Spring 2023 **Chemistry 2000 Final Exam** ____/108 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 0/108 on this exam.

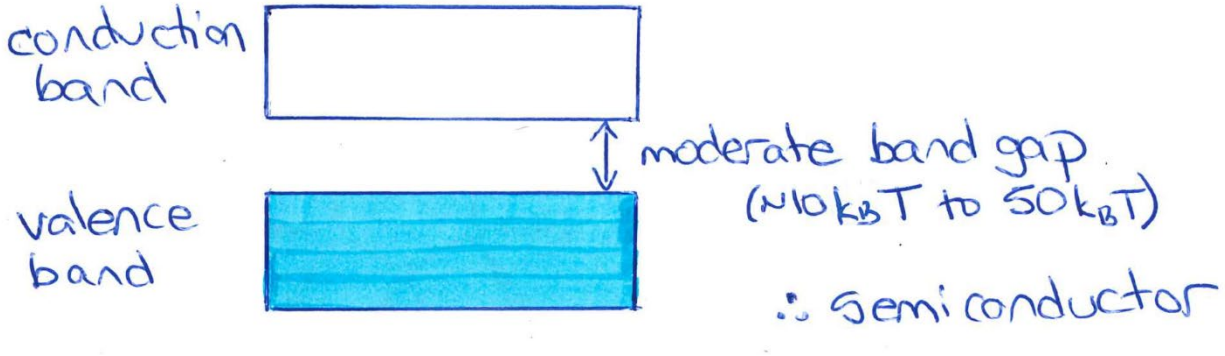
Signature: _____ Date: _____

1) Please read the test carefully before starting. It has 12 pages of questions (six 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) You may use a calculator but only for calculation. No other electronic devices are allowed. Any non-trivial use of a calculator must be described. For example, if you use a calculator to solve a nonlinear equation, you need to make it clear what equation was solved and provide any other inputs you used to the calculation.
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) Marks will be deducted for improper use of significant figures and for missing or incorrect units. Show units in every step of all calculations. Significant figures will only be checked in final answers. If a question has subparts (a, b, c, etc.), the answer to each subpart is considered a "final answer".
9) You have 3 hours to complete this test.

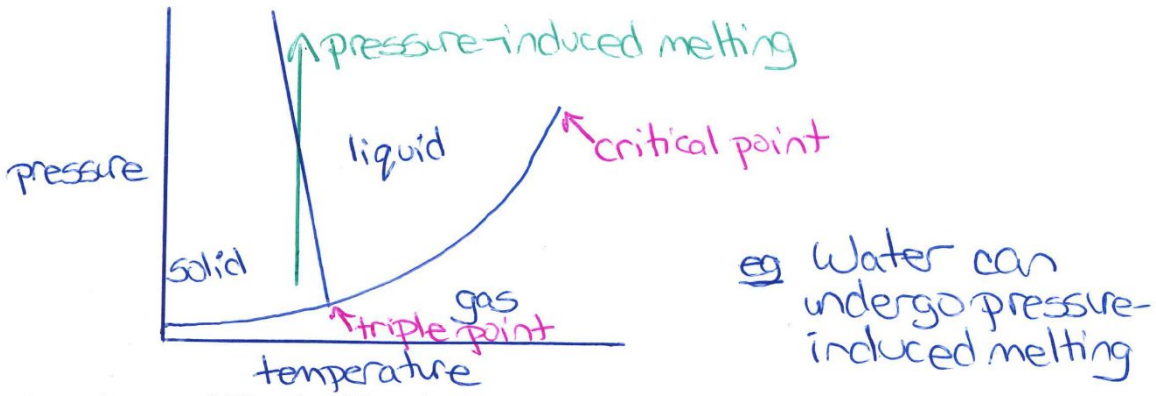
Question Breakdown

Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12	Q13	Q14	Q15			Total
/ 4	/ 4	/ 3	/ 5	/ 2	/ 2	/ 5	/ 4	/ 2	/ 18	/ 11	/ 8	/ 15	/ 24	/ 1			/ 108

1. Draw and label a band diagram for germanium (Ge). Identify whether Ge is a conductor, a semiconductor or an insulator, and explain how this is shown by your diagram. **[4 marks]**



2. Sketch and label a phase diagram for a substance that can undergo pressure-induced melting. Clearly show this phase change on your diagram, and give an example of one substance that can undergo pressure-induced melting. **[4 marks]**



3. Compare solid H_2 and solid HD at the same temperature. Which of the two substances will have a higher entropy? Justify your answer using any relevant equations. **[3 marks]**

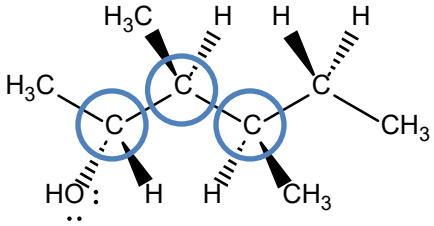
HD has higher entropy.

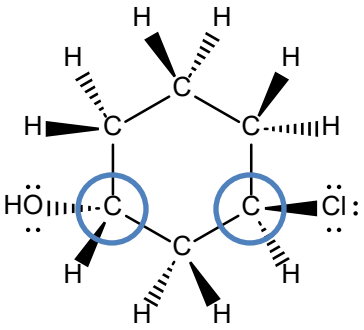
Each molecule of HD can be oriented either $H-D$ or $D-H$; however, all molecules of H_2 will be oriented $H-H$. As such, HD has more possible microstates.

Since entropy increases as the number of microstates increase ($S = k_B ln\Omega$ where Ω is number of microstates), the substance with more microstates has higher entropy.

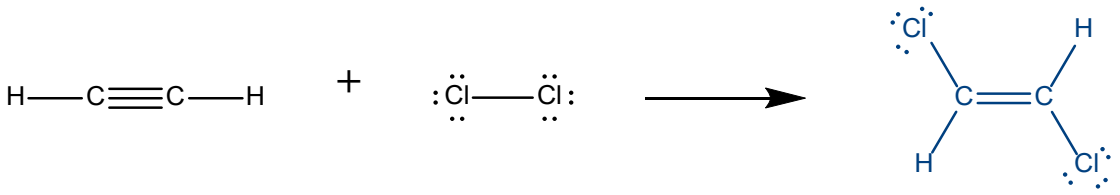
4. Circle all the chiral carbon atoms in each of the substances drawn below. **[5 marks]**

Marks will be deducted for incorrectly circled atoms.

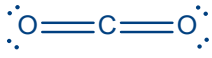




5. Draw the product of the reaction below. Pay attention to stereochemistry. **[2 marks]**



6. Draw a Lewis diagram for carbon dioxide (CO_2). What is the hybridization of the carbon atom in CO_2? **[2 marks]**



C is sp-hybridized

7. What happens to the freezing point of water when you dissolve an equimolar amount of a nonvolatile solute in it? In other words, when you add 1 mole of solute for every 1 mole of water. **[5 marks]**

Your answer should include any relevant equations; however, you are not being asked to calculate the new freezing point – just to indicate whether it's higher, lower or the same as the freezing point of pure water and explain why that is the case.

Adding a nonvolatile solute lowers the freezing point of water. This is because it lowers the activity of the liquid water which raises the equilibrium constant for the freezing process:

$$H_2O_{(l)} \rightleftharpoons H_2O_{(s)} \qquad K = \frac{a_{H_2O_{(s)}}}{a_{H_2O_{(l)}}} \text{ where } a_{H_2O_{(s)}} = 1 \text{ and } a_{H_2O_{(l)}} = X_{H_2O}$$

For pure water, $a_{H_2O_{(l)}} = 1$ and therefore $K_1 = 1$. The freezing point is $T_1 = 0\ ℃ = 273.15\ K$

For an equimolar solution, $a_{H_2O_{(l)}} = \frac{1}{1+1} = \frac{1}{2}$ and therefore $K_2 = \frac{1}{\left(\frac{1}{2}\right)} = 2$

Solve for T_2 using $ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

8. For the electrochemical cell described below, identify which species is the cathode, which species is the anode and write a balanced half-reaction for each half-cell. **[4 marks]**

$$Ag(s) \mid Ag^+(aq) \parallel H^+(aq) \mid H_2(g) \mid Pt(s)$$

The cathode is made of _____Pt_____. The anode is made of _____ Ag_____.

The oxidation half-reaction is:

$$Ag(s) \rightarrow Ag^+(aq) + e^-$$

The reduction half-reaction is:

$$2\ H^+(aq) + 2\ e^- \rightarrow H_2(g)$$

9. O_2 is ionized in a UV-photoelectron spectroscopy experiment. Use your knowledge of molecular orbital labeling conventions to answer the following questions. **[2 marks]**

(a) Signals are observed for ionization from various molecular orbitals including 1σ, 1π and $2\pi^*$. Which of the three listed MOs will require the highest energy light for one of its electrons to be ionized?

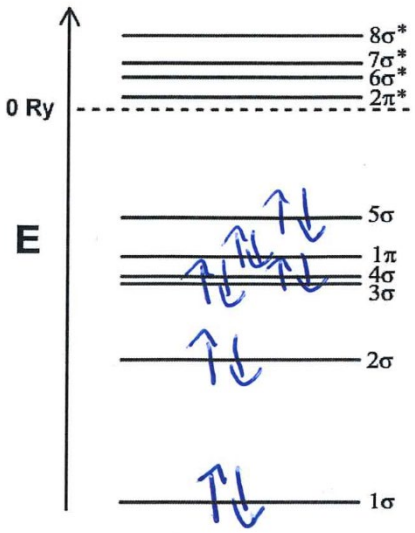
1σ

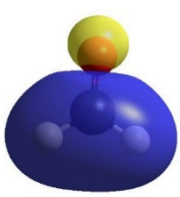
(b) Signals are observed for ionization from various molecular orbitals including 1σ, 1π and $2\pi^*$. Which of the three listed MOs will give a signal with the widest spacing between its lines?

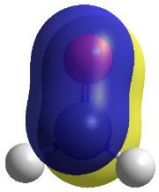
$2\pi^*$

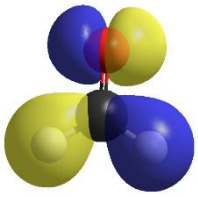
10. The valence molecular orbital energy level diagram for formaldehyde $(H_2C = O)$ is shown below. Drawings of some MOs have also been provided (each labeled with a letter for easy reference). **[18 marks]**

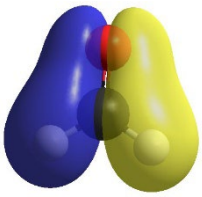
In all MO drawings, oxygen is at the top and carbon is at the bottom (with two hydrogen atoms attached).

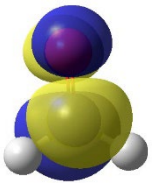


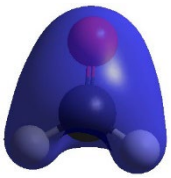

A

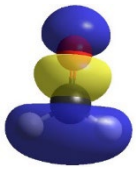

B


C


D


E


F

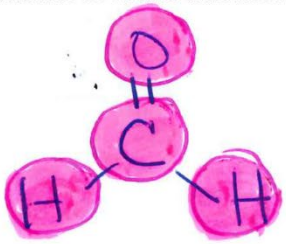

G

(a) Complete the energy level diagram by adding the appropriate number of valence electrons. *[1 mark]*

see above

(b) Identify which of the MO drawings corresponds to the 1σ orbital. Explain your choice and indicate which atomic orbitals combine to make this molecular orbital. *[2 marks]*

F



$2s(O) + 2s(C) + 1s(H) + 1s(H)$

all combine in phase (constructively)

(c) Identify which of the MO drawings corresponds to the 1π orbital. Explain your choice and indicate which atomic orbitals combine to make this molecular orbital. *[2 marks]*

B



$2p_z(O) + 2p_z(C)$

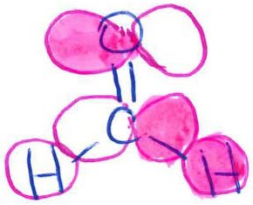
combine in phase (constructively)

continued on next page…

10. *...continued*

(d) Drawing **C** corresponds to the HOMO of formaldehyde. Identify which MO that is and indicate which atomic orbitals combine to make this molecular orbital. *[2 marks]*

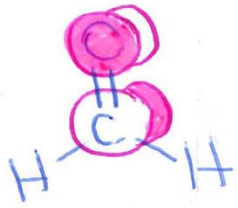
5σ



$2p_x(O) + 2p_x(C)$ combine out-of-phase (destructively); $1s(H) + 1s(H)$ combine constructively with $2p_x(C)$

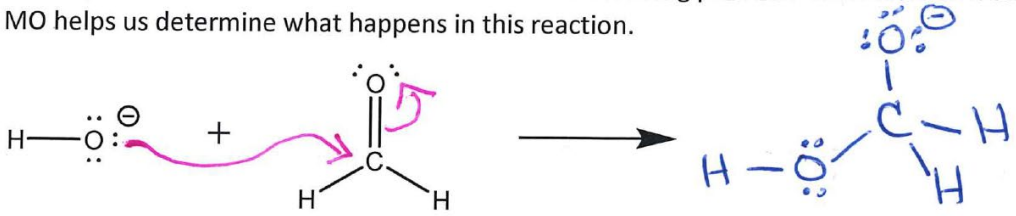
(e) Drawing **E** corresponds to the LUMO of formaldehyde. Identify which MO that is and indicate which atomic orbitals combine to make this molecular orbital. *[2 marks]*

$2\pi^*$



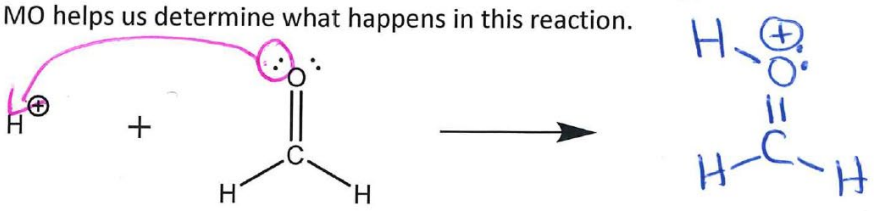
$2p_z(O) + 2p_z(C)$ combine out-of-phase (destructively)

(f) When formaldehyde acts as an electrophile, which MO accepts the electrons? Which atom is attacked? Does adding electrons to this MO make the bond order of an existing bond increase or decrease? Add curved arrows to the reaction below and draw the resulting product. Then comment on how the relevant MO helps us determine what happens in this reaction. *[5 marks]*



LUMO ($2\pi^*$) accepts electrons. It's polarized toward C so attack is at C. It's antibonding so C-O bond order decreases

(g) When formaldehyde acts as a nucleophile, which MO donates the electrons? Which atom attacks? Add curved arrows to the reaction below and draw the resulting product. Then comment on how the relevant MO helps us determine what happens in this reaction. *[4 marks]*

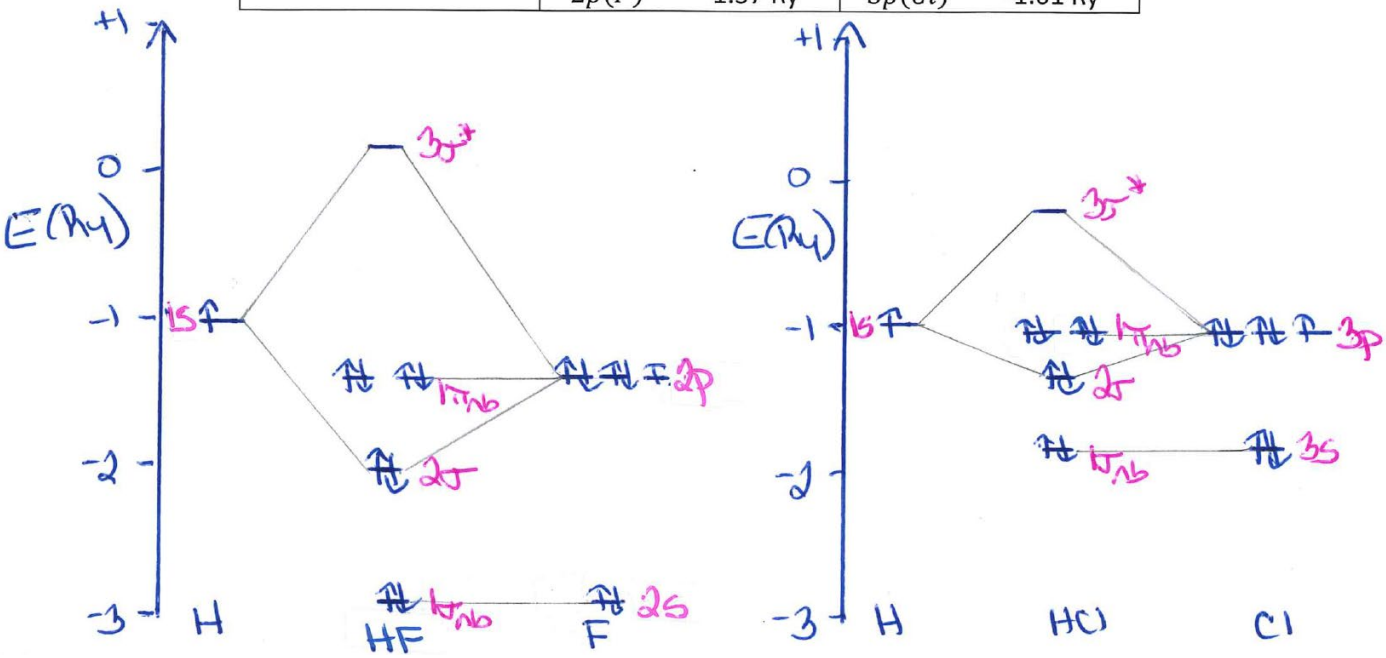


HOMO (5σ) donates electrons. It's polarized toward O (looks like lone pair on O) so O attacks H^+

11. Compare the molecular orbital energy level diagrams (MO diagrams) for HF and HCl. **[11 marks]**

(a) Draw MO diagrams for HF and HCl side by side on the same scale. Your diagrams should include labeled energy levels (clearly indicating whether each MO is bonding, nonbonding or antibonding) and the appropriate number of electrons, but you do not need to include drawings of the orbitals. *[6 marks]*
For simplicity, DO NOT invoke sp-mixing when building the MO diagram for HCl.

Atomic Orbital Energies					
$1s(H)$	-1.00 Ry	$2s(F)$	-2.95 Ry	$3s(Cl)$	-1.86 Ry
		$2p(F)$	-1.37 Ry	$3p(Cl)$	-1.01 Ry



(b) Calculate the bond order for HF and for HCl. Even though these bonds have the same bond order, it requires more energy to break the $H-F$ bond. With reference to the MO diagrams, explain why this is the case. *[2 marks]*

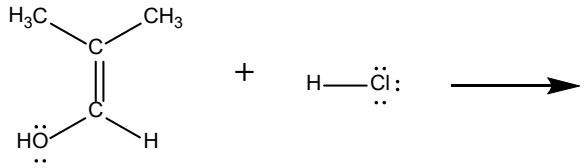
$bond\ order = \frac{2-0}{2} = 1$ for both compounds

The $H-F$ bond requires more energy to break because the difference in energy between the electrons in MOs vs. the electrons in AOs is greater for HF.

(c) When a base reacts with HF, it attacks the hydrogen atom not the fluorine atom. With reference to the MO diagram, explain why that is the case. *[3 marks]*

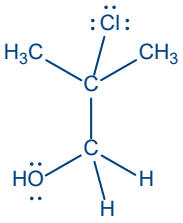
When a base reacts with HF, it donates electrons into the LUMO $(3\sigma^*)$. Because this orbital is closer in energy to $1s(H)$ than to $2p(F)$, it is polarized toward H, so attack is at H.

12. Consider the following addition reaction: **[8 marks]**

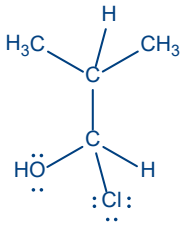


(a) Draw the two possible organic products of this reaction. Label one as **A** and the other as **B**. *[2 marks]*

A



B

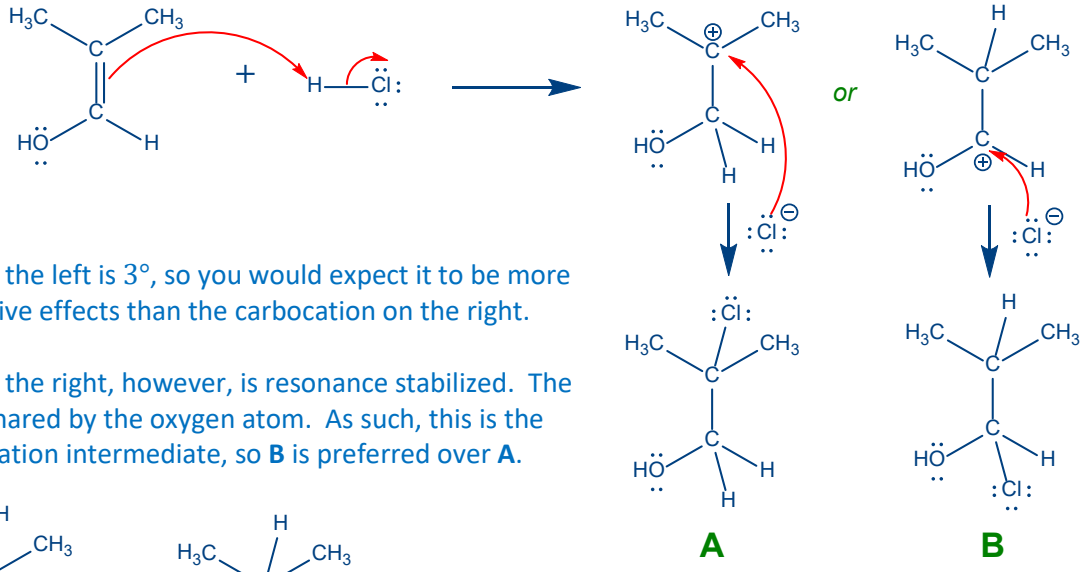


It doesn't matter which is labeled "A" and which is labeled "B"

(b) According to Markovnikov's rule, which of your answers to part (a) is predicted to be the major product? Briefly explain your choice. *[2 marks]*

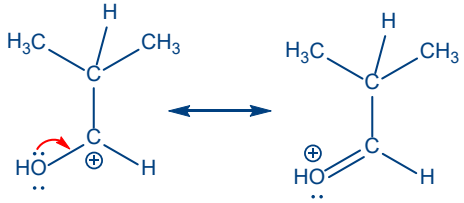
According to Markovnikov's rule, the H is added to the carbon atom that already has more hydrogen atoms attached. So, Markovnikov's rule predicts product **A** as the major product.

(c) In fact, the product predicted by the traditional version of Markovnikov's rule is not the major product in this case. Explain why the other product is actually favoured for this particular alkene. You should find it helpful to draw the two possible carbocation intermediates as part of your explanation. *[4 marks]*



The carbocation on the left is 3°, so you would expect it to be more stabilized by inductive effects than the carbocation on the right.

The carbocation on the right, however, is resonance stabilized. The positive charge is shared by the oxygen atom. As such, this is the more stable carbocation intermediate, so **B** is preferred over **A**.



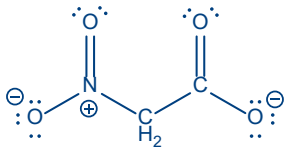
13. The pK_a of acetic acid (CH_3CO_2H) is 4.74. The pK_a of nitroacetic acid ($NO_2CH_2CO_2H$) is 1.68. **[15 marks]**

(a) Briefly explain why the pK_a of nitroacetic acid is so much smaller than that of acetic acid. *[2 marks]*

(b) Calculate the pH of a solution prepared by adding 100.0 g acetic acid to 1.000 L water. *[9 marks]*

(c) Calculate the pH of a solution prepared by adding both 100.0 g acetic acid and 200.0 g sodium acetate (CH_3CO_2Na) to 1.000 L water. *[4 marks]*

(a) Nitroacetic acid has a lower pK_a than acetic acid because nitroacetic acid is a stronger acid than acetic acid. This is because the nitro group is electron-withdrawing, pulling negative charge away from the O^- atoms in the conjugate base:



(b)

Step 1: Calculate K_a of acetic acid from pK_a

$pK_a = -logK_a$ therefore $K_a = 10^{-pK_a} = 10^{-4.74} = 1.8 \times 10^{-5}$

Step 2: Calculate nominal molarity of acetic acid solution

$$n_{HA} = 100.0\ g \times \frac{1\ mol}{60.0524\ g} = 1.665\ mol$$

$$M_{HA} = \frac{1.665\ mol}{1.000\ L} = 1.665\ M$$

Step 3: Set up ICE table and make reasonable assumptions

	$HA_{(aq)}$	$\rightleftharpoons$	$H^+_{(aq)}$	+	$A^-_{(aq)}$
I (M)	1.67		10^{-7}		0
C (M)	$-x$		$+x$		$+x$
E (M)	$1.665 - x \approx 1.665$		$10^{-7} + x \approx x$		x

Step 4: Write equilibrium constant expression and use it to solve for x

$$K_a = \frac{(a_{H^+})(a_{A^-})}{a_{HA}} \text{ therefore } 1.8 \times 10^{-5} = \frac{(x)(x)}{1.665} \text{ therefore } x^2 = (1.8 \times 10^{-5})(1.665)$$

Therefore $x = \sqrt{(1.8 \times 10^{-5})(1.665)} = \sqrt{3.0 \times 10^{-5}} = 0.0055$

Step 5: Check assumptions. If invalid, repeat calculation without the invalid assumption.

Assumption #1: $10^{-7} + \boldsymbol{x} \approx x$	$10^{-7} + 0.0055 = 0.0055$	assumption is okay
Assumption #2: $1.665 - \boldsymbol{x} \approx 1.665$	$1.665 - 0.0055 = 1.660$	assumption is okay

Step 6: Calculate pH from a_{H^+}

$$a_{H^+} = x = 0.0055$$
$$pH = -log(a_{H^+})$$
$$pH = -log(0.0055)$$
$$pH = 2.26$$

(c)

Step 1: Carry forward nominal molarity of acetic acid from part (b)

$$M_{HA} = \frac{1.665\ mol}{1.000\ L} = 1.665\ M$$

Step 2: Calculate nominal molarity of sodium acetate

$$n_{NaA} = 200.0\ g\ \times \frac{1\ mol}{82.0343\ g} = 2.438\ mol$$

$$M_{A^-} = M_{NaA} = \frac{2.438\ mol}{1.000\ L} = 2.438\ M$$

Step 3: Calculate pH of solution using Henderson-Hasselbalch equation or other valid approach

$$pH = pK_a + log\frac{a_{A^-}}{a_{HA}} = 4.74 + log\frac{(2.438)}{(1.665)} = 4.91$$

14. The partial electrochemical oxidation of methanol produces formaldehyde and water: **[24 marks]**

$$____\ CH_3OH_{(l)} + ____\ O_{2(g)} \rightarrow ____\ CH_2O_{(g)} + ____\ H_2O_{(l)}$$

(a) Balance this reaction using the method of half reactions. *[5 marks]*
For full credit, you must show both balanced half reactions.

(b) Using the thermodynamic data provide, calculate $\Delta H°$ and $\Delta S°$ for this reaction. *[5 marks]*

(c) Calculate $\Delta G°$ for this reaction at 25 °C. Is the reaction product- or reactant-favoured at this temperature? *[4 marks]*

(d) Calculate the equilibrium constant for this reaction at 25 °C. *[3 marks]*

(e) Calculate the potential for an electrochemical cell based on this reaction at 25 °C in which the pressure of oxygen is 10.0 bar and the pressure of formaldehyde is 0.0020 bar. *[7 marks]*

	$\Delta_f H°$	$S°$
$CH_3OH_{(l)}$	$-238.7\ \frac{kJ}{mol}$	$126.8\ \frac{J}{mol \cdot K}$
$O_{2(g)}$		$205.0\ \frac{J}{mol \cdot K}$
$CH_2O_{(g)}$	$-108.6\ \frac{kJ}{mol}$	$218.8\ \frac{J}{mol \cdot K}$
$H_2O_{(l)}$	$-285.83\ \frac{kJ}{mol}$	$69.9\ \frac{J}{mol \cdot K}$

(a)
$$\left(CH_3OH_{(l)} \rightarrow CH_2O_{(g)} + 2\,H^+_{(aq)} + 2\,e^-\right) \times 2$$
$$O_{2(g)} + 4\,H^+_{(aq)} + 4\,e^- \rightarrow 2\,H_2O_{(l)}$$
$$2\,CH_3OH_{(l)} + O_{2(g)} \rightarrow 2\,CH_2O_{(g)} + 2\,H_2O_{(l)}$$

(b)
$$\Delta_r H° = 2\,\Delta_f H°\left(CH_2O_{(g)}\right) + 2\,\Delta_f H°\left(H_2O_{(l)}\right) - 2\,\Delta_f H°\left(CH_3OH_{(l)}\right) - \Delta_f H°\left(O_{2(g)}\right)$$
$$\Delta_r H° = 2\left(-108.6\ \tfrac{kJ}{mol}\right) + 2\left(-285.83\ \tfrac{kJ}{mol}\right) - 2\left(-238.7\ \tfrac{kJ}{mol}\right) - \left(0\ \tfrac{kJ}{mol}\right)$$
$$\Delta_r H° = -311.46\ \tfrac{kJ}{mol} = -311.5\ \tfrac{kJ}{mol}$$

$$\Delta_r S° = 2\,S°\left(CH_2O_{(g)}\right) + 2\,S°\left(H_2O_{(l)}\right) - 2\,S°\left(CH_3OH_{(l)}\right) - S°\left(O_{2(g)}\right)$$
$$\Delta_r S° = 2\left(218.8\ \tfrac{J}{mol \cdot K}\right) + 2\left(69.9\ \tfrac{J}{mol \cdot K}\right) - 2\left(126.8\ \tfrac{J}{mol \cdot K}\right) - \left(205.0\ \tfrac{J}{mol \cdot K}\right)$$
$$\Delta_r S° = 118.8\ \tfrac{J}{mol \cdot K}$$

(c) $\Delta_r G° = \Delta_r H° - T\Delta_r S°$

$\Delta_r G° = \left(-311.5\ \frac{kJ}{mol}\right) - (298.15\ K)\left(118.8\ \frac{J}{mol \cdot K}\right)\left(\frac{1\ kJ}{1000\ J}\right)$

$\Delta_r G° = -346.9\ \frac{kJ}{mol}$

$\Delta_r G° < 0$ therefore the reaction is product-favoured under these conditions.

(d) $\Delta_r G° = -RTlnK$ therefore $K = e^{-\frac{\Delta_r G°}{RT}}$

$K = e^{-\frac{\left(-346.9\ \frac{kJ}{mol}\right)\left(\frac{1000\ J}{1\ kJ}\right)}{\left(8.314\,462\ \frac{J}{mol \cdot K}\right)(298.15\ K)}} = e^{139.9} = 5.9 \times 10^{60}$

(e) $\Delta_r G° = -\nu_e F E°$ therefore $E° = -\frac{\Delta_r G°}{\nu_e F}$

$E° = -\frac{\left(-346.9\ \frac{kJ}{mol}\right)\left(\frac{1000\ J}{1\ kJ}\right)}{(4)\left(96485\ \frac{C}{mol}\right)} \times \frac{1\ V}{1\ \frac{J}{C}} = +0.8988\ V$

$Q = \frac{(a_{CH_2O})^2 (a_{H_2O})^2}{(a_{CH_3OH})^2 (a_{O_2})}$ where $a_{CH_2O} = \frac{P_{CH_2O}}{1\ bar} = \frac{0.0020\ bar}{1\ bar} = 0.0020$ $a_{H_2O} = 1$

$a_{CH_2OH} = 1$ $a_{O_2} = \frac{P_{O_2}}{1\ bar} = \frac{10.0\ bar}{1\ bar} = 10.0$

$Q = \frac{(0.0020)^2 (1)^2}{(1)^2 (10.0)} = 4.0 \times 10^{-7}$

$E = E° - \frac{RT}{\nu_e F} lnQ$

$E = (+0.8988\ V) - \frac{\left(8.314\,462\ \frac{J}{mol \cdot K}\right)(298.15\ K)}{(4)\left(96485\ \frac{C}{mol}\right)} ln(4.0 \times 10^{-7}) \times \frac{1\ V}{1\ \frac{J}{C}}$

$E = (+0.8988\ V) - (-0.0946\ V)$

$E = +0.9934\ V$

15. What was the most useful and/or interesting thing you learned in CHEM 2000? **[1 mark]**