

Spring 2018

Chemistry 2000 Final Exam A

____/116 marks

- 1) Please read over the test carefully before beginning. You should have 13 pages of questions, a blank “overflow” page and a double-sided data sheet with periodic table.
- 2) **DO NOT WRITE ON THE QR CODE!!!** Work on pages without a QR code will not be graded.
- 3) If your work is not legible, it will be given a mark of zero. Show your work for all calculations.
- 4) Marks will be deducted for incorrect information added to an otherwise correct answer.
- 5) You may use a calculator but only for calculation. No text-capable calculators are allowed.
- 6) You have 3 hours to complete this test.

Confidentiality Agreement:

I agree not to discuss (or in any other way divulge) the contents of this exam until after 12:00 noon Mountain Time on Wednesday, April 18th, 2018. I understand that breaking this agreement would constitute academic misconduct. The minimum punishment would be a mark of 0/116 on this exam and removal of the “overwrite midterm mark with final exam mark” option for my grade in this course; the maximum punishment would include expulsion from this university.

Signature: _____

Date: _____

Course: CHEM 2000 (General Chemistry II)

Semester: Spring 2018

The University of Lethbridge

Question Breakdown

Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12	Q13	Q14	Total
/ 9	/ 5	/ 6	/ 12	/ 12	/ 14	/ 4	/ 6	/ 6	/ 10	/ 12	/ 12	/ 7	/ 1	/ 116

1. Fill in each blank with the word or phrase that best completes the sentence. **[9 marks]**
- (a) The second law of thermodynamics states that for a reaction to be thermodynamically allowed, the entropy of the universe must increase. [3 marks]
- (b) On a phase diagram, the critical point lies at the end of the curve separating the liquid phase and the gas phase. At pressures and temperatures above the critical point, the substance is a supercritical fluid.
- (c) A semiconductor consisting of one pure substance is a(n) intrinsic semiconductor.
- (d) In an electrochemical cell, the electrode at which oxidation occurs is called the anode.
- (e) Two molecules that are nonsuperimposable mirror images of each other are a pair of enantiomers.

2. The overall reaction in the lead-acid battery involves $Pb_{(s)}$ reacting with $PbO_{2(s)}$. The main product in both half-reactions is $PbSO_{4(s)}$. **[5 marks]**

- (a) Which lead species gets oxidized? **[1 mark]**

$Pb_{(s)}$ *oxidation state of Pb increases from 0 to +2*

- (b) Which lead species gets reduced? **[1 mark]**

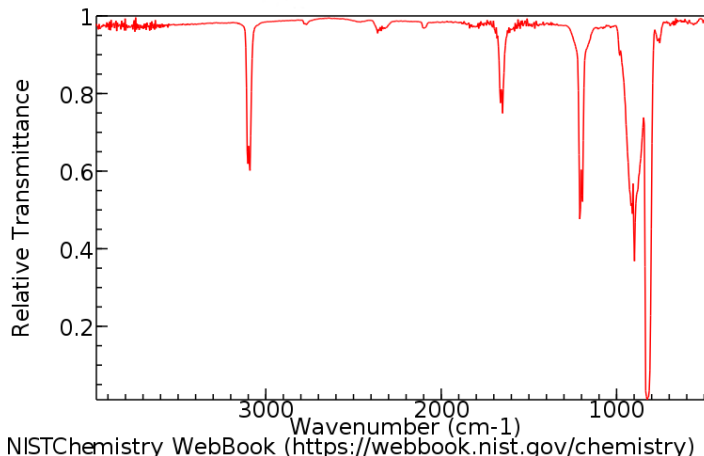
$PbO_{2(s)}$ *oxidation state of Pb decreases from +4 to +2*

- (c) Unbalanced half-reactions are provided below. Balance them then use the balanced half-reactions to write a balanced equation for the overall reaction. **[3 marks]**



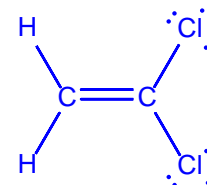
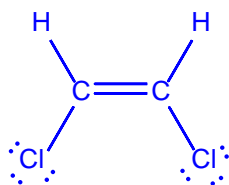
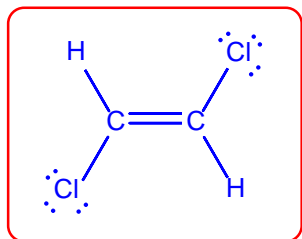
3. A compound has the formula $C_2H_2Cl_2$. This compound is non-polar. The IR spectrum for this compound is shown below.

[6 marks]



NISTChemistry WebBook (<https://webbook.nist.gov/chemistry>)

- (a) Draw the structure of this compound. Explain how the information provided supports your answer. You must reference the IR spectrum in your answer. [3 marks]



The isomer in the red box is the correct answer.

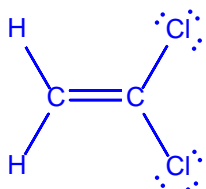
The three structures shown above are the only three isomers of $C_2H_2Cl_2$. The two at the right are both polar. The one on the left is nonpolar since it has no net dipole.

The IR spectrum is consistent with this answer. A peak at approximately 3100 cm^{-1} corresponds to the $C-H$ bonds where the carbon is trigonal planar (due to the $C=C$ double bond). A peak at approximately 1650 cm^{-1} corresponds to the $C=C$ double bond.

- (b) According to Valence Bond theory, what is the hybridization of the carbon atoms in this compound? [1 mark]

sp^2

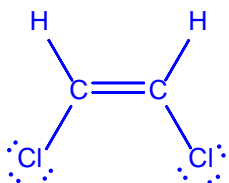
- (c) Draw one structural isomer of this compound. [1 mark]



Structural isomers have different connectivity.

In this case, the difference is between both Cl being attached to the same C vs. one Cl being attached to each C.

- (d) Draw one stereoisomer of this compound. [1 mark]



Stereoisomers have the same connectivity.

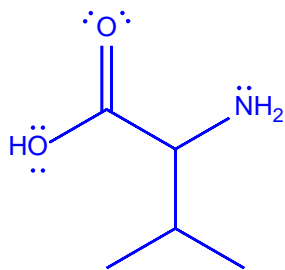
In this case, both stereoisomers (the answers to parts (a) and (d)) have one Cl attached to each C and one H attached to each C.

This is the cis isomer while the answer to part (a) is the trans isomer.

4. As we saw in class, an amino acid consists of a central carbon atom attached to: **[12 marks]**
- a carboxylic acid, ($-CO_2H$)
 - an amine, ($-NH_2$ in an amino acid; however, either H can be replaced by C in other amines; amino acids were specifically discussed in class)
 - a variable (R) group, and
 - a hydrogen atom.

In the amino acid valine, the variable group is an isopropyl group ($-CH(CH_3)_2$).

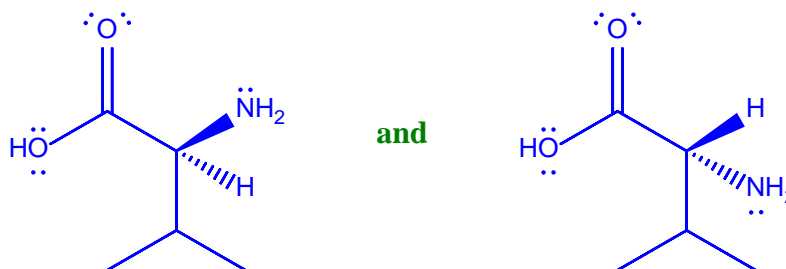
- (a) Draw a line-bond structure for valine. *Include lone pairs.* **[3 marks]**



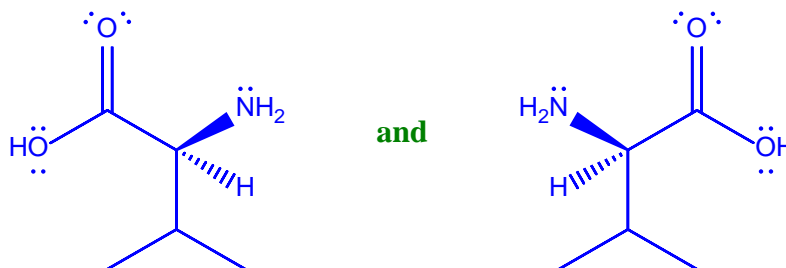
- (b) Is valine chiral? Demonstrate whether or not it is chiral using appropriate drawings. **[3 marks]**

Yes, valine is chiral.

Two nonsuperimposable mirror images (enantiomers) can be drawn for valine:



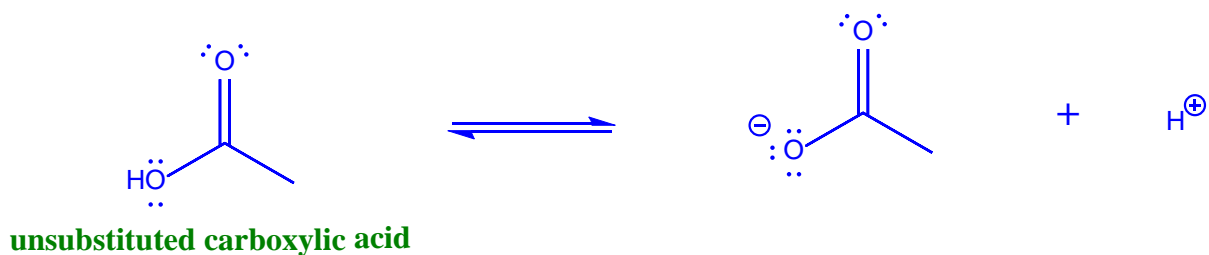
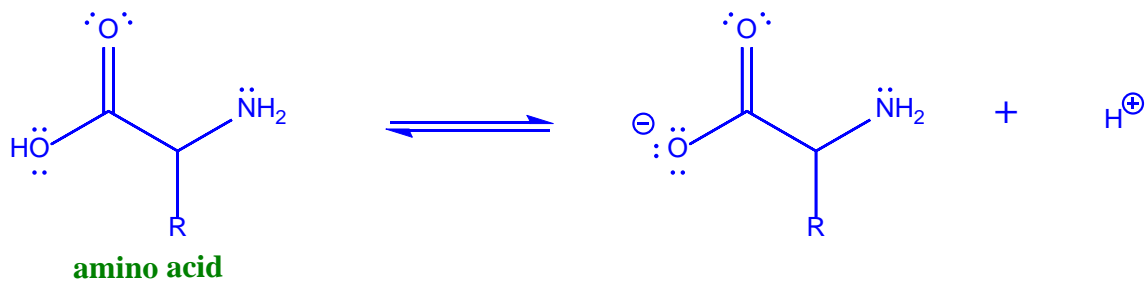
The enantiomers could also be drawn as:



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4. ...continued
 (c) In amino acids, the carboxylic acid functional group is more acidic ($pK_a \sim 2$) than is typical of carboxylic acids (pK_a between 3 and 5). Explain why. [2 marks]

Compare an amino acid with an unsubstituted carboxylic acid. Since we are interested in acidity, focus on the stability of the conjugate base of each acid:



In the conjugate base of the amino acid, the electronegative nitrogen atom pulls electron density away from the negatively charged oxygen atoms, further stabilizing the anion via the inductive effect.

Note that this effect is stronger than the pictures above imply due to the fact that the nitrogen atom is also protonated (and therefore has a positive charge) at all pH values at which the carboxylic acid group is protonated. A positively charged nitrogen atom is more electron withdrawing than a neutral nitrogen atom, strengthening this inductive effect. See part (d).

*Both conjugate bases are stabilized by delocalization of the negative charge over both oxygen atoms – the resonance effect. The **difference** in acidity is due to the addition of the inductive effect for the conjugate acid of the amino acid.*

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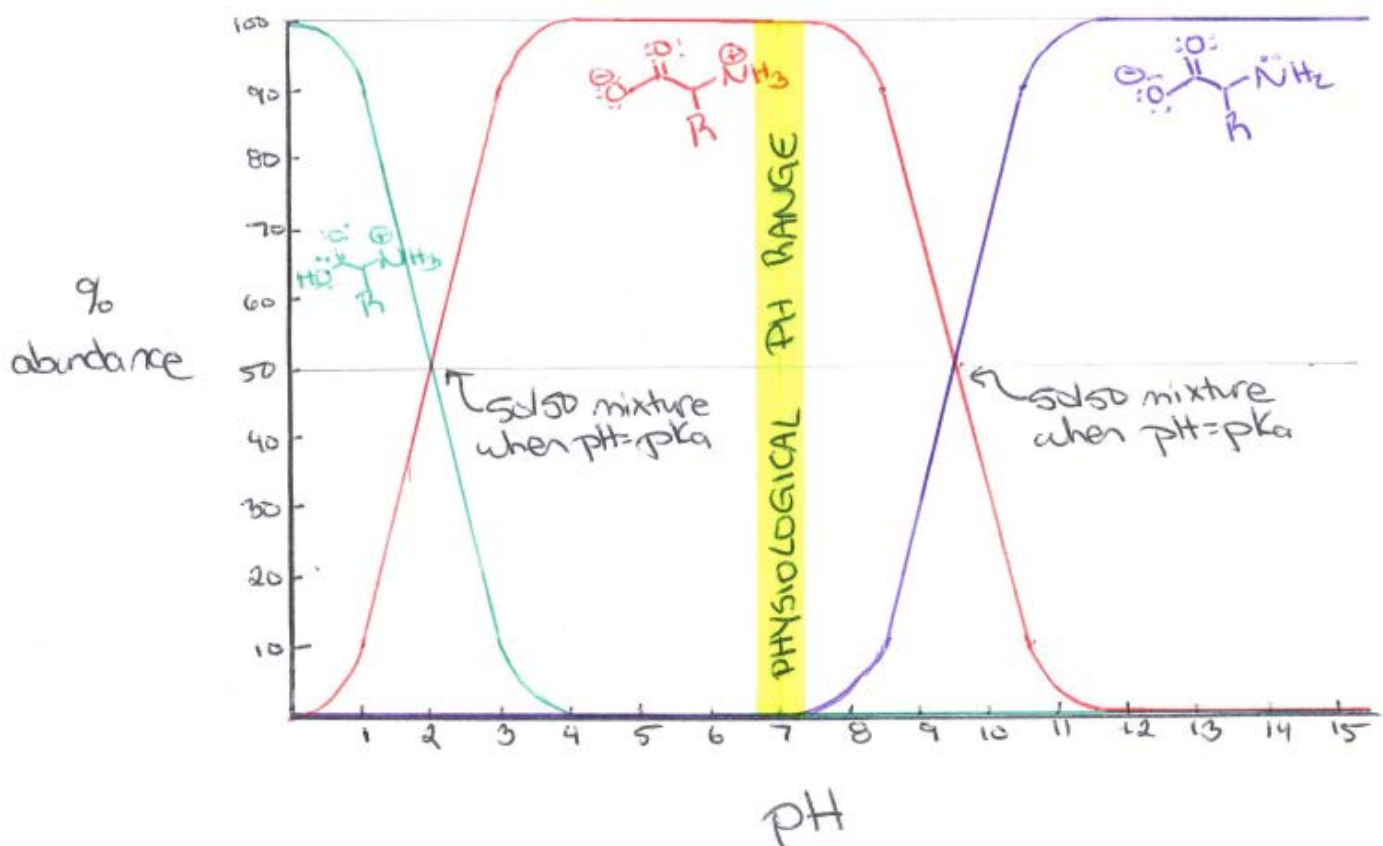
4. ...continued

- (d) What is a zwitterion, and why would valine (and the other amino acids) be a zwitterion under physiological (pH ~7) conditions? Distribution curves may be helpful for answering this question. [4 marks]

A zwitterion is a species whose overall charge is neutral but which contains charged atoms. e.g. An amino acid under physiological conditions contains a -CO_2^- group and a -NH_3^+ group for an overall charge of 0 (unless the R group is charged).

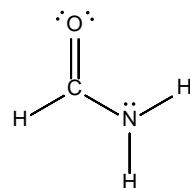
The pK_a of the carboxylic acid group in valine is approximately 2. (see question) The pK_a of the protonated amino group in valine is approximately 9 to 10. (see data sheet) As such, the carboxylic acid group is mostly protonated at pH values below 2 while the amino group is mostly protonated at pH values below 9 to 10.

See the distribution curve below for the forms in which valine exists at different pH values. It clearly shows that the zwitterion dominates at pH values near 7 (the yellow bar).



5. A Lewis structure for formamide is shown below.

[12 marks]



VSEPR suggests that the nitrogen should be trigonal pyramidal but, in fact, it's trigonal planar. For parts (a) and (b), count and sort the AOs. The molecule is planar, so only the p_z orbitals will be π -symmetric.

The σ -symmetric AOs are:

- Three $1s(H)$ – one for each H.
- One $2s(C)$
- One $2s(N)$
- One $2s(O)$
- $2p_x(C)$ and $2p_y(C)$
- $2p_x(N)$ and $2p_y(N)$
- $2p_x(O)$ and $2p_y(O)$

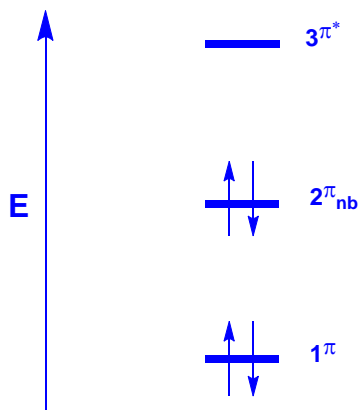
This gives a total of 12 σ -symmetric AOs.

The π -symmetric AOs are:

- $2p_z(C)$
- $2p_z(N)$
- $2p_z(O)$

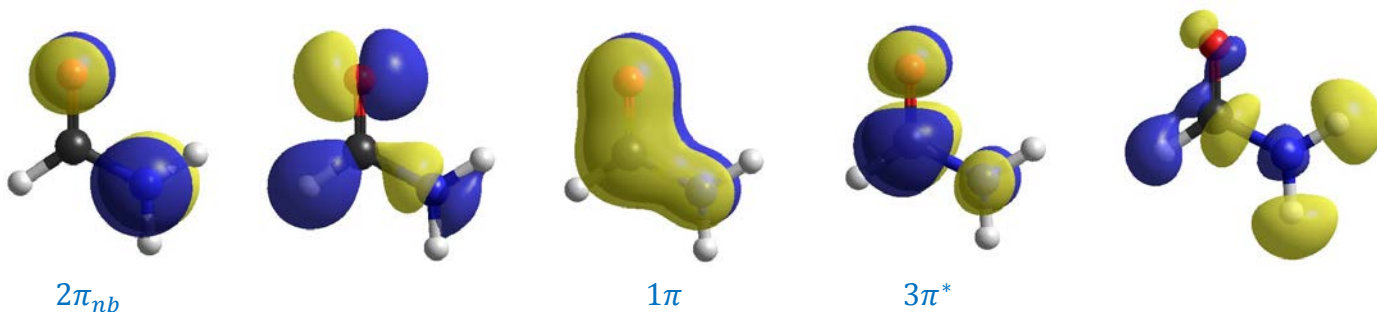
This gives a total of 3 π -symmetric AOs.

- (a) How many valence σ -symmetric MOs does formamide have? [1 mark]
12
- (b) How many valence π -symmetric MOs does formamide have? [1 mark]
3
- (c) Draw a valence π MO energy level diagram for formamide. Your diagram should include energy levels, electrons and labels for the MOs. You do **not** need to include atomic orbitals. [4 marks]



Due to the lack of symmetry, it is also acceptable to label the second MO as 2π instead of $2\pi_{nb}$.

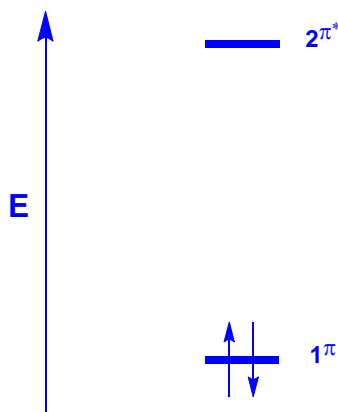
- (d) The pictures below show some of the MOs of formamide. Circle the pictures showing π MOs, and label each π MO, matching it to an energy level in your answer to part (c). You do **not** need to label the σ MOs. [3 marks]



- (e) How would your answers to parts (a), (b) and (c) have changed if the nitrogen atom in formamide had been trigonal pyramidal? [3 marks]

If the nitrogen atom had been trigonal pyramidal instead of trigonal planar, it would not participate in the π system and would therefore not have any π -symmetric AOs. As such, there would only be two π -symmetric AOs making two π -symmetric MOs ($2p_z(C)$ and $2p_z(O)$). That would leave thirteen σ -symmetric AOs making thirteen σ -symmetric MOs.

The valence π MO diagram would therefore only have two energy levels. There would be two pi electrons (since the lone pair on N would no longer belong to the π system):



Some would argue that since the molecule was no longer fully planar, there would no longer be a π system and all the MOs would be σ -symmetric. Even according to this view, two of the MOs would look very much like π MOs. If you took this approach to the question, you would be arguing that there would be zero π -symmetric MOs and fifteen σ -symmetric MOs in a nonplanar conformation of formamide.

6.

[14 marks]

(a) Draw a valence molecular orbital energy level diagram for the hypofluorite anion (OF^-).

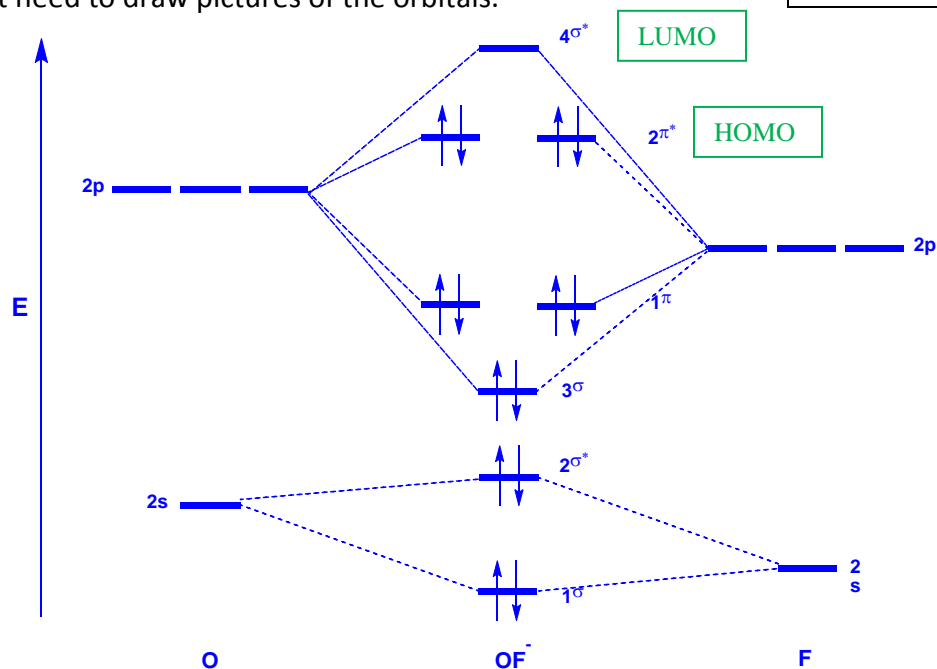
Your diagram should include:

[10 marks]

- energy levels for atomic and molecular orbitals
- tie lines connecting MOs to the appropriate AOs
- labels for atomic and molecular orbitals (including whether MOs are bonding, nonbonding or antibonding)
- electrons in the molecular orbitals
- identification of the HOMO and LUMO

You do not need to draw pictures of the orbitals.

Atomic Orbital	Energy (Ry)
O 2s	-2.38
O 2p	-1.17
F 2s	-2.95
F 2p	-1.37



(b) Calculate the $O - F$ bond order in OF^- .

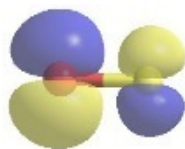
[1 mark]

$$\frac{8-6}{2} = \frac{2}{2} = 1$$

(c) The hypofluorite anion would be a very powerful Lewis base. Based on your MO diagram, which end of the ion (O or F) is most strongly basic? Explain briefly. Your explanation should include a picture of the relevant MO.

[3 marks]

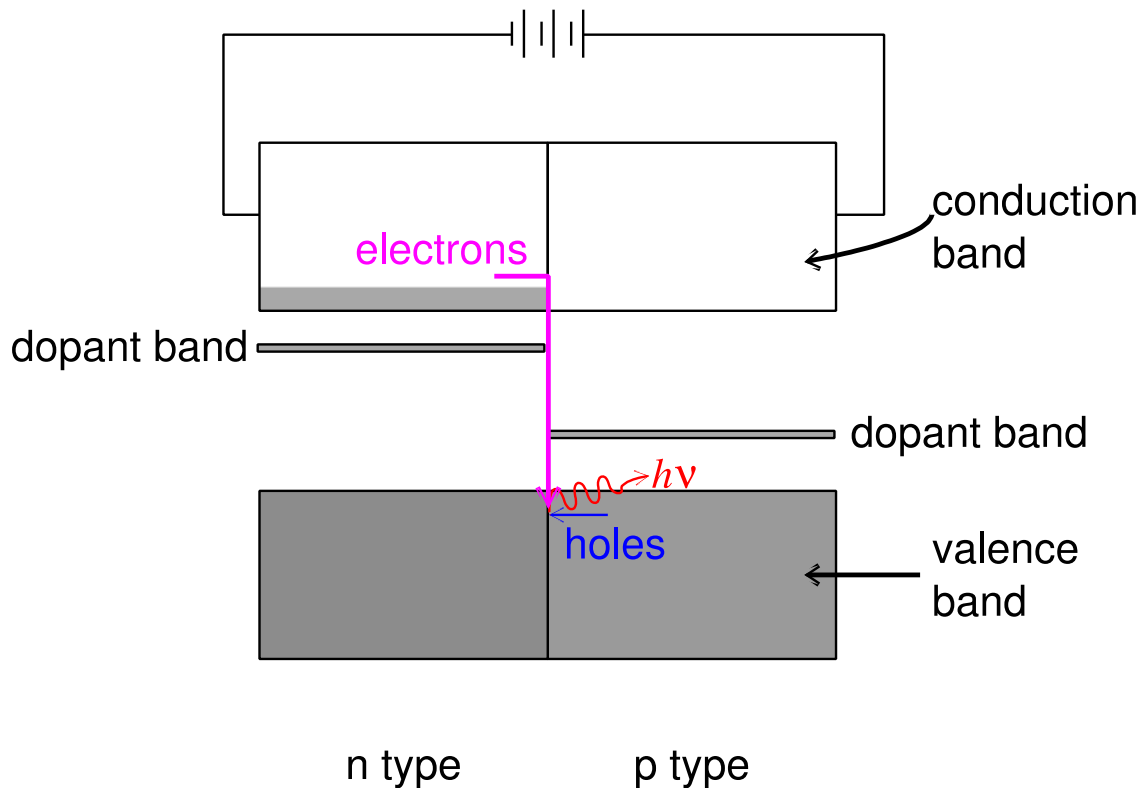
A Lewis base is an electron pair donor. Electrons are donated from the HOMO ($2\pi^*$) therefore that is the relevant MO:



The HOMO is polarized toward the oxygen atom (as shown in the picture above). This is because $2\pi^*$ is closer in energy to $2p(O)$ than to $2p(F)$.

As such, the oxygen end of the ion is most strongly basic.

7. Explain how a light-emitting diode (LED) works using a band diagram. What feature of the diagram is related to the color of the LED? [4 marks]

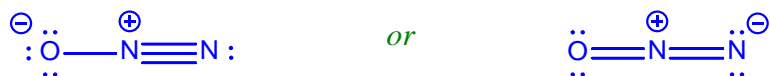


The basis of an LED is an n-p junction (diode). Electrons are fed into the n side of the junction by an external power source, shown here as a battery. The electrons naturally tend to migrate to the p side of the junction due to the relatively empty conduction band on that side. However, LEDs are engineered so that, right at the junction, there is a high probability that electrons will combine with holes in the valence band of the p-type semiconductor.

The energy lost on dropping from the conduction to the valence band is emitted as a photon. The band gap between the conduction and valence bands sets the amount of energy lost by electrons when dropping into the valence band at the junction, and therefore controls the color of the LED via the well-known equation $E = h\nu$.

8. The entropy of N_2O at 0 K is $4.7 \frac{J}{mol \cdot K}$. This is called the residual entropy. [6 marks]

(a) Draw a Lewis diagram for N_2O . The connectivity is $N - N - O$. [2 marks]
 Include all non-zero formal charges.



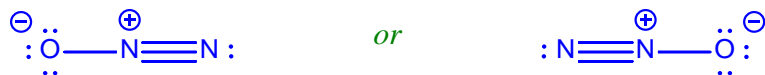
The Lewis diagram on the left is preferable since it shows the negative charge on the more electronegative atom. Both resonance structures contribute to the average structure, but the one on the left is the major contributor.

(b) According to VSEPR, what is the geometry of N_2O ? [1 mark]

linear

(c) Explain the probable origin of the residual entropy of N_2O . Support your argument with a calculation. *Do not expect a perfect match with the measured entropy reported above.* [3 marks]

Even in a perfect crystal, each molecule of N_2O has two possible orientations:



Since every molecule has two possible orientations, that generates 2^n possible microstates (where n is the number of molecules of N_2O in the crystal).

Based on this argument, one would expect a residual entropy of:

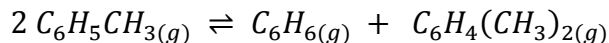
$$S = k_B \ln(\Omega) = k_B \ln(2^n) = k_B \cdot n \cdot \ln(2)$$

To calculate a molar residual entropy, set n to Avogadro's number (the number of molecules in a mole):

$$\begin{aligned} S &= k_B \cdot N_A \cdot \ln(2) \\ S &= \left(1.380649 \times 10^{-23} \frac{J}{K}\right) \left(6.022141 \times 10^{23} \frac{1}{mol}\right) \ln(2) \\ S &= 5.763147 \frac{J}{mol \cdot K} \end{aligned}$$

While this is not a perfect match for the measured residual entropy, it has the same order of magnitude. Possibly the partial charges favour having the molecules line up so that N of one molecule is next to O of the next (to minimize repulsion of the negative charges).

9. In the gas phase, toluene ($C_6H_5CH_3$) can react with itself to make benzene (C_6H_6) and xylenes ($C_6H_4(CH_3)_2$). **[6 marks]**



At 25 °C, the equilibrium constant for this reaction is 0.16.

If we start with a rigid container holding 0.75 bar of toluene, what will the pressures of all reactants and products be once the system reaches equilibrium?

	$2 C_6H_5CH_3(g)$	\rightleftharpoons	$C_6H_6(g)$	+	$C_6H_4(CH_3)_2(g)$
I (bar)	0.75		0		0
C (bar)	$- 2x$		$+ x$		$+ x$
E (bar)	$0.75 - 2x$		x		x

Step 1: Write a balanced chemical equation for the reaction

see above

Step 2: Organize all known information

see above

ICE tables are useful tools to solve equilibrium problems; they can be constructed using any property that is directly proportional to moles for all species – in this case, pressure at constant volume

Step 3: Write equilibrium constant expression

$$K = \frac{(a_{C_6H_6(g)})(a_{C_6H_4(CH_3)_2(g)})}{(a_{C_6H_5CH_3(g)})^2}$$

Step 4: Calculate x

$$K = \frac{(a_{C_6H_6(g)})(a_{C_6H_4(CH_3)_2(g)})}{(a_{C_6H_5CH_3(g)})^2}$$

$$0.16 = \frac{(x)(x)}{(0.75-2x)^2}$$

$$\sqrt{0.16} = \sqrt{\frac{x^2}{(0.75-2x)^2}}$$

$$0.4 = \frac{x}{0.75-2x}$$

$$0.4(0.75 - 2x) = x$$

$$0.3 - 0.8x = x$$

$$0.3 = 1.8x$$

$$x = \frac{0.3}{1.8}$$

$$x = 0.17$$

Step 5: Calculate equilibrium pressures of gases from x.

$$p_{\text{benzene}} = x \text{ bar} = 0.17 \text{ bar}$$

$$p_{\text{xylenes}} = x \text{ bar} = 0.17 \text{ bar}$$

$$p_{\text{toluene}} = (0.75 - 2x) \text{ bar} = (0.75 - (2 \times 0.17)) \text{ bar} = 0.42 \text{ bar}$$

Step 8: Check your work

Does your answer seem reasonable?

All pressures are positive. The equilibrium pressure for toluene is less than the initial pressure (makes sense since the system only contained toluene at the start). The equilibrium constant was close to 1, and the pressures of the three products and reactants are similar (have the same order of magnitude).

10.

[10 marks]

- (a) Calculate the pH of a solution prepared by adding 0.71 g HCl to 1.00 L water.
- [2 marks]

Assume that the addition of HCl does not significantly affect the volume of the solution.

HCl is a strong monoprotic acid. As such, it fully dissociates in water, generating 1 mol H^+ for every 1 mol HCl. Thus, calculating the molarity of HCl gives the molarity of H^+ .

The molar mass of HCl is $36.4606 \frac{g}{mol}$ (calculated from molar masses on periodic table).

Step 1: Calculate molarity of $H^+_{(aq)}$

$$M_{H^+} = M_{HCl} = \frac{0.71 g}{1.00 L} \times \frac{1 mol}{36.4606 g} = 0.019 \frac{mol}{L}$$

Step 2: Calculate activity of $H^+_{(aq)}$

pH is calculated from activity of H^+ . Assuming an ideal solution,

$$a_{H^+} = \frac{M_{H^+}}{1 \frac{mol}{L}} = \frac{0.019 \frac{mol}{L}}{1 \frac{mol}{L}} = 0.019$$

Step 3: Calculate pH

$$pH = -\log(a_{H^+}) = -\log(0.019) = 1.71$$

Step 4: Check your work

Does your answer seem reasonable?

The pH of an acidic solution should be below 7. If the concentration of HCl had been 1×10^{-2} , we'd have expected a pH of 2. So, this answer is reasonable.

- (b) Calculate the pH of a solution prepared by adding 0.15 g acetic acid (
- CH_3CO_2H
-) to 1.00 L water. Assume that the addition of acetic acid does not significantly affect the volume of the solution.
- [8 marks]

Acetic acid is a weak monoprotic acid. As such, it partially dissociates in water, 1 mol H^+ for every mole of acetic acid that dissociates.

How much of the acetic acid dissociates is determined by the equilibrium constant ($pK_a = 4.74$; see data sheet) and is most easily found using an ICE table.

The molar mass of acetic acid is $60.0524 \frac{g}{mol}$ (calculated from molar masses on periodic table).

Step 1: Calculate molarity of acetic acid

$$M_{acetic\ acid} = \frac{0.15 g}{1.00 L} \times \frac{1 mol}{60.0524 g} = 0.0025 \frac{mol}{L}$$

Step 2: Calculate K_a from pK_a

$$pK_a = -\log K_a$$

$$K_a = 10^{-pK_a}$$

$$K_a = 10^{-4.74}$$

$$K_a = 1.8 \times 10^{-5}$$

Step 3: Set up ICE table

	$HA_{(aq)}$	\rightleftharpoons	$H^+_{(aq)}$	$+$	$A^-_{(aq)}$
I (M)	0.0025		10^{-7}		0
C (M)	$-x$		$+x$		$+x$
E (M)	$0.0025 - x$		$10^{-7} + x \approx x$		x

Step 4: Write equilibrium constant expression

$$K_a = \frac{(a_{H^+})(a_{A^-})}{a_{HA}}$$

Step 5: Calculate x

$$1.8 \times 10^{-5} = \frac{(x)(x)}{0.0025 - x}$$

$$(1.8 \times 10^{-5})(0.0025 - x) = x^2$$

$$x^2 + (1.8 \times 10^{-5})x - (4.5 \times 10^{-8}) = 0$$

We can solve for x using the quadratic equation (as shown below) or using a graphing calculator (either by finding the intercepts or using an equation solving function).

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-(1.8 \times 10^{-5}) \pm \sqrt{(1.8 \times 10^{-5})^2 - 4(1)(-4.5 \times 10^{-8})}}{2(1)} = \frac{-(1.8 \times 10^{-5}) \pm (4.3 \times 10^{-4})}{2}$$

$$x = 2.0 \times 10^{-4} \text{ or } -2.2 \times 10^{-4}$$

Since x cannot be negative (since that would give negative concentrations), $x = 2.0 \times 10^{-4}$

Step 6: Calculate concentration of $H^+_{(aq)}$ and check assumption

$$M_{H^+} = \left(10^{-7} \frac{\text{mol}}{\text{L}}\right) + \left(x \frac{\text{mol}}{\text{L}}\right) = \left(10^{-7} \frac{\text{mol}}{\text{L}}\right) + \left(2.0 \times 10^{-4} \frac{\text{mol}}{\text{L}}\right) = 2.0 \times 10^{-4} \frac{\text{mol}}{\text{L}}$$

The initial $10^{-7} \frac{\text{mol}}{\text{L}} H^+$ in pure water is negligible relative to the amount produced by dissociation of the acid. Therefore, the assumption that $10^{-7} + x \approx x$ was reasonable.

Step 7: Calculate activity of $H^+_{(aq)}$

pH is calculated from activity of H^+ . Assuming an ideal solution,

$$a_{H^+} = \frac{M_{H^+}}{1 \frac{\text{mol}}{\text{L}}} = \frac{x \frac{\text{mol}}{\text{L}}}{1 \frac{\text{mol}}{\text{L}}} = \frac{2.0 \times 10^{-4} \frac{\text{mol}}{\text{L}}}{1 \frac{\text{mol}}{\text{L}}} = 2.0 \times 10^{-4}$$

Step 8: Calculate pH

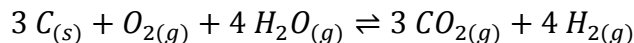
$$pH = -\log(a_{H^+}) = -\log(2.0 \times 10^{-4}) = 3.69$$

Step 9: Check your work

Does your answer seem reasonable?

The pH of an acidic solution should be below 7. This solution has a lower concentration than the one in part (a) and it's a weaker acid. Therefore, we expect this pH to be higher than the answer to part (a).

11. The reformation of coal to hydrogen using high pressure steam can be described by the following chemical equation: [12 marks]



- (a) Calculate K for this reaction performed at 25 °C. [8 marks]

The equilibrium constant can be calculated from the standard free energy of reaction. That can, in turn, be calculated from thermodynamic data on the data sheet.

Step 1: Calculate the standard enthalpy change for the reaction

$$\Delta_r H^\circ = \sum \Delta_f H^\circ(\text{products}) - \sum \Delta_f H^\circ(\text{reactants})$$

$$\Delta_r H^\circ = [3 \Delta_f H^\circ(CO_{2(g)}) + 4 \Delta_f H^\circ(H_{2(g)})] - [3 \Delta_f H^\circ(C_{(s)}) + \Delta_f H^\circ(O_{2(g)}) + 4 \Delta_f H^\circ(H_2O_{(g)})]$$

$$\Delta_r H^\circ = \left[3 \left(-393.50 \frac{\text{kJ}}{\text{mol}} \right) + 4 \left(0 \frac{\text{kJ}}{\text{mol}} \right) \right] - \left[3 \left(0 \frac{\text{kJ}}{\text{mol}} \right) + \left(0 \frac{\text{kJ}}{\text{mol}} \right) + 4 \left(-241.8 \frac{\text{kJ}}{\text{mol}} \right) \right]$$

$$\Delta_r H^\circ = -213.3 \frac{\text{kJ}}{\text{mol}}$$

Step 2: Calculate the standard entropy change for the reaction

$$\Delta_r S^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$$

$$\Delta_r S^\circ = [3 S^\circ(CO_{2(g)}) + 4 S^\circ(H_{2(g)})] - [3 S^\circ(C_{(s)}) + S^\circ(O_{2(g)}) + 4 S^\circ(H_2O_{(g)})]$$

$$\Delta_r S^\circ = \left[3 \left(213.7 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) + 4 \left(130.7 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) \right] - \left[3 \left(5.686 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) + \left(205.0 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) + 4 \left(188.8 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) \right]$$

$$\Delta_r S^\circ = 186.6 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$

Step 3: Calculate the standard free energy change for the reaction

$$\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ$$

$$\Delta_r G^\circ = \left(-213.3 \frac{\text{kJ}}{\text{mol}} \right) - (298.15 \text{ K}) \left(186.6 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) \left(\frac{1 \text{ kJ}}{1000 \text{ J}} \right)$$

$$\Delta_r G^\circ = -268.9 \frac{\text{kJ}}{\text{mol}}$$

Step 4: Calculate the equilibrium constant for the reaction at 25 °C

$$\Delta_r G^\circ = -RT \ln K$$

$$\ln K = -\frac{\Delta_r G^\circ}{RT}$$

$$\ln K = -\frac{\left(-268.9 \frac{\text{kJ}}{\text{mol}} \right)}{\left(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} \right) (298.15 \text{ K})} \times \frac{1000 \text{ J}}{1 \text{ kJ}}$$

$$\ln K = 108.5$$

$$K = e^{108.5}$$

$$K = 1 \times 10^{47}$$

Step 5: Check your work

Does your answer seem reasonable?

5 moles of gas in reactants gives 7 moles of gas in products; therefore, expect a large positive entropy change. Reaction is used industrially therefore expect a negative free energy change (thermodynamically allowed reaction).

(b) Calculate K for this reaction performed at 125 °C. [4 marks]

This is a "two temperatures; two equilibrium constants" question using $\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$.

Step 1: Match equilibrium constants to the corresponding temperature

$$T_1 = 298.15 \text{ K}$$

$$T_2 = 398.15 \text{ K}$$

$$K_1 = 1 \times 10^{47}$$

$$K_2 = ???$$

Step 2: Calculate the standard enthalpy change for the reaction

This was done in part (a).

$$\Delta_r H^\circ = -213.3 \frac{\text{kJ}}{\text{mol}} = -2.133 \times 10^5 \frac{\text{J}}{\text{mol}}$$

Step 3: Crunch the numbers

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{K_2}{1 \times 10^{47}}\right) = \left(\frac{-2.133 \times 10^5 \frac{\text{J}}{\text{mol}}}{8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}}\right) \left(\frac{1}{298.15 \text{ K}} - \frac{1}{398.15 \text{ K}}\right)$$

$$\ln\left(\frac{K_2}{1 \times 10^{47}}\right) = -21.61$$

$$\frac{K_2}{1 \times 10^{47}} = e^{-21.61}$$

$$\frac{K_2}{1 \times 10^{47}} = 4.1 \times 10^{-10}$$

$$K_2 = (1 \times 10^{47})(4.1 \times 10^{-10})$$

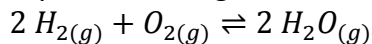
$$K_2 = 5 \times 10^{37}$$

Step 5: Check your work

Does your answer seem reasonable?

This reaction is exothermic ($\Delta_r H^\circ < 0$), so it is expected to have a smaller equilibrium constant at the higher temperature.

12. The hydrogen fuel cell is governed by the following reaction: [12 marks]



For the purposes of this question, consider a hydrogen fuel cell operating under acidic conditions.

- (a) What is the stoichiometric coefficient for electrons (ν_e) for this reaction? [2 marks]

4

This value can be obtained by writing the two half-reactions then adding them to give the overall balanced equation.



4 electrons are cancelled when the half-reactions are combined; therefore, $\nu_e = 4$

- (b) Calculate the standard cell potential for this reaction at 25 °C. [4 marks]

Step 1: Calculate the standard free energy change for the reaction

$$\Delta_r G^\circ = \sum \Delta_f G^\circ(\text{products}) - \sum \Delta_f G^\circ(\text{reactants})$$

$$\Delta_r G^\circ = 2 \Delta_f G^\circ(\text{H}_2\text{O}_{(g)}) - [2 \Delta_f G^\circ(\text{H}_{2(g)}) + \Delta_f G^\circ(\text{O}_2)]$$

$$\Delta_r G^\circ = 2 \left(-228.6 \frac{\text{kJ}}{\text{mol}} \right) - \left[2 \left(0 \frac{\text{kJ}}{\text{mol}} \right) + \left(0 \frac{\text{kJ}}{\text{mol}} \right) \right]$$

$$\Delta_r G^\circ = -457.2 \frac{\text{kJ}}{\text{mol}}$$

Step 2: Calculate standard potential from standard free energy change

$$\Delta_r G^\circ = -\nu_e F E^\circ$$

$$E^\circ = -\frac{\Delta_r G^\circ}{\nu_e F}$$

$$E^\circ = -\frac{\left(-457.2 \frac{\text{kJ}}{\text{mol}} \right)}{(4) \left(96\,485 \frac{\text{C}}{\text{mol}} \right)} \times \frac{1000 \text{ J}}{1 \text{ kJ}}$$

$$E^\circ = +1.185 \frac{\text{J}}{\text{C}} = +1.185 \text{ V}$$

Step 3: Check your work

Does your answer seem reasonable? Are sig. fig. correct?

The standard free energy change is negative therefore the standard potential should be positive.

- (c) Calculate the cell potential for this reaction at 25 °C if the input stream provides 66 bar $H_{2(g)}$ and 33 bar $O_{2(g)}$ while the pressure of water vapour is kept at 0.001 bar. Is this reaction product-favoured under those conditions. Why or why not? [6 marks]

Step 1: Calculate reaction quotient

$$Q = \frac{(a_{H_2O(g)})^2}{(a_{H_2(g)})^2 (a_{O_2(g)})} = \frac{(0.001)^2}{(66)^2 (33)} = 7.0 \times 10^{-12}$$

Step 2: Calculate potential for reaction under nonstandard conditions

$$E = E^\circ - \frac{RT}{\nu_e F} \ln Q$$

$$E = (1.185 \text{ V}) - \frac{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})}{(4)(96485 \frac{\text{C}}{\text{mol}})} \ln(7.0 \times 10^{-12}) \times \frac{1 \text{ V}}{1 \frac{\text{J}}{\text{C}}}$$

$$E = 1.185 \text{ V} - (-0.165 \text{ V})$$

$$E = 1.350 \text{ V}$$

Step 3: Check your work

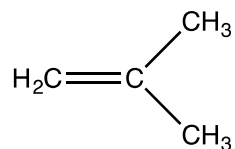
Does your answer seem reasonable?

High pressures of reactants, low pressures of products and a reaction that is thermodynamically allowed under standard conditions strongly suggest that the reaction should be thermodynamically allowed under these conditions (positive cell potential).

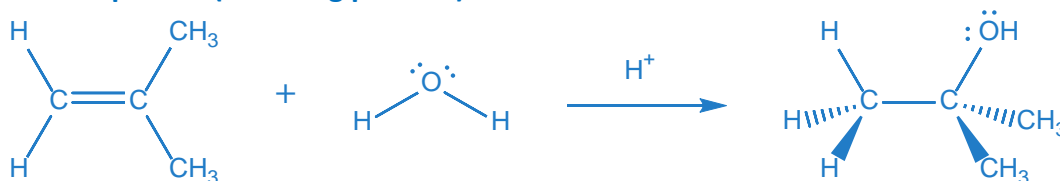
Step 4: Answer the question!

Yes, the reaction is product-favoured under those conditions. The cell potential is positive.

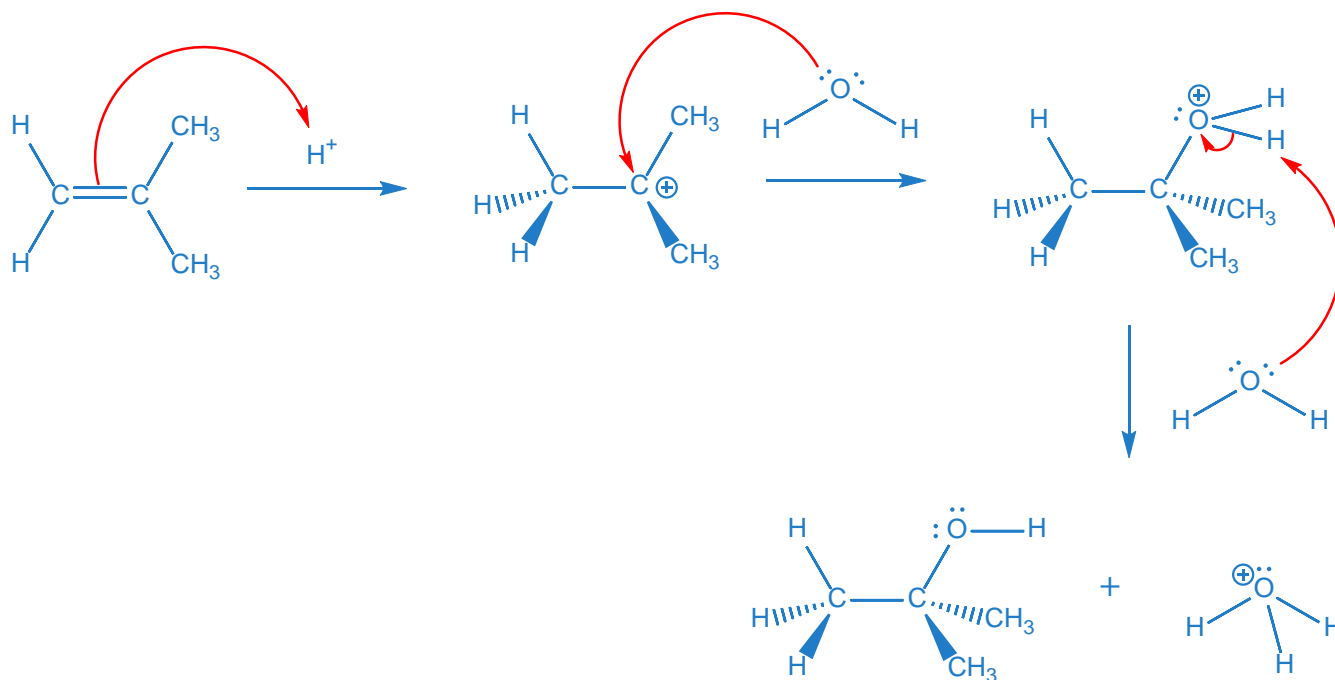
13. What is the product in the acid-catalyzed addition of water to the following molecule? Show the mechanism, including the electron movement using the curved arrow notation. **[7 marks]**



Reaction equation (including product):



Mechanism:



Note that the CH₂ is protonated (not the C with two CH₃ groups attached) so as to give the tertiary carbocation intermediate. (Protonating the other C would have given a primary carbocation intermediate – which is less stable.)

Also note that water is NOT a strong enough acid to protonate the alkene. This is why an acid catalyst is required!

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