

Name

Student number

Test 2 for AESB1120ST

10 October 2014, from 10.45 - 12.30

On chapter 7-11, 15,18 from "Principles of Chemistry", Nivaldo Tro

- **FIRST, PLEASE READ THIS PAGE CAREFULLY**
- Please mark each page of this exam with your name and student number.
- This exam consists of 4 problems and counts 8 pages, including this cover page. Each problem consists of a number of questions.
- You will have 1 hour and 45 minutes (105 minutes) to complete this test.
- During the first 30 minutes of the test you are not allowed to leave the room.
- You will be able to score 90 points for this exam, and 10 points for marking each page of your answers to this exam with your name and student number.
- $\text{Mark Test 1} = (\text{total number of earned points}) / 10$
- First, study the problem carefully and prepare your answer on scratch paper. Then, write your answer in the open space on the problems sheets.
- The problems should be answered in either Dutch or English, in clear hand-written text.
- The completed exam consisting of the problem sheets with answers should be handed in. You are not allowed to keep this exam.
- The exam with the correct answers will be published on the Blackboard pages for this course the next working day following the exam.
- The results of this exam will be published on the Blackboard pages for this course on October 17.
- This exam was composed by J. van Esch and R. Eelkema.
- Mobile telephones and other communication devices should be switched off and stored out of reach.
- **Before continuing, mark each page of this exam with your name and student number.**

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Problem 1 (25 points)

a) For the following elements, (1) give the electron configuration with the correct atomic orbitals, (2) clearly indicate which electrons are the core electrons and which electrons are the valence electrons, and (3) give the charge and electron configuration of the most stable ion formed by these elements. (9 points)

(i) Br

35 electrons. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4p^2 4px^2 4py^2 4pz^1$
($1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$) core ($4p^2 4px^2 4py^2 4pz^1$) valence
 Br^- $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4p^2 4px^2 4py^2 4pz^2$

(ii) P

15 electrons. $1s^2 2s^2 2p^6 3s^2 3px^1 3py^1 3pz^1$
($1s^2 2s^2 2p^6$) core ($3s^2 3px^1 3py^1 3pz^1$) valence
 P^{3-} $1s^2 2s^2 2p^6 3s^2 3p^6$

(iii) Ca

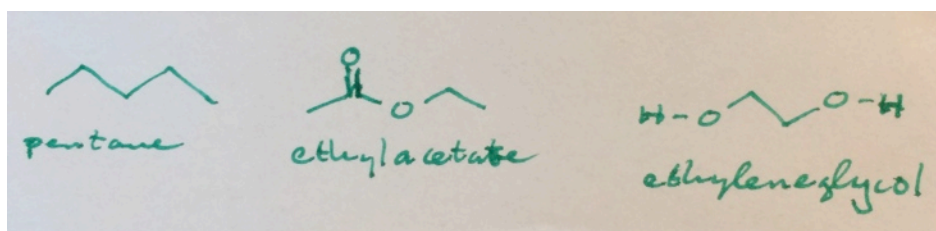
20 electrons. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
($1s^2 2s^2 2p^6 3s^2 3p^6$) core ($4s^2$) valence
 Ca^{2+} $1s^2 2s^2 2p^6 3s^2 3p^6 (4s^0)$

b) Organize the following compounds in terms of viscosity (lower to higher), and explain your answer (8 points):

$HOCH_2CH_2OH$ (ethylene glycol), $CH_3CH_2CH_2CH_2CH_3$ (*n*-pentane), $CH_3C(=O)OCH_3$ (ethyl acetate)

pentane < ethylacetate < ethylene glycol

viscosity scales with the magnitude of intermolecular interactions. pentane has only dispersion forces, ethylacetate has dispersion forces and a dipole moment, ethylene glycol has dispersion forces, a dipole moment and hydrogen bonds. Typically forces are dispersion \ll dipole-dipole < hydrogen bonds, hence the order.



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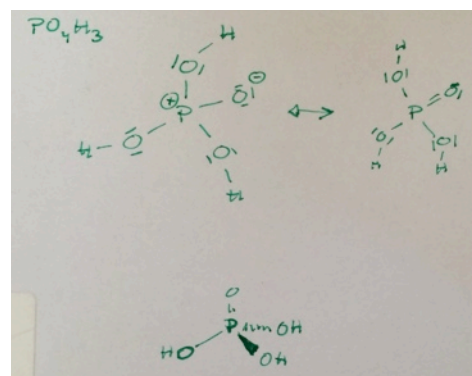
c) What is the 3D structure of (i) PO_4H_3 , and (ii) CH_3COCH_3 ? Explain your answer using Lewis structure drawings and VSEPR theory (8 points).

(i) PO_4H_3

valence electrons: $\text{P}=5$, $\text{O} = 4 \cdot 6$, $\text{H}=3 \cdot 1$, combined = 32 electrons = 16 pairs

4 groups around P, no lone pairs \Rightarrow VSEPR says tetrahedron.

we only marked the 3D geometry around the central atom.



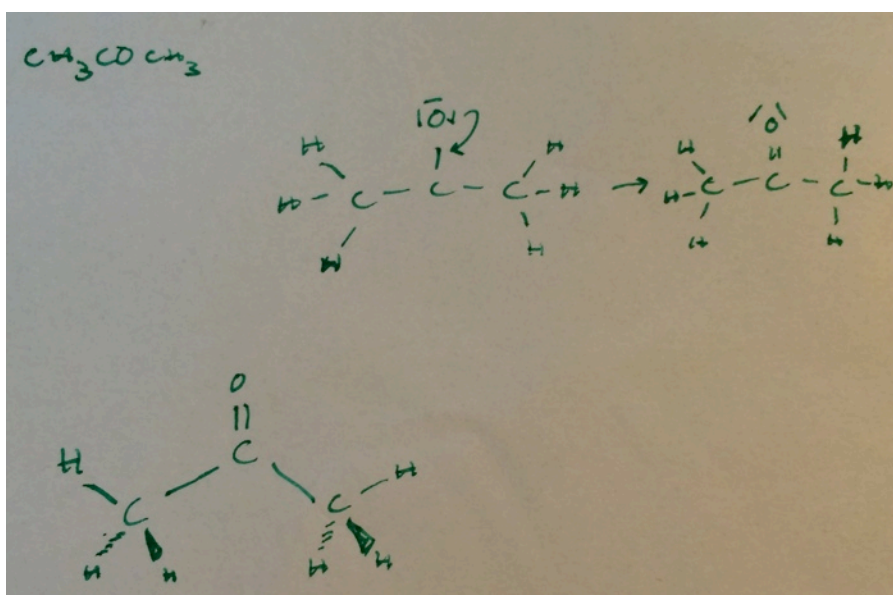
(ii) CH_3COCH_3

valence electrons: $\text{O}=6$, $\text{C} = 3 \cdot 4$, $\text{H}=6 \cdot 1$, combined = 24 electrons = 12 pairs

outer carbons: 4 groups around C, no lone pairs \Rightarrow VSEPR says tetrahedron.

inner carbon: 3 groups around C, no lone pairs \Rightarrow VSEPR says trigonal planar.

we only marked the 3D geometry around the central atom.



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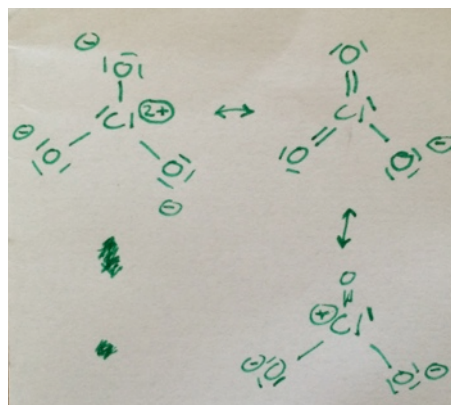
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Problem 2 (22 points)

a) Draw the complete Lewis structure (including free electron pairs) of the following compounds. (6 points)

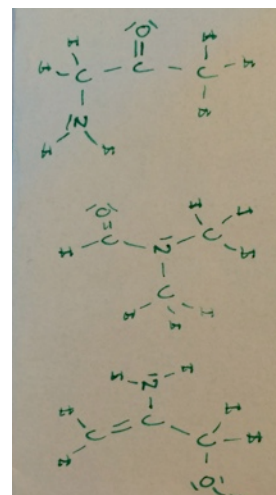
(i) ClO_3^-

valence electrons: $\text{Cl}=7$, $\text{O} = 3 \cdot 6$, charge = 1,
combined = 26 electrons = 13 pairs



(ii) $\text{C}_3\text{H}_7\text{NO}$ (several isomers possible, draw two)

valence electrons: $\text{N}=5$, $\text{O} = 6$, $\text{C} = 3 \cdot 4$, $\text{H} = 7 \cdot 1$, combined = 30
electrons = 15 pairs



b) True or False? Indicate if the statements below are true or false. When you indicate False, explain your answer in 1-2 lines or a simple drawing. (16 points)

(i) Because of the polarizability of oxygen, ClO_4H is a stronger acid than ClOH

False: oxygen is hardly polarizable. In this case it is either the electronegativity of O, or resonance in the conjugate base (more possible forms for ClO_4^-).

(ii) Atomic orbitals: the $n=4$ level has 16 orbitals.

True

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(iii) The Aufbau principle says that you fill degenerate orbitals first.

False: Aufbau says that you fill the lowest energy orbitals first.

(iv) At the Triple Point in a typical phase diagram, when you lower the temperature you get a solid.

True

(v) NH_4Cl has a high melting point because of the dipole in the NH_4^+ cation.

False: NH_4^+ has a tetrahedral geometry and hence no dipole. The high melting point stems from the strong ion-ion interactions.

(vi) A liquid reaches its boiling point when its vapor pressure is equal to the external pressure.

True

(vii) Dispersion forces are generally stronger than dipole-dipole interactions.

False: dispersion forces are the weakest intermolecular forces known.

(viii) Na^+ is smaller than K^+ because of shielding.

False: Shielding experience by the outer shell electrons is equal in both; the size depends on the distance of the $n=2$ (Na^+) and $n=3$ (K^+) shells to the nucleus.

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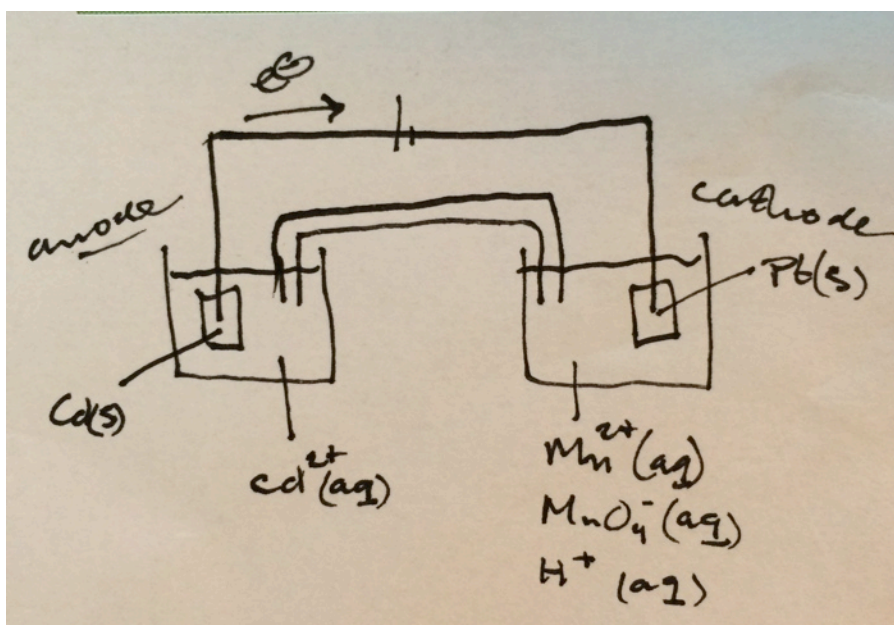
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Problem 3 (25 points)

A hypothetical electrochemical cell has the following cell diagram:



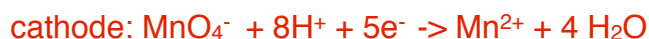
- a) draw such a galvanic cell, consisting of a platinum electrode in 100 mL aqueous 1M $\text{Mn}(\text{NO}_3)_2$ solution, and a cadmium electrode in 100 mL aqueous 1M $\text{Cd}(\text{NO}_3)_2$ solution. The solutions are connected by a salt bridge, and the electrodes can be connected with a copper wire. Indicate in your drawing what are the cathode and the anode, the contents of each half cell, and in which direction the current will flow when the anode and cathode are connected. (6p).



Electrons flow from anode to cathode. Formally, current goes in the opposite direction. Both were awarded points.

WARNING: we mistakenly left out the MnO_4^- and H^+ concentrations in this question. In the current setup, the current would actually run the other direction. The drawing is the cell under standard conditions. Both answers are correct, as long as they are motivated. Answers involving solid Mn were also awarded points but not full marks as Mn is not listed.

- b) What is the potential of the simple galvanic cell in problem 3a? Explain your answer using a simple calculation. Give the two half reactions, the final reaction and the cell potential under standard conditions. (8p)



$$\text{cathode: } +1.51\text{V}; \text{ anode } -0.40\text{V}; E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = 1.51 - (-0.4) = +1.91\text{V}$$

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- c) When the cathode and anode are connected through a lamp, this lamp will light up because the cell will generate a current. Indicate what happens in the galvanic cell with the concentrations of the Cd^{2+} ions, the Mn^{2+} ions, and the cell potential after the cell has generated a current for some time, and explain your answer. (5 points).

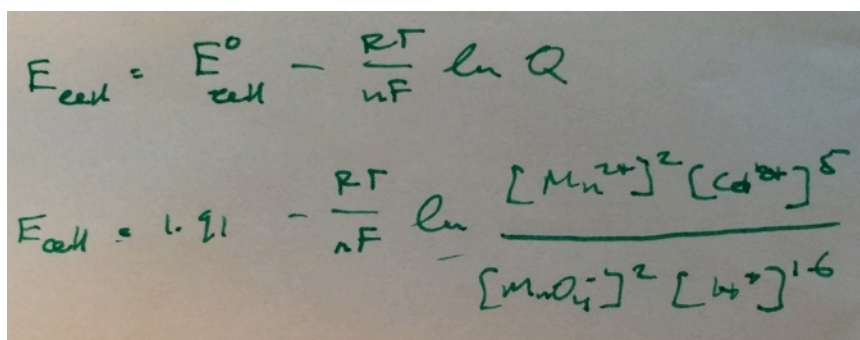
$[\text{Cd}^{2+}]$, $[\text{Mn}^{2+}]$ will increase over time. As they increase, the potential of the cell will drop as more product is made and reactants are depleted, making the reaction less favorable. Using the Nernst equation you can show that Q increases, making E_{cell} decrease. Finally the potential will reach zero.

WARNING: we mistakenly left out the MnO_4^- and H^+ concentrations in question 3a. So if you say that this is a (nearly) dead cell, you'd be correct and get points. The answer above is under standard conditions, also correct.

- d) How would you increase the cell potential of this cell? Provide a method that does not involve changing the chemical elements involved and explain what will happen using a simple calculation. (6 points)



Nernst equation:


$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln Q$$
$$E_{\text{cell}} = 1.91 - \frac{RT}{nF} \ln \frac{[\text{Mn}^{2+}]^2 [\text{Cd}^{2+}]^5}{[\text{MnO}_4^-]^2 [\text{H}^+]^{16}}$$

so either increasing the concentration of MnO_4^- or H^+ , or decreasing the concentration of Mn^{2+} or Cd^{2+} will increase E_{cell} .

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Problem 4 (18 points)

Acetone (C_3H_6O) is a common solvent, widely used in consumer products and in the chemical industry. Acetone has the following physical properties:

b.p. 329.3 K (1 atm)

m.p. 178.7 K (1 atm)

vapor pressure at various temperatures: 9.39 kPa (0 °C); 30.6 kPa (25 °C); 374 kPa (100 °C); 2.8 MPa (200 °C)

triple point 178.5 K at $2.75 \cdot 10^{-5}$ bar

critical point 508 K at 48 bar

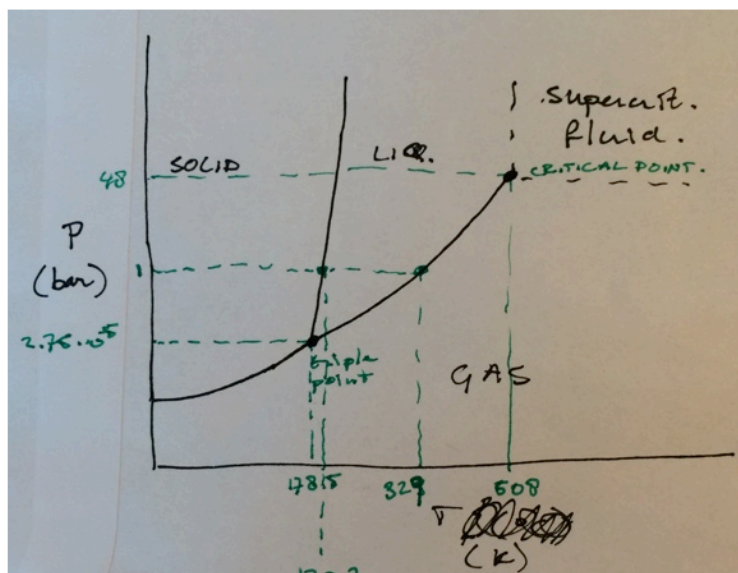
ΔH_{fus} 5.69 kJ/mol (assume independent of temperature)

ΔH_{vap} 31 kJ/mol (assume independent of temperature)

Heat capacities: C_p (liquid) 125.5 J/(mol*K) (assume independent of temperature)

C_p (gas) 75 J/(mol*K) (assume independent of temperature)

a) Using the data listed, draw the phase diagram of acetone, indicating the various phases, the melting point, boiling point, triple point and critical point. (9 points)



b) Acetone (200 grams) is heated from 89 °C to 124 °C at a constant pressure of 374 kPa. Calculate the amount of heat needed for this process, and clearly show how you obtained your answer. (9 points)

200 grams acetone (molecular weight = 58): $200/58 = 3.45$ mol.

at 374 kPa, acetone boils at 100 degrees C, where the vapor pressure is equal to the external pressure. Then, three calculations:

heating 89-100 degrees C: 11 degrees. $q = n \cdot C_p(\text{liq}) \cdot \Delta T = 3.45 \cdot 125.5 \cdot 11 = 4.8$ kJ

heating 100-124 degrees C: 24 degrees. $q = n \cdot C_p(\text{gas}) \cdot \Delta T = 3.45 \cdot 75 \cdot 24 = 6.2$ kJ

vaporization: $q = n \cdot \Delta H_{vap} = 3.45 \cdot 31 = 1.1 \cdot 10^2$ kJ

adding up: $4.8 + 6.2 + 11 \cdot 10^1 = 1.2 \cdot 10^2$ kJ. (120 kJ, 118 kJ)