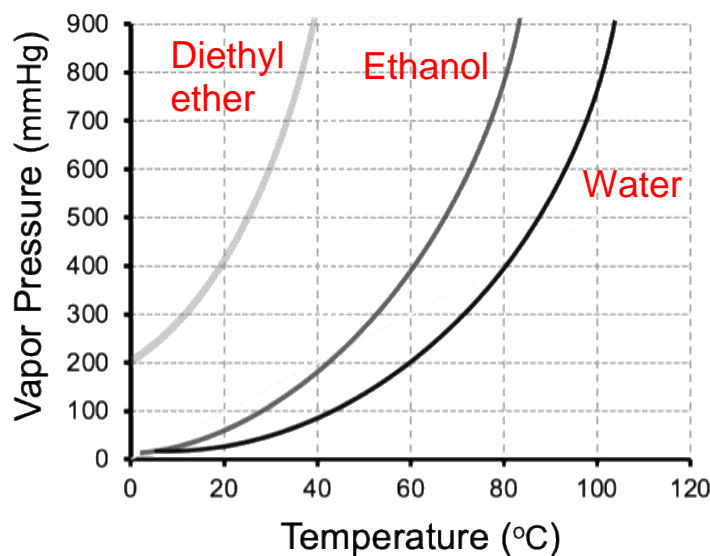
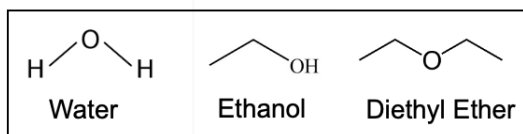


2023 CHEM 154 Midterm Examination Solutions

1. [4 marks total] The graph to the right shows plots of the vapour pressure for water, ethanol, and diethyl ether.



- a) Label each plot with the corresponding molecule and in the space below, write the reasons for your assignments.

Diethyl ether has the highest vapour pressure due to the weakest intermolecular forces among the three molecules (dipole-dipole and dispersion), allowing molecules to escape from the liquid phase more readily. Ethanol, with its polar character due to its hydroxyl (OH) group, exhibits dipole-dipole interactions in addition to dispersion forces and H-bonding resulting in a lower vapour pressure than diethyl ether. Water, with a strong dipole and hydrogen bonding (with two hydrogen atoms that can form hydrogen bonds, making it capable of forming multiple hydrogen bonds simultaneously), has the lowest vapour pressure, as the hydrogen bonds significantly hinder the escape of water molecules into the gas phase at room temperature.

- b) Estimate the boiling point of water, in °C, when the external pressure is 40 kPa. 68-72°C

Note: 40 kPa = 300 mmHg

- c) A beaker of diethyl ether, a beaker of water and two beakers of ethanol are placed inside an initially evacuated container, and heated to 40 °C. After some time, it is observed that all the beakers have liquids and the total pressure inside the container is constant. Calculate the resulting mole fraction of ethanol in the gas phase.

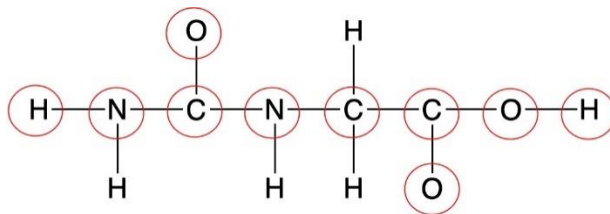
After some time we expect equilibria to exist between each liquid and its vapour, so each species should be at its vapour pressure at 40 °C, and the total pressure should be the sum of these.

Assuming ideal gases then gives (estimating each vapour pressure from the graph)

$$\text{Molar fraction (ethanol)} = \frac{P_{\text{ethanol}}}{P_{\text{diethyl ether}} + P_{\text{water}} + P_{\text{ethanol}}} = \frac{185 \text{ mmHg}}{(900 + 90 + 185) \text{ mmHg}} = 0.16$$

2. [1 mark total] The skeletal structure to the right shows the atom connectivity of a neutral molecule. Multiple bonds and lone pair electrons are not shown. Circle all the atoms that could simultaneously lie in the same plane.

The other H atom on the terminal N could also have been selected instead.



3. [5 marks total] A perspective diagram of penicillin is shown to the right.

- a) In the boxes, write the molecular shape at the indicated atoms.
- b) Enter below the ideal values of the labelled bond angles, in degrees.

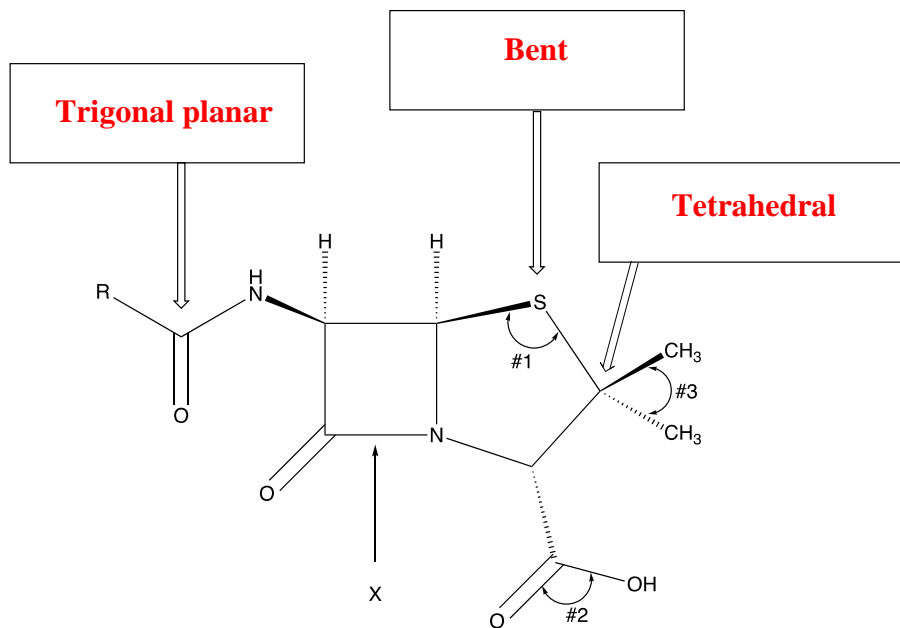
#1 109.5 #2 120

#3 109.5

- c) Write the electron configuration (using noble gas notation) for a neutral sulphur atom. **[Ne] 3s² 3p⁴**

- d) Estimate the bond order of the bond indicated by X (please show your work).

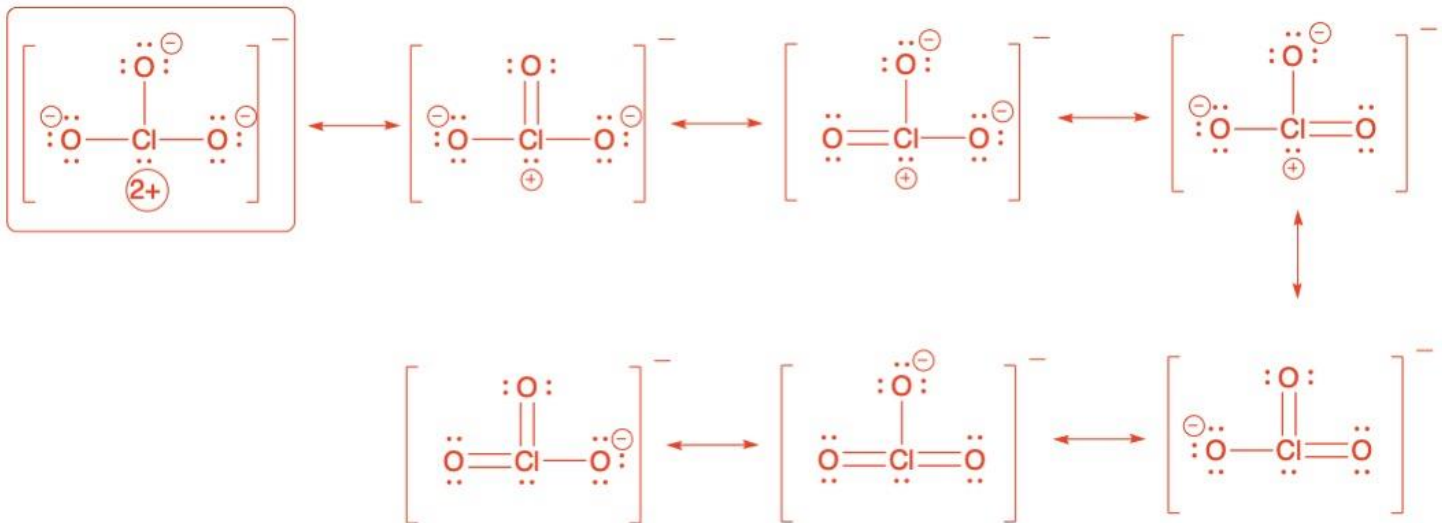
There are two possible resonance contributors: one with no formal charges (as shown), and one with formal charges (with the C double bonded to N and single bonded to O). If the resonances contributed equally, the calculated bond order would be $(1+2)/2 = 1.5$. However, the one with no formal charges is more stable so will contribute more towards the resonance hybrid. Therefore, the actual bond order for the bond indicated by X would be in the range of 1 – 1.5.



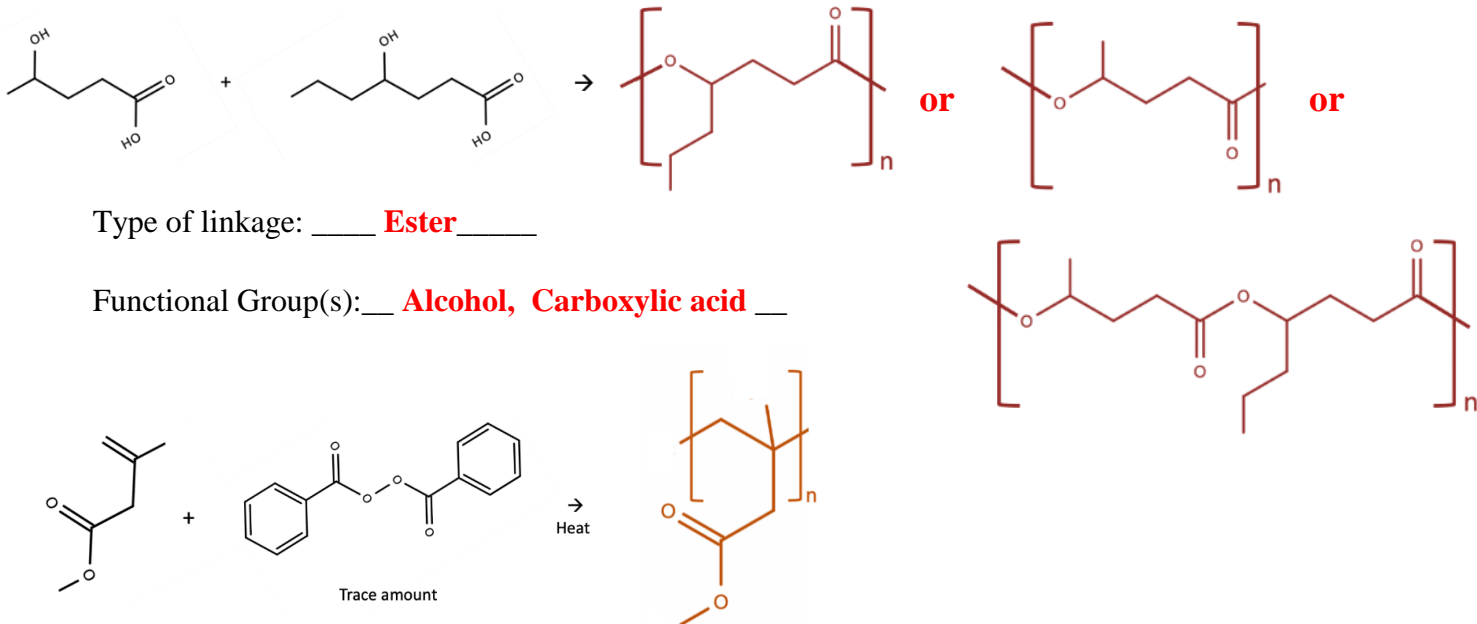
4. [4 marks total] Complete the table below for each molecule by drawing the best Lewis structure and the corresponding perspective diagram, as well as by writing the names of the parent and molecular shapes.

Molecule	Best Lewis structure	Shape	Perspective diagram
SOF₂		Parent: Tetrahedral Molecular: Trigonal pyramidal	
SCl₄		Parent: Trigonal bipyramidal Molecular: Seesaw	

5. [3 marks total] Draw all chemically reasonable Lewis structures for ClO_3^- and circle the one(s) that contribute the **least** to the resonance hybrid. Show all lone pairs as dots and indicate formal and overall charges where applicable.

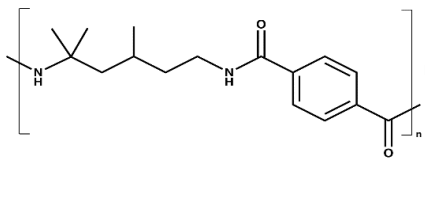
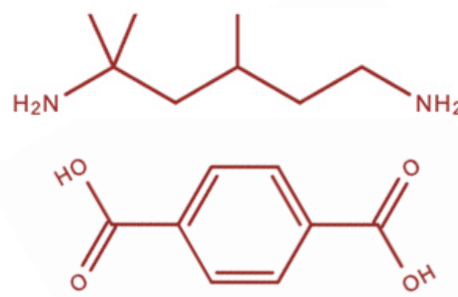
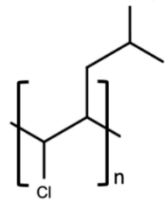
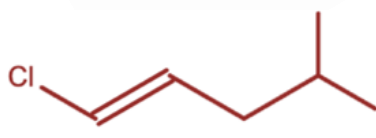


6. [10 marks total] Use line-bond drawings to represent chemical structures when answering this question.
- a) For each reaction shown, i) draw the polymer product(s) (if more than one product is possible, draw 2 possible ones), ii) write the type of linkage, and iii) write the names of all the functional groups in the monomer(s).



- b) In the table, draw the structure of the smallest possible monomer(s) corresponding to each polymer.
- c) Calculate the average degree of polymerization for a sample of Polymer B with average molecular weight $296,000 \text{ g mol}^{-1}$.

The molecular mass of a repeat unit is $118.607 \text{ g mol}^{-1}$ (1 Cl, 11 H, 6 C)
The average degree of polymerization is then
 $296,000 \text{ g mol}^{-1} / 118.607 \text{ g mol}^{-1} = 2496 \sim 2500$

Polymer	Monomer(s)
A 	
B 	

- d) Explain which of the two polymers, A or B, is more flexible.

Polymer B is more flexible than A because it has weaker intermolecular forces (IMF). Polymer A has NH and CO bonds, enabling hydrogen bonding and dipole-dipole interactions. Additionally, its benzene rings, with their planar structures and pi-pi stacking, can restrict flexibility. On the other hand, Polymer B relies primarily on dipole interactions through its Cl substituent and London dispersion forces (LDF), weaker IMFs that result in greater flexibility.

7. [13 marks total] In its standard state allotrope at 80.0°C , elemental phosphorus molecules, $\text{P}_4(\text{l})$, have 4 atoms located at the corners of a tetrahedron (each P is singly bonded to the three others). This liquid was reacted with chlorine gas to produce gaseous PCl_3 in a container with flexible walls, under a constant external pressure of 1.00 bar. Oil circulating through the system kept the temperature constant at 80.0°C . After the reaction, the measured work was 220 J and the heat from the reaction increased the temperature of 2.50 kg of oil by 11.5°C . ($C_{p,\text{oil}} = 1.67 \text{ J/(g K)}$)

- a) Calculate the mass of chlorine gas, in g, that reacted.

The overall reaction is: $\frac{1}{4} \text{P}_4(\text{l}) + \frac{3}{2} \text{Cl}_2(\text{g}) \rightarrow \text{PCl}_3(\text{g})$

Let n be the number of moles of chlorine gas that reacted, thus producing $2n/3$ moles of PCl_3 . The process is isothermal at temperature $80.0^\circ\text{C} = 353.15 \text{ K}$, and isobaric at pressure 1.00 bar, thus

$$\Delta V = V_2 - V_1 = n_2 \frac{RT}{P} - n_1 \frac{RT}{P} = \frac{RT}{P} \left(\frac{2}{3}n - n \right) = -\frac{nRT}{3P}$$

Equating this to work using $w = -P\Delta V$ and solving for n then gives

$$n = \frac{3w}{RT} = \frac{3 \times 220 \text{ J}}{8.314 \text{ J/(K mol)} \times 353.15 \text{ K}} = 0.2248 \text{ mol}$$

which gives the mass of chlorine gas reacted as $0.2248 \text{ mol} \times 70.906 \text{ g/mol} = 15.9 \text{ g}$

b) Calculate ΔU , in kJ, for the reaction.

Calculate the heat transferred to the oil and use this in the First Law to get the change in internal energy, that is (note that heat gained by the oil is lost by the system so q should be negative)

$$q_p = -mc_p\Delta T = -2500\text{g} \times 1.67 \frac{\text{J}}{\text{gK}} \times 11.5\text{K} = -48.0125\text{kJ}$$

$$\Delta U = q + w = -48.0125\text{kJ} + 0.220\text{kJ} = -47.79\text{kJ}$$

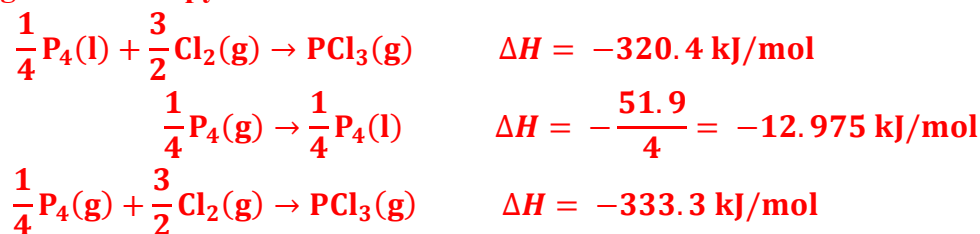
c) Calculate the standard enthalpy of formation for $\text{PCl}_3(\text{g})$ at 80°C , in kJ/mol.

The reaction in a) is precisely the formation reaction for $\text{PCl}_3(\text{g})$ at 80°C , and at constant pressure the heat is just the value of ΔH , for that reaction. From part a) we know that the number of moles of $\text{PCl}_3(\text{g})$ produced is $2/3 \times 0.2248 = 0.1499\text{ mol}$. The enthalpy of formation is for the production of 1 mol of product, therefore

$$\Delta H_f^\circ(\text{PCl}_3) = \frac{-48.0125\text{kJ}}{0.1499\text{mol}} = -320.4\text{kJ/mol}$$

d) Calculate the enthalpy, in kJ, for producing 1 mol of $\text{PCl}_3(\text{g})$ from chlorine gas and gaseous $\text{P}_4(\text{g})$, given $\Delta H^\circ_{\text{vap}}(\text{P}_4(\text{l})) = 51.9\text{kJ/mol}$.

Use Hess's Law to get the enthalpy for the desired reaction



e) Use the result from d) to calculate the P—P bond enthalpy in $\text{P}_4(\text{g})$, in kJ/mol, given the bond enthalpy for P—Cl is 326 kJ/mol.

Use the equation from part d) to estimate the enthalpy change using bond energies. Also, $\text{P}_4(\text{g})$, has 6 P—P bonds (each of the atoms is bonded to 3 others). Putting all this together gives

$$\Delta H = \frac{3}{2}E(\text{Cl}-\text{Cl}) + \frac{1}{4} \times 6E(\text{P}-\text{P}) - 3E(\text{P}-\text{Cl})$$

Solving for $E(\text{P}-\text{P})$ then gives

$$\begin{aligned} E(\text{P}-\text{P}) &= \frac{2}{3} \left(\Delta H - \frac{3}{2}E(\text{Cl}-\text{Cl}) + 3E(\text{P}-\text{Cl}) \right) \\ &= \frac{2}{3} \left(-333.3 \frac{\text{kJ}}{\text{mol}} - \frac{3}{2} \times 239 \frac{\text{kJ}}{\text{mol}} + 3 \times 326 \frac{\text{kJ}}{\text{mol}} \right) = 190.8\text{kJ/mol} \end{aligned}$$