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## AATM 504 – Thermodynamics, Adiabatic Processes, Moist Unsaturated Air

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Homework 6

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### Problem 1

#### Derivations

1. We can repeat the derivation of potential temperature for unsaturated moist air ( $\theta_m$ ) in terms of air temperature ( $T$ ), pressure ( $p$ ), gas constant for dry air ( $R_d$ ), specific heat for dry air ( $C_{pd}$ ), and specific humidity ( $q$ ). Note that a function of  $(1 + 0.61x)/(1 + 0.84x)$  can be approximated by a function of  $(1 - 0.23x)$ .
2. What is the effect of water vapor on the potential temperature for an air parcel (a) with temperature  $T = 303K$  and mixing ratio  $w = 0.020kg/kg$ , and (b)  $T = 273K$  and  $0.006kg/kg$ ? Use the equation for calculation of the moist air potential temperature

$$\theta_m = T \left[ \frac{P_0}{P} \right]^{x(1-0.23q)} \quad (1.1)$$

and compare it to the value of potential temperature of dry air. Discuss the error one makes if one ignores the water vapor in the calculations.

3. Assume that two moist air masses mix adiabatically (no heat added) and isobaric without condensation taking place. One with mass  $m_1$ , specific humidity  $q_1$ , and temperature  $T_1$ , and the other with mass  $m_2$ , specific humidity  $q_2$ , and temperature  $T_2$ . Let the mixed air has a total mass of  $m$  ( $m = m_1 + m_2$ ), specific humidity of  $q$ , and potential temperature of  $\theta$ . Derive the final temperature  $T$  and specific humidity  $q$  in terms of the individual mass and specific humidity for each air mass.

*Solution.*

1. We can follow the exact same procedure as deriving the potential temperature for dry air, except we use different constants for moist air. For adiabatic processes, the 1st law of thermodynamics becomes

$$C_{pm}dT - \alpha dp = 0 \quad (1.2)$$

where  $C_{pm} = C_{pd}(1 + 0.84q)$  (from lecture slides 17) is the specific heat capacity of moist air. Here,  $q = \frac{m_v}{m_d + m_v}$  is the specific humidity. Substituting  $\alpha$  using the ideal gas law,

$$\frac{dT}{T} = \frac{R_m}{C_{pm}} \frac{dp}{p} \quad (1.3)$$

where  $R_m$  is the gas constant for moist air. Integrating and simplifying both sides, we get

$$\begin{aligned}
\int_T^{\theta_m} \frac{dT}{T} &= \frac{R_m}{C_{pm}} \int_p^{p_0} \frac{dp}{p} \\
\ln\left(\frac{\theta_m}{T}\right) &= \frac{R_m}{C_{pm}} \ln\left(\frac{p_0}{p}\right) \\
\left(\frac{\theta_m}{T}\right) &= \left(\frac{p_0}{p}\right)^{\frac{R_m}{C_{pm}}} \\
\theta_m &= T \left(\frac{p_0}{p}\right)^{\frac{R_m}{C_{pm}}}
\end{aligned} \tag{1.4}$$

We can obtain an expression for  $R_m$  in terms of the gas constant for dry air  $R_d$  similar to the previous HW. The ideal gas law can be written as the following for dry air, water vapor, and moist air.

$$\begin{aligned}
p_d V &= m_d R_d T \quad (\text{dry air}) \\
p_v V &= m_v R_v T \quad (\text{water vapor}) \\
p_m V &= m_m R_m T = (m_d + m_v) R_m T \quad (\text{moist air})
\end{aligned} \tag{1.5}$$

From Dalton's law of partial pressures,  $p_m = p_d + p_v$ . Thus, combining our three equations, we get

$$\frac{T}{V} (m_d R_d + m_v R_v) = \frac{T}{V} (m_d + m_v) R_m \tag{1.6}$$

Isolating  $R_m$ , we obtain

$$\begin{aligned}
R_m &= \frac{m_d R_d + m_v R_v}{m_d + m_v} \\
&= (1 - q) R_d + q R_v \\
&= (1 - q) R_d + 1.61 q R_d \\
R_m &= R_d (1 + 0.61 q)
\end{aligned} \tag{1.7}$$

Note that since  $R_v = 461.5 \text{ J kg}^{-1} \text{ K}^{-1}$  and  $R_d = 287.05 \text{ J kg}^{-1} \text{ K}^{-1}$ , then  $R_v = 1.61 R_d$ . Plugging back into Poisson's equation our expressions for  $C_{pm}$  and  $R_m$  in terms of  $q$ , we get

$$\theta_m = T \left(\frac{p_0}{p}\right)^{\frac{R_d(1+0.61q)}{C_{pd}(1+0.84q)}} \tag{1.8}$$

Since we can approximate  $(1 + 0.61q)/(1 + 0.84q)$  as  $(1 - 0.23q)$ , this simplifies into

$$\theta_m = T \left(\frac{p_0}{p}\right)^{\frac{R_d}{C_{pd}}(1-0.23q)} \tag{1.9}$$

2. The specific humidity can be written in terms of the mixing ratio as  $q = \frac{w}{1+w}$ . Thus, we can rewrite Poisson's equation for moist air as

$$\theta_m = T \left(\frac{p_0}{p}\right)^{0.2859[1-0.23(\frac{w}{1+w})]} \tag{1.10}$$

For (a), this becomes

$$\theta_m = 303 \text{ K} \left(\frac{p_0}{p}\right)^{0.2846} \tag{1.11}$$

If we apply Poisson's equation for dry air, this becomes

$$\theta_d = 303 \text{ K} \left( \frac{p_0}{p} \right)^{0.2859} \quad (1.12)$$

Doing the same for (b), we get

$$\begin{aligned} \theta_m &= 273 \text{ K} \left( \frac{p_0}{p} \right)^{0.2855} \\ \theta_d &= 273 \text{ K} \left( \frac{p_0}{p} \right)^{0.2859} \end{aligned} \quad (1.13)$$

The difference between the dry air and moist air calculations are very small. When I plotted them, they overlap very well. Thus, even if we ignore the presence of water vapor, we would still get a value very close to the correct one. However, at much higher mixing ratio, we may need to already account for water vapor.

3. By conservation of the water vapor mass, we can say that  $m_v = m_{v1} + m_{v2}$ . Similarly, from conservation of mass,  $m = m_1 + m_2$ . Using the definition of the specific humidity (ratio of water vapor mass to total air mass), we can say that

$$\begin{aligned} q_1 &= \frac{m_{v1}}{m_1} \\ q_2 &= \frac{m_{v2}}{m_2} \\ q &= \frac{m_v}{m} = \frac{m_v}{m_1 + m_2} \end{aligned} \quad (1.14)$$

Rearranging this, we get

$$\begin{aligned} m_{v1} &= m_1 q_1 \\ m_{v2} &= m_2 q_2 \\ m_v &= (m_1 + m_2) q \end{aligned} \quad (1.15)$$

Applying this to our conservation of water vapor,

$$\begin{aligned} (m_1 + m_2) q &= m_1 q_1 + m_2 q_2 \\ q &= \frac{m_1 q_1 + m_2 q_2}{m_1 + m_2} \end{aligned} \quad (1.16)$$

Under an isobaric process, the 1st law of thermodynamics (with enthalpy) can be written as  $dQ = dH = mC_p dT$ . In integrated form, this is just  $H = mC_p T$ , where  $H$  is enthalpy. Thus, the enthalpy of the two gases can be expressed as

$$\begin{aligned} h_1 &= m_1 C_{p1} T_1 \\ h_2 &= m_2 C_{p2} T_2 \end{aligned} \quad (1.17)$$

and the enthalpy of the gas mixture is

$$h_f = (m_1 + m_2) C_{pf} T \quad (1.18)$$

From conservation of enthalpy (adiabatic process), the total enthalpy of the gas mixture is just the sum of the total enthalpy from the two gases.

$$(m_1 + m_2)C_{pf}T = m_1C_{p1}T_1 + m_2C_{p2}T_2 \quad (1.19)$$

For simplicity, we can work with the same specific heat capacity for all the gases following an average specific humidity  $\bar{q}$  such that  $C_{pm} = (1 + 0.84\bar{q})C_{pd}$ . Writing our equation in terms of specific humidity, we get

$$(m_1 + m_2)(1 + 0.84\bar{q})C_{pd}T = m_1(1 + 0.84\bar{q})C_{pd}T_1 + m_2(1 + 0.84\bar{q})C_{pd}T_2 \quad (1.20)$$

Through simplification and isolating  $T$ , we see that

$$\begin{aligned} (m_1 + m_2)T &= m_1T_1 + m_2T_2 \\ T &= \frac{m_1T_1 + m_2T_2}{m_1 + m_2} \end{aligned} \quad (1.21)$$

□

## Problem 2

### Calculations

1. A cylinder filled with helium (a monatomic ideal gas) has a volume of  $1.8 \times 10^6 \text{ cm}^3$ , a pressure of  $1.2 \times 10^5 \text{ mb}$ , and a temperature of  $300 \text{ K}$ . The cylinder is contained in an evacuated room with a volume of  $16 \text{ m}^3$ . The cylinder ruptures and helium fills the room. Calculate the following and explain the physical laws/assumptions made in your calculations.
  - a) the work done by the expanding helium
  - b) the temperature in the room after the cylinder ruptures
  - c) the pressure in the room after the cylinder ruptures
2. Determine the mean molecular weight of the Venusian atmosphere assuming that it consists of 95%  $\text{CO}_2$  and 5%  $\text{N}_2$  by volume. What is the gas constant for  $1 \text{ kg}$  of such an atmosphere? What is the specific heat capacity (at constant volume, at constant pressure?).

*Solution.*

1.
  - a) The helium does no external work, since it just expanded to fill the evacuated room. It did not change the volume of the room. So,  $dW = 0$ .
  - b) According to Joule's law, when an ideal gas expands without doing external work and without heat exchange, the gas' temperature does not change. Thus, the temperature of the room is just the unchanged temperature of helium,  $T_{\text{room}} = 300 \text{ K}$ .
  - c) According to Boyle's law, at constant temperature,  $P_1 V_1 = P_2 V_2$ . Using this and our given values, we get

$$\begin{aligned} P_2 &= P_1 \frac{V_1}{V_2} \\ &= (1.2 \times 10^5 \text{ mb}) \frac{1.8 \times 10^6 \text{ cm}^3}{16 \times 10^6 \text{ cm}^3} \\ P_2 &= 1.35 \times 10^4 \text{ mb} \end{aligned} \tag{2.1}$$

2. The volume percentages give the molar fractions per molecule:  $0.95 \text{ mol/mol}$  air for  $\text{CO}_2$  and  $0.05 \text{ mol/mol}$  air for  $\text{N}_2$ . The molecular weight of  $\text{CO}_2$  is  $44 \text{ g/mol}$ , while the molecular weight of  $\text{N}_2$  is  $28 \text{ g/mol}$ . Thus, the molecular weight of the Venusian atmosphere is a weighted sum of these two gases depending on their molar fractions in Venus's atmosphere.

$$\begin{aligned} M_{\text{Venus}} &= (0.95 \text{ mol/mol air})(44 \text{ g/mol}) + (0.05 \text{ mol/mol air})(28 \text{ g/mol}) \\ M_{\text{Venus}} &= 43.2 \text{ g/mol air} \equiv 0.0432 \text{ kg/mol air} \end{aligned} \tag{2.2}$$

From the ideal gas law for mixed gases (in the lecture 16 slides),  $R_{\text{Venus}} = \frac{R^*}{M_{\text{Venus}}}$ , where  $R^* = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$  is the universal gas constant. Plugging in our given values, we get

$$R_{\text{Venus}} = \frac{8.314 \text{ JK}^{-1} \text{ mol}^{-1}}{0.0432 \text{ kg/mol}} = 192 \text{ JK}^{-1} \text{ kg}^{-1} \tag{2.3}$$

At constant volume, the relationship between heat change and temperature change for  $CO_2$ ,  $Q_{CO_2}$ , and  $N_2$ ,  $Q_{N_2}$ , are given by the 1st law of thermodynamics.

$$\begin{aligned} Q_{CO_2} &= m_{CO_2} C_{CO_2} \Delta T \\ Q_{N_2} &= m_{N_2} C_{N_2} \Delta T \end{aligned} \quad (2.4)$$

where  $C_{CO_2}$  and  $C_{N_2}$  are the specific heat capacities at constant volume for  $CO_2$  and  $N_2$ , respectively. Similarly, using the conservation of mass for the whole Venusian atmosphere, we get

$$Q_{Venus} = m_{Venus} C_{Venus} \Delta T = (m_{CO_2} + m_{N_2}) C_{Venus} \Delta T \quad (2.5)$$

The total heat change for Venus's atmosphere must be the sum of the heat changes for its components:  $Q_{Venus} = Q_{CO_2} + Q_{N_2}$ .

$$m_{CO_2} C_{CO_2} \Delta T + m_{N_2} C_{N_2} \Delta T = (m_{CO_2} + m_{N_2}) C_{Venus} \Delta T \quad (2.6)$$

Isolating  $C_{Venus}$ ,

$$C_{Venus} = \frac{m_{CO_2} C_{CO_2} + m_{N_2} C_{N_2}}{m_{CO_2} + m_{N_2}} = q_{CO_2} C_{CO_2} + q_{N_2} C_{N_2} \quad (2.7)$$

where  $q$  indicates the mass fractions per molecule. For  $CO_2$ , this is just

$$\begin{aligned} q_{CO_2} &= 0.95 \text{ mol/mol air} \left( \frac{M_{CO_2}}{M_{Venus}} \right) = 0.95 \text{ mol } CO_2 / \text{mol air} \left( \frac{44 \text{ g } CO_2 / \text{mol } CO_2}{43.2 \text{ g air/mol air}} \right) \\ q_{CO_2} &= 0.97 \frac{\text{g } CO_2}{\text{g air}} \equiv 0.97 \frac{\text{kg } CO_2}{\text{kg air}} \end{aligned} \quad (2.8)$$

Doing the same for  $N_2$ , we get  $q_{N_2} = 0.03 \frac{\text{kg } CO_2}{\text{kg air}}$ . The specific heat capacities of our two molecules at constant volume are  $C_{CO_2} = 0.655 \text{ kJ K}^{-1} \text{ kg}^{-1}$  and  $C_{N_2} = 0.743 \text{ kJ K}^{-1} \text{ kg}^{-1}$ . Plugging in all these values back to our equation for the specific heat capacity of Venus, we get

$$\begin{aligned} C_{Venus} &= \left( 0.97 \frac{\text{kg } CO_2}{\text{kg air}} \right) (0.655 \text{ kJ K}^{-1} \text{ kg}^{-1}) + \left( 0.03 \frac{\text{kg } CO_2}{\text{kg air}} \right) (0.743 \text{ kJ K}^{-1} \text{ kg}^{-1}) \\ C_{Venus} &= 0.658 \text{ kJ K}^{-1} \text{ kg}^{-1} \quad (\text{at constant volume}) \end{aligned} \quad (2.9)$$

We can repeat the exact same process to get Venus's specific heat capacity at constant pressure, except we use the specific heat capacity of our molecules at constant pressure. The specific heat capacities of our two molecules at constant pressure are  $C_{CO_2} = 0.844 \text{ kJ K}^{-1} \text{ kg}^{-1}$  and  $C_{N_2} = 1.04 \text{ kJ K}^{-1} \text{ kg}^{-1}$ . Thus,

$$\begin{aligned} C_{Venus} &= \left( 0.97 \frac{\text{kg } CO_2}{\text{kg air}} \right) (0.844 \text{ kJ K}^{-1} \text{ kg}^{-1}) + \left( 0.03 \frac{\text{kg } CO_2}{\text{kg air}} \right) (1.04 \text{ kJ K}^{-1} \text{ kg}^{-1}) \\ C_{Venus} &= 0.850 \text{ kJ K}^{-1} \text{ kg}^{-1} \quad (\text{at constant pressure}) \end{aligned} \quad (2.10)$$

□

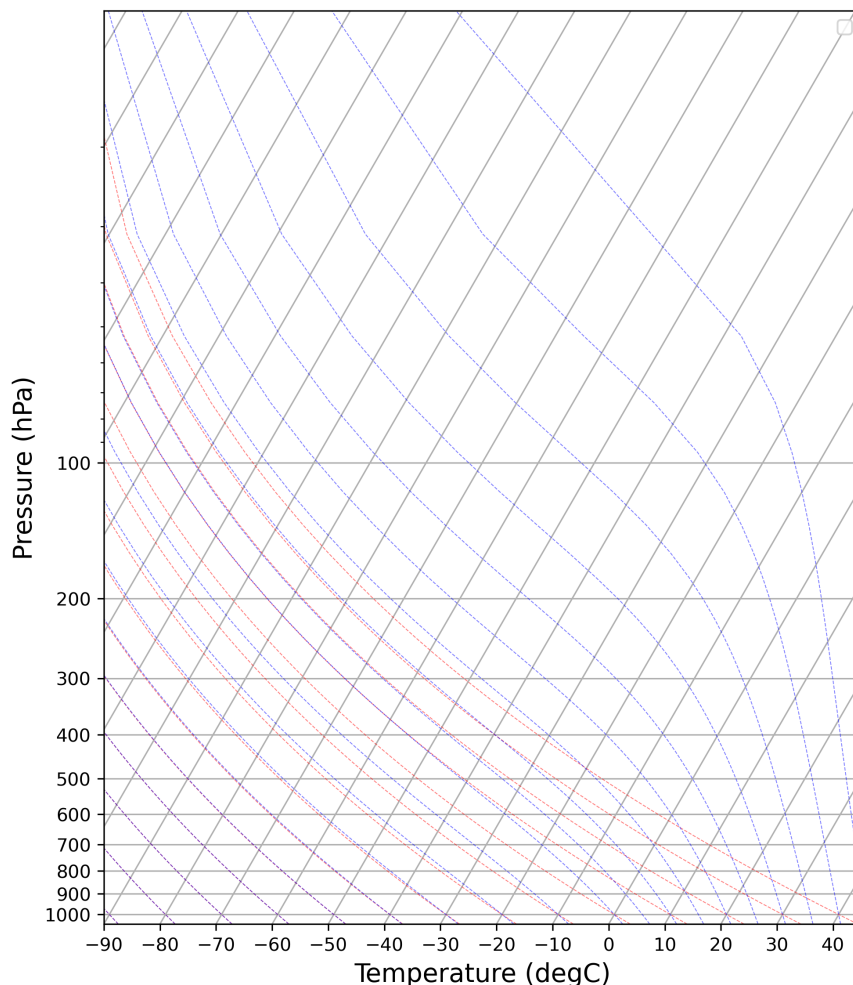
### Problem 3

#### Additional Questions

1. The following figure shows the P-V diagram of air parcel via an adiabatic versus isothermal expansion from the same initial state  $(P_i, V_i)$  to the final state  $(P_f, V_f)$ . The expansion ends up with the same volume  $V_f$ . Please identify and explain which one is correct labeling of the two process curves, isothermal, and adiabatic.
2. Draw the isothermal and adiabatic process into a skew-T- $\ln p$  (short skew-T) diagram.

*Solution.*

1. The first law of thermodynamics can be expressed as  $dQ = mC_v dT + pdV$ . For an adiabatic process this becomes  $mC_v dT = -pdV$ . Since  $V_f > V_i$ ,  $-pdV$  must be negative, so  $dT$  is also negative. Thus, the final temperature for the adiabatic process is lower than its initial temperature. Consequently, the final adiabat temperature must also be lower than the final isotherm temperature (which didn't change from its initial). From the ideal gas law, a lower temperature also means lower pressure, so the final adiabat pressure must be lower than the final isotherm pressure. The diagram to the right is correct.
2. Shown below is a skew-T diagram, and highlighted are the isothermal and adiabatic processes.



□