

THE UNIVERSITY OF BRITISH COLUMBIA
CHEMISTRY 123 EXAMINATION

20 April 2002

This examination consists of this cover and 14 numbered pages.
PLEASE CHECK THAT YOU HAVE A COMPLETE PAPER

TIME LIMIT:
2.5 HOURS

GIVEN NAME(S): <u>ANSWER KEY</u> (IN INK)	SURNAME: _____ (CAPITALS) (IN INK)
STUDENT NUMBER: _____ (IN INK)	SIGNATURE: _____ (IN INK)

NO CALCULATORS ALLOWED PREPROGRAMMED WITH ANY CHEMISTRY OR PHYSICS FORMULAE OR TEXTUAL MATERIAL. MOLECULAR MODELS ARE ALLOWED.

Lecture Section (check \checkmark your section)
<input type="checkbox"/> 201 (MWF 1:00) Drs. Patey/Tanner
<input type="checkbox"/> 202 (MWF 2:00) Drs. Patey/Tanner
<input type="checkbox"/> 209 (MWF 9:00) Drs. Brion/Sherman
<input type="checkbox"/> 210 (MWF 10:00) Drs. Brion/Sherman
<input type="checkbox"/> 211 (MWF 11:00) Drs. Bizzotto/Comisarow
<input type="checkbox"/> 299 (T,Th 9:30) Drs. Bizzotto/Comisarow
<input type="checkbox"/> 222 (T,Th 2:00) Dr. McIntosh

Question	Maximum	Obtained	Initials
1	10		
2	5		
3	6		
4	12		
5	16		
6	13		
7	18		
8	12		
9	6		
10	15		
11	17		
TOTAL	130		
MARK	65		

REGULATIONS FOR EXAMINATIONS

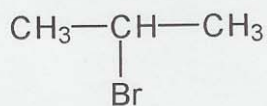
1. Each candidate must be prepared to produce upon request, a Library/AMS card for identification.
2. Candidates are not permitted to ask questions of the invigilators, except in cases of supposed errors or ambiguities in examination questions.
3. No candidates shall be permitted to enter the examination room after the expiration of one-half hour from the scheduled starting time, or to leave during the first half hour of the examination.
4. Candidates guilty of any of the following, or similar, dishonest practices shall be immediately dismissed from the examination and shall be liable to disciplinary action:
 - (a) Making use of any books, papers or memoranda, calculators, audio or visual cassette players or other memory and devices, other than those authorized by the examiners.
 - (b) Speaking or communicating with other candidates.
 - (c) Purposely exposing written papers to the view of other candidates. The plea of accident or forgetfulness shall not be received.
5. Candidates must not destroy or mutilate any examination material; must hand in all examination papers; and must not take any examination material from the examination room without permission of the invigilator.

ANSWER ALL QUESTIONS

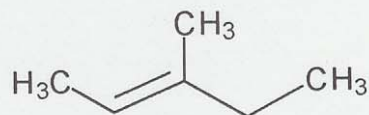
***** ADDITIONAL DATA *****

$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$
 $1 \text{ L atm} = 101.3 \text{ J}$
 $F = 96,500 \text{ coulombs mol}^{-1}$
 $1 \text{ J} = 1 \text{ volt coulomb}$
 $K_w = 1.00 \times 10^{-14} \text{ at } 25^\circ\text{C (298 K)}$

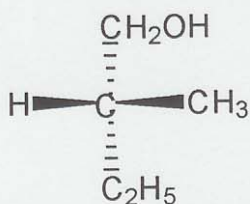
1. Name the following compounds, including as necessary designation of stereochemistry.



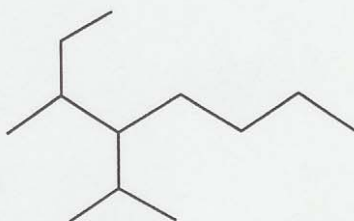
a) 2-bromopropane



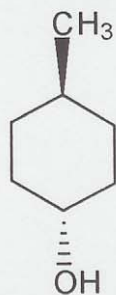
b) (E)-3-methyl-2-pentene



c) (R)-2-methyl-1-butanol

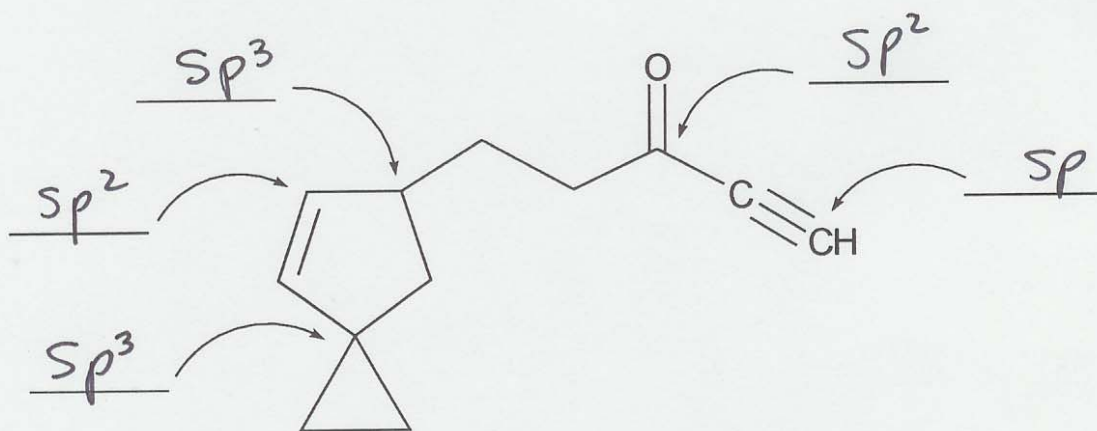


d) 3-methyl-4-ispropyloctane

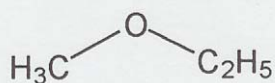


e) trans-4-methylcyclohexanol

2. What is the state of hybridization at the indicated carbon atoms?



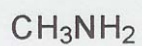
3. What functional groups are present in the following molecules?



a) ether



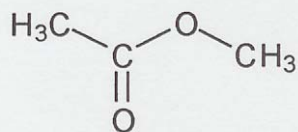
b) alcohol



c) amine



d) ketone



e) ester



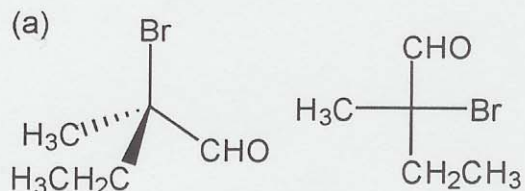
e) alkyne

4. Shown below are a number of pairs of structural formulas. In the box below each pair, place the number (related to one of the terms listed below) that best describes the relationship between the two structures.

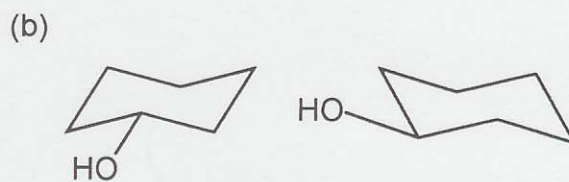
NOTE: Each term may be used more than once and not all of the terms need be used.

1. constitutional isomers 2. diastereomers

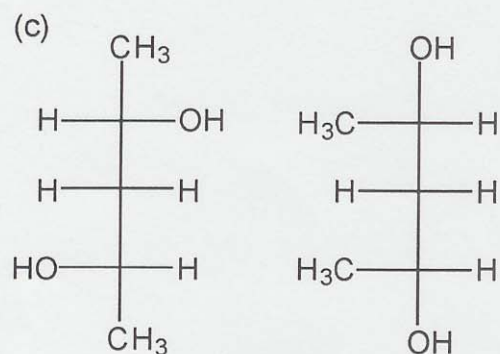
3. identical 4. enantiomers



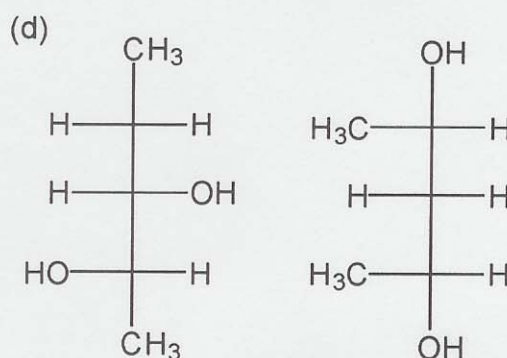
3



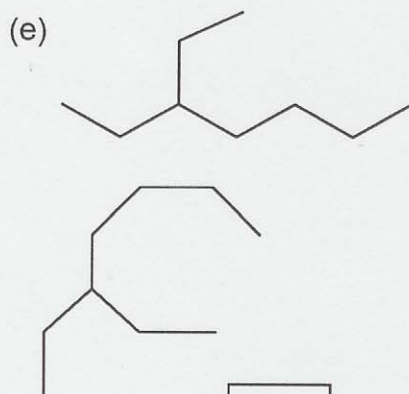
3



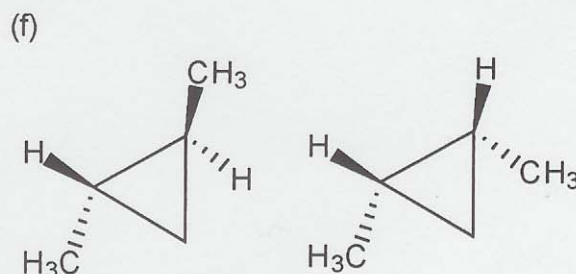
2



1



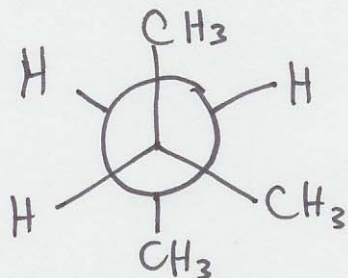
3



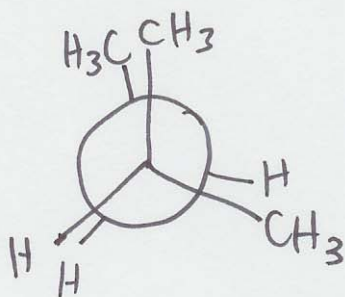
2

5. Clearly draw three dimensional representations of the following molecules/conformations.

a) The most stable conformation of 2-methylbutane. Use a Newman projection viewing along the C2-C3 bond.



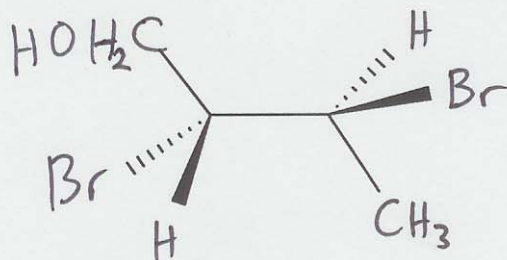
b) The least stable conformation of 2-methylbutane. Use a Newman projection viewing along the C2-C3 bond.



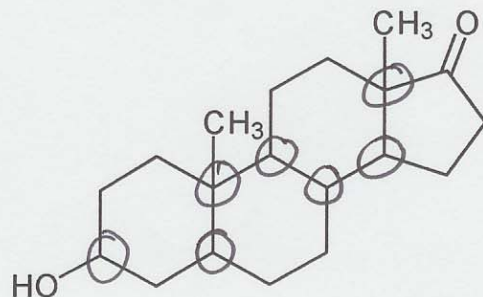
c) The most stable conformation of *cis*-1-*tert*-butyl-4-methylcyclohexane.



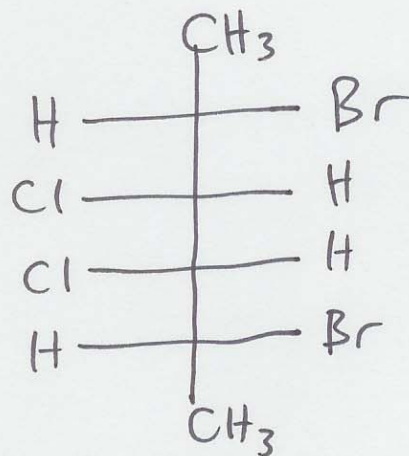
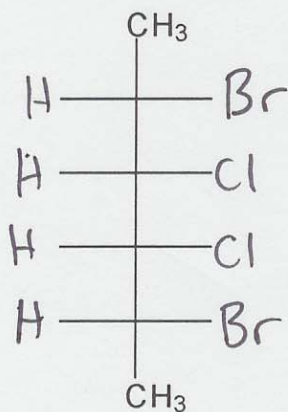
d) Complete the template below to clearly show the structure of (2*R*,3*S*)-2,3-dibromo-1-butanol. Show all the hydrogen, carbon, and oxygen atoms that are required to complete the structure.



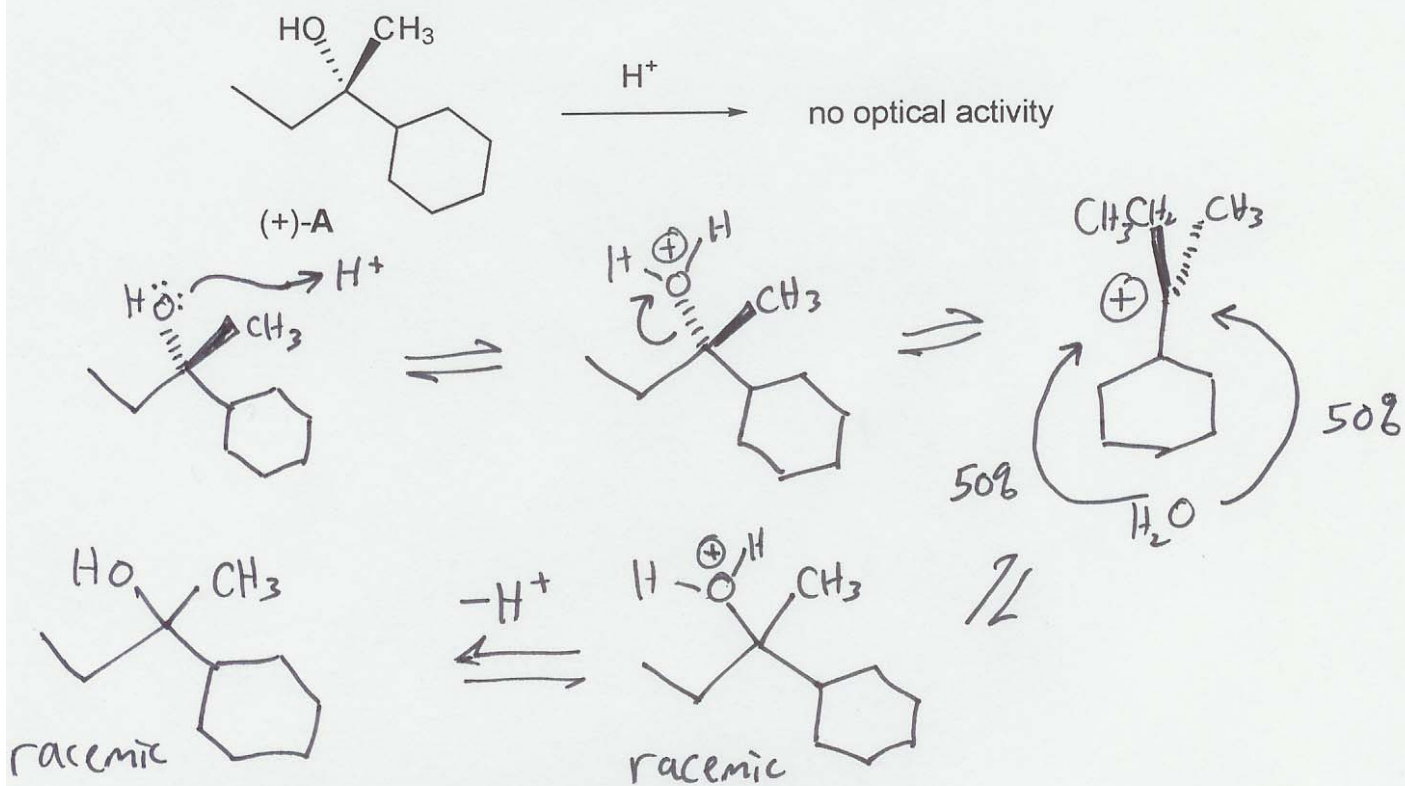
6a) Circle all of the stereogenic centres in the following steroid molecule.



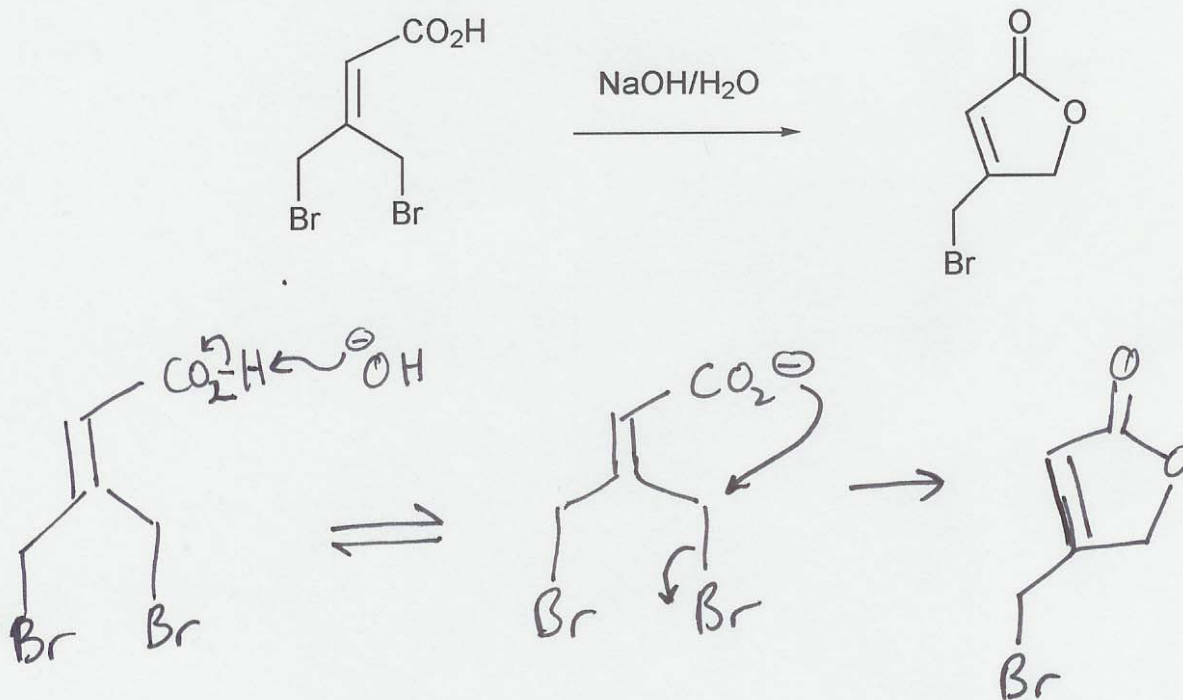
6b) Draw the Fisher projection(s) of all the achiral (optically inactive) stereoisomers of 2,5-dibromo-3,4-dichlorohexane. Use the template below and re-draw the template as necessary. Draw each isomer only once.



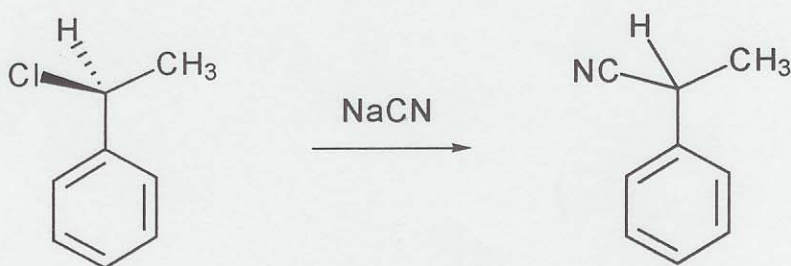
7a) The optical activity of (+)-A (shown below) becomes zero in the presence of acid. Propose a reaction mechanism that would account for this observation.



7b) Propose a mechanism for the reaction below.



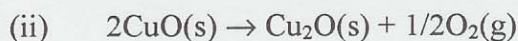
7c) The chloro compound on the left, below, was converted to the nitrile (ie. RCN) on the right. The stereochemistry of the product is not shown. A student wondered whether the mechanism of this reaction was S_N1 or S_N2 and decided to answer this question using a kinetic study. What experiment should the student perform and what results would enable the student to decide which mechanism is correct?



vary the $[NaCN]$. If the rate is dependant on $[NaCN]$, it is an S_N2 reaction. If it is ~~is~~ independent of $[NaCN]$, it is S_N1 .

End of organic section.....

8. If you wished to prepare $\text{Cu}_2\text{O}(\text{s})$ under standard conditions at 25°C , two possible reactions could be considered:



(a) From the data given below, calculate ΔH° , ΔE° , ΔS° and ΔG° for both reactions at 25°C .

	$\text{O}_2(\text{g})$	$\text{Cu}(\text{s})$	$\text{CuO}(\text{s})$	$\text{Cu}_2\text{O}(\text{s})$
ΔH_f° (kJ mole ⁻¹)			-159.2	-168.5
S° (J mole ⁻¹ K ⁻¹)	204.8	33.12	42.59	93.05

Answers:	Reaction (i)	Reaction (ii)
ΔH°	-9.3 kJ	+ 149.9 kJ
ΔE°	-9.3 kJ	+ 148.7 kJ
ΔS°	+17.34 JK ⁻¹	+ 110.27 JK ⁻¹
ΔG°	-14.5 kJ	+ 117.0 kJ

Show work for reaction (i):

$$\Delta H^\circ = -168.5 - (0 - 1.59.2) = -9.3 \text{ kJ}$$

$$\Delta E^\circ = \Delta H^\circ - \Delta(pV) = \Delta H^\circ - 0 = -9.3 \text{ kJ}$$

$$\Delta S^\circ = 93.05 - (33.12 + 42.59) = +17.34 \text{ JK}^{-1}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -9.3 - 298 \times 17.34 \times 10^{-3} = -14.5 \text{ kJ}$$

Show work for reaction (ii):

$$\Delta H^\circ = -168.5 + \frac{1}{2} \times 0 - 2(-159.2) = +149.9 \text{ kJ}$$

$$\begin{aligned} \Delta E^\circ &= \Delta H^\circ - \Delta(pV) = \Delta H^\circ - \Delta nRT \\ &= +149.9 - \left(\frac{1}{2} - 0\right)(8.314 \times 10^{-3})(298) \\ &= +148.7 \text{ kJ} \end{aligned}$$

$$\Delta S^\circ = 93.05 + \frac{1}{2}(204.8) - 2(42.59) = 110.27 \text{ JK}^{-1}$$

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = +149.9 - (298)(110.27 \times 10^{-3}) \\ &= +117.0 \text{ kJ} \end{aligned}$$

- (b) Which of reactions (i) and (ii) would you attempt to use for preparing $\text{Cu}_2\text{O}(s)$ at 25°C ? Give a reason for your choice.

reaction (i) because $\Delta G^\circ < 0$
(negative)

9. (a) State the 1st law of thermodynamics (words and/or equations).

$$\Delta E = q + W$$

(or) Energy is conserved
The Energy of the universe is constant

(b) State the 2nd law of thermodynamics (words and/or equations).

$$\Delta S_{\text{TOTAL}} = \Delta S_{\text{SYSTEM}} + \Delta S_{\text{SURROUNDINGS}} \geq 0$$

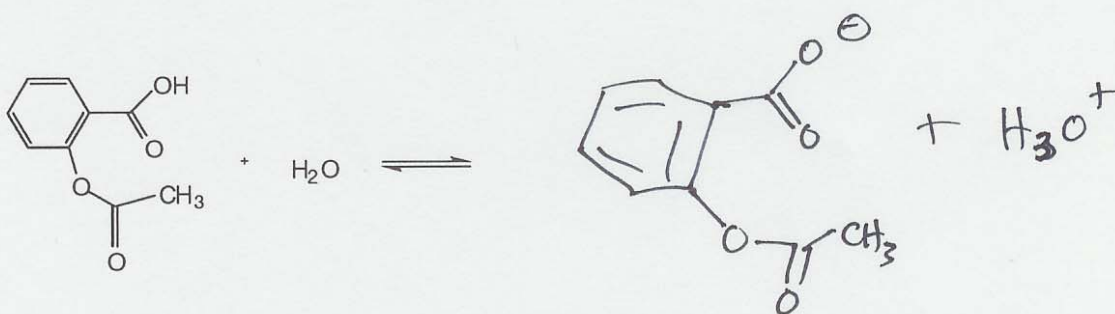
The entropy of the Universe is increasing

(c) State the 3rd law of thermodynamics (words and/or equations).

$$S^{\circ} = 0$$

The entropy of a (perfect) crystalline ~~substance~~ substance at absolute zero is zero

10. (a) Complete the following equilibrium acid-base expression by drawing the structures of all products formed when acetylsalicylic acid (aspirin) is dissolved in pure water.



- (b) You have prepared a 1 Litre solution containing 0.10 M of acetylsalicylic acid and 0.20 M of its conjugate base, sodium acetylsalicylate, in pure water at 25°C. Using a very accurate pH meter, you find that the pH of this solution is 3.80. What is the K_a value for acetylsalicylic acid at 25°C?

$$K_a = \underline{3.17 \times 10^{-4}}$$

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

$$pK_a = 3.80 - \log \left(\frac{0.2}{0.1} \right) = 3.499$$

$$K_a = 3.169 \times 10^{-4}$$

- (c) What is the K_b for sodium acetylsalicylate at 25°C?

$$K_b = \underline{3.15 \times 10^{-11}}$$

$$K_b = \frac{K_w}{K_a} = \frac{10^{-14}}{3.169 \times 10^{-4}} = 3.155 \times 10^{-11}$$

- (d) You have just swallowed a small tablet of pure aspirin. Upon dissolving in your stomach, which has a pH < 2, what is the predominant charge state of this compound? (circle the answer)

positive

neutral

negative

Upon passing into your intestine, which has a pH > 7, what is the predominant charge state of this compound? (circle the answer)

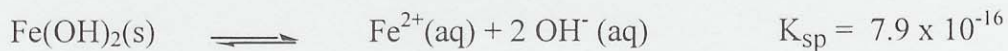
positive

neutral

negative

11. (a) Some inorganic salts do not completely dissolve when placed in water. The degree of dissociation is given by an equilibrium constant, called K_{sp} .

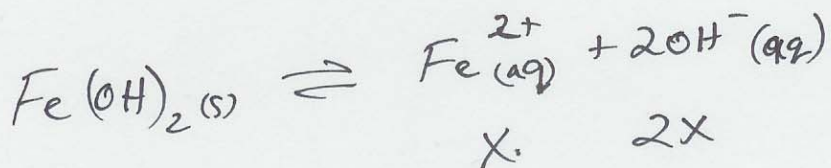
- (i) Given the following reaction, write an expression for the K_{sp} of $Fe(OH)_2(s)$ in terms of activities.



$$K_{sp} = \frac{a_{Fe^{2+}} a_{OH^-}^2}{a_{Fe(OH)_2(s)}} \approx [Fe^{2+}][OH^-]^2$$

- (ii) 10 g of $Fe(OH)_2(s)$ (MW = 89.85 g/mol) is added to 100 mL of water. Calculate the $[Fe^{2+}]$ and pH of the solution at equilibrium.

$$[Fe^{2+}] = \underline{5.82 \times 10^{-6} M} \quad pH = \underline{9.07}$$



$$K_{sp} = x(2x)^2 = 4x^3 \quad x = [Fe^{2+}] = \left(\frac{K_{sp}}{4}\right)^{1/3}$$

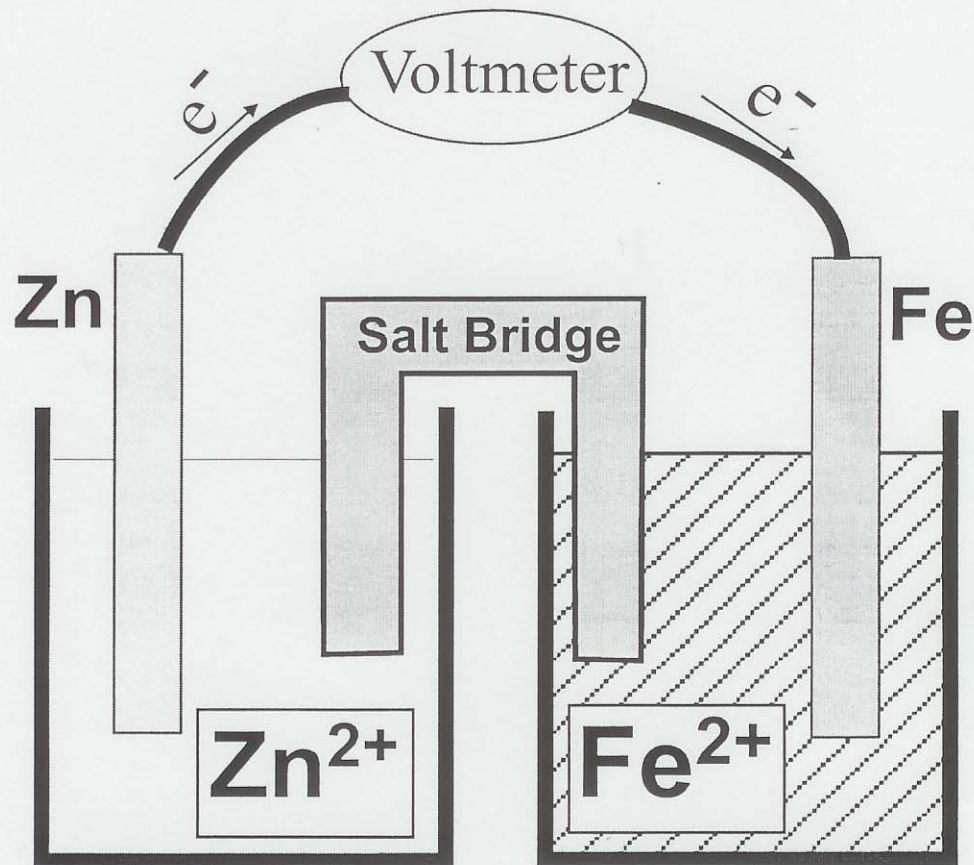
$$[Fe^{2+}] = \left(\frac{7.9 \times 10^{-16}}{4}\right)^{1/3} = 5.82 \times 10^{-6} M$$

$$[OH^-] = 2x = 1.16 \times 10^{-5} M$$

$$pOH = 4.93 \quad pH = 9.07$$

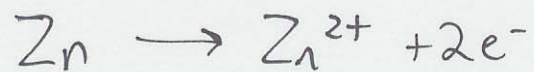
11. (b) Electrochemistry can measure the $[\text{Fe}^{2+}]$ at equilibrium and therefore can be used to determine equilibrium constants or the K_{sp} values for various complexes. This method is utilized in chemical analysis of sea water.

(i) One example of an electrochemical cell that can be constructed for this purpose is shown below (counter ions are not indicated):

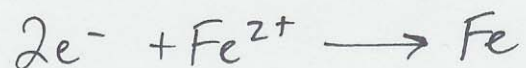


Noting the direction of electron flow, write the following:

Anodic half reaction:



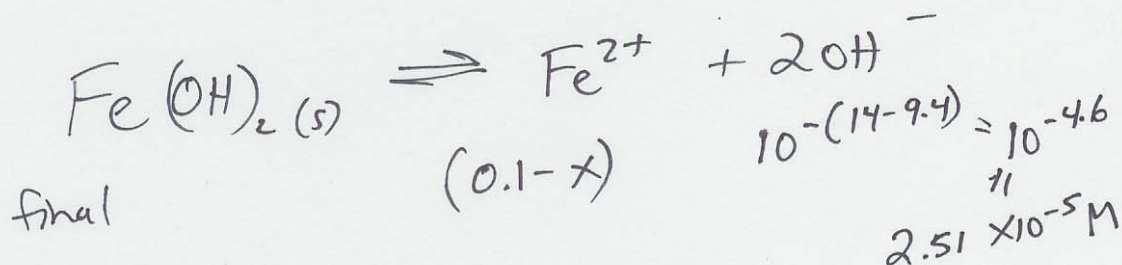
Cathodic half reaction:



Net cell reaction:



- (ii) Calculate the cell potential at 25°C if the iron electrode is immersed in a 100 mL solution to which 0.90g Fe(OH)₂(s) was added. This solution is also buffered to pH = 9.4. The [Zn²⁺] = 1.0 M and the standard cell potential is 0.324 V.
(Hint: use the K_{sp} value from 11(a), and then the Nernst equation.)



$$K_{sp} = 7.9 \times 10^{-16} = (0.1 \text{ M} - x)(2.51 \times 10^{-5} \text{ M})^2$$

$$[\text{Fe}^{2+}] = \frac{7.9 \times 10^{-16}}{(2.51 \times 10^{-5})^2}$$

$$[\text{Fe}^{2+}] = 1.25 \times 10^{-6} \text{ M}$$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Zn}^{2+}]}{[\text{Fe}^{2+}]} = 0.324 - \frac{8.314(298)}{2(96485)} \ln \left(\frac{1}{1.25 \times 10^{-6}} \right)$$

$$= 0.324 - 0.175$$

$$= 0.149 \text{ V}$$