CHEM 1001 A, N and T Midterm Test #1
October 2, 2015

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

A1. Boyle's law states that the product of p and V is a constant. Why is this "law" not obeyed at very high pressure?

At very high pressure, the molecules are close together and experience attractive forces. This causes the volume to decreases faster than the pressure increases, so pV actually decreases.

A2. State Dalton's law of partial pressures.

Dalton's law states that the total pressure is the sum of the partial pressures of the gases in a mixture, or $p_{tot} = \sum_i p_i$

A3. Why is the rate of effusion or diffusion of a gas molecule proportional to the square root of the inverse of its molecular weight?

This is because the rate of effusion or diffusion is proportional to molecular speed, which in turn is inversely proportional to the square rood of the inverse of the molecular weight according to

$$\bar{v} = \left(\frac{3RT}{M}\right)^{1/2}$$

A4. Why does the concentration of ozone (O_3) go through a maximum at an altitude of approximately 30 km?

Above this altitude, there is very little oxygen, so the reaction $O_2 + h\upsilon \rightarrow O + O$ goes very slowly, thus produces very little O, which is needed in the reaction $O + O_2 \rightarrow O_3$ which produces the O_3.
Below this altitude, the reaction $O_2 + h\upsilon \rightarrow O + O$ also goes slowly because the light intensity is so low.
At this altitude, the rate of $O_2 + h\upsilon \rightarrow O + O$ is maximized, thus so is the rate of production of O, thus also of O_3.

A5. Under what conditions is it true that $\Delta H = q$?

This is true only in an open system at constant pressure.

A6. What does the term "state function" mean? Also give an example of a state function.

A state function is a function whose value does not depend on the path or rate of a chemical reaction. The only state function we have studied so far is ΔH, although there are others…

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) [4 marks] Use the ideal gas law to calculate the pressure (in bar) exerted by 100 moles of nitrogen gas in a 15.0 L container at 75.0°C.

$$p = \frac{nRT}{V} = \frac{100\ \text{mol}(0.08314\ \frac{\text{L bar}}{\text{mol K}})(75+273)\text{K}}{15.0\ \text{L}} = 193\ \text{bar}$$

(b) [8 marks] Use the van der Waals equation to calculate the pressure (in bar) exerted by 100 moles of nitrogen gas in a 15.0 L container at 75.0°C. For nitrogen, *a* = 1.408 bar L^2 mol^{-2} and *b* = 0.0391 L mol^{-1}.

$$\begin{aligned} p &= \frac{nRT}{V-nb} - a\left(\frac{n}{V}\right)^2 \\ &= \frac{100\ \text{mol}(0.08314\ \frac{\text{L bar}}{\text{mol K}})(75+273)\text{K}}{15.0\ \text{L} - 100\ \text{mol}(0.0391\ \text{L mol}^{-1})} - 1.408\ \text{bar L}^2\text{mol}^{-2}\left(\frac{100\ \text{mol}}{15.0\ \text{L}}\right)^2 \\ &= 261\ \text{bar} - 63\ \text{bar} \\ &= 198\ \text{bar} \end{aligned}$$

(c) [4 marks] Explain the difference in the two values calculated in part (a) and part (b) above. Be specific.

This is a very high pressure, so the molecules are close together. Their volumes and the attractive forces among them become significant under these conditions, so the pressure is very different from what the ideal gas law would predict. In this case, the molecular volumes are more important than the attractive forces, so the van der Waals pressure is larger than the ideal pressure.

(d) [4 marks] Why does $H_2O_{(g)}$ exert a lower pressure than $O_{2(g)}$ under the same conditions of n, V and T?

The intermolecular attractive forces in water are greater than in oxygen. This pulls the molecules closer together and they therefore exert a small pressure.

B2. (a) [4 marks] Calculate the density of helium gas (in g L^{-1}) at 20.0 bar and 100°C.

$$\rho = \frac{pM}{RT}$$

$$= \frac{20.0\ \text{bar}(4.00\ \text{g mol}^{-1})}{(0.08314\ \frac{\text{L bar}}{\text{mol K}})(100+273)\text{K}} = 2.58\ \text{g L}^{-1}$$

(b) [4 marks] Calculate the ratio of the diffusion rates of $PCl_{3(g)}$ and $PCl_{5(g)}$ under the same conditions. Which gas diffuses faster?

$$\frac{\text{rate}_{PCl_3}}{\text{rate}_{PCl_5}} = \sqrt{\frac{M_{PCl_5}}{M_{PCl_3}}} = \sqrt{\frac{208.2\ \text{g mol}^{-1}}{134.3\ \text{g mol}^{-1}}} = 1.25 \quad \text{(would be 0.90 if inverted)}$$

The PCl_3 diffuses faster.

(c) [4 marks] Calculate the molecular weight (in g mol^{-1}) of a gas whose average speed at 150°C is 513.9 m s^{-1}.

$$\bar{v} = \left(\frac{3RT}{M}\right)^{1/2}$$

$$\bar{v}^2 = \frac{3RT}{M}$$

$$M = \frac{3RT}{\bar{v}^2} = \frac{3(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(150+273)\text{K}}{(513.9\ \text{m s}^{-1})^2} = 0.03995\ \text{kg mol}^{-1} = 39.95\ \text{g mol}^{-1}$$

(d) [8 marks] A 6.50 L vessel contains 2.0 g of each of $Ne_{(g)}$ and $F_{2(g)}$ at 35°C. Calculate the total pressure and the partial pressure of each gas (in bar).

$$\frac{2.0\ \text{g Ne}}{20.18\ \text{g mol}^{-1}} = 0.0991\ \text{mol Ne} \qquad \frac{2.0\ \text{g}\ F_2}{38.0\ \text{g mol}^{-1}} = 0.0526\ \text{mol}\ F_2$$

n_{tot} = 0.0991 + 0.0526 = 0.1517 mol

$$p_{tot} = \frac{n_{tot}RT}{V} = \frac{0.1517\ \text{mol}(0.08314\ \frac{\text{L bar}}{\text{mol K}})(35+273)\text{K}}{6.50\ \text{L}} = 0.598\ \text{bar}$$

$$p_{Ne} = X_{Ne}p_{tot} = \frac{n_{Ne}}{n_{tot}}p_{tot} = \frac{0.0991\ \text{mol}}{0.1517\ \text{mol}}0.598\ \text{bar} = 0.391\ \text{bar}$$

$$p_{F_2} = X_{F_2}p_{tot} = \frac{n_{F_2}}{n_{tot}}p_{tot} = \frac{0.0526\ \text{mol}}{0.1517\ \text{mol}}0.598\ \text{bar} = 0.207\ \text{bar}$$

B3. (a) [12 marks] Calculate ΔH (in kJ mol^{-1}) for the reaction:

$$2\ N_{2(g)} + 5\ O_{2(g)} \rightarrow 2\ N_2O_{5(g)}$$

given the following data:

$N_2O_{5(g)} + H_2O_{(l)} \rightarrow 2\ HNO_{3(l)}$ $\quad \Delta H = -77\ \text{kJ mol}^{-1}$
$1/2\ N_{2(g)} + 3/2\ O_{2(g)} + 1/2\ H_{2(g)} \rightarrow HNO_{3(l)}$ $\quad \Delta H = -174\ \text{kJ mol}^{-1}$
$H_{2(g)} + 1/2\ O_{2(g)} \rightarrow H_2O_{(l)}$ $\quad \Delta H = -286\ \text{kJ mol}^{-1}$

$2\ N_{2(g)} + 6\ O_{2(g)} + 2\ H_{2(g)} \rightarrow 4\ HNO_{3(l)}$ $\quad \Delta H = 4(-174\ \text{kJ}) = -696\ \text{kJ mol}^{-1}$

$4\ HNO_{3(l)} \rightarrow 2\ N_2O_{5(g)} + 2\ H_2O_{(l)}$ $\quad \Delta H = -2(-77\ \text{kJ}) = +154\ \text{kJ mol}^{-1}$

$2\ H_2O_{(l)} \rightarrow 2\ H_{2(g)} + O_{2(g)}$ $\quad \Delta H = -2(-286) = +572\ \text{kJ mol}^{-1}$

$2\ N_{2(g)} + 5\ O_{2(g)} \rightarrow 2\ N_2O_{5(g)}$ $\quad \Delta H = -696 + 154 + 572 = +30\ \text{kJ mol}^{-1}$

(b) [4 marks] It takes 100.0 J of heat to raise the temperature of 52.5 g of lead ($Pb_{(s)}$) from 28.0 to 47.6°C. Calculate the <u>molar</u> heat capacity of lead.

$$q = mC\Delta T$$

$$C = \frac{q}{m\Delta T}$$

$$= \frac{100.0\ \text{J}}{52.5\ \text{g}(47.6 - 28.0)^{\circ}\text{C}}$$

$$= 0.0972\ \text{J g}^{-1}\ {}^{\circ}\text{C}^{-1}$$

$$\times\ 207.2\ \text{g mol}^{-1} = 20.1\ \text{J mol}^{-1}\ {}^{\circ}\text{C}^{-1}$$

(c) [4 marks] Calculate the amount of heat required to raise the temperature of 1.5 L of liquid water from 25°C to the boiling point. For water, $C = 4.18\ \text{J}\ {}^{\circ}\text{C}^{-1}\ \text{g}^{-1}$, and the density of water is $0.997\ \text{g cm}^{-3}$.

$$q = mC\Delta T$$

$$= \left[1.5\ \text{L} \times \left(\frac{1000\ \text{cm}^3}{1\ \text{L}}\right) \times \left(\frac{0.997\ \text{g}}{1\ \text{cm}^3}\right)\right] \times \left(\frac{4.18\ \text{J}}{{}^{\circ}\text{C g}}\right) \times (100 - 25)^{\circ}\ \text{C} = 4.69 \times 10^5\ \text{J}$$

B4. (a) [15 marks] Use the following standard enthalpies of formation to calculate how many litres of propane gas (measured at 0.95 bar and 15°C) must be burned in oxygen to produce enough energy to heat 10.0 L of liquid water from 15°C to 100°C. For water, C = 4.18 J $^{o}C^{-1}$ g^{-1}, and the density of water is 0.997 g cm^{-3}.

	$C_3H_{8(g)}$	$CO_{2(g)}$	$H_2O_{(g)}$
ΔH^o_f (kJ mol^{-1})	-103.8	-393.5	-241.8

The (unbalanced) reaction is $C_3H_{8(g)} + O_{2(g)} \rightarrow CO_{2(g)} + H_2O_{(g)}$

The amount of heat that must be supplied is $q = mC\Delta T$

$$= \left[10.0\ \mathrm{L} \times \left(\frac{1000\ \mathrm{cm}^3}{1\ \mathrm{L}}\right) \times \left(\frac{0.997\ \mathrm{g}}{1\ \mathrm{cm}^3}\right)\right] \times \left(\frac{4.18\ \mathrm{J}}{{}^o\mathrm{C\ g}}\right) \times (100-15)^o\ \mathrm{C} = 3.54 \times 10^6\ \mathrm{J}$$

The reaction must first be balanced: $C_3H_{8(g)} + 5\ O_2 \rightarrow 3\ CO_{2(g)} + 4\ H_2O_{(g)}$

$\Delta H^o = 3\ \Delta H^o_f\ (CO_{2(g)}) + 4\ \Delta H^o_f\ (H_2O_{(g)}) - \Delta H^o_f\ (C_3H_{8(g)}) - 5\ \Delta H^o_f\ (O_{2(g)})$
= 3(-393.5) + 4(-241.8) – (-103.8) – 5(0)
= -2043.9 kJ mol^{-1} = 2.04 $\times 10^6$ J mol^{-1}

The amount of propane required is therefore $\dfrac{3.54 \times 10^6\ \mathrm{J}}{2.04 \times 10^6\ \mathrm{J\ mol}^{-1}} = 1.74\ \mathrm{mol}$

Using the ideal gas law, $V = \dfrac{nRT}{p} = \dfrac{1.74\ \mathrm{mol}(0.08314\ \mathrm{L\ bar\ K}^{-1}\ \mathrm{mol}^{-1})(15+273)\mathrm{K}}{0.95\ \mathrm{bar}} = 43.8\ \mathrm{L}$

(b) [5 marks] Some propane gas is expanded from 20.0 to 50.0 L at a pressure of 1.00 bar. Calculate the work (in kJ) and explain why it is negative.

$w = -p\Delta V = -10^5 Pa(0.050 - 0.020)m^3 = -3000\ Pa\ m^3 = -3000\ J = -3.00\ kJ$

The system (i.e. the propane) had to do work during expansion to “push back” the atmosphere. This required an expenditure of energy, i.e. the energy of the system decreased, and by convention this means the work is negative.