

Fall 2011: 5.112 PRINCIPLES OF CHEMICAL SCIENCE

Problem Set #4 solutions

This problem set was graded out of 99 points

Question 1 (out of 7 points)

(i) For each pair, determine which compound has bonds with greater ionic character. (3 points)

- (a) NH_3 or AsH_3 : The N-H bond is more ionic than the As-H bond since the difference in electronegativity of N and H (3.0 vs. 2.2) is greater than the difference between As and H (2.2 vs. 2.2).
- (b) SiO_2 or SO_2 : S and O have similar electronegativities (3.0 and 3.4) whereas for Si and O the difference is greater (1.9 vs. 3.4) so the Si-O bonds have greater ionic character.
- (c) SF_6 or IF_5 : S and I have very similar electronegativities (2.6 and 2.7), thus the bonds are very similar. S-F bonds may have a slightly higher ionic character, but it would be difficult to determine experimentally.

(ii) In which molecule, $\text{O}=\text{C}=\text{O}$ or $\text{O}=\text{C}=\text{CH}_2$, do you expect the C-O bond to be more ionic? (2 points)

The C-O bond in $\text{O}=\text{C}=\text{O}$ will have greater ionic character because O is more electronegative than the carbon in the CH_2 fragment, so in absolute values, the C in CO_2 has twice as much charge removed as the C attached to one O and the CH_2 fragment.

(iii) In which molecule do you expect the bonds to be more ionic, CCl_4 or SiCl_4 ? (2 points)

The difference in electronegativity between C and Cl is less than the difference between Si and Cl, so the bonds in SiCl_4 will be have greater ionic character.

Question 2 (out of 3 points)

The gaseous potassium chloride molecule has a dipole moment of 10.3 D, which indicates that it is a very polar molecule. The separation between the nuclei in this molecule is 2.67 Å. Calculate the dipole moment of a KCl molecule if there were opposite charges of one fundamental unit (1.60×10^{-19} C) at the nuclei?

We can calculate the dipole moment of the molecule if it was completely ionic from the following formula:

$$\mu = \frac{QR}{3.336 \times 10^{-30} \text{ C m/D}} = \frac{(1.602 \times 10^{-19} \text{ C})(2.67 \times 10^{-10} \text{ m})}{3.336 \times 10^{-30} \text{ C m/D}} = 12.8 \text{ D}$$

The dipole moment of KCl is 12.8 D if it were 100% ionic in character.

Question 3 (out of 6 points)

Consider two diatomic molecules with 100% ionic character. One has a bond length of 1.75 Angstroms, the other a bond length of 3.25 Angstroms.

(a) Calculate the dipole moment for each molecule. (3 points)

The equation for dipole moment is: $\mu = QR$, where Q = the charge and R is the distance separating the two ions, if we want to have the dipole moment to be in debye, we need to have the conversion fact of 0.2082 A D^{-1} .

We can now go ahead and calculate the dipole moments for the two molecules:

For the 1.75 Å bond length:

$$\mu = \frac{QR}{0.2082 \text{ C Å D}^{-1}} = \frac{(e) \left(1.75 \text{ Å} \right)}{0.2082 \text{ e Å D}^{-1}} = 8.41 \text{ D}$$

For the 3.25 Å bond length:

$$\mu = \frac{QR}{0.2082 \text{ C Å D}^{-1}} = \frac{(e) \left(3.25 \text{ Å} \right)}{0.2082 \text{ e Å D}^{-1}} = 15.6 \text{ D}$$

(b) Calculate the Coulombic potential energy for each molecule. (3 points)

We need to remember the equation for Coulombic potential: $\Delta E_{\text{coulomb}} = \frac{q_1 q_2}{4\pi\epsilon_0 r}$, where q is the charge on the ion multiplied by the fundamental charge (e).

Now we can calculate the Coulombic potential energy for each molecule:

For the 1.75 Å bond length:

$$\Delta E_{\text{coulomb}} = \frac{q_1 q_2}{4\pi\epsilon_0 r} = \frac{(1.60218 \times 10^{-19} \text{ C})(1.60218 \times 10^{-19} \text{ C})}{4\pi(8.85419 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1})(1.75 \times 10^{-10} \text{ m})}$$

$$= 1.31829 \times 10^{-18} \text{ J}$$

$$= 1.32 \times 10^{-18} \text{ J}$$

For the 3.25 Å bond length:

$$\Delta E_{\text{coulomb}} = \frac{q_1 q_2}{4\pi\epsilon_0 r} = \frac{(1.60218 \times 10^{-19} \text{ C})(1.60218 \times 10^{-19} \text{ C})}{4\pi(8.85419 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1})(3.25 \times 10^{-10} \text{ m})}$$

$$= 7.09875 \times 10^{-19} \text{ J}$$

$$= 7.10 \times 10^{-19} \text{ J}$$

Question 4 (out of 4 points)

Estimate the percent ionic character of the bond in each of the following species. All the species are unstable or reactive under ordinary laboratory conditions, but are observed in interstellar space.

| | Average Bond Length (Å) | Dipole Moment (D) |
|--------------------|-------------------------|-------------------|
| (a) OH | 0.980 | 1.66 |
| (b) CH | 1.131 | 1.46 |
| (c) CN | 1.175 | 1.45 |
| (d) C ₂ | 1.246 | 0 |

The percentage ionic character is calculated by determining the δ (fraction of unit charge on each atom) and multiplying δ by 100.

(a) OH

$$\delta = \frac{\left[0.2082 \text{ Å D}^{-1} \right]}{0.980 \text{ Å}} [1.66 \text{ D}] = 0.353 \quad \text{For OH, the percentage ionic character is 35.3 \%}$$

(b) CH

$$\delta = \frac{\left[0.2082 \text{ Å D}^{-1} \right]}{1.131 \text{ Å}} [1.46 \text{ D}] = 0.269 \quad \text{For CH, the percentage ionic character is 26.9 \%}$$

(c) CN

$$\delta = \frac{\left[0.2082 \text{ Å D}^{-1} \right]}{1.175 \text{ Å}} [1.45 \text{ D}] = 0.257 \quad \text{For CN, percentage ionic character is 25.7 \%}$$

(d) C₂ For C₂ the percentage ionic character is 0 %.

Question 5 (out of 6 points)

Consider KF, which has an ionic bond. The bond length is 2.17×10^{-10} m or 217 pm.

(a) Calculate the energy (in kJ/mol) required to dissociate the KF molecule into the ions K^+ and F^- .

This energy is the Coulomb energy of interaction between the ions of K^+ and F^- :

$$\begin{aligned}\Delta E_{\text{coulombic}} &= \frac{Q_1 Q_2}{4\pi\epsilon_0 r} \\ &= \frac{(1)(1)(1.602 \times 10^{-19} \text{ C})^2 (6.022 \times 10^{23} \text{ mol}^{-1})}{4\pi(8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1})(2.17 \times 10^{-10} \text{ m})} \\ &= 640113 \text{ J mol}^{-1} = 6.40 \times 10^2 \text{ kJ mol}^{-1}\end{aligned}$$

The energy required to dissociate KF into its ions is 6.40×10^2 kJ mol⁻¹. The energy is positive because we are going from molecule to ions (up on the energy scale).

(b) The energy required to dissociate KF into neutral atoms is 498 kJ/mol. Given that the first ionization energy for K is 419 kJ/mol, calculate the electron affinity (in kJ/mol) for F.

We can calculate the electron affinity for F by using the following equation:

$$\Delta E_d = \frac{Q_1 Q_2}{4\pi\epsilon_0 R} - [IE_1(K) - EA(F)]$$

We are given the ΔE_d (498 kJ mol⁻¹). We calculated the coulomb interaction energy in part (a) (640 kJ mol⁻¹) and we are given IE_1 for potassium (419 kJ mol⁻¹), so we can calculate the electron affinity for F by substitution into the above equation:

$$\begin{aligned}\Delta E_d &= \frac{Q_1 Q_2}{4\pi\epsilon_0 r} - [IE_1(K) - EA(F)] \\ 498 \text{ kJ mol}^{-1} &= 6.40 \times 10^2 \text{ kJ mol}^{-1} - [419 \text{ kJ mol}^{-1} - EA(F)] \\ EA(F) &= 498 \text{ kJ mol}^{-1} - 6.40 \times 10^2 \text{ kJ mol}^{-1} + 419 \text{ kJ mol}^{-1} \\ &= 277 \text{ kJ mol}^{-1}\end{aligned}$$

The electron affinity for F is 277 kJ mol⁻¹. (The electron affinity is actually 328 kJ mol⁻¹). Since this method is an approximation, the agreement is reasonable.

Question 6 (out of 6 points)

Consider the SrO molecule that has an ionic bond length of 1.54×10^{-10} m.

a) Calculate the energy in kJ mol⁻¹ required to dissociate SrO into its ions Sr^{+2} and O^{2-} . Treat the ions as point charges.

The energy the question asked for is the $\Delta E_{\text{coulomb}}$ which can be calculated from the following equation:

$$\begin{aligned}\Delta E_{\text{coulomb}} &= \frac{e^2}{4\pi\epsilon_0 r} = \frac{(2)^2 (1.602176 \times 10^{-19} \text{ C})^2 (6.02214 \times 10^{23} \text{ mol}^{-1})}{4\pi(8.85419 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1})(1.54 \times 10^{-10} \text{ m})} \\ &= \frac{6.183456 \times 10^{-14} \text{ C}^2 \text{ mol}^{-1}}{1.713482 \times 10^{-20} \text{ C}^2 \text{ J}^{-1}} \\ &= 3.60871 \times 10^6 \text{ J mol}^{-1} \\ &= 3.61 \times 10^3 \text{ kJ mol}^{-1}\end{aligned}$$

The energy required to dissociate SrO into its ions Sr^{+2} and O^{2-} is 3.61×10^3 kJ mol⁻¹.

b) Write 5 reactions which when summed will result in the reaction: $\text{SrO} \rightarrow \text{Sr} + \text{O}$. Four of these reactions are related to the energies for the processes given in the table below.

| | |
|-----------------------|-------------|
| IE ₁ of Sr | 549 kJ/mol |
| IE ₂ of Sr | 1064 kJ/mol |
| EA of O | 141 kJ/mol |
| EA of O ⁻ | -844 kJ/mol |

Then, calculate the bond dissociation energy of CaO into its neutral atoms, Ca and O.

Five possible reactions are:

| Reaction | ΔE |
|---|---|
| $\text{Sr}^{+1} + e^{-1} \rightarrow \text{Sr}$ | $\Delta E_A = -(\text{IE}_1 \text{ of Sr}) = -549 \text{ kJ mol}^{-1}$ |
| $\text{Sr}^{+2} + e^{-1} \rightarrow \text{Sr}^{+1}$ | $\Delta E_B = -(\text{IE}_2 \text{ of Sr}) = -1064 \text{ kJ mol}^{-1}$ |
| $\text{O}^{-1} \rightarrow \text{O} + e^{-1}$ | $\Delta E_C = +141 \text{ kJ mol}^{-1}$ |
| $\text{O}^{-2} \rightarrow \text{O}^{-1} + e^{-1}$ | $\Delta E_D = -844 \text{ kJ mol}^{-1}$ |
| $\text{SrO} \rightarrow \text{Sr}^{+2} + \text{O}^{-2}$ | $\Delta E_{\text{coulomb}} = 3610 \text{ kJ mol}^{-1}$ |
| $\text{CaO} \Rightarrow \text{Ca} + \text{O}$ | |

We can now calculate the energy required to dissociate into neutral atoms (which is called the dissociation energy);

$$\begin{aligned} \Delta E &= \Delta E_A + \Delta E_B + \Delta E_C + \Delta E_D + \Delta E_{\text{Coulomb}} \\ &= (-549 \text{ kJ mol}^{-1}) + (-1064 \text{ kJ mol}^{-1}) + (141 \text{ kJ mol}^{-1}) + (-844 \text{ kJ mol}^{-1}) + (3610 \text{ kJ mol}^{-1}) \\ &= 1294 \text{ kJ mol}^{-1} \end{aligned}$$

The dissociation energy is 1294 kJ mol^{-1} .

Question 7 (out of 3 points)

Because of its particle nature, light can exert pressure on a surface. Suppose a 1.5-W laser is focused on a circular area 0.15 mm in radius. The wavelength of the laser light is 569 nm. Assume that the photons travel perpendicular to the surface and are perfectly reflected, and their momenta change sign after reflection from the wall. Using results from the kinetic theory of gases, calculate the pressure exerted by the light on the surface. The momentum p of a photon is related to its energy through $E = pc$.

The fall of photons on a surface exerts a pressure. Use the deBroglie relation to compute the momentum of the photons:

$$p = \frac{h}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J s}}{569 \times 10^{-9} \text{ m}} = 1.1645 \times 10^{-27} \text{ kg m s}^{-1}$$

Each photon bounces away from the wall with momentum of the same magnitude but opposite sign. The change in momentum per collision is:

$$\Delta p = p_2 - p_1 = (1.1645 \times 10^{-27} \text{ kg m s}^{-1}) - (-1.1645 \times 10^{-27} \text{ kg m s}^{-1}) = 2.33 \times 10^{-27} \text{ kg m s}^{-1}$$

The number of photons colliding per second equals the power of the laser (1.5 watt = 1.5 J s^{-1}) divided by the energy delivered per photon. The energy transported by one 569 nm photon is:

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J s})(2.9979 \times 10^8 \text{ m s}^{-1})}{(569 \times 10^{-9} \text{ m})} = 3.491 \times 10^{-19} \text{ J}$$

Clearly, it requires lots of such photons to transport 1.5 J s^{-1} :

$$\left(\frac{1.5 \text{ J}}{1 \text{ s}}\right) \times \left(\frac{1 \text{ photon}}{3.49 \times 10^{-19} \text{ J}}\right) = \frac{4.30 \times 10^{18} \text{ photons}}{\text{second}}$$

As developed in Section 4-13, the total force equals the change in momentum per collision multiplied by the number of collisions per second:

$$F = (2.33 \times 10^{-27} \text{ kg m s}^{-1}) \times (4.30 \times 10^{18} \text{ s}^{-1}) = 1.00 \times 10^{-8} \text{ kg m s}^{-2}$$

Pressure is defined as force divided by area. The area of the circular wall is πr^2 where r is the radius. Hence:

$$\begin{aligned} P &= \frac{F}{A} = \frac{F}{\pi r^2} = \frac{1.00 \times 10^{-8} \text{ kg m s}^{-2}}{\pi (0.15 \times 10^{-3} \text{ m})^2} \\ &= 0.1415 \text{ Pa} \\ &= 0.14 \text{ Pa (correct sig figs)} \end{aligned}$$

So the pressure exerted by the light on the surface is 0.21 Pa.

Question 8 (out of 6 points)

In an optical atomic trap, beams of tightly focused laser light replace the physical walls of conventional containers. They briefly (for 0.500 s) exert enough pressure to confine 695 sodium atoms in a volume of $1.0 \times 10^{-15} \text{ m}^3$. The temperature of this gas is 0.00024 K, the lowest temperature ever reached for a gas.

a) Compute the root-mean-square speed of the atoms in this confinement.

The root-mean-square speed of the molecules of a gas is $v_{\text{rms}} = \sqrt{\frac{3RT}{M}}$

where M is the molar mass of the gas. We substitute $M = 0.02299 \text{ kg mol}^{-1}$, $R = 8.315 \text{ J mol}^{-1}\text{K}^{-1}$, and $T = 0.00024 \text{ K}$ to compute

$$\begin{aligned} v_{\text{rms}} &= \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3(8.315 \text{ J mol}^{-1}\text{K}^{-1})(2.4 \times 10^{-4} \text{ K})}{0.02299 \text{ kg mol}^{-1}}} \\ &= 0.5103 \text{ m s}^{-1} \\ &= 0.51 \text{ m s}^{-1} \end{aligned}$$

$$v_{\text{rms}} = 0.51 \text{ m s}^{-1}$$

Common errors here are to use M in g mol^{-1} instead of kg mol^{-1} or to use R in the wrong units.

b) Assume ideal gas behavior to compute the pressure exerted on the "walls" of the optical bottle in this experiment.

Since we are making the assumption that the Na atoms are acting as an ideal gas, we can use the equation $PV = nRT$. We have to first determine V . The volume of the trap is expressed in liters ($1 \text{ L} = 10^{-3} \text{ m}^3$) and we can convert the volume of $1.0 \times 10^{-15} \text{ m}^3$ to L;

$$1.0 \times 10^{-15} \text{ m}^3 \left(\frac{1 \text{ L}}{10^{-3} \text{ m}^3}\right) = 1.0 \times 10^{-12} \text{ L}$$

The amount of its contents is expressed in moles

$$n = \frac{695 \text{ atoms}}{6.022 \times 10^{23} \text{ atoms mol}^{-1}} = 1.1541 \times 10^{-21} \text{ mol}$$

Then, the problem becomes a substitution into $PV = nRT$;

$$P = \frac{(1.15341 \times 10^{-21} \text{ mol}) 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} (2.4 \times 10^{-4} \text{ K})}{1.0 \times 10^{-12} \text{ L}} = 2.273 \times 10^{-14} \text{ atm}$$

The atoms exert a pressure of 2.3×10^{-14} atm.

Question 9 (out of 2 points)

Equal numbers of atoms of Helium-4 and Xenon-129 exert the same pressure at constant volume and temperature, despite the large difference in the masses. Based on kinetic theory, explain what this tells you about the velocities of the atoms.

Since pressure is defined as the force exerted on a unit area of the walls of a container by atoms of the gas, an average helium atom must exert the same force as an average xenon atom. According to the definition of an ideal gas, these collisions must be elastic. Since force exerted in an elastic collision by an impact is proportional to the momentum of the atom, helium atoms must move much faster than xenon atoms to exert the same force.

Question 10 (out of 6 points)

The "escape velocity" necessary for objects to leave the gravitational field of the earth is 11.2 km/s. Calculate the ratio of the escape velocity to the root-mean-square speed of helium, argon, and xenon atoms at 2200 K. Does your result help explain the low abundance of the light gas helium in the atmosphere? Explain.

To calculate the rms speeds of helium, argon, and xenon atoms at 2000 K (1 significant figure!), we substitute the molar masses in kg mol^{-1} of the three gases successively into the expression u_{rms} , taking $T = 2000 \text{ K}$ and $R = 8.315 \text{ J mol}^{-1} \text{ K}^{-1}$.

For He

$$v_{\text{rms}} = \sqrt{\frac{3(8.315 \text{ J mol}^{-1} \text{ K}^{-1})(2200 \text{ K})}{(4.0026 \times 10^{-3} \text{ kg mol}^{-1})}} = 3.703 \times 10^3 \text{ m s}^{-1}$$

$$v_{\text{rms}} = 3.7 \times 10^3 \text{ m s}^{-1} \text{ (correct sig figs)}$$

$$\begin{aligned} \text{Ratio of } \frac{\text{escape velocity}}{\text{root-mean square velocity}} &= \frac{3.703 \times 10^3 \text{ m s}^{-1}}{11.2 \times 10^3 \text{ m s}^{-1}} \\ &= 0.33061 \\ &= 0.33 \end{aligned}$$

For Ar

$$v_{\text{rms}} = \sqrt{\frac{3(8.315 \text{ J mol}^{-1} \text{ K}^{-1})(2200 \text{ K})}{(39.948 \times 10^{-3} \text{ kg mol}^{-1})}} = 1.1172 \times 10^3 \text{ m s}^{-1}$$

$$v_{\text{rms}} = 1.1 \times 10^3 \text{ m s}^{-1} \text{ (correct sig figs)}$$

$$\begin{aligned} \text{Ratio of } \frac{\text{escape velocity}}{\text{root-mean square velocity}} &= \frac{1.12 \times 10^3 \text{ m s}^{-1}}{11.2 \times 10^3 \text{ m s}^{-1}} (100) \\ &= 0.10465 \\ &= 0.10 \text{ (correct sig figs)} \end{aligned}$$

For Xe

$$v_{\text{rms}} = \sqrt{\frac{3(8.315 \text{ J mol}^{-1} \text{ K}^{-1})(2200 \text{ K})}{(131.29 \times 10^{-3} \text{ kg mol}^{-1})}} = 646.53 \text{ m s}^{-1}$$

$$v_{\text{rms}} = 6.5 \times 10^2 \text{ m s}^{-1} \text{ (correct sig figs)}$$

$$\begin{aligned} \text{Ratio of } \frac{\text{escape velocity}}{\text{root-mean square velocity}} &= \frac{6.46 \times 10^2 \text{ m s}^{-1}}{11.2 \times 10^3 \text{ m s}^{-1}} (100) \\ &= 0.05773 \\ &= 0.058 \text{ (correct sig figs)} \end{aligned}$$

The ratio of the escape velocity to the root mean square speeds are 0.33 (for He), 0.10 (for Ar) and 0.058 (for Xe). Helium is much more likely to escape than the heavier gases so this means that it will not be found at high abundance in our atmosphere.

Question 11 (out of 2 points)

A confined gas of Ar is heated so that its pressure is tripled. If the volume remains the same, how much kinetic energy does the gas gain or lose?

Think about the ideal gas law, $PV=nRT$. If the pressure is doubled, volume stays the same, we can determine how the temperature has changed:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\text{know that } P_2 = 3P_1 \quad \text{and} \quad V_1 = V_2$$

simplifying the relationship:

$$\frac{P_1}{T_1} = \frac{3P_1}{T_2} \quad \text{therefore : } T_2 = 3T_1$$

So, the temperature has tripled. Because $E = \frac{3}{2}RT$, the gas triples its kinetic energy

Question 12 (out of 4 points: 1 for part (a), 3 for part (b))

Six Rb atoms, with speeds of 1.2, 1.4, 1.6, 1.6, 2.0 and 2.5 m/s, are trapped in a laser trap.

(a) Determine the most probable speed for this distribution of six atoms.

The most probable speed is 1.6 m s^{-1} . There are two atoms with that speed.

(b) Calculate the root mean square speed for this distribution of six atoms.

The root mean square speed is:

$$\begin{aligned} \left(\overline{v^2}\right)^{\frac{1}{2}} &= \left(\frac{\left(1.2 \text{ m s}^{-1}\right)^2 + \left(1.4 \text{ m s}^{-1}\right)^2 + 2\left(1.6 \text{ m s}^{-1}\right)^2 + \left(2.0 \text{ m s}^{-1}\right)^2 + \left(2.5 \text{ m s}^{-1}\right)^2}{6} \right)^{\frac{1}{2}} \\ &= \left(\frac{1.44 \text{ m}^2 \text{ s}^{-2} + 2.074 \text{ m}^2 \text{ s}^{-2} + 5.12 \text{ m}^2 \text{ s}^{-2} + 4.0 \text{ m}^2 \text{ s}^{-2} + 6.25 \text{ m}^2 \text{ s}^{-2}}{6} \right)^{\frac{1}{2}} \\ &= \left(\frac{18.77 \text{ m}^2 \text{ s}^{-2}}{6} \right)^{\frac{1}{2}} = 1.7687 \text{ m s}^{-1} = 1.8 \text{ m s}^{-1} \end{aligned}$$

The root mean square speed for the six Rb atoms is 1.8 m s^{-1} .

(c) Calculate the temperature that corresponds to your answer for (b).

From our lectures #12 notes, we know that: $v_{\text{rms}} = \left(\frac{3RT}{M}\right)^{\frac{1}{2}}$

For the equation:

- v_{rms} that we calculated in part (b) = 1.8 m s^{-1}
- R which is the universal gas constant = $8.31447 \text{ J K}^{-1} \text{ mol}^{-1}$ (Use this value because a Joule is a Newton.meter, and a Newton = m kg s^{-2} which once you cancel units gives:

$$\begin{aligned} v_{\text{rms}} &= \left(\frac{3RT}{M}\right)^{\frac{1}{2}} \\ &= \left(\frac{(\text{m}^2 \text{ kg s}^{-2} \text{ K}^{-1} \text{ mol}^{-1})(\text{K})}{\text{kg mol}^{-1}}\right)^{\frac{1}{2}} \\ &= \left(\frac{\text{m}^2}{\text{s}^2}\right)^{\frac{1}{2}} \end{aligned}$$

- M which is the molar mass in $\text{kg mol}^{-1} = 85.47 \times 10^{-3} \text{ kg mol}^{-1}$
- T is the unknown:

Now we can solve for T:

$$\begin{aligned} v_{\text{rms}} &= \left(\frac{3RT}{M}\right)^{\frac{1}{2}} \\ 1.8 \text{ m s}^{-1} &= \left(\frac{3(8.31447 \text{ J K}^{-1} \text{ mol}^{-1} \text{ T})}{85.47 \times 10^{-3} \text{ kg}}\right)^{\frac{1}{2}} \\ 3.24 \text{ m}^2 \text{ s}^{-2} &= \left(\frac{3(8.31447 \text{ J K}^{-1} \text{ mol}^{-1} \text{ T})}{85.47 \times 10^{-3} \text{ kg}}\right) \\ T &= 0.011 \text{ K} \end{aligned}$$

Question 13 (out of 12 points: 3 for each speed)

Consider Ne gas at $T=298 \text{ K}$. For every million molecules traveling at the root mean square speed, approximately how many travel at $0.1 v_{\text{rms}}$; at $1.2 v_{\text{rms}}$; at $2 v_{\text{rms}}$; at $3 v_{\text{rms}}$.

This is a problem looking at the Maxwell-Boltzmann speed distribution function;

$$\frac{\Delta N}{N} = f(v)\Delta v, \text{ where } f(v) = 4\pi \left(\frac{M}{2\pi RT}\right)^{\frac{3}{2}} (v)^2 \exp\left(\frac{-Mv^2}{2RT}\right)$$

So we can compare the functions for the different speeds remembering that m is $20.180 \times 10^{-3} \text{ kg mol}^{-1}$, R is $8.315 \text{ J mol}^{-1} \text{ K}^{-1}$, T is 298 K and v is going to be v_{rms} .

We have to first determine v_{rms}

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3(8.31451 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{20.180 \times 10^{-3} \text{ kg}}} = 606.91 \text{ m s}^{-1}$$

Substituting the first ratios;

$$\frac{(1,000,000)_{\text{rms}}}{\Delta N_{0.1 v_{\text{rms}}}} = \left(\frac{v_{\text{rms}}}{0.1 v_{\text{rms}}} \right)^2 \exp \left[\left(\frac{-20.180 \times 10^{-3} \text{ kg mol}^{-1}}{2 \left(8.315 \text{ J mol}^{-1} \text{ K}^{-1} \right) (298 \text{ K})} \right) \left[(606.91)^2 - (60.691)^2 \right] \right]$$

$$\frac{(1,000,000)_{\text{rms}}}{\Delta N_{0.1 v_{\text{rms}}}} = 100 \exp \left[(-4.07205 \times 10^{-6}) (3.64656 \times 10^5) \right]$$

$$\frac{(1,000,000)_{\text{rms}}}{\Delta N_{0.1 v_{\text{rms}}}} = (100) \exp(-1.48490) = (100) (.22653)$$

$$\frac{(1,000,000)_{\text{rms}}}{\Delta N_{0.1 v_{\text{rms}}}} = 22.653$$

$$\Delta N_{0.1 v_{\text{rms}}} = 44,144$$

For every 1,000,000 molecules traveling at v_{rms} , 40 thousand molecules travel at $0.1v_{\text{rms}}$.

We can now do the same calculation for $1.2v_{\text{rms}}$:

$$\frac{(1,000,000)_{\text{rms}}}{\Delta N_{1.2 v_{\text{rms}}}} = \left(\frac{v_{\text{rms}}}{1.2 v_{\text{rms}}} \right)^2 \exp \left[\left(\frac{-20.180 \times 10^{-3} \text{ kg mol}^{-1}}{2 \left(8.315 \text{ J mol}^{-1} \text{ K}^{-1} \right) (298 \text{ K})} \right) \left[(606.91)^2 - (728.292)^2 \right] \right]$$

$$\frac{(1,000,000)_{\text{rms}}}{\Delta N_{1.2 v_{\text{rms}}}} = 0.6944 \exp \left[(-4.07205 \times 10^{-6}) (-1.6207 \times 10^5) \right]$$

$$\frac{(1,000,000)_{\text{rms}}}{\Delta N_{1.2 v_{\text{rms}}}} = 0.6944 \exp(0.659955) = (0.6944) (1.93470) = 1.34346$$

$$\Delta N_{1.2 v_{\text{rms}}} = 7.44345 \times 10^5$$

$$= 7.4 \times 10^5$$

For every 1,000,000 molecules traveling at v_{rms} , 7.4×10^5 molecules travel at $1.2v_{\text{rms}}$.

We can now do the same calculation for $2v_{\text{rms}}$:

$$\frac{(1,000,000)_{\text{rms}}}{\Delta N_{2v_{\text{rms}}}} = \left(\frac{v_{\text{rms}}}{2v_{\text{rms}}} \right)^2 \exp \left[\left(\frac{-20.180 \times 10^{-3} \text{ kg mol}^{-1}}{2 \left(8.315 \text{ J mol}^{-1} \text{ K}^{-1} \right) (298 \text{ K})} \right) \left[(606.91)^2 - (1213.82)^2 \right] \right]$$

$$\frac{(1,000,000)_{\text{rms}}}{\Delta N_{2v_{\text{rms}}}} = 0.25 \exp \left[(-4.07205 \times 10^{-6}) (-1.10502 \times 10^6) \right]$$

$$\frac{(1,000,000)_{\text{rms}}}{\Delta N_{2v_{\text{rms}}}} = (0.25) \exp(4.49969) = (0.25) (89.9896) = 22.49$$

$$\Delta N_{2v_{\text{rms}}} = 44,450$$

For every 1 million molecules traveling at v_{rms} there are 40 thousand molecules traveling at twice the v_{rms} .

We can now do the same calculation for $3v_{rms}$:

$$\frac{(1,000,000)_{rms}}{\Delta N_{3v_{rms}}} = \left(\frac{v_{rms}}{3v_{rms}}\right)^2 \exp\left[\left(\frac{-20.180 \times 10^{-3} \text{kg mol}^{-1}}{2(8.315 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})}\right)\left[(606.91)^2 - (1820.73)^2\right]\right]$$

$$\frac{(1,000,000)_{rms}}{\Delta N_{3v_{rms}}} = 0.1111 \exp\left[(-4.07205 \times 10^{-6})(-2.94672 \times 10^6)\right]$$

$$\frac{(1,000,000)_{rms}}{\Delta N_{3v_{rms}}} = 0.1111 \exp(11.9992) = (0.1111)(162622) = 18067.3$$

$$\Delta N_{3v_{rms}} = 55.3$$

For every 1 million molecules traveling at v_{rms} , there are 55 molecules traveling at three times the v_{rms} .

Here is another way to set up the problem using symbols:

The probability ratio, r , of two velocities is given by:

$$r = \frac{f(v)}{f(v_{rms})} = \frac{4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 \exp\left(-\frac{Mv^2}{2RT}\right)}{4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v_{rms}^2 \exp\left(-\frac{Mv_{rms}^2}{2RT}\right)}$$

$$= \left(\frac{v}{v_{rms}}\right)^2 \exp\left(-\frac{M}{2RT}(v^2 - v_{rms}^2)\right)$$

In this scenario, it is convenient to redefine v as a constant times v_{rms} :

$$v = cv_{rms}$$

Then we have:

$$r = \left(\frac{cv_{rms}}{v_{rms}}\right)^2 \exp\left(-\frac{M}{2RT}((cv_{rms})^2 - v_{rms}^2)\right)$$

$$= c^2 \exp\left(-\frac{Mv_{rms}^2}{2RT}(c^2 - 1)\right)$$

but we notice that

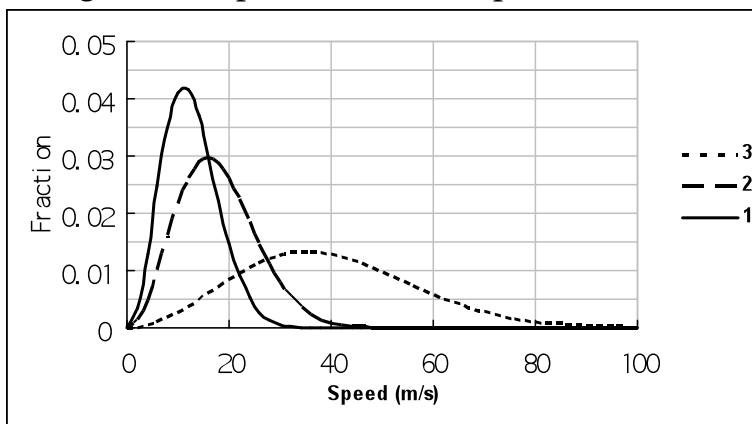
$$v_{rms}^2 = \frac{3RT}{M} \quad \text{so}$$

$$r = c^2 \exp\left(-\frac{3}{2}(c^2 - 1)\right)$$

And there is no dependence on M or T . The final answer is given by $10^6 r$, with $v = cv_{rms}$.

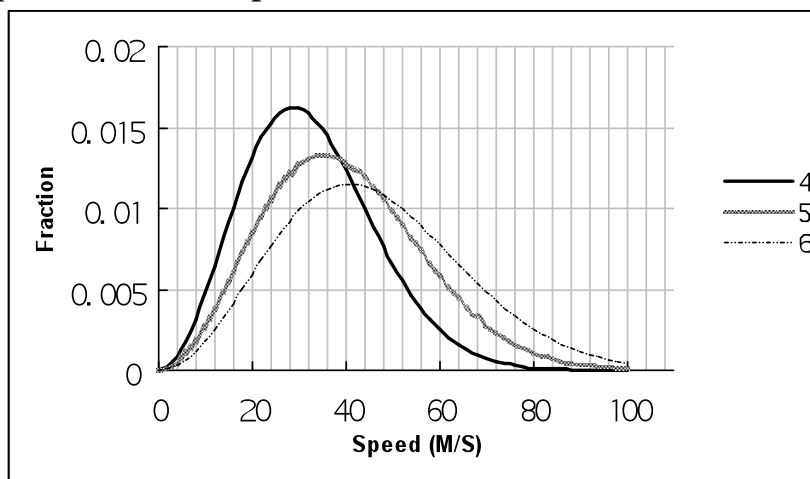
Question 14 out of 6 points)

(a) The following graph shows the range of molecular speeds for three gases, He, Ne and Ar, as given by the Maxwell distribution. Each of the curves (1, 2 and 3) correspond to 325 K. Match the curves with the gases, and provide a brief explanation.



Curve 1, 2 and 3 correspond to Ar, Ne and He, respectively, because according to the Maxwell distribution of speeds, the greater the molar mass, the lower the average speed and the narrower the spread of speeds.

(b) The following graph shows the range of molecular speeds for Gas 3 in the above question, at 225 K, 325 K and 425 K as given by the Maxwell distribution. Match the curves with the temperatures, and provide a brief explanation.



Curve 4, 5 and 6 correspond to 225 K, 325 K and 425 K, respectively, because according to the Maxwell distribution of speeds, the higher the temperature, the higher the average speed and the broader the spread of speeds.

Question 15 (out of 3 points)

The number of molecules in a gas sample that have the most probably speed (v_{mp}) at a temperature T is one-quarter the number of the same type of molecules that have the most probably speed at 355 K. What is the temperature?

Using the Maxwell distribution of speeds...

$$f(v) = 4\pi \left(\frac{M}{2\pi RT} \right)^{\frac{3}{2}} v^2 e^{-\frac{Mv^2}{2RT}}$$

$$\frac{df(v)}{dv} = \left(\frac{M}{2\pi RT} \right)^{\frac{3}{2}} e^{-\frac{Mv^2}{2RT}} \left[8\pi v + 4\pi v^2 \left(\frac{-Mv}{RT} \right) \right] = 0$$

Solving for v_{mp} in terms of T:

$$v_{mp} = \left(\frac{2RT}{M} \right)^{\frac{1}{2}}$$

Substitution into $f(v)$ gives:

$$f(v_{mp}) = 4\pi \left(\frac{M}{2\pi RT} \right)^{\frac{3}{2}} \left(\frac{2RT}{M} \right) e^{-1} = 4\pi \left(\frac{M}{2\pi RT} \right)^{\frac{1}{2}} e^{-1}$$

The problem asks for the temperature that satisfies this relationship:

$$f(v_{mp})_T = \frac{1}{4} f(v_{mp})_{355}$$

$$4\pi \left(\frac{M}{2\pi RT} \right)^{\frac{1}{2}} e^{-1} = \frac{1}{4} 4\pi \left(\frac{M}{2\pi R(355 \text{ K})} \right)^{\frac{1}{2}} e^{-1}$$

$$\left(\frac{1}{T} \right)^{\frac{1}{2}} = \left(\frac{1}{4} \right) \left(\frac{1}{355 \text{ K}} \right)^{\frac{1}{2}}$$

$$\left(\frac{1}{T} \right) = \left(\frac{1}{16} \right) \left(\frac{1}{355 \text{ K}} \right)$$

$$T = 16(355 \text{ K}) = 5680 \text{ K}$$

The second temperature is 5680 K

Question 16 (out of 6 points)

Consider methane (CH_4) gas at a temperature T.

- (a) Calculate the ratio, to 3 significant figures, of the number of methane molecules that have the average speed \bar{v} to the number of molecules that have twice the average speed, $2\bar{v}$.

Let's first consider the Maxwell-Boltzmann speed distribution;

$$\frac{\Delta N}{N} = f(u)\Delta u, \text{ where } f(u) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} u^2 \exp\left(\frac{-mu^2}{2k_B T} \right),$$

We can compare the fraction of total number of molecules traveling at the average speed \bar{v} and compare that to the fraction of total number of molecules traveling at $2\bar{v}$

$$\frac{f(\bar{v})}{f(2\bar{v})} = \frac{(\bar{v})^2 \exp\left(\frac{-M(\bar{v})^2}{2RT} \right)}{(2\bar{v})^2 \exp\left(\frac{-M(2\bar{v})^2}{2RT} \right)}$$

$$\begin{aligned}
&= \frac{(\bar{v})^2}{(2\bar{v})^2} \exp\left[-\frac{M}{2RT}\left((\bar{v})^2 - 4(\bar{v})^2\right)\right] \\
&= \frac{1}{4} \exp\left[-\frac{3M(\bar{v})^2}{2RT}\right] \\
&= \frac{1}{4} \exp\left[\left(\frac{3M}{2RT}\right)\left(\frac{8RT}{\pi M}\right)\right] \\
&= \frac{1}{4} \exp\left[\frac{12}{\pi}\right] \\
&= (.25000)(45.5913) \\
&= 11.3978 \\
&= 11.4
\end{aligned}$$

The ratio of the number of molecules with speed \bar{v} to that of $2\bar{v}$ is 11.4.

- (b) Calculate the ratio, to 3 significant figures, of the number of methane molecules that have the average energy \bar{E} to the number of molecules that have twice the average energy, $2\bar{E}$.**

We need to look at the energy distribution equation:

$$f(E) = 2\pi \left(\frac{1}{\pi RT}\right)^{\frac{3}{2}} E^{\frac{1}{2}} e^{\frac{-E}{RT}}$$

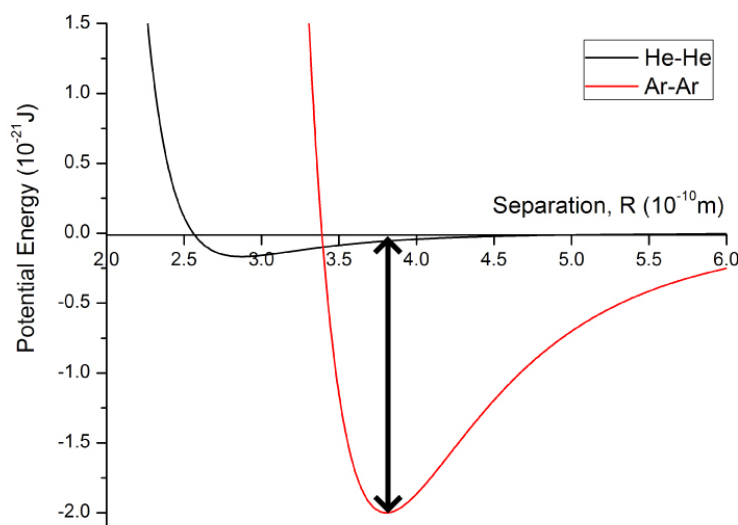
We can substitute into the equation and look at the ratios:

$$\begin{aligned}
\frac{f(E)}{f(2E)} &= \frac{2\pi \left(\frac{1}{\pi RT}\right)^{\frac{3}{2}} E^{\frac{1}{2}} e^{\frac{-E}{RT}}}{2\pi \left(\frac{1}{\pi RT}\right)^{\frac{3}{2}} (2E)^{\frac{1}{2}} e^{\frac{-2E}{RT}}} \\
&= \left(\frac{E}{2E}\right)^{\frac{1}{2}} e^{\left(\frac{-E}{RT} + \frac{2E}{RT}\right)} \\
&= \left(\frac{1}{2}\right)^{\frac{1}{2}} e^{\frac{E}{RT}} \\
&= \left(\frac{1}{2}\right)^{\frac{1}{2}} e^{\left(\frac{1}{RT}\right)\left(\frac{3RT}{2}\right)} \\
&= \left(\frac{1}{2}\right)^{\frac{1}{2}} e^{\frac{3}{2}} \\
&= (0.70711)(4.48169) \\
&= 3.1690 \\
&= 3.17
\end{aligned}$$

The ratio of methane molecules that have the average energy \bar{E} to the number of molecules that have twice the average energy, $2\bar{E}$ is 3.17.

Question 17 (out of 4 points)

The following figure is a plot of the potential energy versus separation distance for two neutral noble-gas atoms:



Lennard-Jones potential for the He-He (black) and Ar-Ar dimers.

Commonly referred to as the Lennard-Jones potential, the equation that describes these functions is:

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

where ϵ and σ are constants that depend on the system of interest. The L-J potential is a useful model because it captures the essential physics of interaction at long and short separation: attraction between the atoms at long r and repulsion at short.

a) Determine which terms in $V(r)$ correspond to attraction and repulsion. (2 points)

Let us look at the equation from the question: $V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$

The attractive interaction is going to stabilize the formation of the molecule, so it has the negative sign in front of it. The attractive interaction term is therefore: $\left(\frac{\sigma}{r} \right)^6$

The repulsive interaction is going to destabilize the dimer, so it will have the positive sign in front of it. The repulsive interaction is therefore: $\left(\frac{\sigma}{r} \right)^{12}$.

b) What does the depth of the potential energy well correspond to (indicated by the black arrow)? (1 point)

The depth of the potential energy well, (ϵ) is the binding energy between two neutral noble atoms (or the dissociation energy of the dimer)

The potential energy minimum for the helium dimer is at an intermolecular distance of 0.287 nm, while the minimum for argon is 0.380 nm.

c) Why does argon have a greater separation distance at the minimum than helium? (1 point)

Argon has a larger atomic radius (lower in the group on the periodic table), therefore (in hard sphere model) unable to come "closer to each other."

d) (Bonus) Was Lennard-Jones one person or two? Answer ONE!

Question 18 (out of 4 points)

Name the types of attractive forces that will contribute to the interactions among atoms, molecules, or ions in the following substances. Indicate the one(s) you expect to predominate.

- (a) KF Potassium and fluorine differ considerably in electronegativity. The bonding in the compound potassium fluoride is expected to be ionic. These ion-ion attractions predominate in this compound; dispersion forces are also present.
- (b) Cl₂ Dispersion forces are the only intermolecular forces possible between molecules of Cl₂.
- (c) HBr Dipole-Dipole attractions predominate in the interactions between molecules in hydrogen bromide. The positive (H) end of one molecule is attracted by the negative (Br) end of another, but repelled by its positive (H) end. Dispersion forces are also present.
- (d) Kr Dispersion forces are the only forces operating among the atoms in a sample of Krypton. Single Kr atoms have completely symmetrical (spherically symmetrical) distributions of charge. Two neighboring Kr atoms induce temporary dipoles in each other that cause them to attract each other.

Question 19 (out of 2 points)

Predict whether a bromide ion will be most strongly attracted to a sodium ion, a molecule of hydrogen chloride, or an atom of krypton.

A bromide ion should be most strongly attracted to a sodium ion. The attraction between ions of unlike charge such as these is stronger than the ion-dipole attraction between Br⁻¹ and HCl and the ion-induced dipole attraction between Br⁻¹ and Kr.

Question 20 (out of 3 points)

Under room conditions, fluorine and chlorine are gases, bromine is a liquid, and iodine is a solid. Explain the origin of this trend in the physical state of the halogens.

The boiling point and melting point of a substance depend on the strength of the attractive forces operation amount the particles that comprise the liquid or solid substance. These forces tend to increase with increasing molar mass in a group of related substances. The halogens are certainly closely related chemically. Therefore their boiling and melting points tend to rise with increasing molar mass.

Question 21 (out of 4 points)

List the following substances in order of increasing normal boiling points T_b , and explain your reasoning: NO, NH₃, Ne, RbCl.

Substances with the strongest intermolecular forces require the highest temperature to make them boil. Liquid RbCl has strong Coulomb (electrostatic) forces holding its ions together. It has the highest boiling point. Liquid NH₃ has dipole-dipole attractions, as does liquid NO. In liquid NH₃, these are particularly strong. They are hydrogen bonds. In liquid NO, the dipole-dipole

attractions are weaker. Liquid NH_3 boils at a higher temperature than liquid NO . Induced dipole-induced dipole forces are the only intermolecular attractions in liquid neon. Consequently, it has the lowest boiling point of all. The order of the molecules in increasing boiling points are: $\text{Ne} < \text{NO} < \text{NH}_3 < \text{RbCl}$.