Spring 2023 **Chemistry 2000 Midterm #1** ____/45 marks

Confidentiality Agreement:
I agree not to discuss (or in any other way divulge) the contents of this exam with (or in the presence of) any CHEM 2000 student who has yet to write it. I understand that breaking this agreement would constitute academic misconduct. The minimum penalty would be a mark of 0/45 on this exam.

Signature: _____ Date: _____

1) Please read the test carefully before starting. It has 6 pages of questions (3 pages double-sided).
2) You have also been given a data sheet. It does not have a QR code, so nothing written on it will be graded.
3) **DO NOT WRITE ON ANY QR CODE!!!** Work on pages without a QR code will not be graded.
4) Neither calculators nor any other electronic devices may be used while writing this test.
5) If your work is not legible, it will be given a mark of zero.
6) Show your work. Answers without supporting reasoning or calculations will not get full credit
7) Marks will be deducted for incorrect information added to an otherwise correct answer.
8) You have 90 minutes to complete this test.

Question Breakdown

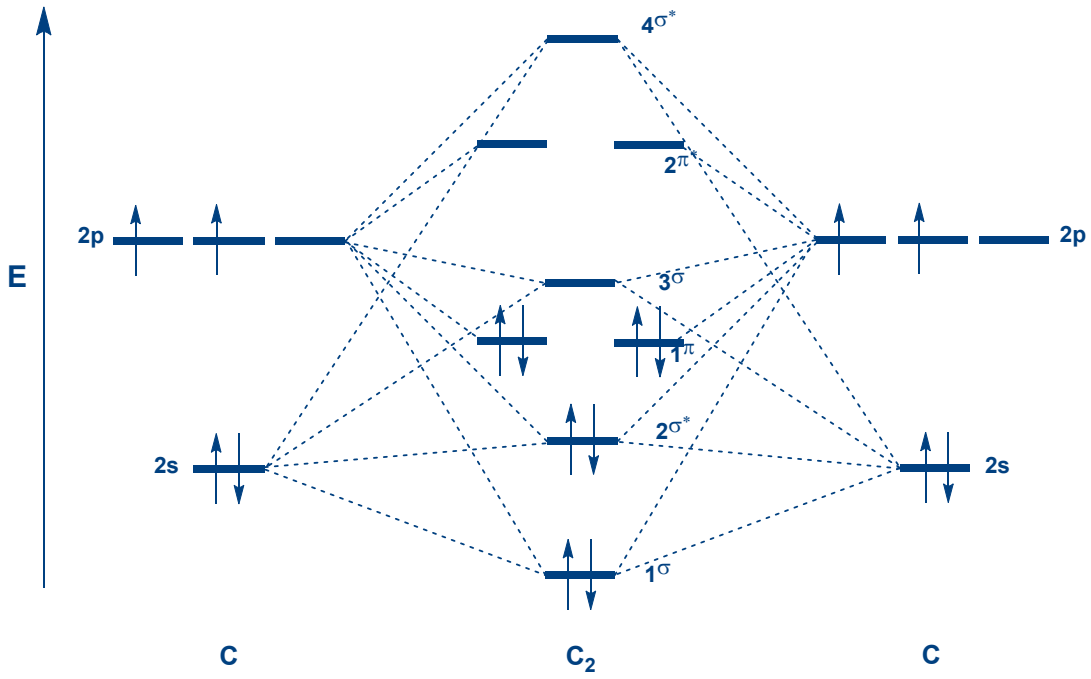
Q1	**Q2**	**Q3**	**Q4**	**Q5**									**Total**
/ 11	/ 17	/ 7	/ 5	/ 5									/ 45

1. **[11 marks]**

(a) Draw the valence molecular orbital energy level diagram (MO diagram) for C_2. *[7 marks]*

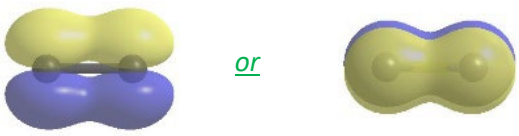
Your diagram must include:

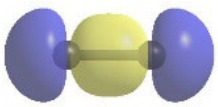
- labeled molecular orbital energy levels (you don't need to draw pictures of the MOs)
- identification of each molecular orbital as bonding, nonbonding or antibonding
- electrons in the appropriate molecular orbitals



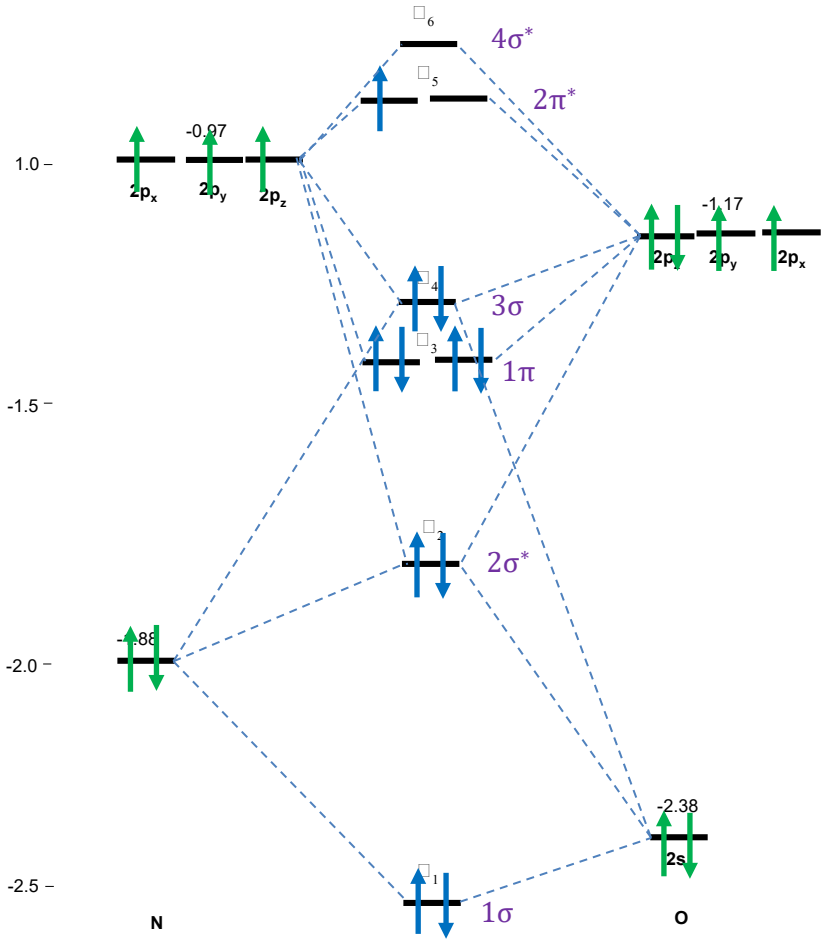
(b) Identify the HOMO and LUMO of C_2. Draw a picture showing each. If there are two degenerate MOs for either answer, you only need to draw a picture of one of them. *[4 marks]*

HOMO: 1π LUMO: 3σ





2. The partial molecular orbital energy level diagram (MO diagram) below is for NO. Each molecular orbital energy level has been labeled with a numbered Ψ so that specific energy levels can be referenced. **[17 marks]**



(a) Complete this diagram by: *[8 marks]*

- adding the appropriate number of electrons to the molecular orbitals,
- adding tie lines to show which atomic orbitals combine to make each molecular orbital,
- labeling each molecular orbital using notation that shows its symmetry and whether it is bonding, antibonding or nonbonding (i.e. 1π, $2\sigma^*$, etc.), and

(b) Write the electron configuration (or "orbital occupancy") for a neutral molecule of NO. *[1 mark]*

$(1\sigma)^2(2\sigma^*)^2(1\pi)^4(3\sigma)^2(2\pi^*)^1$

(c) Calculate the bond order for a neutral molecule of NO. *[1 mark]*

$$bond\ order = \frac{\#\ bonding\ e^- - \#\ antibonding\ e^-}{2} = \frac{8-3}{2} = \frac{5}{2} = 2\frac{1}{2}$$

continued on next page…

2. *…continued*

(d) Based on what you see in your completed MO diagram, explain why NO is very reactive. *[1 mark]*

NO is very reactive because it has an unpaired electron in $2\pi^*$.

(e) Consider how the vibrational line spacing will change when NO is ionized to NO^+. Do you expect ionization to make the N-O bond more rigid, less rigid or not particularly affect rigidity? What is the consequence for the spacing between the vibrational energy levels? How would that affect the spacing of the lines on a photoelectron spectrum? *[6 marks]*

Imagine three different scenarios:

i. How will the vibrational line spacing change if the electron is removed from Ψ_1?

Ψ_1 is a bonding MO so removing an electron from it will decrease the bond order and therefore decrease the rigidity of the bond. This will decrease the spacing between the vibrational levels leading to closely spaced lines on the photoelectron spectrum.

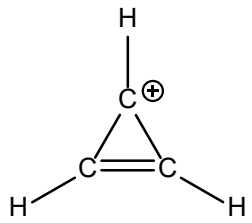
ii. How will the vibrational line spacing change if the electron is removed from Ψ_3?

Ψ_3 is a bonding MO so removing an electron from it will decrease the bond order and therefore decrease the rigidity of the bond. This will decrease the spacing between the vibrational levels leading to closely spaced lines on the photoelectron spectrum.

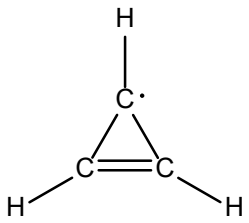
iii. How will the vibrational line spacing change if the electron is removed from Ψ_5?

Ψ_5 is an antibonding MO so removing an electron from it will increase the bond order and therefore increase the rigidity of the bond. This will increase the spacing between the vibrational levels leading to widely spaced lines on the photoelectron spectrum.

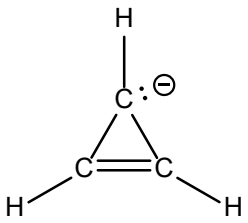
3. Consider the following three species: **[7 marks]**



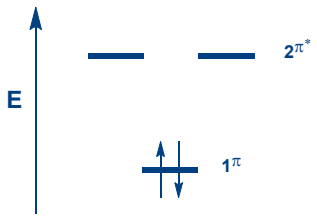
$C_3H_3^+$

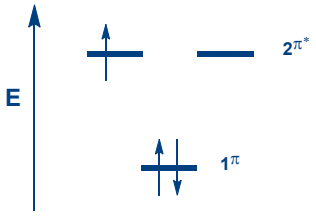


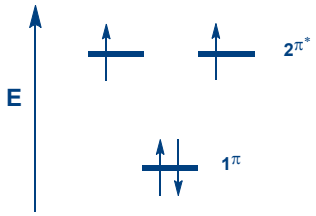
C_3H_3



$C_3H_3^-$







(a) In the space underneath each species, draw its pi MO diagram. Each diagram should include energy levels (labeled using the convention taught in this class that clearly indicates whether MOs are bonding, antibonding or nonbonding) and the appropriate number of electrons. You do NOT need to draw pictures of the MOs. *[5 marks]*

see pi MO diagrams drawn below Lewis diagrams

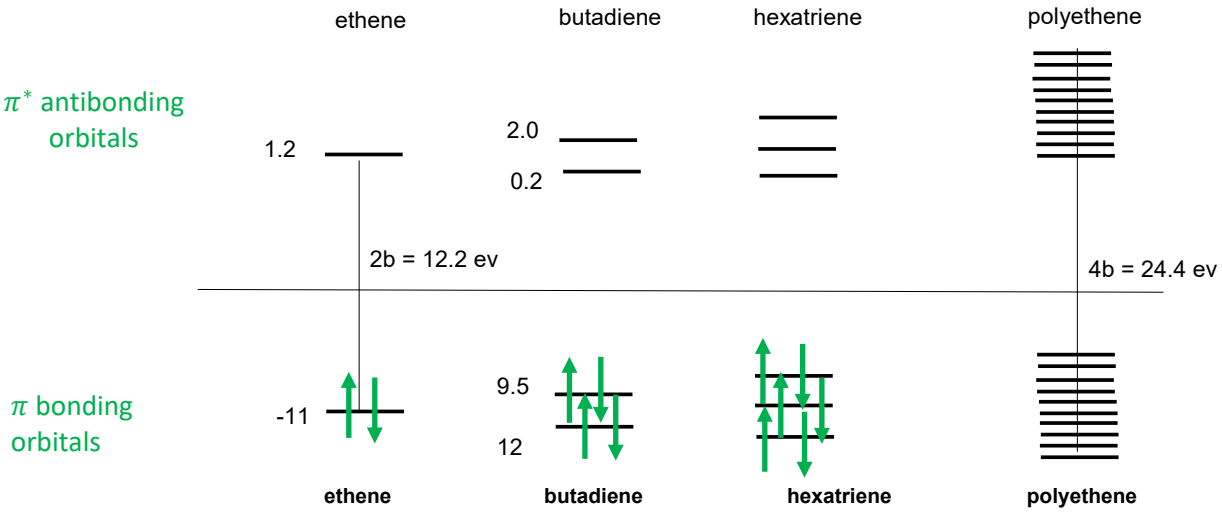
See Exercise 4.6 for a detailed explanation of how these diagrams are drawn. For a cyclic pi system that is symmetric, you draw the polygon point-down inside a circle ("Frost circle") to predict the energy levels.

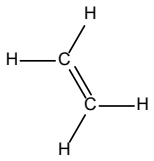
(b) With reference to the three MO diagrams, explain why the cation is favoured over both the anion and the neutral species. *[2 marks]*

To form the cation from the neutral species, you remove an antibonding electron – which is a high energy electron and therefore easily removed. To form the anion from the neutral species, you add an antibonding electron – which will be a high energy electron and this is therefore not favourable.

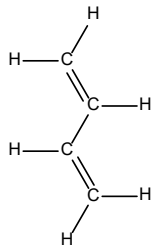
4. The diagrams below show pi MO diagrams for increasingly long pi systems: **[5 marks]**

At 20 °C, $1\ eV \approx 40\ k_B T$.

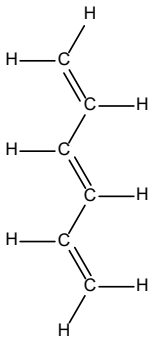




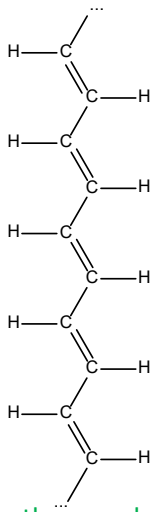
two $\pi\ e^-$



four $\pi\ e^-$



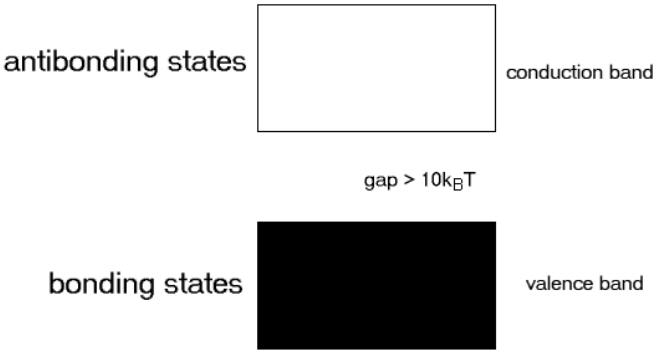
six $\pi\ e^-$



exactly enough $\pi\ e^-$ to fill the lower band

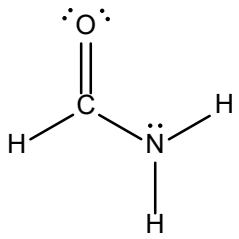
Based on this information, draw a labeled band diagram for polyethene and, with reference to that diagram, explain whether you expect polyethene to be a conductor, an insulator or a semiconductor.

Polyethene is an insulator. The valence band is completely full while the conduction band is completely empty, so conduction requires excitation of an electron in the valence band into the conduction band. Based on the energies in the diagram provided, the band gap appears to be approximately 10 eV – which is equivalent to approximately 400 $k_B T$ and far too large for polyethene to be a conductor or semiconductor.

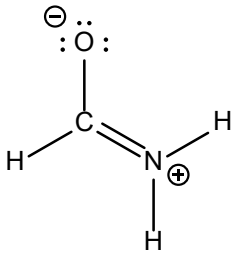


5. Consider Lewis diagrams **A** and **B**. **[5+2 marks]**

For each of parts (a) to (d), look only at the diagram referred to by that part of the question.



A



B

(a) According to valence bond theory, what is the hybridization of the carbon atom in diagram **A**?

sp^2

(b) According to valence bond theory, what is the hybridization of the nitrogen atom in diagram **A**?

sp^3

(c) According to valence bond theory, what is the hybridization of the carbon atom in diagram **B**?

sp^2

(d) According to valence bond theory, what is the hybridization of the nitrogen atom in diagram **B**?

sp^2

(e) What is the relationship between diagrams **A** and **B**?

In other words, complete the statement "**A** and **B** are resonance structures."

BONUS *(2 marks)*

In light of your answers to parts (a) to (e) of this question, comment on why valence bond theory may not be the best approach to describing the bonding in this case.

Resonance structures are just different ways to draw the same molecule. It doesn't make sense for the nitrogen atom to have different hybridizations in different resonance structures. If hybridization were real, the nitrogen atom could only be hybridized in one way – not in two different ways at the same time.