Part A. Problems to be graded (5 points each)

1. In the absence of turbulent mixing, the partial pressure of each gas that makes up the air would decrease as elevation from sea level increases according to $P_i = P_i^E e^{-\frac{g z}{M_i RT}}$. $P_i$ is the partial pressure of gas $i$ at elevation $z$ (m), $P_i^E$ is its partial pressure at sea level, $g$ is the acceleration of gravity (m/s$^2$), $R$ is the gas constant (8.3145 J/mol K), $T$ is the temperature (K), and $M_i$ is the molar mass of the gas (kg/mol). [The argument of the exponential function must have no units. I am giving you the units, in parenthesis, that you need to use in order to accomplish unit cancellation. You can use any units that you want for those variables, but if you use other units, you will have to use conversion factors to cancel them out. You can use any units you want for $P_i$ and $P_i^E$, as long as you use the same for both.]

As a result of turbulent mixing, the composition of the Earth’s atmosphere is constant below 100 km, but the total pressure decreases with altitude as $P = P_E e^{-\frac{g z}{M_{ave} RT}}$, where $M_{ave}$ is the mean molecular weight of air (28.9×10$^{-3}$ kg/mol). At sea level, $x_{N_2} = 0.78084$ and $x_{He} = 5.24×10^{-6}$. Let’s assume also that $T = 300$ K (and constant for all points in your calculations).

A. Calculate the total pressure at 4000 m (the elevation of Potosí, Bolivia) and at 8.85 km.

B. Calculate the value $x_{N_2}/x_{He}$ would have at 8.85 km (the elevation of Mount Everest) in the absence of turbulent mixing. Compare your answer with the correct value.

Note that when I say “compare”, I don’t mean for you to tell me that they are different. Give a percent difference or, if the numbers are too different, tell me how many times one is larger than the other. Acceptable answers could be “the calculated number is 12.7% higher than the actual value” or “the actual value is 3.5 times larger than the calculated value.”

2. Evaluate $\alpha$, the thermal expansivity, and $\kappa$, the isothermal compressibility, for an ideal gas at 250 K and 1.00 bar.

Note. You can do this problem way before we cover this material in class. Simply check out equations 1.43 and 1.44 to get the expressions for these two terms.

3. Two thermometers, one filled with ethanol and one filled with mercury, are calibrated at 0°C and at 100°C. [This means that the length of the column of fluid is recorded at these two temperatures and then the space between these two marks is divided into 100 parts of equal length, each of which represents a degree (1°C).] We are going to explore how accurate these two thermometers are. In other words, we want to know how far off the correct temperature each thermometer is when making a reading far from the calibration points. For your calculations, you can assume that the pressure is constant and that the expansion or contraction of the glass container is negligible.

You place the two thermometers in a container that is at 50.00°C. What temperatures would you read in the ethanol and mercury thermometers?

Data: $\alpha$(ethanol) = 1.0414×10$^{-3}$ + 1.5672×10$^{-6}$ $t$ + 5.148×10$^{-8}$ $t^2$

$\alpha$(mercury) = 1.8146×10$^{-4}$ + 1.8410×10$^{-8}$ $t$ (t = temperature in °C)

4. $z = y^3 \sin(x^2) + \sin(x^2y^2) e^{(x-y)}$. Evaluate $\frac{\partial^3 z}{\partial y^2 \partial x}$. 

Part B. Two of the following problems will be graded (5 points each)

Levine, 6th Edition: 1.14, 1.21, 1.34, 1.52, 1.54, 1.57
Levine, 5th Edition: 1.13, 1.20, 1.33, 1.50, 1.52, 1.56
Chem/Phys 301  First Problem Set

1.

(a) \( P = P_0 e^{-\frac{g z^2}{RT}} \)

At 4000 m: \( \frac{g z^2}{RT} = \frac{28.9 \times 10^{-3} \text{ kg/m} \cdot 9.81 \text{ m/s}^2 \cdot 4000 \text{ m}}{8.3145 \frac{\text{J}}{\text{mol K}}} = 0.4546 \) (in units)

\[ P = 1 \text{ atm} \cdot e^{-0.4546} = 0.635 \text{ atm} = P_{4000} = 482 \text{ torr} \]

At 8.85 km: \( \frac{g z^2}{RT} = \frac{28.9 \times 10^{-3} \text{ kg/m} \cdot 9.81 \text{ m/s}^2 \cdot 8850 \text{ m}}{8.3145 \frac{\text{J}}{\text{mol K}}} = 1.006 \)

\[ P = 1 \text{ atm} \cdot e^{-1.006} = 0.366 \text{ atm} = P_{8850} = 278 \text{ torr} \]

(b) Recall that \( x_i = \frac{P_i}{P_{\text{tot}}} \). Get \( P_i \) in the absence of mixing.

\[ P_{N_2} = \frac{M_i \cdot g z^2}{RT} = \frac{28.014 \times 10^{-3} \text{ kg/mol} \cdot 9.81 \text{ m/s}^2 \cdot 8850 \text{ m}}{8.3145 \frac{\text{J}}{\text{mol K}}} = 0.9351 \]

\[ P_{N_2} = p_{N_2} \cdot e^{-0.9351} = 0.78084 \cdot 1 \text{ atm} \cdot e^{-0.9351} = 0.2945 \text{ atm} \]

\[ x_{N_2} = \frac{0.2945 \text{ atm}}{0.3657 \text{ atm}} = 0.8053 = x_{N_2} \]

\[ P_{He} = \frac{M_i \cdot g z^2}{RT} = \frac{4.003 \times 10^{-3} \text{ kg/mol} \cdot 9.81 \text{ m/s}^2 \cdot 8850 \text{ m}}{8.3145 \frac{\text{J}}{\text{mol K}}} = 0.1343 \]

\[ P_{He} = p_{He} \cdot e^{-0.1343} = 5.24 \times 10^{-6} \text{ atm} \cdot e^{-0.1343} = 4.558 \times 10^{-6} \text{ atm} \Rightarrow X_{He} = \frac{4.558 \times 10^{-6} \text{ atm}}{0.3657 \text{ atm}} \]

\[ X_{He} = 1.246 \times 10^{-5} \]

If no mixing \( \frac{x_{N_2}}{x_{He}} = \frac{0.8053}{1.246 \times 10^{-5}} = 6.46 \times 10^4 \rightarrow \] Actual ratio is 2.31 times bigger than if no mixing (2.31 was \( N_2 \) per given amount of \( He \))
\[ \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \quad K = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T \]

for an ideal gas: \( PV = nRT \Rightarrow V = \frac{nRT}{P} \)

\[ \left( \frac{\partial V}{\partial T} \right)_p = \frac{nR}{P} \Rightarrow \alpha = \frac{1}{nRT} \frac{nR}{P} = \frac{R}{nRT} \frac{nRT}{P} = \frac{1}{T} \]

\[ \Rightarrow \alpha = \frac{1}{T} \]

at 250 K \( \Rightarrow \alpha = \frac{1}{250K} = \frac{1}{4.00 \times 10^{-3} \text{ K}^{-1}} = \alpha \)

\[ \left( \frac{\partial V}{\partial p} \right)_T = nRT \left( \frac{\partial p}{\partial p} \right)_T = nRT \left( \frac{-1}{P^2} \right) \]

\[ K = -\frac{nRT}{P} \left( \frac{\partial V}{\partial p} \right)_T = -\frac{P}{nRT} \left( -\frac{nRT}{P^2} \right) = \frac{1}{P} \]

\[ \Rightarrow K = \frac{1}{P} \]

at 1.00 bar \( \Rightarrow K = \frac{1}{1.00 \text{ bar}} = 1.00 \text{ bar}^{-1} = K \)
The idea here is that the fluid expands with temperature, so that \( V = V_0 + \Delta V \). If the cylinder has constant radius, the volume is proportional to the length. Also, since pressure is constant, we ignore the effect of \( \frac{\partial V}{\partial P} \).

In other words, \( \Delta V = \int_{V_0}^{V} \frac{\partial V}{\partial T} \, dt + \int_{P_1}^{P_2} \frac{\partial V}{\partial P} \, dP \)

\( \frac{\partial V}{\partial T} = \alpha \cdot V_0 \), so we have that
\( \Delta V = \int_{V_0}^{V} \alpha \cdot V_0 \, dt \)

What we want is to see how \( \Delta V \) at 50°C compares to \( \Delta V \) at 100°C.

If the thermometer is exact, \( \Delta V_{50} = \frac{1}{2} \Delta V_{100} \)

\( \Delta V_{50} = \int_{0}^{50} \alpha \cdot V_0 \, dt \quad \Delta V_{100} = \int_{0}^{100} \alpha \cdot V_0 \, dt \)

For ethanol, \( \Delta V_{50}^{eth} = \int_{0}^{50} V_0 \left( 1.0414 \cdot 10^{-3} + 3.6472 \cdot 10^{-6} t + 5.148 \cdot 10^{-8} t^2 \right) dt = \)

\( = V_0 \left( [1.0414 \cdot 10^{-3}]_{50} + 1.36472 \cdot 10^{-6} \left[ t^2 \right]_{0}^{50} + 3.314 \cdot 10^{-8} \left[ t^3 \right]_{0}^{50} \right) = \)

\( = V_0 \cdot 0.05467 = \Delta V_{50}^{eth} \Rightarrow \Delta V_{50}^{eth} = 0.05467 \cdot V_0 \)

Likewise, plugging 100°C into the integrated expression, I get

\( \Delta V_{100}^{eth} = 0.1291 \cdot V_0 \)

From the second expression, we know that every degree should be
\( \frac{\Delta V_{100}^{eth}}{V_0} \) the difference of volume between \( V_0 \) at \( 100°C \Rightarrow 0.00129V_0 \)

Since, at 50°C, we read 0.05467 \( V_0 \Rightarrow \) the reading in the thermometer is

\( \frac{0.05617 \cdot V_0}{0.05467 \cdot V_0} = 43.5°C \)
The same procedure applies to mercury.

\[
\Delta V_{50}^{Hg} = \int_0^{50} V_0^{Hg} \left( 1.8146 \cdot 10^{-4} + 1.8410 \cdot 10^{-8} t \right) dt = \\
= V_0^{Hg} \left[ 1.8146 \cdot 10^{-4} t \bigg|_0^{50} + 1.8410 \cdot 10^{-8} \frac{t^2}{2} \bigg|_0^{50} \right] = \\
= V_0^{Hg} \cdot 0.009096 \Rightarrow \Delta V_{50}^{Hg} = 0.009096 V_0^{Hg}.
\]

For \( \Delta V_{100}^{Hg} \), I get \( \Delta V_{100}^{Hg} = 0.01824 V_0^{Hg} \)

which means that the length of 1°C is proportional to 0.0001824 \( V_0^{Hg} \)

\[\Rightarrow \text{thermometer reading } \frac{0.009096 V_0^{Hg}}{0.0001824 V_0^{Hg}} = 49.87°C\]

as you can see, a mercury thermometer is much more accurate than an ethanol thermometer.
\( z = y^3 \sin(x^2) + \sin(x^2y^2) e^{(x-y)} \)

\[
\left( \frac{\partial^2 z}{\partial x \partial y} \right)_y = y^2 \cdot (2x) \cdot \cos(x^2) + 2xy^2 \cos(x^2y^2) e^{(x-y)} + \sin(x^2y^2) e^{(x-y)} \\
= 2xy^2 \cos(x^2) + e^{(x-y)} \left[ 2xy^2 \cos(x^2y^2) + \sin(x^2y^2) \right]
\]

\[
\left( \frac{\partial^2 z}{\partial y \partial x} \right)_x = 3y^2 \cdot \sin(x^2) + 2x^2y \cos(x^2y^2) e^{(x-y)} + \sin(x^2y^2) (-1) e^{(x-y)} \\
= 3y^2 \sin(x^2) + e^{(x-y)} \left[ 2x^2y \cos(x^2y^2) - \sin(x^2y^2) \right]
\]

\[
\left( \frac{\partial}{\partial x} \right)_y \left( \frac{\partial}{\partial y} \right)_x \left( \frac{\partial}{\partial x} \right)_y = -1 \Rightarrow \left( \frac{\partial}{\partial x} \right)_y = -\left( \frac{\partial^2}{\partial x \partial y} \right)_x = - \left( \frac{\partial}{\partial x} \right)_x \left( \frac{\partial}{\partial y} \right)_x
\]

\[
\left( \frac{\partial}{\partial y} \right)_x = - \frac{2xy^3 \cos(x^2) + e^{(x-y)} \left[ 2xy^2 \cos(x^2y^2) + \sin(x^2y^2) \right]}{3y^2 \sin(x^2) + e^{(x-y)} \left[ 2x^2y \cos(x^2y^2) - \sin(x^2y^2) \right]}
\]
PART B

(119)

a. \( P = \frac{E}{A} = \frac{m \cdot g}{A} = \frac{V \cdot P \cdot g}{A} = A \cdot \frac{h \cdot P \cdot g}{A} = h \cdot p \cdot g \)

i. \( P_{hg} = P_{h_2o} \Rightarrow h_{hg} \cdot P_{hg} \cdot g = h_{h_2o} \cdot P_{h_2o} \cdot g \)

\[ \Rightarrow h_{h_2o} = \frac{h_{hg} \cdot P_{hg}}{P_{h_2o}} = \frac{30.0 \text{ in} \times 13.53 \text{ g/cm}^3}{0.999 \text{ g/cm}^3} = 407 \text{ in} \]

\[ h_{h_2o} = 10.3 \text{ m} \]

5. \( P = h \cdot p \cdot g = 30.0 \text{ in} \left( \frac{0.0254 \text{ m}}{1 \text{ in}} \right) \left( \frac{13.53 \text{ g}}{\text{cm}^3} \right) \left( \frac{100 \text{ cm}^3}{1 \text{ in}^3} \right) \left( \frac{1 \text{ kg}}{1000 \text{ g}} \right) \left( \frac{9.8 \text{ cm}}{\text{s}^2} \right) \left( \frac{1 \text{ m}}{100 \text{ cm}} \right) = \\
\]

\[ = 100830 \text{ Pa} \left( \frac{760 \text{ torr}}{1.013 \times 10^5 \text{ Pa}} \right) = 756 \text{ torr} = P \]

in contrast, if \( g = 9.80 \text{ m/s}^2 \) (the mean value of \( g \)) \( \Rightarrow \)

\[ P(30.0 \text{ in}) = 762 \text{ torr} \]

(121)

\[ \frac{P}{\rho} \quad \text{PV} = nRT = \frac{m}{MM} \quad RT \Rightarrow \frac{P}{V} = \frac{\rho}{MM} \Rightarrow \frac{P}{\rho} = \frac{RT}{MM} \]

\[ \Rightarrow \frac{P}{\rho} = \frac{RT}{MM} \]

In the plot (see next page), the extrapolation to \( P=0 \), i.e. the finding of the \( y \)-intercept, yields \( \frac{RT}{MM} \)

\[ y \text{- intercept} = \frac{RT}{MM} \]
\[
\begin{align*}
P (\text{atm}) & \quad \rho (\text{g/L}) & \quad P/\rho & \quad \text{fit} \\
0.2000 & \quad 0.2796 & \quad 0.7153 & \quad 0.7153 \\
0.5000 & \quad 0.7080 & \quad 0.7062 & \quad 0.7062 \\
0.8000 & \quad 1.1476 & \quad 0.6971 & \quad 0.6971 \\
\end{align*}
\]

Regression Output:
- Constant: 0.7214
- Std Err of Y Est: 0.0000
- R Squared: 1.0000
- No. of Observations: 3.0000
- Degrees of Freedom: 1.0000

\[
\begin{align*}
\gamma - \text{int} & = 0.7214 \quad \text{atm} \cdot \text{L} \quad \text{J} = \frac{RT}{M} \Rightarrow M = \frac{0.082056 \text{ atm} \cdot \text{L} \cdot \text{mol} \cdot \text{K}}{0.7214 \text{ atm} \cdot \text{L} / \text{J}} = 181.67 \text{ g/mol} = M \\
\text{ammonia} & \quad \text{CH}_3 - \text{NH}_2 \\
\text{NH}_2 & \quad \text{L} \Rightarrow M (\text{L}) = 15 \quad \text{CH}_3 \\
\text{ammonia:} & \quad \text{CH}_3 - \text{NH}_2
\end{align*}
\]

\[\text{Eqn 1.34}\]

\((\text{a})\) \quad \frac{P_i}{P_T} = x_i \Rightarrow P_i = x_i \cdot P_T

\((\text{b})\) \quad P_T = 1.00 \text{ atm} \Rightarrow P_{N_2} = 0.78 \text{ atm} \quad (593 \text{ torr})

\quad P_{O_2} = 0.21 \text{ atm} \quad (160 \text{ torr})

\quad P_{Ar} = 0.0093 \text{ atm} \quad (7.1 \text{ torr})

\quad P_{CO_2} = 0.0002 \text{ atm} \quad (0.2 \text{ torr})

\(\text{L}\) \quad V_{\text{total}} = 15 \text{ ft} \times 20 \text{ ft} \times 10 \text{ ft} \times 3000 \text{ ft}^3 = 3000 \text{ ft}^3 \frac{(3.048 \text{ cm}^3)}{(1 \text{ ft}^3)} \frac{1 \text{ cm}^3}{1 \text{ dm}^3} = 8.5 \times 10^4 \text{ L}

\quad P_{\text{total}} = 740 \text{ torr} \quad \frac{1 \text{ atm}}{760 \text{ torr}} = 0.974 \text{ atm}

\quad P_{N_2} = 0.759 \text{ atm} \quad P_{O_2} = 0.204 \text{ atm} \quad P_{Ar} = 0.0096 \text{ atm} \quad P_{CO_2} = 2.9 \times 10^{-4} \text{ atm}

\quad PV = nRT = \frac{M}{M} \cdot RT = \frac{M}{RT} \Rightarrow M = \frac{PV}{M}

\quad V = \frac{8.5 \times 10^4 \text{ L}}{0.082 \text{ atm} \cdot \text{L} \cdot \text{mol} \cdot \text{K}} \cdot 293 \text{ K} = 3538 \text{ mol} \cdot \text{atm}

\quad N_2 \Rightarrow M = 0.759 \text{ atm} \cdot 3538 \text{ mol} \cdot \text{atm} \cdot \frac{28 \text{ g}}{1 \text{ mol}} \cdot \frac{1 \text{ kg}}{1000 \text{ g}} = 75 \text{ kg}

\quad Ar \Rightarrow M = 0.0096 \text{ atm} \cdot 3538 \text{ mol} \cdot \frac{40 \text{ g}}{1 \text{ mol}} \cdot \frac{1 \text{ kg}}{1000 \text{ g}} = 1.3 \text{ kg}

\quad O_2 \Rightarrow M = 0.204 \text{ atm} \cdot 3538 \text{ mol} \cdot \frac{32 \text{ g}}{1 \text{ mol}} \cdot \frac{1 \text{ kg}}{1000 \text{ g}} = 23 \text{ kg}

\quad CO_2 \Rightarrow M = 2.9 \times 10^{-4} \text{ atm} \cdot 3538 \text{ mol} \cdot \frac{44 \text{ g}}{1 \text{ mol}} \cdot \frac{1 \text{ kg}}{1000 \text{ g}} = 0.05 \text{ kg}
\[ m_{\text{total}} = 75 \text{ kg} + 73 \text{ kg} + 1.2 \text{ kg} + 0.05 \text{ kg} = 99 \text{ kg} \] (a mass larger than that of most people)

\[ c = \frac{m}{V} = \frac{99 \text{ kg}}{8.5 \cdot 10^{-4} \text{ L}} = 1.16 \text{ g/L} \]

\[ PV = nRT (1 + \alpha p) \Rightarrow V = \frac{nRT}{p} (1 + \alpha p) = \frac{nRT}{p} + nRT \alpha \]

\[ \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T \left( \frac{\partial V}{\partial T} \right)_p = \frac{nR}{p} + nRT \Rightarrow \frac{nR}{p} (1 + \alpha p) = \frac{V}{T} \]

\[ \Rightarrow \alpha = \frac{1}{V} \frac{V}{T} \Rightarrow \alpha = \frac{1}{T} \]

\[ K = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T \Rightarrow \left( \frac{\partial V}{\partial T} \right)_p = \frac{nRT}{p} \left( -\frac{1}{p^2} \right) = -\frac{nRT}{p^2} \]

\[ K = \frac{-\frac{nRT}{p^2}}{\frac{nRT}{p} (1 + \alpha p)} = \frac{1}{p(1 + \alpha p)} \Rightarrow K = \frac{1}{p(1 + \alpha p)} \]

\[ \left( \frac{\partial p}{\partial T} \right)_V \Rightarrow PV = nRT (1 + \alpha p) = nRT + nRT \alpha p \Rightarrow PV - nRT \alpha p = nRT \]

\[ \Rightarrow p = \frac{nRT}{V - nRT a} \Rightarrow \left( \frac{\partial p}{\partial T} \right)_V = -\frac{nR (V - nRT a - nRT \alpha p)}{(V - nRT a)^2} = \frac{nR \alpha p V}{(V - nRT a)^2} \]

\[ \Rightarrow \left( \frac{\partial p}{\partial T} \right)_V = \frac{nR \alpha \left( V - nRT a \right)}{(V - nRT a)^2} + \frac{n^2 R^2 a T}{(V - nRT a)^2} = \frac{nRT}{(V - nRT a)} \frac{1}{T} + \frac{n^2 R^2 a T}{(V - nRT a)^2} = \]

\[ = \frac{p}{T} + \frac{\alpha p^2}{T} = \frac{1}{T} p (1 + \alpha p) = \frac{(\partial p)}{(\partial T)_V} \]

\[ \frac{\alpha}{K} = \frac{\alpha}{\frac{V}{T}} = \frac{V \left( \frac{\partial V}{\partial p} \right)_T}{T} = \frac{p (1 + \alpha p)}{T} \]

\[ \Rightarrow \frac{\alpha}{K} = \frac{V \left( \frac{\partial V}{\partial p} \right)_T}{T} = \frac{p (1 + \alpha p)}{T} \]

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Tangent of the 300°C $V_m$ vs $P$ at 2000 bar:

Slope: \[ \frac{14 \text{ cm}^3/\text{mol}}{7600 \text{ bar}} = 0.00183 \text{ cm}^3/\text{mol bar} = \frac{\partial V_m}{\partial P} \]

\[ k = -\frac{1}{V_m} \left( \frac{\partial V_m}{\partial P} \right)_T = -\frac{1}{20.5 \text{ cm}^3/\text{mol}} - 0.00113 \text{ cm}^3/\text{mol bar} = 5.5 \times 10^{-5} \text{ bar}^{-1} \]

\[ \Delta V = V \left( -k \int_{P_1}^{P_2} \text{d}P \right) = -k \Delta P V \]

For $\Delta V = 1\%V = 0.01V$

$\Delta P = -\frac{0.01}{k}$ sign just indicates direction of change; if $P \Rightarrow V$

\[ k = 5 \times 10^{-6} \text{ atm}^{-1} \Rightarrow \Delta P = \frac{0.01}{5 \times 10^{-6} \text{ atm}^{-1}} = 2000 \text{ atm} = \Delta P \]

\[ k = 1 \times 10^{-4} \text{ atm}^{-1} \Rightarrow \Delta P = \frac{0.01}{1 \times 10^{-4} \text{ atm}^{-1}} = 100 \text{ atm} = \Delta P \]