

CHM 5423 – Atmospheric Chemistry  
Problem Set 1  
Due date: Thursday, January 24<sup>th</sup>.

Do the following problems. Show your work.

1) The concentration of molecular oxygen (O<sub>2</sub>) for Mars at surface level is 1300 ppm. The total pressure and temperature of the atmosphere at surface level is  $p_{\text{total}} = 0.0060$  bar,  $T = 210$  K. Give the amount of oxygen present at surface level in the following ways:

- $p(\text{O}_2)$  (partial pressure of oxygen, in units of bar, atm, torr, and  $\mu\text{torr}$ .)
- $N(\text{O}_2)$  (number density of oxygen molecules, in units of molecules/cm<sup>3</sup>)
- $D(\text{O}_2)$  (density of oxygen, in units of  $\mu\text{g/L}$ )

2) The following question concerns the escape of molecules from the atmosphere of Mars.

a) Find  $v_{\text{esc}}$  and  $v_{\text{rms}}$  for the following molecules: H<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>, and Ar. Use  $T = 500$  K (an approximate average temperature in the Martian exosphere) in your calculations.

b) Define  $R_v = v_{\text{esc}}/v_{\text{rms}}$ , the ratio of the escape velocity to the rms average speed of a molecule. It can be shown that for the case  $R_v \gg 1$  that  $f$ , the fraction of molecules in a gas at equilibrium that have a speed great enough to leave the gravitational attraction of a planet is given by the expression

$$f \cong (1/6\pi R_v^2)^{1/2} \exp(-3R_v^2/2) \quad (2.1)$$

Find  $f$  for each of the above four molecules in the Martian exosphere.

c) The likelihood of molecules of a particular gas escaping from the gravitational attraction of a planet can be estimated based on the value for  $f$ . In general, the larger the value for  $f$  the more likely escape of the gas becomes. We may use the following approximation to estimate the likelihood that a particular gas has escaped the gravitational attraction of a planet during the 4.5 billion years that the solar system has existed.

If  $f < 10^{-25}$ , then essentially no escape will have occurred.

If  $10^{-15} < f < 10^{-25}$ , then some escape will have occurred

If  $f > 10^{-15}$  then essentially all of the gas will have escaped

Based on your results above, explain why the current atmosphere of Mars contains large amounts of N<sub>2</sub> and Ar but only small amounts of H<sub>2</sub>.

d) There is good reason to believe that the average temperature of the Martian exosphere once was much larger than the value currently observed. Explain the implications of this for the escape of gases from the atmosphere of Mars.

e) The above argument for gas escape ignores the possibility of photochemically assisted escape of gases. For water, for example, the following process can occur in the exosphere



Explain how the above process could lead to the removal of water from the atmosphere of Mars.

3) At what altitude (in km) is the pressure of the Earth's atmosphere equal to the surface pressure on Mars (0.0060 bar)? Use  $H = 7.4$  km for the scale height for Earth.

4) One indirect piece of evidence indicating that free molecular oxygen was uncommon in the early atmosphere of the Earth is the presence of pyrites (metal sulfides) in mineral samples that have been dated several billion years old. Such compounds are thermodynamically unstable in the presence of oxygen. More recent mineral samples have iron oxides present, but usually do not contain iron pyrite.

a) Using the information below, find the equilibrium constant for the process



b) Based on your answer in a, estimate the partial pressure of  $\text{O}_2(\text{g})$  in the atmosphere at which iron pyrite ( $\text{FeS}_2$ ) becomes thermodynamically unstable relative to iron II oxide ( $\text{FeO}$ ). What does this imply about the content of oxygen in the early atmosphere of the Earth? (Note that there are other factors involved, including the rate of reaction 3.1 and the temperature dependence of the equilibrium constant, but the argument based on the thermodynamics of the reaction remains valid).

Substance	$\Delta H^\circ$ (kJ/mol)	$\Delta G^\circ$ (kJ/mol)	$S^\circ$ (J/mol·K)
FeO(s)	- 272.04	- 251.43	60.75
FeS <sub>2</sub> (s)	- 167.36	- 156.16	53.86
O <sub>2</sub> (g)	0.0	0.0	205.14
S(s)	0.0	0.0	31.80

5) Simple calculations can often tell us interesting information about planetary atmospheres.

a) Based on the information in the Chapter 1 handout, find the total mass of the atmosphere of Earth and Venus. Compare the result obtained for the Earth to the value given in the Chapter 1 notes. (HINT: The force exerted by a mass  $m$  in the gravitational field of a planet is  $F = mG_s$ , where  $m$  is mass and  $G_s$  is the gravitational constant for the planet. Force is also related to pressure by the relationship  $p = F/A$ , where  $A$  is area.)

b) Use your result from a and the information on atmospheric composition to find the total mass of argon in the atmosphere of the Earth and Venus. Comment on your results.

6) For an adiabatic expansion of an ideal gas, it may be shown that

$$(T_i/T_f)^\gamma = (p_i/p_f)^{\gamma-1} \quad (6.1)$$

where  $\gamma = C_p/C_v$  is the ratio of the constant pressure heat capacity to the constant volume heat capacity of the gas. Eq 6.1 assumes that over the temperature range of the expansion  $\gamma$  is constant.

a) According to the barometric equation

$$p_z = p_0 \exp(-z/H) \quad (6.2)$$

where  $p_z$  is atmospheric pressure at altitude  $z$  and  $p_0$  is atmospheric pressure at some reference altitude (taken to be sea level for the Earth).

By combining eq 6.1 and 6.2 find an expression for  $T_z$ , the temperature for an air parcel initially at sea level and temperature  $T_0$  after it rises to an altitude  $z$ , and assuming that it expands adiabatically as it rises. Give your expression in terms of  $p_0$ ,  $T_0$ ,  $\gamma$ ,  $H$ ,  $z$ , and/or other constants. (HINT: Let  $T_0$  and  $p_0$  be the temperature and pressure of the air at sea level, where  $z = 0$ . Then  $T_f$  and  $p_f$  are equivalent to  $T_z$  and  $p_z$ , the temperature and pressure at altitude  $z$ .)

b) Using the following values for the terms in your expression for  $T_z$ , find the value for  $T_z - T_0$  for the case  $z = 1.0$  km. Note that this value for  $T_z - T_0$  corresponds approximately to the adiabatic lapse rate for dry air in the Earth's atmosphere.

$$\gamma = 1.40 \quad T_0 = 288. \text{ K} \quad H = 7.4 \text{ km} \quad p_0 = 1.00 \text{ atm}$$

Solutions.

1) a)  $p(\text{O}_2) = (1300/10^6) (0.0060 \text{ bar}) = 7.8 \times 10^{-6} \text{ bar}$

Since  $1 \text{ atm} = 1.01325 \text{ bar}$

$$p(\text{O}_2) = (7.8 \times 10^{-6} \text{ bar}) (1 \text{ atm}/1.01325 \text{ bar}) = 7.70 \times 10^{-6} \text{ atm}$$

Since  $1 \text{ atm} = 760 \text{ torr}$

$$p(\text{O}_2) = (7.70 \times 10^{-6} \text{ atm}) (760 \text{ torr}/1 \text{ atm}) = 5.85 \times 10^{-3} \text{ torr}$$

Finally, since  $1 \text{ torr} = 10^6 \mu\text{torr}$

$$p(\text{O}_2) = (5.85 \times 10^{-3} \text{ torr}) (10^6 \mu\text{torr}/\text{torr}) = 5.85 \times 10^3 \mu\text{torr}$$

b)  $pV = nRT$ , and so  $(n/V) = p/RT$

Multiplying by  $N_A$  (Avogadro's number) gives

$$nN_A/V = N/V = pN_A/RT$$

So 
$$\frac{N}{V} = \frac{(7.8 \times 10^{-6} \text{ bar}) (6.022 \times 10^{23} \text{ molecule/mol})}{(0.08314 \text{ L}\cdot\text{bar/mol}\cdot\text{K}) (210. \text{ K})} \frac{1. \text{ L}}{1000. \text{ cm}^3} = 2.69 \times 10^{14} \text{ molecule/cm}^3$$

c) 
$$D = 2.69 \times \frac{10^{14} \text{ molecule}}{\text{cm}^3} \frac{1000. \text{ cm}^3}{1. \text{ L}} \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ molecule}} \frac{32.0 \text{ g}}{\text{mol}} \frac{10^6 \mu\text{g}}{\text{g}} = 1.43 \times 10^{-5} \text{ g/L}$$

$$= 14.3. \mu\text{g/L}$$

2) a+b)  $\text{H}_2, M = 2.02 \text{ g/mol} = 2.02 \times 10^{-3} \text{ kg/mol}$   
 $\text{H}_2\text{O} = 18.02 \text{ g/mol} = 18.02 \times 10^{-3} \text{ kg/mol}$   
 $\text{N}_2, M = 28.02 \text{ g/mol} = 28.02 \times 10^{-3} \text{ kg/mol}$   
 $\text{Ar}, M = 39.95 \text{ g/mol} = 39.95 \times 10^{-3} \text{ kg/mol}$

$$v_{\text{esc}} = (2M_p G/r_p)^{1/2} = [2 (6.42 \times 10^{23} \text{ kg}) (6.67 \times 10^{-11} \text{ N}\cdot\text{m}^2/\text{kg}^2) / 3400. \times 10^3 \text{ m}]^{1/2} = 5019. \text{ m/s}$$

$$v_{\text{rms}} = (3RT/M)^{1/2} \quad R = 8.314 \text{ J/mol}\cdot\text{K} \quad T = 500. \text{ K}$$

$$R_v = v_{\text{esc}}/v_{\text{rms}}$$

gas	$v_{\text{rms}}$ (m/s)	$R_v = v_{\text{esc}}/v_{\text{rms}}$	f
$\text{H}_2$	2485.	2.02	$2.5 \times 10^{-4}$
$\text{H}_2\text{O}$	832.	6.03	$7.9 \times 10^{-26}$
$\text{N}_2$	667.	7.52	$4.4 \times 10^{-39}$
Ar	559.	8.98	$7.5 \times 10^{-55}$

c) Based on the values for f calculated above, all of the  $\text{H}_2$  originally present in the atmosphere of Mars should have escaped by this time.  $\text{N}_2$  and Ar should not have escaped to any significant degree, given their small values for f. Some, but not all, of the water present in the atmosphere should have escaped, since f is near the upper limit for partial escape from the atmosphere.

d) If the temperature of the exosphere was larger than 500. K, then  $v_{rms}$ ,  $R_v$ , and  $f$  would all be larger. This would make it easier for  $H_2O$  to escape, and might even lead to some escape of  $N_2$  and  $Ar$ . Since  $H_2$  can already escape rapidly from the atmosphere of Mars, a higher temperature for the exosphere would only mean even more rapid escape.

e) If  $H_2O$  photochemically dissociates in the upper atmosphere of Mars, then the  $H$  and  $H_2$  produced would escape from the atmosphere far more rapidly than  $H_2O$ , due to the much smaller masses. The oxygen produced would likely not escape from the atmosphere. Its most likely fate would be removal by chemical reaction with substances on the surface of Mars.

3)  $p_z = p_0 \exp(-z/H)$  and so

$$(p_z/p_0) = \exp(-z/H)$$

$$\ln(p_z/p_0) = -z/H$$

$$z = -H \ln(p_z/p_0) = H \ln(p_0/p_z)$$

For  $p_z = 0.0060$  bar,  $p_0 = 1.000$  bar

$$z = (7.4 \text{ km}) \ln(1.0/0.0060) = 38. \text{ km}$$

4) a)  $\ln K = -\Delta G^\circ_{rxn}/RT$

$$\Delta G^\circ_{rxn} = [2 \Delta G^\circ_f(\text{FeO}(s)) + 4 \Delta G^\circ_f(\text{S}(s))] - [2 \Delta G^\circ_f(\text{FeS}_2(s)) + \Delta G^\circ_f(\text{O}_2(g))]$$

$$[2(-251.43 \text{ kJ/mol})] - [2(-156.16 \text{ kJ/mol})] = -190.54 \text{ kJ/mol}$$

$$\ln K = \frac{(190540. \text{ J/mol})}{(8.314 \text{ J/mol}\cdot\text{K})(298. \text{ K})} = 76.91 \quad K = e^{76.91} = 2.5 \times 10^{33}$$

b) Since everything in the reaction other than  $O_2$  is a solid

$$K = 1/p(O_2) \quad p(O_2) = 1/K = 1/2.5 \times 10^{33} = 4. \times 10^{-34} \text{ bar}$$

This applies at the temperature of the thermochemical data (298. K). While the value of  $K$  might change with temperature, and there is no information on the kinetics of the reaction, thermodynamically  $FeO(s)$  is far more stable than  $FeS_2(s)$ , and would be expected to form if there was any significant partial pressure of  $O_2(g)$  in the atmosphere.

The absence of  $FeO$  and the presence of  $FeS_2$  in ancient rocks therefore implies that initially there was very little free  $O_2$  in the atmosphere of the Earth, as the presence of  $O_2$  in the atmosphere would have meant  $FeO$  would form in preference to  $Fe_2S$ .

5) a)  $F = mG_s$  where  $m = \text{mass}$   $G_s = \text{surface gravity of planet}$

But  $p = F/A$  where  $p = \text{pressure}$   $A = \text{area}$

So  $pA = mG_s$

$$m = pA/G_s$$

Now  $A$  for a sphere is  $A = 4\pi r^2$ , and so

$$m = 4\pi r_p^2 p/G_s$$

For Earth  $m = 4\pi (6380. \times 10^3 \text{ m})^2 \frac{(1.0 \times 10^5 \text{ N/m}^2)}{(9.78 \text{ m/s}^2)} = 5.23 \times 10^{18} \text{ kg}$  (vs  $5.14 \times 10^{18} \text{ kg}$  in Table 1.1)

For Venus  $m = 4\pi (6050. \times 10^3 \text{ m})^2 \frac{(92. \times 10^5 \text{ N/m}^2)}{(8.87 \text{ m/s}^2)} = 4.77 \times 10^{20} \text{ kg}$

b) The mass of argon in a planetary atmosphere is

$$m(\text{Ar}) = \text{fraction of Ar (by number)} \frac{M(\text{Ar})}{M_{\text{ave}}} m(\text{atmosphere})$$

where  $M_{\text{ave}}$  is the average molecular mass of the atmosphere. Note we need the second factor above because we usually give composition by percent (or parts per million) by number, not by mass.

$$M(\text{Ar}) = 39.95 \text{ g/mol} \quad M_{\text{ave}}(\text{Earth}) = 28.96 \text{ g/mol (Table 1.1, Chapter 1)}$$

$$M_{\text{ave}}(\text{Venus}) = 43.45 \text{ g/mol (using 96.5 \% CO}_2, 3.5 \% \text{ N}_2)$$

$$\text{So mass argon for Earth} = (0.0093) (39.95/28.96)(5.23 \times 10^{18} \text{ kg}) = 6.71 \times 10^{16} \text{ kg}$$

$$\text{So mass argon for Venus} = (70. \times 10^{-6}) (39.95/43.45)(4.77 \times 10^{20} \text{ kg}) = 3.07 \times 10^{16} \text{ kg}$$

So the Earth and Venus have roughly equal masses of argon. Since argon is not expected to escape from either atmosphere, that suggests the argon that is present has a similar origin.

6)  $T_i = T_0 \quad T_f = T_z$   
 $p_i = p_0 \quad p_f = p_z = p_0 \exp(-z/H)$

And so  $(T_0/T_i)^\gamma = (p_0/p_z)^{\gamma-1}$

Invert  $(T_z/T_0)^\gamma = (p_z/p_0)^{\gamma-1} = (e^{-z/H})^{\gamma-1}$

$$T_z^\gamma = T_0^\gamma (e^{-z/H})^{\gamma-1}$$

or  $T_z = T_0 (e^{-z/H})^{\gamma-1/\gamma}$

For  $z = 1.0 \text{ km} \quad T_0 = 288. \text{ K} \quad H = 7.4 \text{ km}$

$$\gamma = C_{p,m}/C_{v,m} = 1.40 \text{ (since for N}_2 \text{ and O}_2 \text{ } C_{v,m} = (5/2) \text{ R, and so } C_{p,m} = C_{v,m} + \text{ R} = (7/2) \text{ R)}$$

$$T_z = (288. \text{ K}) (e^{-1.0/7.4})^{0.4/1.4} = 277.1 \text{ K}$$

$$\Delta T = 277.1 \text{ K} - 288.0 \text{ K} = - 10.9 \text{ K}$$

So the adiabatic lapse rate for dry air at sea level is approximately – 11 K/km.