

## ENV-413: Thermodynamics of the Earth systems

### Worksheet 2: Kinetic theory, equations of state

#### Elementary kinetic theory (refer to section 1.6)

1. The pressure of ideal gas on the walls of a container varies in the following ways (all other variables remaining the same):

Variable	Increase	Decrease	Remains the Same
Incr. Speed of Molecules	x		
Incr. Mass of Molecules	x		
Incr. Vol. of Container		x	
Incr. Temperature	x		

2. If the speed of each molecule in an ideal gas were tripled, would the temperature also triple?

Temperature and velocity are not directly proportional. If the velocity tripled the temperature would increase by a factor of 9.

3. If the temperature of an ideal gas doubled from 50 °C to 100 °C, does the average kinetic energy of the molecules double?

No. It is important to remember that the kinetic energy of the gas would not double because we have to assess the changes in terms of absolute temperature. For example, this change is essentially analogous to a 323K to 373K change. This would not cause the KE to double.

4. Is it possible for both the pressure and volume of an ideal gas to change without causing the internal energy of the gas to change?

Yes, because the change in KE is related to the change in temperature. As long as the change is isothermal in nature it is possible.

5. If the atoms in a container of helium gas have the same average speed as the atoms of a container of argon, which one has the higher temperature?

If two atoms have the same speed but one has a heavier mass, the atom with the heavier mass will translate into more energy and a higher temperature.

6. Which, if either, contains a greater number of molecules, one mole of hydrogen or one mole of oxygen? Which, if either, has more mass?

The number of molecules in a mole of hydrogen and a mole of oxygen is the same. This is  $6.02 \times 10^{23}$ . One mole of oxygen has more mass since the molar mass of oxygen is larger than the molar mass of hydrogen.

## Equation of state for mixture of ideal gases (refer to section 1.7)

2. The equation of state for an ideal gas can be written as

$$pV=nR^*T$$

where  $p$  is pressure,  $V$  is volume,  $n$  is the number of moles,  $T$  is temperature, and  $R^*$  is the universal gas constant.

a) which variables are extensive?

Volume  
Number of moles

b) divide both sides of the equation by mass ( $m$ ), thereby converting the two extensive variables to intensive variables.

$$\frac{pV}{m} = \frac{nR^*T}{m}$$

c) Using the following definitions:

Molecular weight:  $M=m/n$

Specific volume:  $v=V/m$

rewrite the original equation of state using only intensive variables.

$$\frac{pv}{M} = \frac{R^*T}{M}$$

d) The specific gas constant,  $R$ , is defined as  $R^*/M$ . Rewrite the ideal gas law using intensive variables and the specific gas constant. (eq 1.12)

$$pv = RT \quad (\text{Note } R^* \text{ represents universal gas const. } R \text{ represents specific gas const})$$

e) Estimate the specific gas constant for nitrogen. (molecular weight for  $N_2$  is 28 g/mole)

$$R = R^*/M = (8.314 \text{ J/mole K})/(28 \text{ g/mole}) = 296.93 \text{ J/kgK}$$

f) For a mixture of ideal gases, an average specific gas constant can be defined as a mass-weighted mean of the gaseous constituents. Since the atmosphere is about 75% (by mass) nitrogen and oxygen is the next most abundant atmospheric gas (about 23% by mass), would the specific gas constant for the mixture of nitrogen and oxygen be greater or less than the value of  $R$  calculated for nitrogen? The specific gas constant for the mixture of all atmospheric gases except for water vapor is generally referred to as the "dry air" gas constant,  $R_d$ .

$$R(O_2) < R(N_2)$$

### Equation of state for moist air

g) Complications are introduced by the presence of water vapor, which has a variable amount. From Dalton's law of partial pressure, the equation of state can be written individually for each gas in a mixture. Write the equation of state for water vapor, using the notation  $e$  for water vapor partial pressure and the subscript  $v$  to denote vapor.

$$pv = RT$$

$$ev = R_v T$$

h) By combining the equations of state for the "dry air" gases with that for water vapor (see details in section 1.7), a gas constant for dry air plus water vapor (moist air) can be written

$$R = R_d(1 + 0.608 q_v)$$

where  $q_v$  is the specific humidity, defined as the fractional mass of water vapor. Write an equation of state for moist air, using the specific gas constant for moist air.

$$pv = RT$$

$$pv = R_d(1 + 0.608 q_v)T$$

i) It is awkward to have a variable gas constant, so it is the convention among meteorologists to make the humidity adjustment to the temperature rather than to the gas constant. Thus we define a *virtual temperature*,  $T_v$

$$T_v = (1 + 0.608 q_v)T \quad (1.25)$$

Rewrite the equation of state for moist air using virtual temperature (eq. 1.26)

$$pv = R_d T_v$$

j). Calculate the virtual temperature for the following conditions:

a)  $T=303K, q_v=0.025$

b)  $T=243K, q_v=0.003$

a)  $T_v = (1 + (0.608 * 0.025))303 = 307.6056$

b)  $T_v = (1 + (0.608 * 0.003))243 = 243.4432$