

Felker FIS

First Midterm Examination, CH20A-1, Fall 2015

Thursday, October 29, 7 to 8:50 pm

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This examination is composed of four problems. Do all parts of all the problems. You have one hour and fifty minutes to complete the exam. You may use three pages of notes (front and back), and a noncommunicating calculator of your choice in working the exam. Only exams **worked in pen** will be eligible for any possible regrades.

Possibly useful physical constants:

Avogadro's number: $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

Electron charge: $-e = -1.602 \times 10^{-19} \text{ C}$

Permittivity of vacuum: $\epsilon_0 = 8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$

Two pages that may contain useful data follow this page.

Problem 1: 23 of 25 points

Problem 2: 20 of 25 points

Problem 3: 24 of 25 points

Problem 4: 24 of 25 points

TOTAL:

PHYSICAL PROPERTIES OF THE ELEMENTS

F

APPENDIX

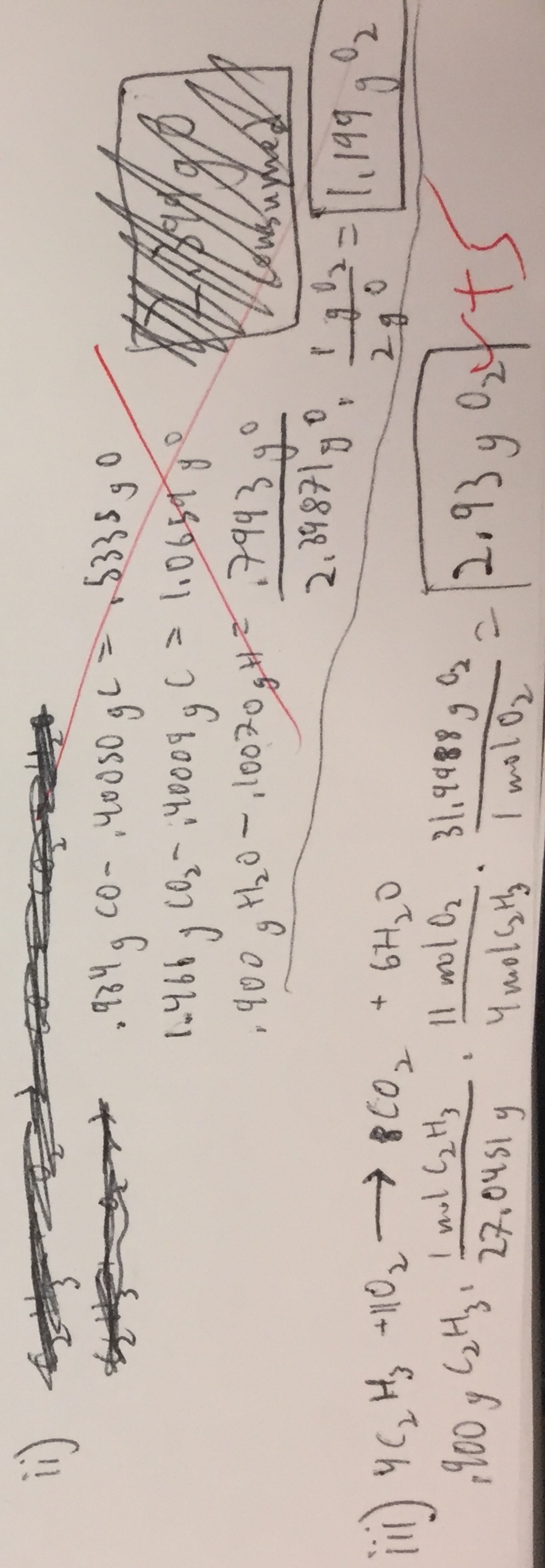
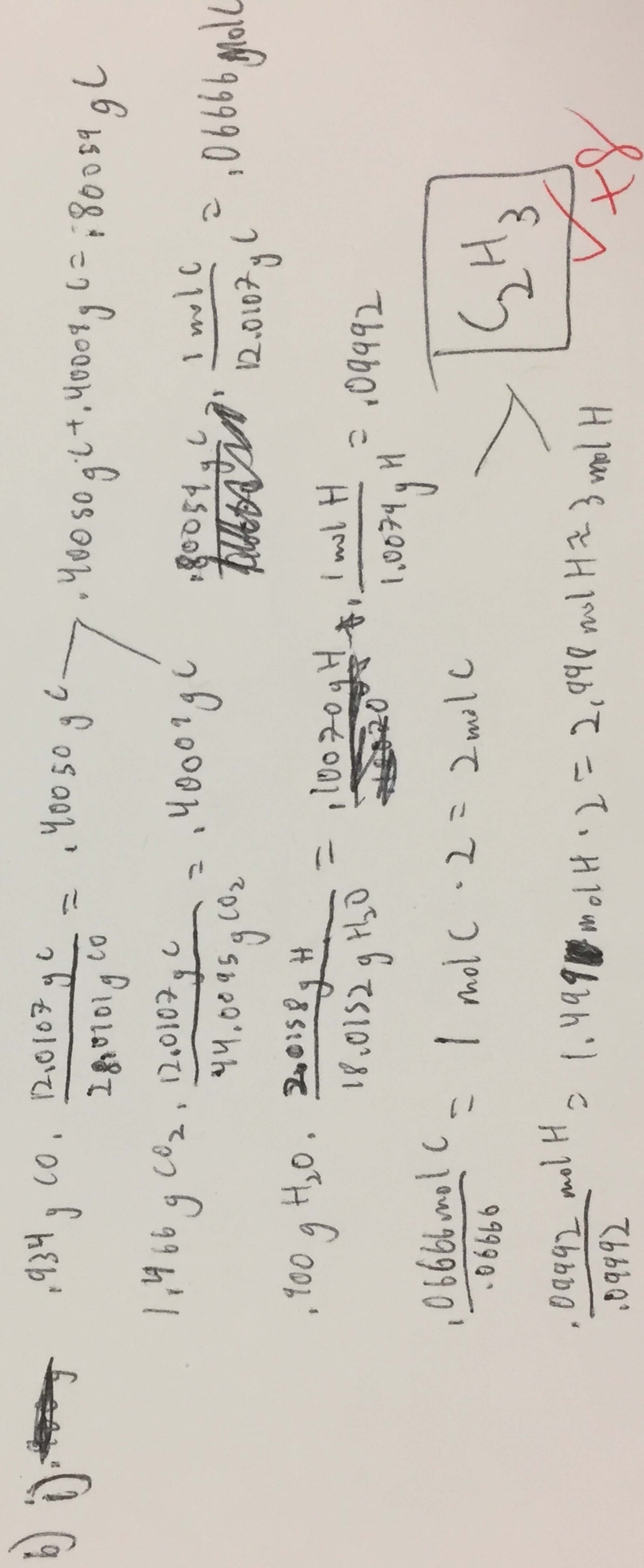
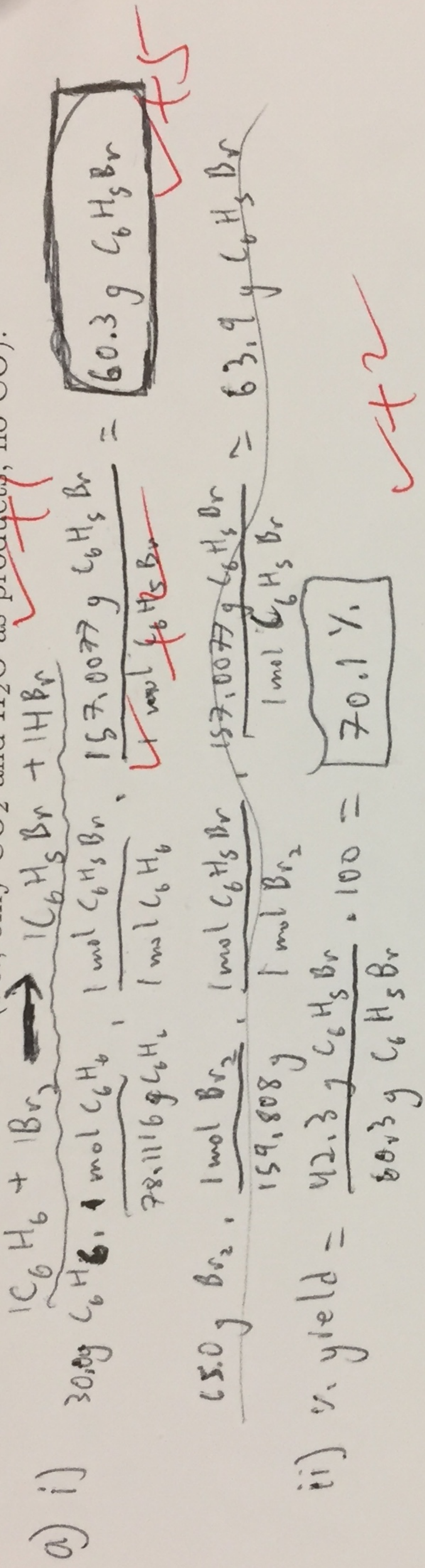
Hydrogen and the Alkali Metals (Group I Elements)

| | Hydrogen | Lithium | Sodium | Potassium | Rubidium | Cesium | Francium |
|--|--------------------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| Atomic number | 1 | 3 | 11 | 19 | 37 | 55 | 87 |
| Atomic mass | 1.00794 | 6.941 | 22.98976928 | 39.0983 | 85.4678 | 132.9054519 | (223.0197) |
| Melting point (°C) | -259.14 | 180.54 | 97.81 | 63.65 | 38.89 | 28.40 | 25 |
| Boiling point (°C) | -252.87 | 1347 | 903.8 | 774 | 688 | 678.4 | 677 |
| Density at 25°C (g cm ⁻³) | 0.070 | 0.534 | 0.971 | 0.862 | 1.532 | 1.878 | |
| | (-253°C) | | | | | | |
| Color | Colorless | Silver | Silver | Silver | Silver | Silver | |
| Ground-state electron configuration | 1s ¹ | [He]2s ¹ | [Ne]3s ¹ | [Ar]4s ¹ | [Kr]5s ¹ | [Xe]6s ¹ | [Rn]7s ¹ |
| Ionization energy [†] | 1312.0 | 520.2 | 495.8 | 418.8 | 403.0 | 375.7 | ≈400 |
| Electron affinity [†] | 72.770 | 59.63 | 52.867 | 48.384 | 46.884 | 45.505 | est. 44 |
| Electronegativity | 2.20 | 0.98 | 0.93 | 0.82 | 0.82 | 0.79 | 0.70 |
| Ionic radius (Å) | 1.46(H ⁻) | 0.68 | 0.98 | 1.33 | 1.48 | 1.67 | ≈1.8 |
| Atomic radius (Å) | 0.37 | 1.52 | 1.86 | 2.27 | 2.47 | 2.65 | ≈2.7 |
| Enthalpy of fusion [†] | 0.1172 | 3.000 | 2.602 | 2.335 | 2.351 | 2.09 | |
| Enthalpy of vaporization [†] | 0.4522 | 147.1 | 97.42 | 89.6 | 76.9 | 67.8 | |
| Bond enthalpy of M ₂ [†] | 436 | 102.8 | 72.6 | 54.8 | 51.0 | 44.8 | |
| Standard reduction potential (volts) | 0 | -3.045 | -2.7109 | -2.924 | -2.925 | -2.923 | ≈2.9 |
| | H ⁺ /H ₂ | Li ⁺ /Li | Na ⁺ /Na | K ⁺ /K | Rb ⁺ /Rb | Cs ⁺ /Cs | Fr ⁺ /Fr |

[†]In kilojoules per mole.

1(a) Benzene (C_6H_6) reacts with molecular bromine (Br_2) to produce bromobenzene (C_6H_5Br) and hydrogen bromide (HBr). (i) (8 points) What is the maximal amount of bromobenzene that can be produced when 30.0 g of benzene reacts with 65.0 g of Br_2 ? (ii) (2 points) If the actual amount of bromobenzene produced from the above mixture is 42.3 g, what is the percentage yield of the reaction?

(b) If a hydrocarbon (a compound containing only C and H) combusts in a limited amount of O_2 then, in addition to H_2O , both CO and CO_2 are produced as products. Suppose 0.900 g of a hydrocarbon is burned in a limited O_2 environment to produce 0.934 g of CO, 1.466 g of CO_2 and 0.900 g of H_2O . (a) (8 points) Determine the empirical formula for the hydrocarbon. (b) (2 points) Determine the mass of O_2 consumed in the reaction. (c) (5 points) Determine the mass of O_2 that would have been required to effect complete combustion (i.e., only CO_2 and H_2O as products, no CO).



2(a) (12 points) A sample containing only $\text{CaCO}_3(s)$ and $\text{SrCO}_3(s)$ has a mass of 0.600 g. Upon dissolution in strong acid the sample produces 0.220 g of $\text{CO}_2(g)$. Determine the mass percentage of CaCO_3 in the original sample under the assumption that all the C in the original sample is converted to CO_2 in the dissolution process.

(b) Acrylonitrile ($\text{C}_3\text{H}_3\text{N}$), an important industrial chemical, can be produced by the reaction of propylene (C_3H_6) with ammonia (NH_3) and diatomic oxygen to produce acrylonitrile and water. (i) (2 points) Write a balanced chemical equation for this reaction. (ii) (8 points) A mixture containing 30 kg each of propylene, ammonia, and oxygen react to produce acrylonitrile. What mass of acrylonitrile is produced, assuming a yield of 100%? (iii) (3 points) What is the limiting reagent for the reaction described in (ii)?

a) $0.220 \text{ g CO}_2 \cdot \frac{12.0107 \text{ g C}}{44.0095 \text{ g CO}_2} = 0.004999 \text{ mol C}$ X1

$x \text{ mol C} \cdot \frac{1 \text{ mol CaCO}_3}{1 \text{ mol C}} + (0.600 - x) \text{ mol C} \cdot \frac{1 \text{ mol SrCO}_3}{1 \text{ mol SrCO}_3} = 0.004999 \text{ mol C}$ X1

how did you get this equation?

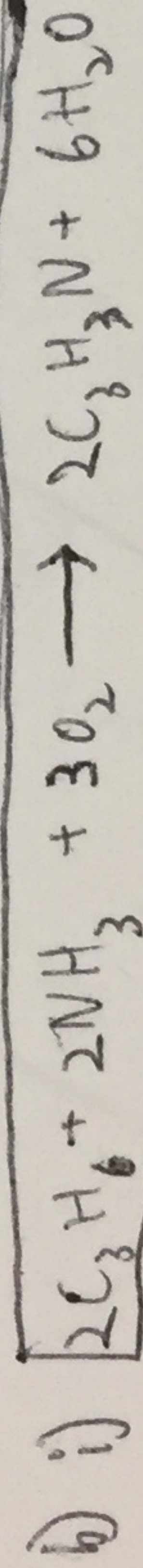
$100.0869x \text{ g CaCO}_3 + (0.600 - x) \text{ g SrCO}_3 = 0.600 \text{ g sample}$

$-47.542x = -0.13799$

$x = 0.0029024$ +2

$0.0029024 \text{ mol C} \cdot \frac{100.0869 \text{ g CaCO}_3}{1 \text{ mol CaCO}_3} = 0.29049 \text{ g CaCO}_3$ +2

mass % $\text{CaCO}_3 = \frac{0.29049 \text{ g CaCO}_3}{0.600 \text{ g sample}} \cdot 100 = 48.41\% \text{ CaCO}_3$ +2



ii) $30 \text{ kg C}_3\text{H}_6 \cdot \frac{1000 \text{ g}}{1 \text{ kg}} \cdot \frac{1 \text{ mol C}_3\text{H}_6}{42.0795 \text{ g C}_3\text{H}_6} = 714.286 \text{ mol C}_3\text{H}_6$

$30 \text{ kg NH}_3 \cdot \frac{1000 \text{ g}}{1 \text{ kg}} \cdot \frac{1 \text{ mol NH}_3}{17.0304 \text{ g NH}_3} = 1755.3 \text{ mol NH}_3$

$30 \text{ kg O}_2 \cdot \frac{1000 \text{ g}}{1 \text{ kg}} \cdot \frac{1 \text{ mol O}_2}{31.9988 \text{ g O}_2} = 937.5 \text{ mol O}_2$

$2 \text{ mol C}_3\text{H}_6 \rightarrow 2 \text{ mol C}_3\text{H}_3\text{N}$

$714.286 \text{ mol C}_3\text{H}_6 \cdot \frac{2 \text{ mol C}_3\text{H}_3\text{N}}{2 \text{ mol C}_3\text{H}_6} = 714.286 \text{ mol C}_3\text{H}_3\text{N}$

$714.286 \text{ mol C}_3\text{H}_3\text{N} \cdot \frac{53.0625 \text{ g C}_3\text{H}_3\text{N}}{1 \text{ mol C}_3\text{H}_3\text{N}} = 37830 \text{ g C}_3\text{H}_3\text{N}$

$37830 \text{ g C}_3\text{H}_3\text{N} = 37.83 \text{ kg C}_3\text{H}_3\text{N}$

iii) O_2 produced the least $\text{C}_3\text{H}_3\text{N}$, so O_2 is the limiting reagent

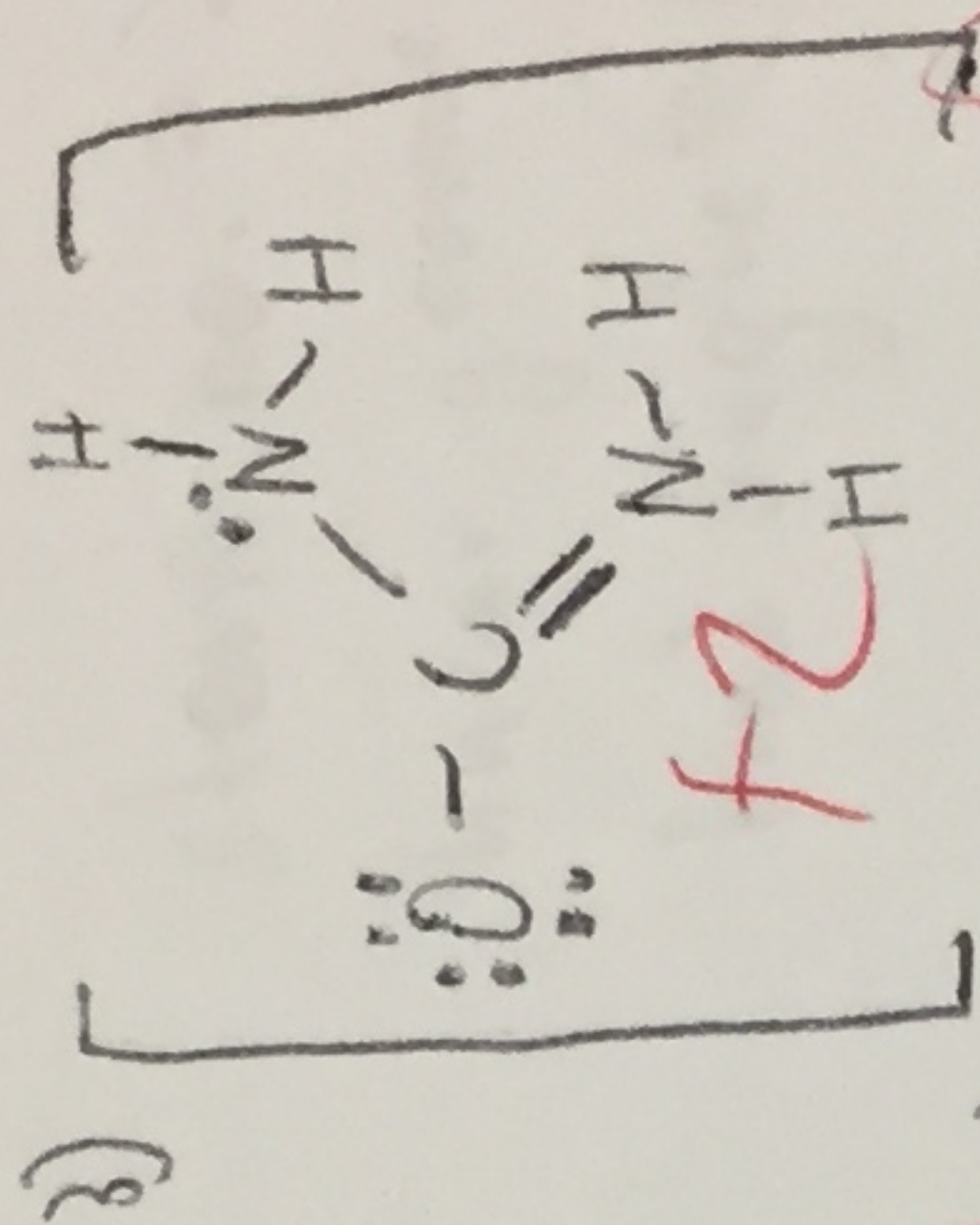
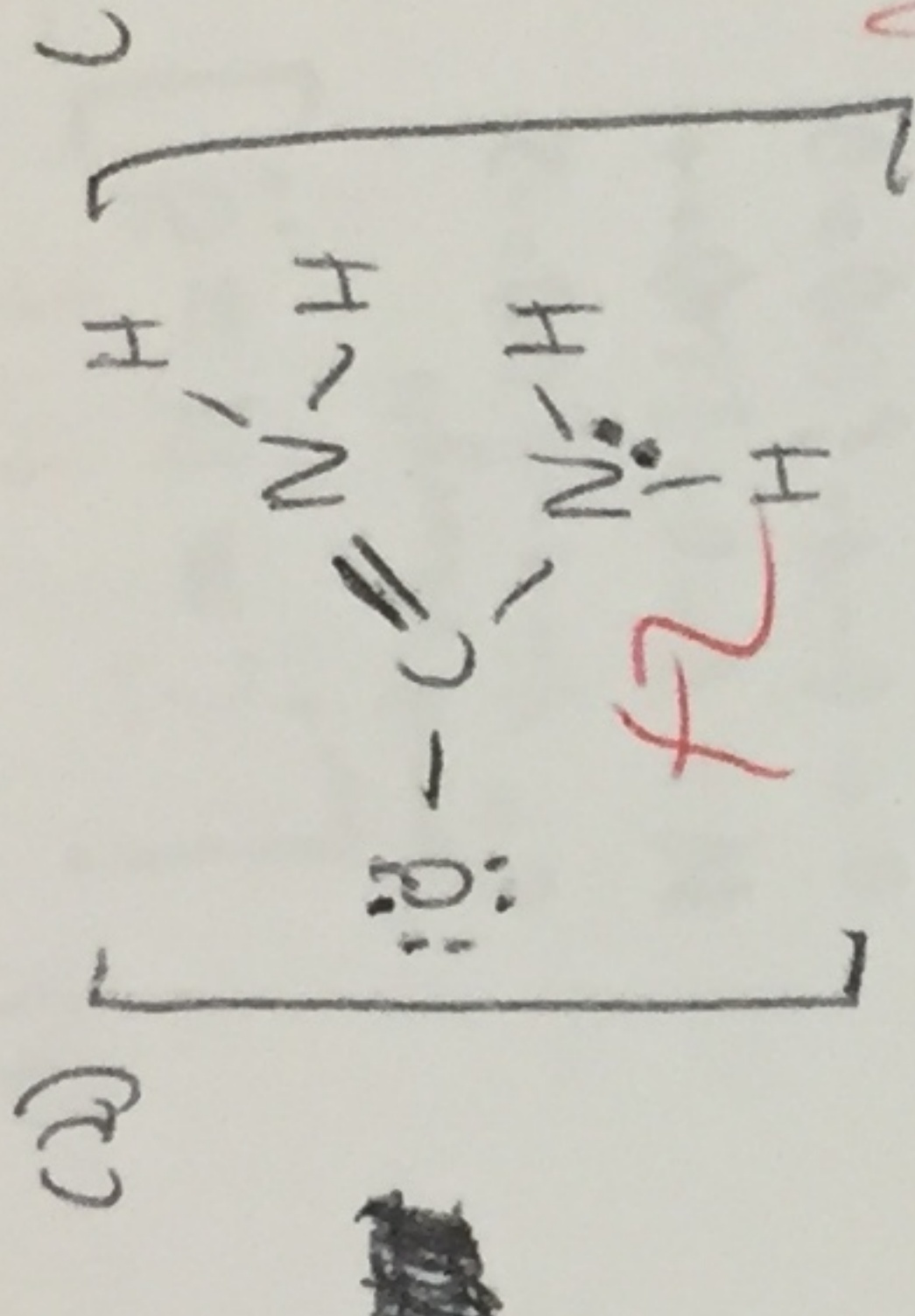
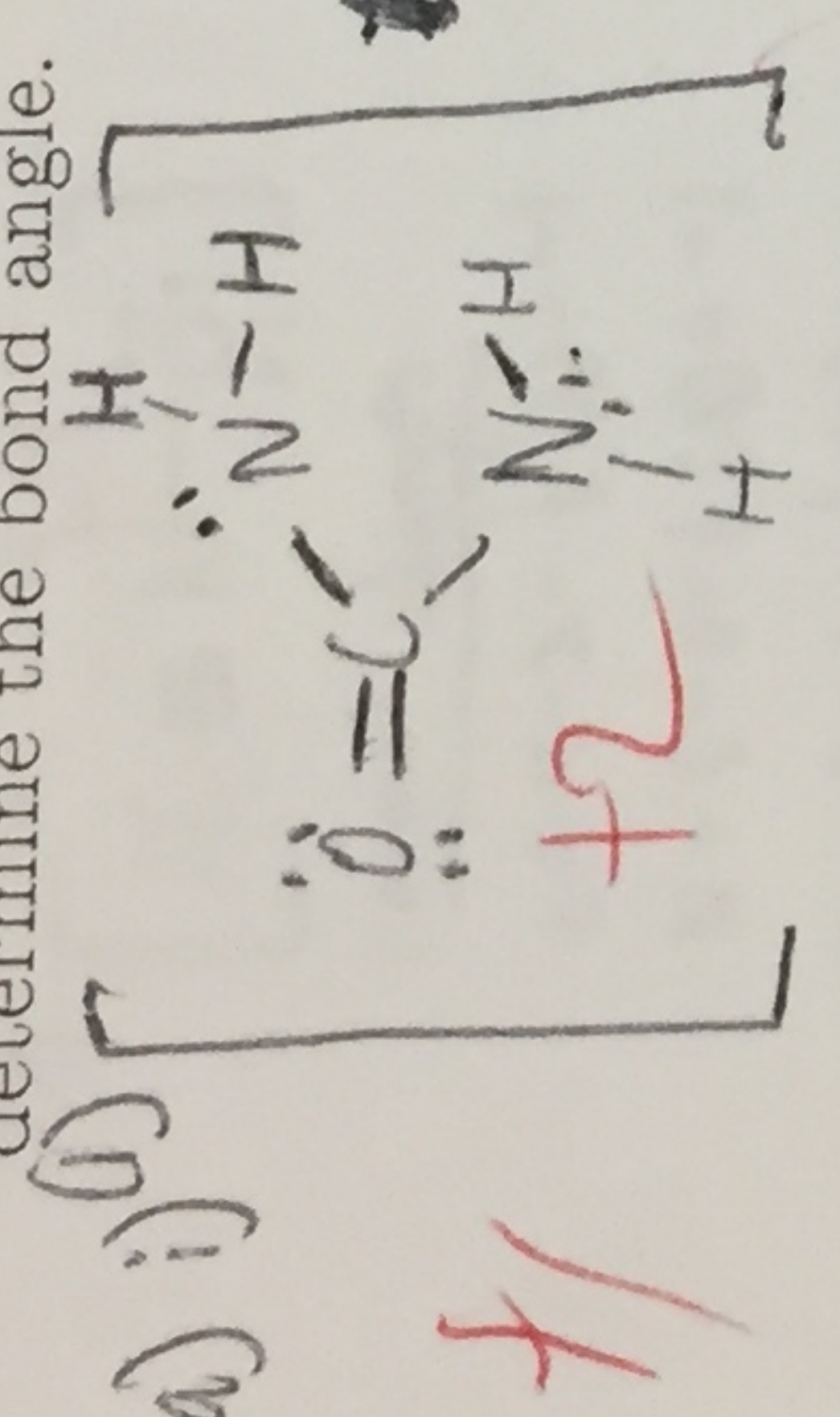
+13

3(a) Urea has the chemical formula $\text{OC}(\text{NH}_2)_2$. It has one CO bond and two CN bonds. Each of the N atoms is also bonded to two H atoms. (i) (7 points) Draw the three most important Lewis-structure resonance forms for the molecule (these need not all be equivalent resonance structures). (ii) (3 points) Based on a formal charge analysis predict which resonance structure(s) is(are) likely to contribute most to the bonding in the molecule. (iii) (5 points) It happens that urea is a planar species with all its bond angles equal to roughly 120° . Is this geometry consistent with the "dominant" resonance structure from (ii)? Explain your answer fully by making reference to VSEPR theory.

(b) (10 points) Draw two acceptable (i.e., all valence shells filled) Lewis structures for both (i) NCO^- (the C is bonded to the N and to the O) and (ii) CNO^- (the N is bonded to the C and to the O). For each identify the Lewis structure that would be expected to contribute most to the bonding in the molecule and apply VSEPR to determine the bond angle.

$\text{C}: 4e^- \cdot 1 = 4e^-$
 $\text{O}: 6e^- \cdot 1 = 6e^-$
 $\text{N}_1: 5e^- \cdot 2 = 10e^-$
 $\text{H}: 1e^- \cdot 4 = 4e^-$
Total valence $e^- = 24e^-$

N_1 is top N,
 N_2 is bottom N



ii) (i) $\text{FC}(\text{O}) = 6 - 4 - \frac{1}{2}(4) = 0$
 $\text{FC}(\text{C}) = 4 - 0 - \frac{1}{2}(8) = 0$
 $\text{FC}(\text{N}_1) = 5 - 2 - \frac{1}{2}(6) = 0$
 $\text{FC}(\text{N}_2) = 5 - 2 - \frac{1}{2}(6) = 0$
 $\text{FC}(\text{H}) = 1 - 0 - \frac{1}{2}(2) = 0$

(ii) $\text{FC}(\text{O}) = 6 - 6 - \frac{1}{2}(2) = -1$
 $\text{FC}(\text{C}) = 4 - 0 - \frac{1}{2}(8) = 0$
 $\text{FC}(\text{N}_1) = 5 - 0 - \frac{1}{2}(8) = +1$
 $\text{FC}(\text{N}_2) = 5 - 2 - \frac{1}{2}(6) = 0$
 $\text{FC}(\text{H}) = 1 - 0 - \frac{1}{2}(2) = 0$

(iii) $\text{FC}(\text{O}) = 6 - 6 - \frac{1}{2}(2) = -1$
 $\text{FC}(\text{C}) = 4 - 0 - \frac{1}{2}(8) = 0$
 $\text{FC}(\text{N}_1) = 5 - 2 - \frac{1}{2}(6) = 0$
 $\text{FC}(\text{N}_2) = 5 - 0 - \frac{1}{2}(8) = +1$
 $\text{FC}(\text{H}) = 1 - 0 - \frac{1}{2}(2) = 0$

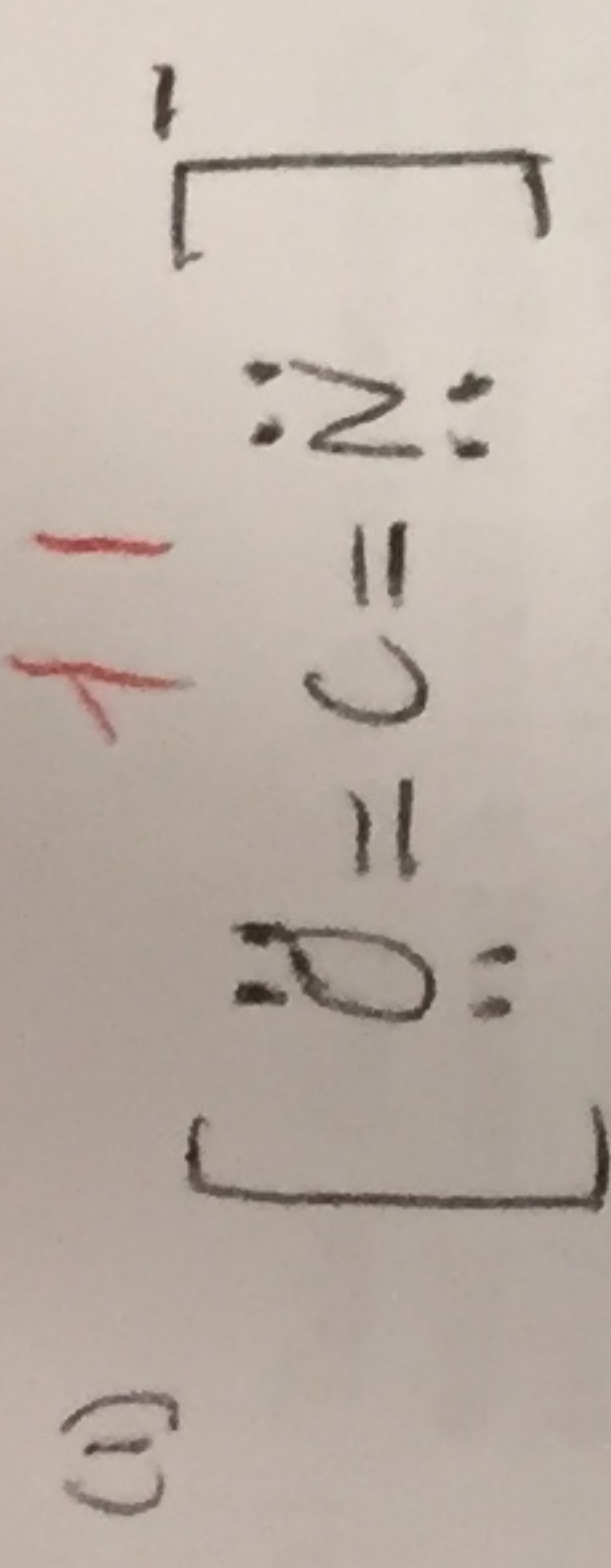
Since structure (i) has all atoms with formal charges of zero as well as the sum of the formal charges equal to zero, it will contribute most to the bonding in the molecule. Though (ii) and (iii) have sums of zero, each has a formal charge of -1 on the O atom and a formal charge of +1 on an N atom, making each less dominant than structure (i).

iii) In structure (i), the geometry at the C atom will be planar as its steric number of 3 and lack of lone pairs gives it trigonal planar geometry. However, at each N atom, the geometry will be trigonal pyramidal due to the steric number of 4 with one lone pair. This causes the H atoms to break from the plane created by the geometry about the C atom at an angle of approximately 109.5° . This means the geometry of the urea molecule is inconsistent with the geometry of the "dominant" resonance structure from (ii).

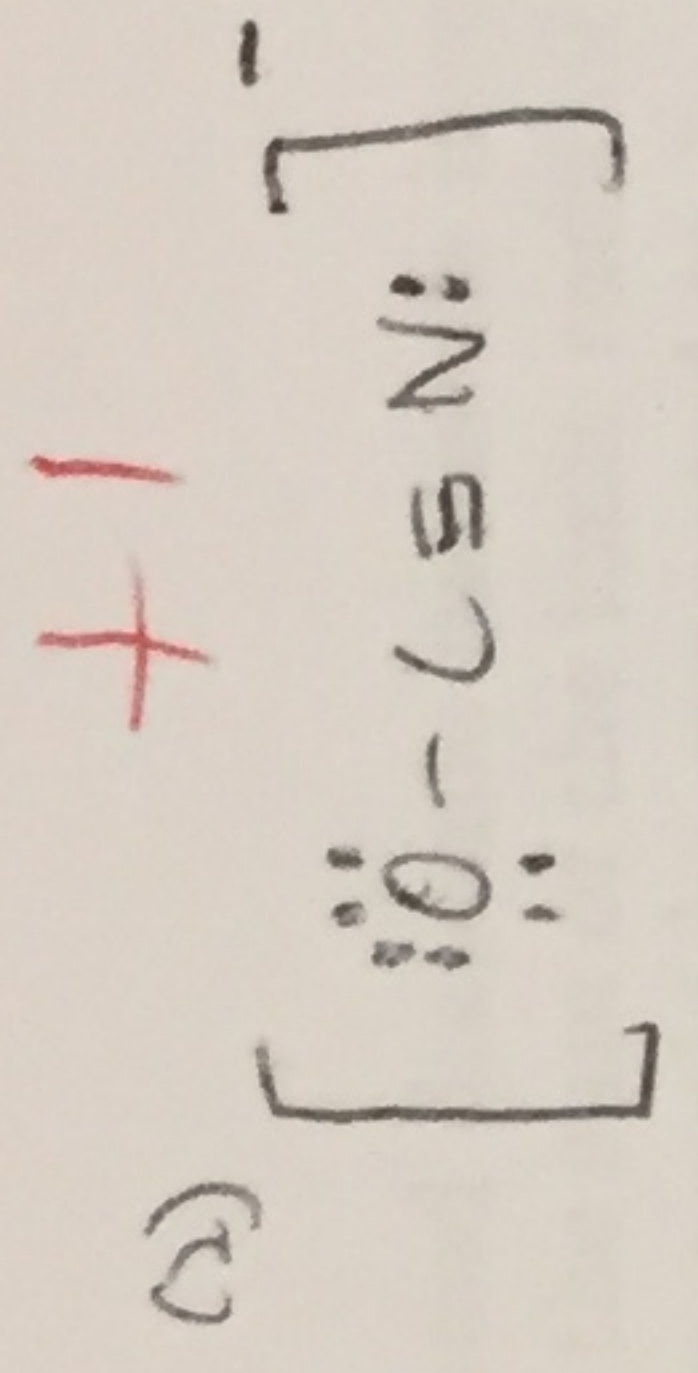
(Part b on next page)

b) i) NCO^-

$\text{C} = 4e^-$
 $\text{O} = 6e^-$
 $\text{charge} = 1e^-$
 total $16e^-$
 volume



Formal charges:
 $\text{O} = 6 - 4 - \frac{1}{2}(4) = 0$
 $\text{C} = 4 - 0 - \frac{1}{2}(8) = 0$
 $\text{N} = 5 - 4 - \frac{1}{2}(4) = -1$

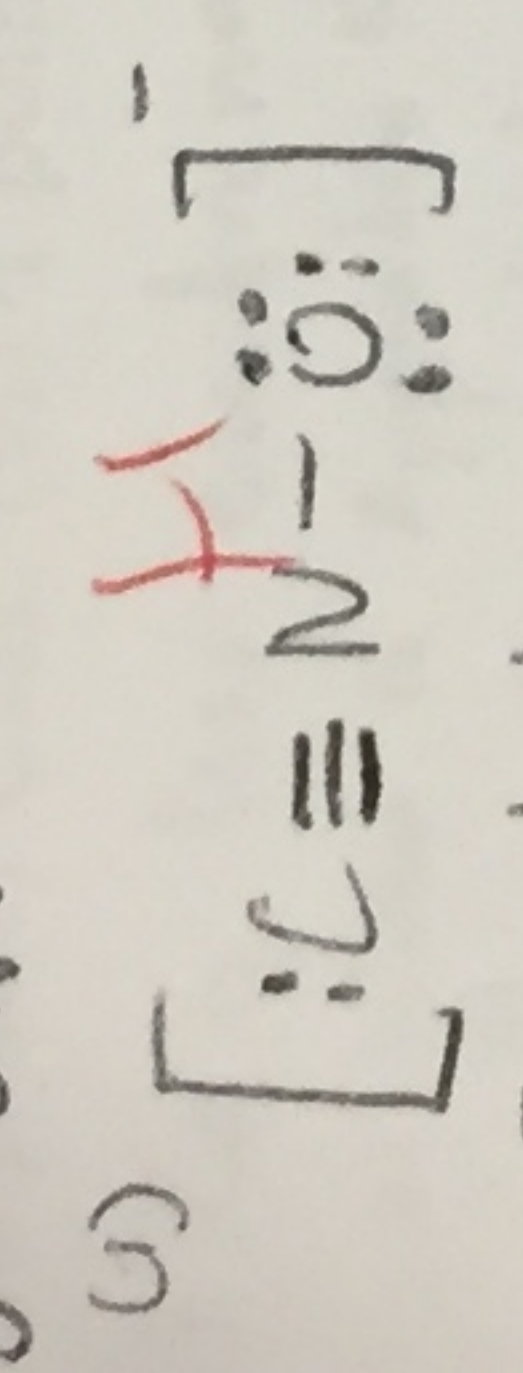


Formal charges:
 $\text{O} = 6 - 6 - \frac{1}{2}(2) = -1$
 $\text{C} = 4 - 0 - \frac{1}{2}(8) = 0$
 $\text{N} = 5 - 2 - \frac{1}{2}(6) = 0$

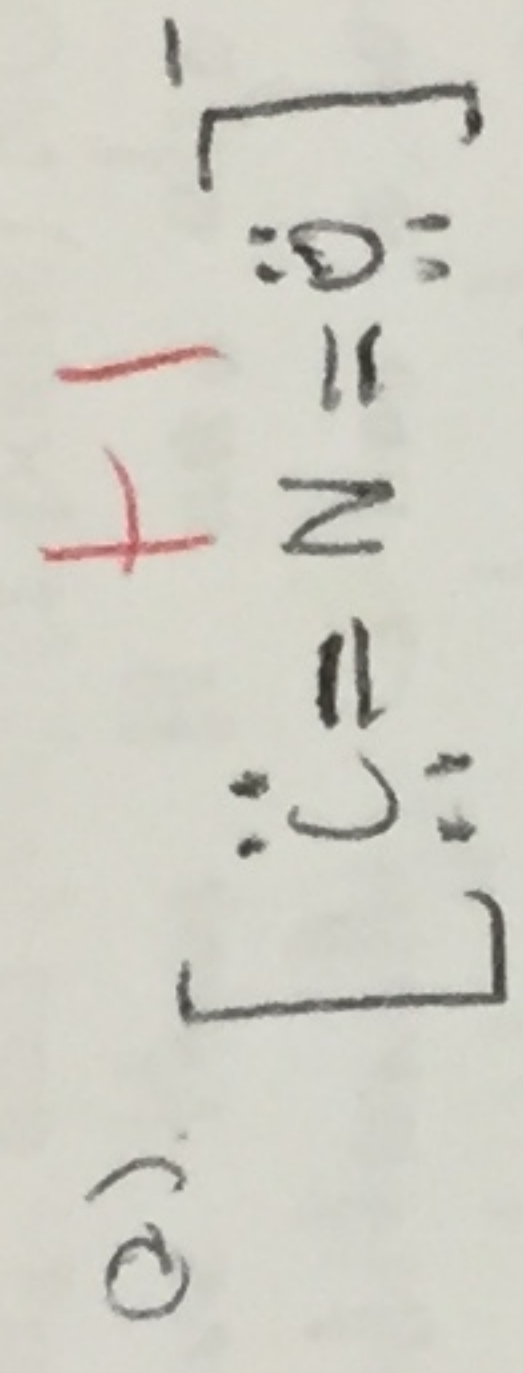
steric no. = 2
 linear geometry
 bond angle = 180°

Structure (2) is expected to contribute most since O is more electronegative than N, so it is more likely to adapt a formal charge of -1, both are likely to contribute, though.

ii) CNO^-



Formal charges:
 $\text{C} = 4 - 2 - \frac{1}{2}(6) = -1$
 $\text{N} = 5 - 0 - \frac{1}{2}(8) = +1$
 $\text{O} = 6 - 6 - \frac{1}{2}(2) = -1$



Formal charges:
 $\text{C} = 4 - 4 - \frac{1}{2}(4) = -2$
 $\text{N} = 5 - 0 - \frac{1}{2}(8) = +1$
 $\text{O} = 6 - 4 - \frac{1}{2}(4) = 0$

steric no. = 2
 linear geometry
 bond angle = 180°

Structure (1) will be favored since there is a more even distribution of formal charge across the molecule, with no atom's charge having a magnitude greater than 1, whereas structure (2) has a magnitude of 2 in the negative on carbon.

9

Same

4(a) Take CsH to be an ionically bonded diatomic molecule involving singly-charged ions and having a bond length that is the sum of the ionic radii of the cation and the anion. (i) (3 points) Identify which atom would be expected to be the cation. Support your answer fully. (ii) (6 points) Estimate the energy required to dissociate the diatomic to form the separated neutral atoms. In making this estimate neglect the short-range repulsion contribution to the diatomic's energy. (iii) (7 points) Sketch a diagram of the potential energy of the diatomic as a function of the distance between the nuclei. On this diagram set the zero of the potential energy to that of the separated neutrals. Indicate on the diagram the energy of dissociation from part (ii) and the equilibrium bond distance of the diatomic.

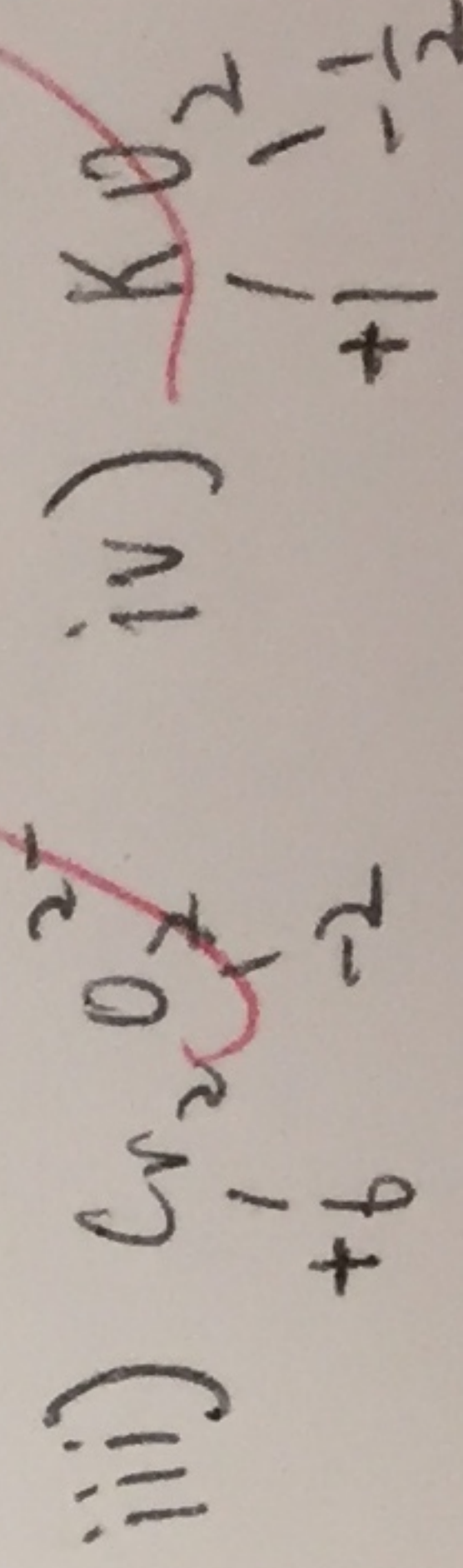
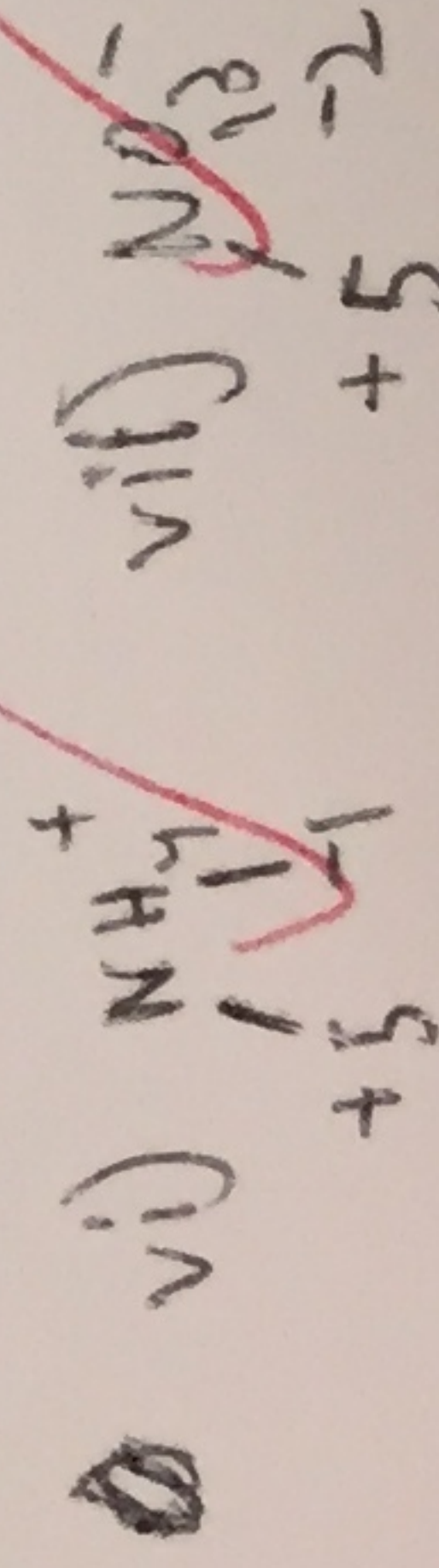
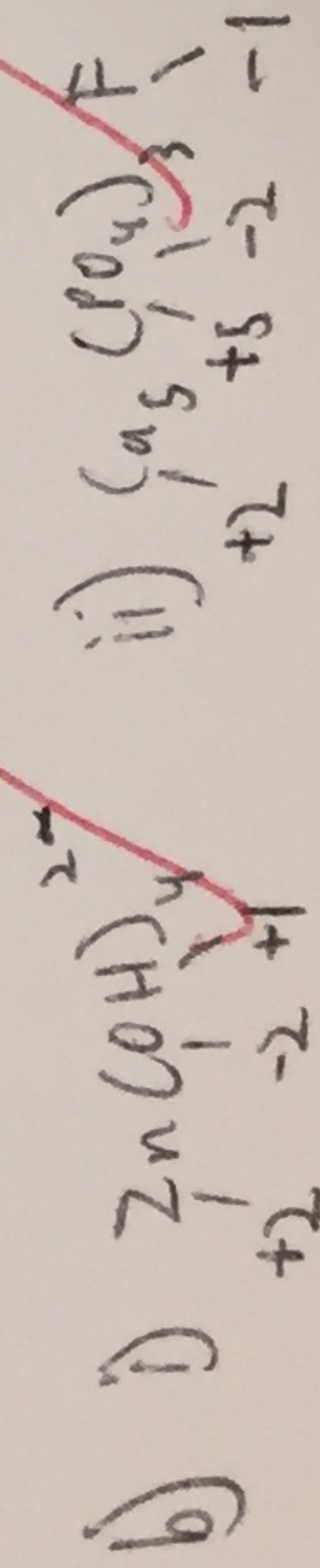
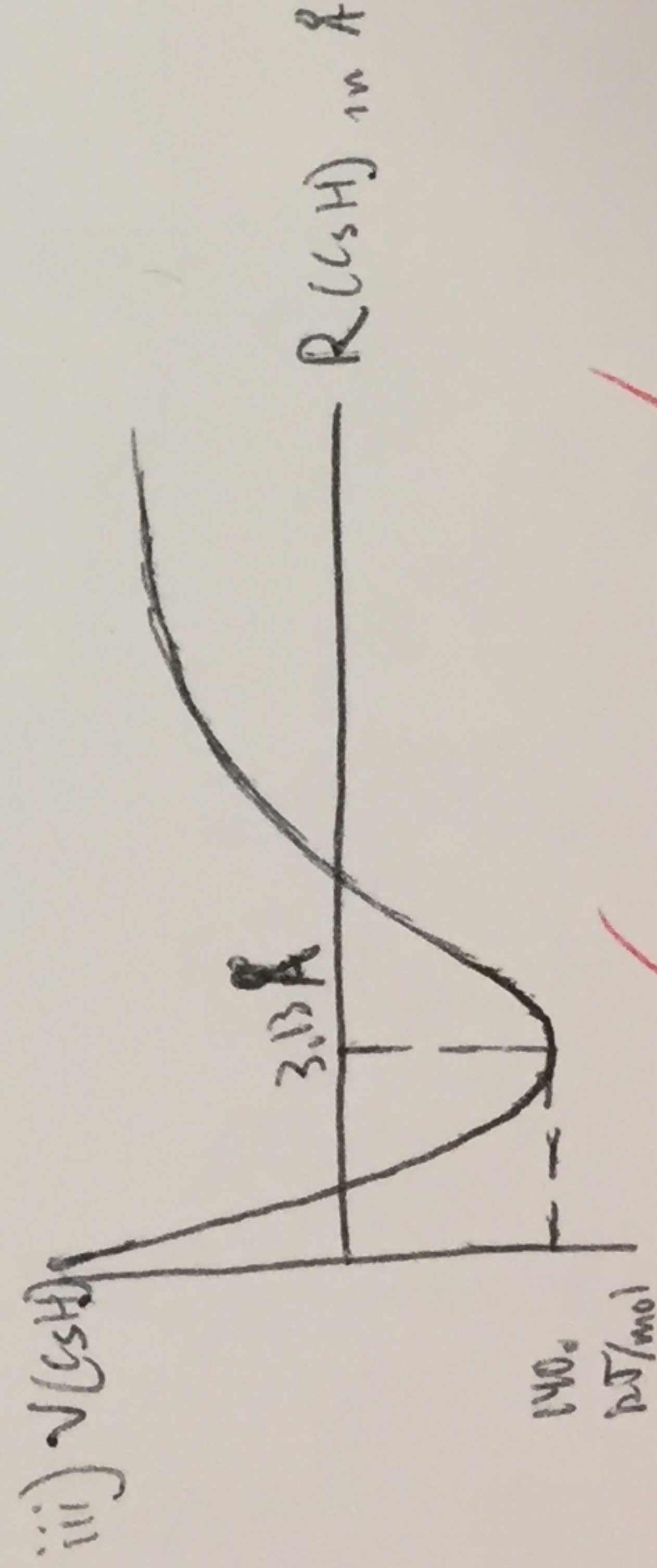
(b) Assign oxidation numbers to the atoms in each of the following species: (i) (2 points) $\text{Zn}(\text{OH})_4^{2-}$, (ii) (2 points) $\text{Ca}_5(\text{PO}_4)_3\text{F}$, (iii) (1 point) $\text{Cr}_2\text{O}_7^{2-}$, (iv) (1 point) KO_2 , (v) (1 point) CsH , (vi) (1 point) NH_4^+ , and (vii) (1 point) NO_3^- .

a) i) Cs is less electronegative than H and also has a lower electron affinity as given in Appendix F. Additionally, Cs has a lower first ionization energy as its valence electrons are held more loosely since they are farther from the nucleus, as evidenced again by Appendix F. As such, Cs is expected to lose an electron and become the cation while H gains an electron and becomes the anion.

$$\text{ii) } \Delta E_d = \frac{-q_1 q_2}{4\pi \epsilon_0 r} - E_{\infty} - E_{\infty}, \quad E_{\infty} = \text{IE}_1(\text{Cs}) - \text{EA}(\text{H}) = 302.43 \text{ kJ/mol}$$

$$\Delta E_d = \frac{-(-1.602 \times 10^{-19} \text{ C})(1.602 \times 10^{-19} \text{ C})}{4\pi (8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1})(3.13 \times 10^{-10} \text{ m})} - 302.43 \text{ kJ/mol}$$

$$= 44361 \frac{\text{kJ}}{\text{mol}} - 302.43 \text{ kJ/mol} = \boxed{140. \text{ kJ/mol}}$$



(1)