CHEM 1001 A, N and T Midterm Test #1
October 17, 2014

Part A. Answer each of the six questions with a few sentences or equations where necessary. (5 Marks each)

1. State Dalton’s law of partial pressures.

   Dalton’s law of partial pressure states that the total pressure of a gas sample is equal to the sum of the partial pressures of the gases making up that sample. Or, $p_{tot} = \sum_i p_i$

2. Under what conditions is $q = \Delta H$?

   $q = \Delta H$ only if the system is open and the pressure is constant.

3. What chemical species are mostly responsible for absorption of UV light from the sun in the following wavelength ranges?

0 – 100 nm	N_2O
100 – 200 nm	O_2
200 – 300 nm	O_3

4. What two ideas about the nature of light are brought together in the Planck equation, $E = h\nu$?

   The idea that light is wavelike with a frequency ν, and that it is particle–like, with photons each having energy E.

5. Why does $Ne_{(g)}$ have a lower pressure than an equal amount of $He_{(g)}$ at the same volume and temperature?

   Ne is a larger atom than He. Thus the intermolecular forces among Ne atoms are larger, and these attractive forces cause the Ne atoms to be attracted to one another, effectively lowering the number of particles in the gas phase, hence lowering the pressure.

6. Considering the known elements, which of the following five sets of quantum numbers are allowed and which are not?

n	**l**	**m_l**	**m_s**	**Allowed? (Yes or No)**
2	2	0	+½	**No**
2	1	1	–½	**Yes**
3	0	0	+½	**Yes**
4	3	-1	–½	**Yes**
4	2	+2	+½	**Yes**

Part B. Answer any three of the following four questions (B1, B2, B3, B4). If you answer all four, the best three answers will count. (20 marks each)

B1. (a) [5] 0.5 mol $CO_{2(g)}$ at 50°C in a volume of 15.0 L is compressed to a pressure of 1.5 bar and cooled to 25°C. Calculate the new volume (L).

$$p_1 = \frac{nRT_1}{V_1} = \frac{0.5\,\text{mol}(0.08314\ \text{L bar K}^{-1}\text{mol}^{-1})(273+50)\text{K}}{15.0\ \text{L}} = 0.895\ \text{bar}$$

$$\frac{p_1V_1}{n_1T_1} = \frac{p_2V_2}{n_2T_2}$$

In this case, $n_1 = n_2$, so $\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$

or, $V_2 = \frac{p_1V_1T_2}{p_2T_1} = \frac{0.895\ \text{bar}(15.0\ \text{L})(273+25)\text{K}}{1.5\ \text{bar}(273+50)\text{K}} = 8.26\ \text{L}$

(b) [5] Use the van der Waals equation to calculate the pressure (in bar) that results from putting 5.0 mol $H_2O_{(g)}$ in a 1.0 L container at 300°C. For $H_2O_{(g)}$, a = 5.54 bar L^2 mol^{-2} and b = 0.0305 L mol^{-1}.

$$p = \frac{nRT}{V-nb} - a\left(\frac{n}{v}\right)^2$$

$$= \frac{5.0\,\text{mol}\,(0.08314\,\text{L bar K}^{-1}\text{mol}^{-1})(273+300)\text{K}}{1.0\,\text{L} - 5.0\,\text{mol}\,(0.0305\,\text{L mol}^{-1})} - 5.54\,\text{bar L}^2\text{mol}^{-2}\left(\frac{5.0\,\text{mol}}{1.0\,\text{L}}\right)^2$$

$$= 281.0\ \text{bar} - 138.5\ \text{bar}$$

$$= 142.5\,\text{bar}$$

(c) [2] Calculate the mean speed of $He_{(g)}$ atoms at 25°C

$$\bar{v} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3(8.314\,\text{J K}^{-1}\text{mol}^{-1})(273+25)\text{K}}{0.004\,\text{kg mol}^{-1}}} = 1363\ \text{m s}^{-1}$$

(d) [8] In $He_{(g)}$ at 25°C and 1 bar, the mean free path $\lambda = 0.2 \times 10^{-6}$ m. Use this and the speed calculated in part (c) to calculate the total number of collisions per second among He atoms in a 1m^3 box at 1 bar and 25°C.

If the mean free path is 0.2×10^{-6} m, and the speed is on average 1363 m s^{-1}, the number of collisions experienced by one He atom per second is (as shown in class):

$$\text{Collision frequency} = \frac{\text{speed}}{\text{mean free path}} = \frac{1363\ \text{m s}^{-1}}{0.2\times10^{-6}\ \text{m}} = 6.82\times10^{9}\text{s}^{-1}$$

In a 1 m^3 box at 25°C and 1 bar, the number of He atoms is:

$$N_{Av}\frac{pV}{RT} = 6.02\times10^{23}\text{mol}^{-1}\frac{10^5\,\text{Pa}(1\,\text{m}^3)}{8.314\ \text{Pa m}^3\text{mol}^{-1}\text{K}^{-1}(25+273)\text{K}} = 2.43\times10^{25}$$

The number of collisions is therefore $\frac{6.82\times10^{9}\text{s}^{-1}(2.43\times10^{25})}{2} = 8.28\times10^{34}\text{s}^{-1}$

(divide by two so as not to double count each collision)

B2. (a) [8] Calculate the partial pressures (bar) of each gas in a mixture of 100.0 g $O_{2(g)}$ and 175.0 g $N_{2(g)}$ in a 120.0 L container at 35°C.

$$\frac{100.0\text{ g O}_2}{32.0\text{ g mol}^{-1}} = 3.125\text{ mol CO}_2$$

$$\frac{175.0\text{ g N}_2}{28.0\text{ g mol}^{-1}} = 6.250\text{ mol N}_2$$

$$n_{\text{tot}} = 3.125\text{ mol O}_2 + 6.250\text{ mol N}_2 = 9.375\text{ mol}$$

$$p_{\text{tot}} = \frac{n_{\text{tot}}RT}{V} = \frac{9.375\text{ mol}(0.08314\text{ L bar K}^{-1}\text{mol}^{-1})(273+35)\text{K}}{120\text{ L}} = 2.00\text{ bar}$$

$$X_{O_2} = \frac{3.125\text{ mol}}{3.125\text{ mol} + 6.250\text{ mol}} = 0.333$$

Thus, $p_{O_2} = X_{O_2}(p_{\text{tot}}) = 0.333(2.00\text{ bar}) = 0.666\text{ bar}$

and $p_{N_2} = X_{N_2}(p_{\text{tot}}) = (1-0.333)(2.00\text{ bar}) = 1.33\text{ bar}$

(b) [4] Write the four reactions collectively called the Chapman cycle which explain the existence of ozone in the stratosphere.

$O_2 + h\upsilon \rightarrow O + O$
$O + O_2 \rightarrow O_3$
$O_3 + h\upsilon \rightarrow O_2 + O$
$O + O_3 \rightarrow 2\ O_2$

(c) [4] Why is the radiative forcing of $CH_{4(g)}$ so much greater than that of $CO_{2(g)}$?

$CH_{4(g)}$ has many more modes of vibration than $CO_{2(g)}$, so more photons (of different wavelengths) can be absorbed by $CH_{4(g)}$, resulting in more heating.

(d) [4] Beginning with $NiS_{(s)}$, show the reactions that produce $H_2SO_{4(aq)}$, i.e. acid rain.

$$NiS_{(s)} + \tfrac{3}{2}O_{2(g)} \longrightarrow NiO_{(s)} + SO_{2(g)}$$

$$SO_{2(g)} + \tfrac{1}{2}O_{2(g)} \longrightarrow SO_{3(g)}$$

$$SO_{3(g)} + H_2O_{(l)} \longrightarrow H_2SO_{4(aq)}$$

B3. Calculate ΔH^0 (kJ/mol) for the reaction: $HF_{(g)} \downarrow HF_{(aq)}$ given the following data:

Reaction 1: $2\ Al_{(s)} + 6\ HF_{(aq)} \downarrow 2\ AlF_{3(aq)} + 3\ H_{2(g)}$ $\Delta H^o = -988$ kJ/mol
Reaction 2: $2\ Al_{(s)} + 3\ F_{2(g)} \downarrow 2\ AlF_{3(s)}$ $\Delta H^o = -1561$ kJ/mol
Reaction 3: $H_{2(g)} + F_{2(g)} \downarrow 2\ HF_{(g)}$ $\Delta H^0 = -273$ kJ/mol
Reaction 4: $AlF_{3(s)} \downarrow AlF_{3(aq)}$ $\Delta H^0 = -288$ kJ/mol

$2\ Al_{(s)} + 6\ HF_{(aq)} \downarrow 2\ AlF_{3(aq)} + 3\ H_{2(g)}$ $\Delta H^o = -988$ kJ/mol
$2\ AlF_{3(aq)} \downarrow 2\ AlF_{3(s)}$ $\Delta H^0 = -2(-288$ kJ/mol)
$6\ HF_{(g)} \downarrow 6\ HF_{(aq)}$ $\Delta H^0 = X$
$3\ H_{2(g)} + 3\ F_{2(g)} \downarrow 6\ HF_{(g)}$ $\Delta H^0 = 3(-273$ kJ/mol)

$2\ Al_{(s)} + 3\ F_{2(g)} \downarrow 2\ AlF_{3(s)}$ $\Delta H^o = -700 + 288 + X + 3(-273) = -1561$ kJ/mol

Thus $X = -1561 - (-988 - 2(-288) + 3(-273)) = -330$

But X is the enthalpy change for the reaction $6\ HF_{(g)} \downarrow 6\ HF_{(aq)}$.
Thus for the reaction $HF_{(g)} \downarrow HF_{(aq)}$, $\Delta H^0 = -330/6 = -55$ kJ/mol

[10] for setting up the reactions correctly
[10] for the math

Mark of zero if the reactions do not add up.

B4. (a) [6] Lines in the Lyman series end at m = 1. From which level do electrons fall to result in the emission of light at 102.6 nm?

$$\frac{1}{\lambda} = \mathrm{R}\left[\frac{1}{\mathrm{m}^2} - \frac{1}{\mathrm{n}^2}\right]$$

$$\frac{1}{\mathrm{R}\lambda} = \frac{1}{\mathrm{m}^2} - \frac{1}{\mathrm{n}^2}$$

$$\frac{1}{\mathrm{n}^2} = \frac{1}{\mathrm{m}^2} - \frac{1}{\mathrm{R}\lambda}$$

$$\mathrm{n}^2 = \left(\frac{1}{\mathrm{m}^2} - \frac{1}{\mathrm{R}\lambda}\right)^{-1}$$

$$\mathrm{n} = \left(\frac{1}{\mathrm{m}^2} - \frac{1}{\mathrm{R}\lambda}\right)^{-0.5}$$

$$= \left(\frac{1}{1^2} - \frac{1}{0.01097\mathrm{nm}^{-1}(102.6\,\mathrm{nm})}\right)^{-0.5}$$

$$= 3$$

(b) [6] Calculate the maximum wavelength (nm) of light able to break the bond in Cl_2 knowing that the bond dissociation energy is 240 kJ / mol.

$$\mathrm{E} = \mathrm{h}\upsilon$$

$$= \frac{\mathrm{hc}}{\lambda}$$

$$\lambda = \frac{\mathrm{hc}}{\mathrm{E}}$$

$$\frac{6.63\times10^{-34}\,\mathrm{J\,s}(3.00\times10^{8}\,\mathrm{m\,s}^{-1})}{240000\,\mathrm{J\,mol}^{-1} / 6.02\times10^{23}\,\mathrm{mol}^{-1}}$$

$$= 4.99\times10^{-7}\,\mathrm{m}$$

$$= 499\ \mathrm{nm}$$

(c) [8] How many photons are produced in a light pulse at λ = 653 nm having a total energy of 0.489 J?

$$\mathrm{E} = \mathrm{h}\upsilon$$

$$= \frac{\mathrm{hc}}{\lambda}$$

$$= \frac{6.63\times10^{-34}\,\mathrm{J\,s}(3.00\times10^{8}\,\mathrm{m\,s}^{-1})}{653\times10^{-9}\,\mathrm{m}}$$

$$= 3.05\times10^{-19}\,\mathrm{J\ per\ photon}$$

Thus, a pulse having a total energy of 0.489 J must contain:

$$\frac{0.489\ \mathrm{J}}{3.05\times10^{-19}\,\mathrm{J / photon}} = 1.6\times10^{18}\ \mathrm{photons}$$