ | Density, $\mathrm{g\ mL^{-1}}$ | Van der Waals $b$, $\mathrm{L\ mol^{-1}}$ |
|---|---|---|---|
| Acetic acid | 60.05 | 1.0491 | 0.10680 |
| Acetone | 58.08 | 0.7908 | 0.09940 |
| Acetonitrile | 41.05 | 0.7856 | 0.11680 |
| Ammonia | 17.03 | 0.7710 | 0.03707 |
| Aniline | 93.13 | 1.0216 | 0.13690 |
| Benzene | 78.11 | 0.8787 | 0.11540 |
| Benzonitrile | 103.12 | 1.0102 | 0.17240 |
| iso-Butylbenzene | 134.21 | 0.8621 | 0.21440 |
| Chlorine | 70.91 | 3.2140 | 0.05622 |
| Durene | 134.21 | 0.8380 | 0.24240 |
| Ethane | 30.07 | 0.5720 | 0.06380 |
| Hydrogen chloride | 36.46 | 1.1870 | 0.04081 |
| Mercury | 200.59 | 13.5939 | 0.01696 |
| Methane | 16.04 | 0.4150 | 0.04278 |
| Nitrogen dioxide | 46.01 | 1.4494 | 0.04424 |
| Silicon tetrafluoride | 104.08 | 1.6600 | 0.05571 |
| Water | 18.02 | 1.0000 | 0.03049 |

Notes

[1]We use the over-bar to indicate that the quantity is per mole of substance. Thus, we write $\overline{N}$ to indicate the number of particles per mole. We write $\overline{M}$ to represent the gram molar mass. In Chapter 14, we introduce the use of the over-bar to denote a partial molar quantity; this is consistent with the usage introduced here, but carries the further qualification that temperature and pressure are constant at specified values. We also use the over-bar to indicate the arithmetic average; such instances will be clear from the context.

[2]The unit of temperature is named the kelvin, which is abbreviated as K.

[3]A redefinition of the size of the unit of temperature, the kelvin, is under consideration. The practical effect will be inconsequential for any but the most exacting of measurements.

[4]For a thorough discussion of the development of the concept of temperature, the evolution of our means to measure it, and the philosophical considerations involved, see Hasok Chang, Inventing Temperature, Oxford University Press, 2004.

[5]See T. L. Hill, ***An Introduction to Statistical Thermodynamics***, Addison-Wesley Publishing Company, 1960, p 286.

[6]See S. M. Blinder, ***Advanced Physical Chemistry***, The Macmillan Company, Collier-Macmillan Canada, Ltd., Toronto, 1969, pp 185-189