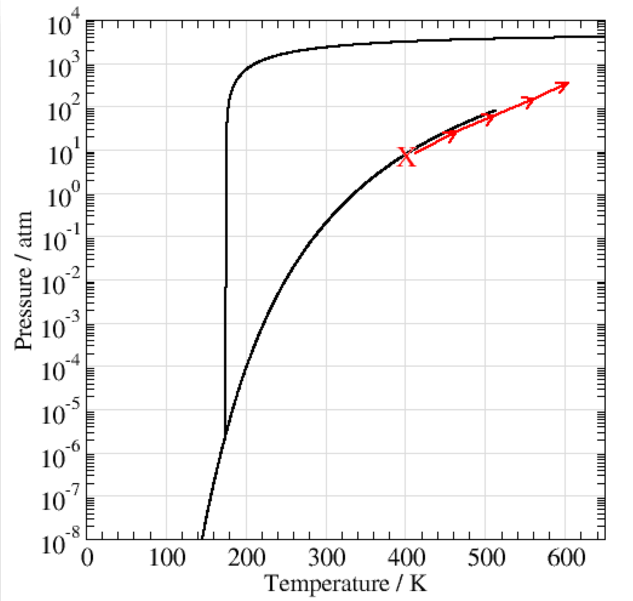
2021 CHEM 154 Midterm Examination Solutions

1. **[8 marks total]** Some methanol (CH_3OH) is placed in an initially evacuated, rigid, 2.00 L container and put in an oven maintained at a constant temperature. After some time, the pressure in the container becomes constant at 7.60 atm, and the container has 1.00 L of gas above 1.00 L of liquid.



Methanol Phase Diagram

a) Treating methanol as an ideal gas, calculate the number of moles of vapour in the container.

The system is at equilibrium so 7.60 atm is the vapour pressure of methanol, that is the system is at point 'X' on the phase diagram, with T ~ 400 K. Thus, the number of moles of vapour, using the ideal gas law, is

$$\mathbf{n = \frac{PV}{RT} = \frac{7.60\ atm \times 1.00\ L}{0.08206\ \frac{L\ atm}{K\ mol} \times 400\ K} = 0.2315\ mol}$$

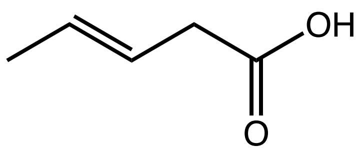
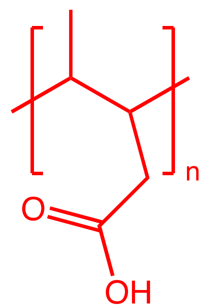
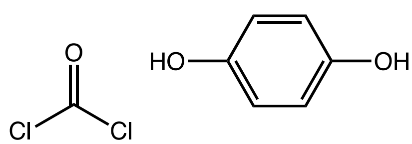
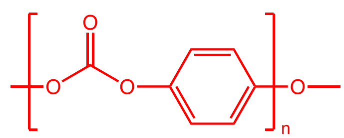
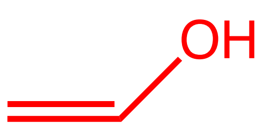
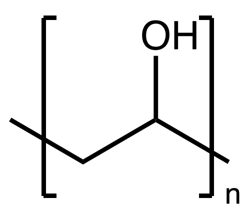
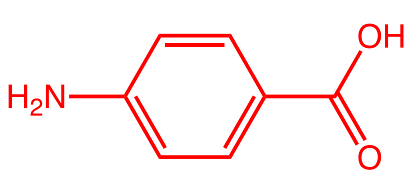
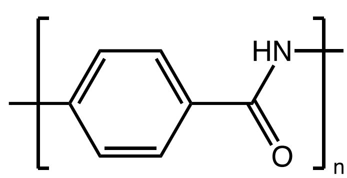
b) If part a) was repeated treating methanol as a real gas, would the expected number of moles of vapour be less than, equal to, or greater than the value calculated in part a)? Please give qualitative arguments to explain your answer. (Do not try to calculate this number.)

For a real gas, at these pressures, one expects PV/nRT < 1 due to the attractive interactions (dipole-dipole) among the gas particles (using the vdW parameters for methanol: a = 9.649 L^2 bar/mol^2 and b = 0.06702 L/mol gives PV/nRT ~ 0.95). Thus, for the same V, T and P, the number of moles of vapour should be greater than that predicted from the ideal gas equation to make the compressibility factor less than one. Put another way, you need more moles of vapour to bring the pressure up to the value expected for an ideal gas.

c) The temperature of the oven is slowly increased to 600 K. Describe what happens in the container, that is the number phases present, any pressure changes, etc.. If desired, please draw on the phase diagram to help explain your answer.

As T increases, more liquid will vapourize but because the system has a fixed volume (the container is rigid) and there is lots of liquid present, equilibrium should persist between the vapour and liquid. In other words, the system will follow the liquid-vapour coexistence curve, as shown by the red line with arrows on the phase diagram. During this time P will increase and the system will have a gas above a liquid. This will change once the critical point is reached at T ~ 520 K, after which one single phase will be present in the container (a supercritical fluid) as the temperature and pressure increase to their final values.

2. **[8 marks total]** Complete the table below by drawing the missing polymer or monomer(s), selecting the type of polymerization reaction, and indicating **all** intermolecular forces (IMF) governing the mechanical properties of the polymer.

Monomer(s)	**Polymer**	**Reaction? (fill in circle)**	**IMFs? (fill in circle(s))**
		Condensation Addition	London Dispersion Forces Dipole-dipole H-bonding
		Condensation Addition	London Dispersion Forces Dipole-dipole H-bonding
		Condensation Addition	London Dispersion Forces Dipole-dipole H-bonding
		Condensation Addition	London Dispersion Forces Dipole-dipole H-bonding

3. **[2 marks total]** Draw all the Lewis structures for NO_2 having zero formal charge on every atom and only one unpaired electron.

4. **[5 marks total]** All quantities are at 298 K. Combusting 1 mole of ethanol ($CH_3CH_2OH(l)$) to $CO_2(g)$ and $H_2O(g)$ releases 1235 kJ. Using this information, and the equations below, as well as knowing $\Delta H°(vap) = 44.00$ kJ mol^{-1} for liquid water, determine the enthalpy of formation of liquid ethanol, in kJ mol^{-1}. Please show your work, and write your final answer on the line indicated below.

$$C(graphite) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H° = -393.5 \text{ kJ}$$
$$H_2(g) + \tfrac{1}{2} O_2(g) \rightarrow H_2O(l) \qquad \Delta H° = -285.8 \text{ kJ}$$

We need to manipulate equations in such a way as to isolate the desired enthalpy of formation. One way to do this is by using the formation equation directly, that is

$$2\ C(graphite) + 2\ O_2(g) \rightarrow 2\ CO_2(g) \qquad \Delta H° = -787.0 \text{ kJ}$$
$$3\ H_2(g) + 3/2\ O_2(g) \rightarrow 3\ H_2O(l) \qquad \Delta H° = -857.4 \text{ kJ}$$
$$3\ H_2O(g) + 2\ CO_2(g) \rightarrow CH_3CH_2OH(l) + 3\ O_2(g) \qquad \Delta H° = +1235 \text{ kJ}$$
$$3\ H_2O(l) \rightarrow 3\ H_2O(g) \qquad \Delta H° = +132 \text{ kJ}$$
$$2\ C(graphite) + 3\ H_2(g) + \tfrac{1}{2} O_2(g) \rightarrow CH_3CH_2OH(l) \qquad \Delta H° = -277.4 \text{ kJ}$$

Alternatively, one could start with the combustion and vapourization reactions and solve for the desired heat of formation, knowing that with the supplied equations one has $\Delta H°_f(CO_2(g)) = -393.5$ kJ mol^{-1} and $\Delta H°_f(H_2O(l)) = -285.8$ kJ mol^{-1}, that is

$$CH_3CH_2OH(l) + 3\ O_2(g) \rightarrow 3\ H_2O(g) + 2\ CO_2(g) \qquad \Delta H°_1 = -1235 \text{ kJ} \quad \text{so that}$$

$$\Delta H°_1 = 3 \text{ mol} \times \Delta H°_f(H_2O(g)) + 2 \text{ mol} \times \Delta H°_f(CO_2(g)) - 1 \text{ mol} \times \Delta H°_f(CH_3CH_2OH(l))$$

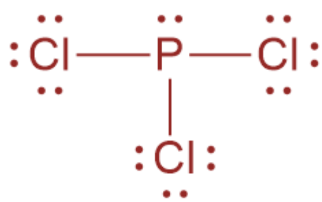
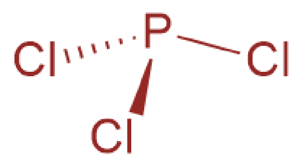
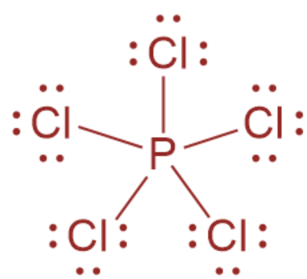
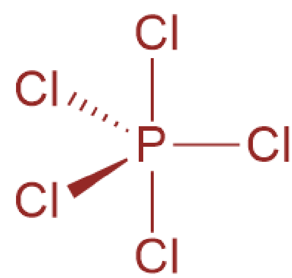
rearranging gives

$$\Delta H°_f(CH_3CH_2OH(l)) = 3\ \Delta H°_f(H_2O(g)) + 2\ (-393.5 \text{ kJ mol}^{-1}) - (-1235 \text{ kJ mol}^{-1})$$

But from $H_2O(l) \rightarrow H_2O(g)$, $44 \text{ kJ mol}^{-1} = \Delta H°_f(H_2O(g)) - \Delta H°_f(H_2O(l))$ **one gets** $\Delta H°_f(H_2O(g)) = 44 \text{ kJ mol}^{-1} + (-285.8 \text{ kJ mol}^{-1}) = -241.8 \text{ kJ mol}^{-1}$ **so that**

$$\Delta H°_f(CH_3CH_2OH(l)) = 3\ (-241.8 \text{ kJ mol}^{-1}) + 2\ (-393.5 \text{ kJ mol}^{-1}) - (-1235 \text{ kJ mol}^{-1}) = -277.4 \text{ kJ mol}^{-1}$$

5. **[7 marks total]** Complete the table by drawing for each molecule the best Lewis structure and a perspective diagram, as well as indicating whether it is polar. For the Lewis structure, show all bonds as lines and lone pairs as dots. Write the parent and molecular shapes for each molecule.

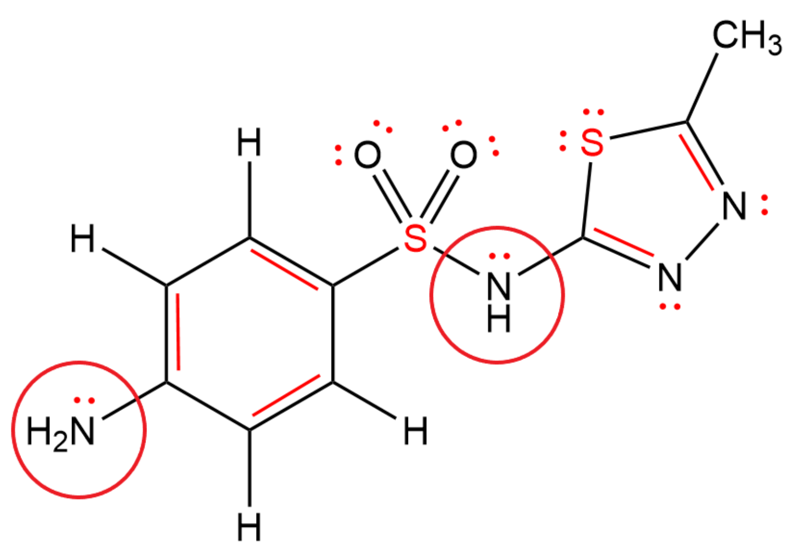
Molecule	Best Lewis Structure	Shape	Perspective Diagram	Polar? Yes/No
PCl_3		Parent: **tetrahedral** Molecular: **trigonal pyramid**		**Yes**
PCl_5		Parent: **trigonal bipyramid** Molecular: **trigonal bipyramid**		**No**

6. **[6 marks total]** The skeletal structure (showing atom connectivity) of an antibiotic is shown below. The formal charge on all atoms of the best Lewis structure is zero, and the boxes represent a missing element with an atomic number less than 20.

a) Produce the best Lewis structure by drawing multiple bonds or lone pairs, as necessary, on the skeletal structure diagram. Write the name of element in the boxes **(both boxes contain the same element)**.

b) Circle all the atoms with a trigonal pyramidal molecular shape

(Note: double bonds in 6-member ring could be other resonant form.)

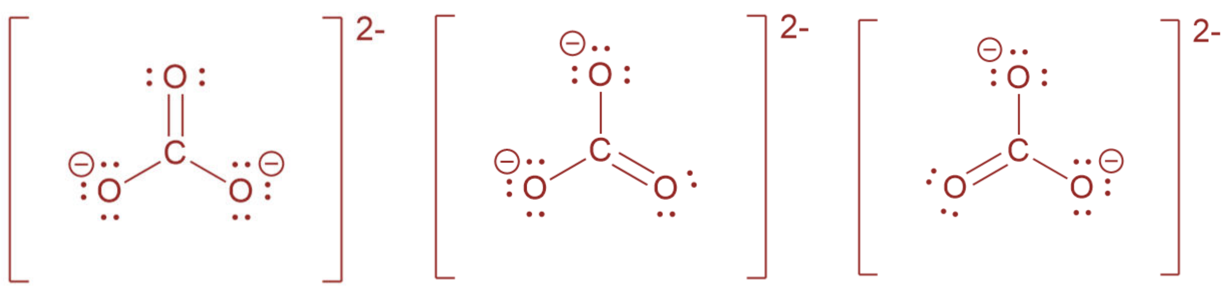


7. **[3 marks total]** Write two balanced equations showing the first and second ionization of helium. For each equation, indicate whether ΔH is positive, negative or zero.

$He(g) \rightarrow He^{+}(g) + e^{-}$ $\qquad$ **$\Delta H > 0$**

$He^{+}(g) \rightarrow He^{2+}(g) + e^{-}$ $\qquad$ **$\Delta H > 0$**

8. **[6 marks total]** Limestone is a sedimentary rock used extensively in building construction and is composed mostly of calcium carbonate ($CaCO_3$). Draw all valid Lewis structures contributing to the resonance hybrid of the carbonate anion (CO_3^{2-}). Show all bonds as lines and lone pairs as dots; indicate formal charges and overall charges where applicable.



Estimate the bond order of the C—O bond in CO_3^{2-} (please show your work).

The three resonance structures are all equivalent, so will weigh equally when estimating the bond order. As well, each C—O bond is identical. Averaging the bond orders across the three structures gives

Bond order = (2 + 1 + 1)/3 = 4/3