

THE UNIVERSITY OF BRITISH COLUMBIA**CHEMISTRY 123 FINAL EXAMINATION**

22 April 2008

This examination consists of 16 numbered pages.

TIME LIMIT:**PLEASE CHECK THAT YOU HAVE A COMPLETE PAPER****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)

- 201 (MWF 1:00) Drs. Wang/Ruddick
 202 (MWF 2:00) Drs. Wang/Ruddick
 203 (MWF 3:00) Drs. MacFarlane/Love
 210 (MWF 10:00) Dr. Liu
 211 (MWF 11:00) Drs. Herring/Sammis
 299 (T,Th 9:30) Drs. Herring/Sherman
 222 (T,Th 2:00) Drs. MacFarlane/Perrin

***** ANSWER ALL QUESTIONS *****

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

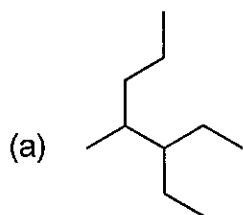
REGULATIONS FOR EXAMINATIONS

- Each candidate must be prepared to produce upon request, a Library/AMS card for identification.
- Candidates are not permitted to ask questions of the invigilators, except in cases of supposed errors or ambiguities in examination questions.
- 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.
- 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:
 - Having at the place of writing any books, papers or memoranda, calculators, audio or visual cassette players or other memory aid devices, other than those authorized by the examiners.
 - Speaking or communicating with other candidates.
 - Purposely exposing written papers to the view of other candidates. The plea of accident or forgetfulness shall not be received.
- 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.

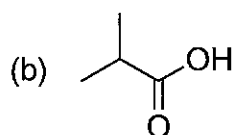
***** ADDITIONAL DATA *****

ATTACHED (LAST TWO PAGES) ARE AN EQUATIONS SHEET AND A PERIODIC TABLE.

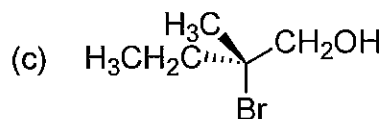
1. [9 points] Name the following compounds according to IUPAC nomenclature:



3-ethyl-4-methylheptane

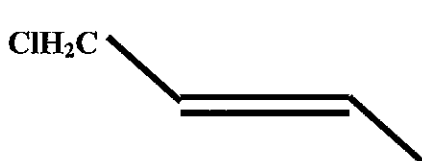


2-methylpropanoic acid

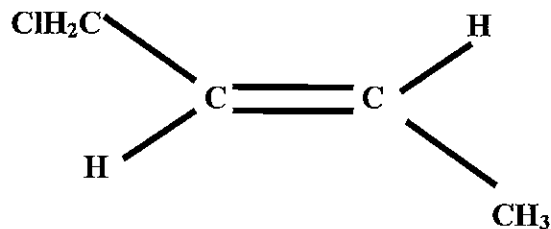


(R)-2-bromo-2-methylbutanol

2. [3 points] Draw the structure of (*E*)-1-chloro-2-butene.



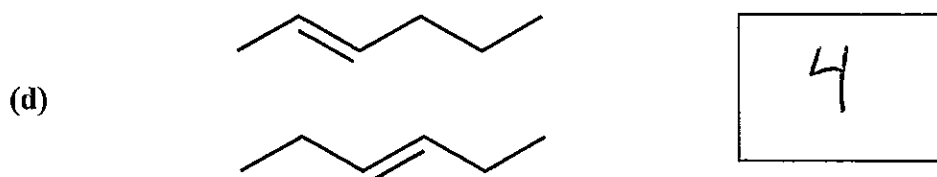
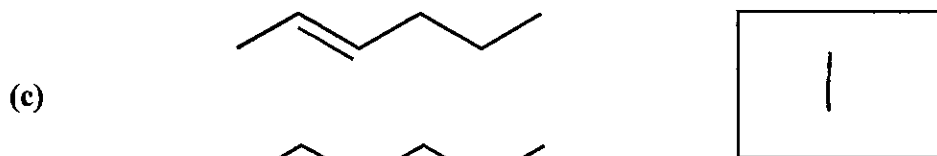
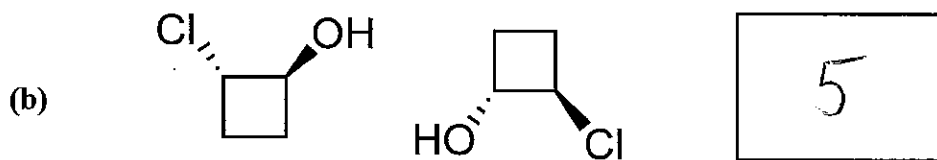
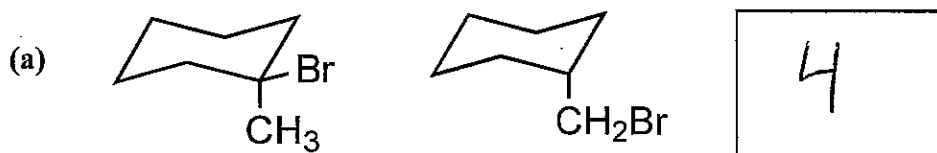
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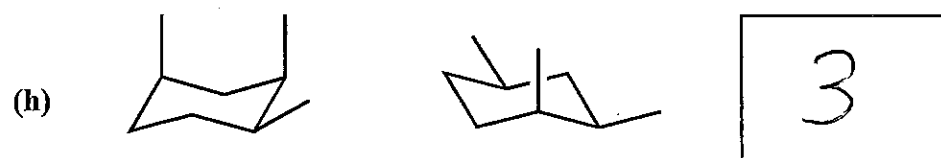
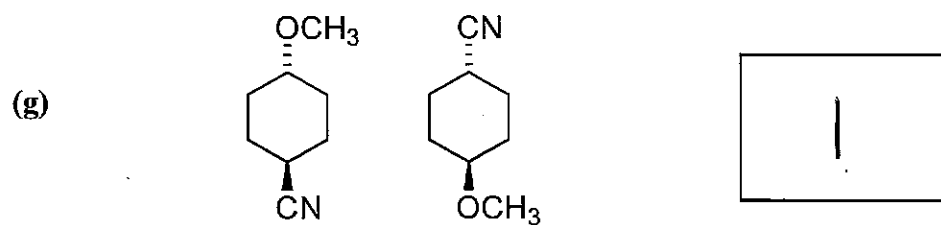
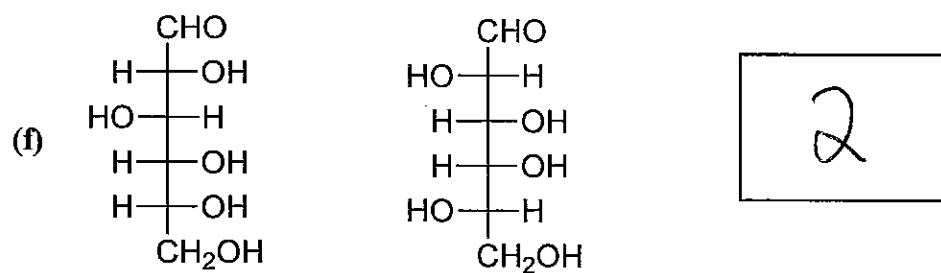
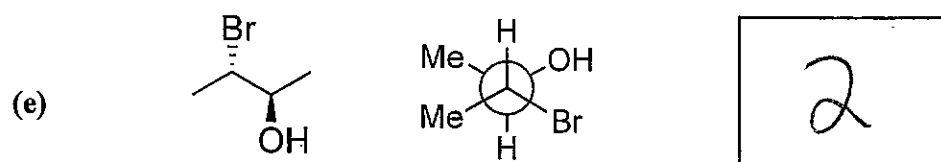
3. [16 points] Below are eight pairs of structural formulas. In the box to the right of each pair, place the number (from the six terms listed below) that BEST describes the relationship between the two structures. NOTE: Each term may be used more than once and not all terms need be used.

1. Identical
2. Diastereomers
3. Conformers

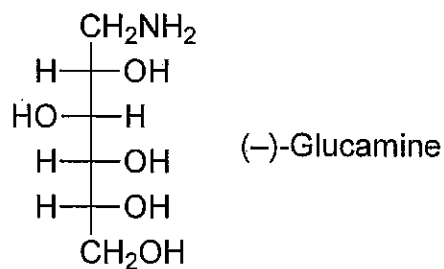
4. Constitutional isomers
5. Enantiomers
6. None of the above relationships



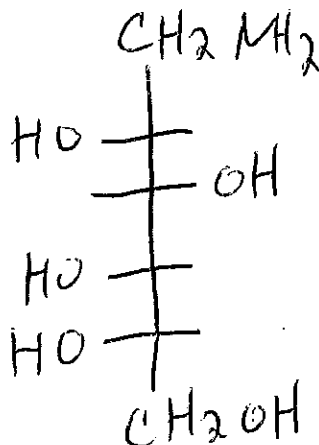
3. (Continued)



4. [11 points] (–)-Glucamine, shown below, has a specific rotation of -7.95° .



- (a) Draw a Fischer Projection of the enantiomer of (–)-glucamine.



- (b) What is the specific rotation of the compound you drew in part (a)? It is (circle one):

(1) $+7.95^\circ$

(2) -7.95°

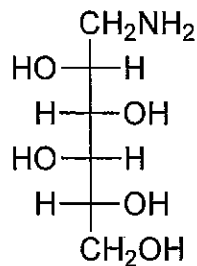
(3) positive, but can't determine the exact rotation based on the given information

(4) negative, but can't determine the exact rotation based on the given information

(5) can't determine the sign or the exact rotation based on the given information

4. (Continued)

(c) The specific rotation of the compound below is (circle one):



(1) $+7.95^\circ$

(2) -7.95°

(3) positive, but can't determine the exact rotation based on the given information

(4) negative, but can't determine the exact rotation based on the given information

(5) can't determine the sign or the exact rotation based on the given information

(d) Calculate the percentage of (-)-glucamine in a mixture of (-)-glucamine and (+)-glucamine that has a specific rotation of $+4.77^\circ$.

$$X = \% (-)$$

$$+4.77 = +7.95(1-X) + (-7.95)(X)$$

$$= 7.95 - 7.95X - 7.95X$$

$$15.9X = 3.18$$

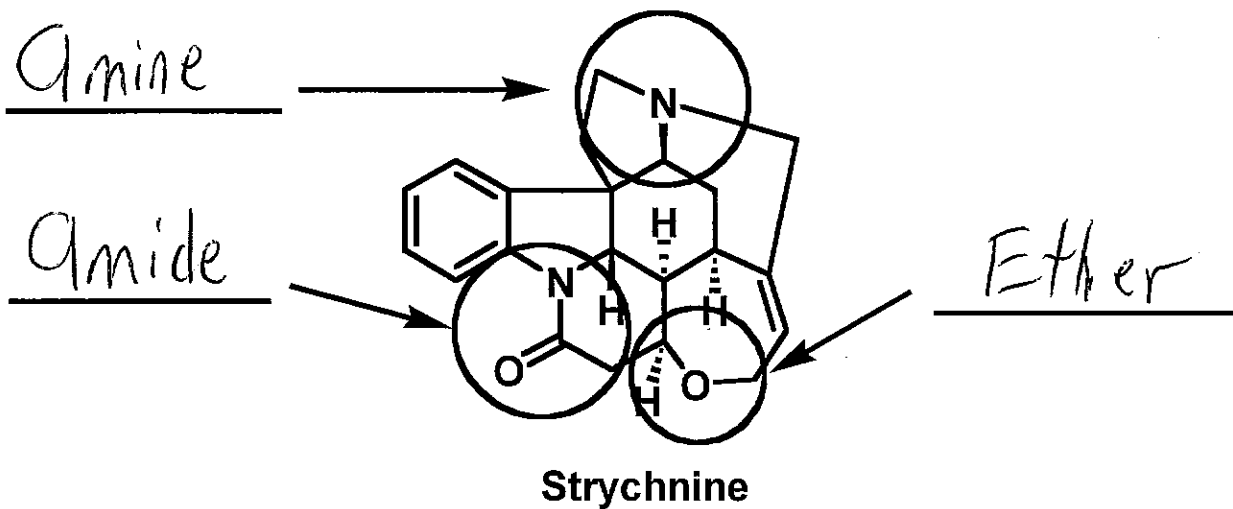
$$X = \frac{3.18}{15.9}$$

$$X = 0.20$$

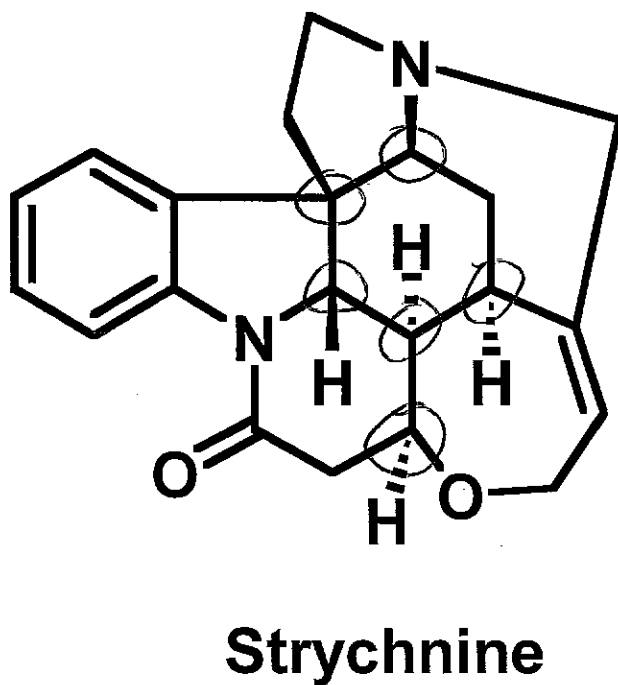
20% (-) glucamine

5. [10 points] Strychnine (structure below) is a highly bitter, toxic (rat poison) natural product isolated from the *Strychnos nux vomica* plant, found in the rainforests of the Southern Asian and Australia.

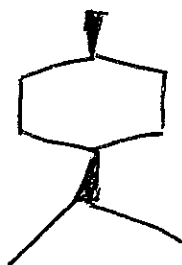
(a) In the space provided, write the name of the circled functional groups:



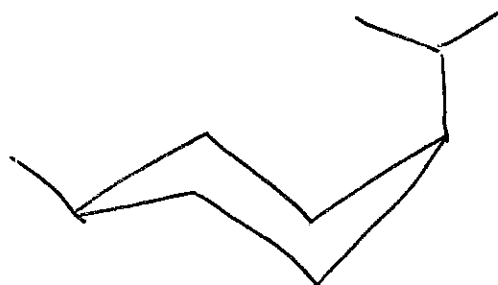
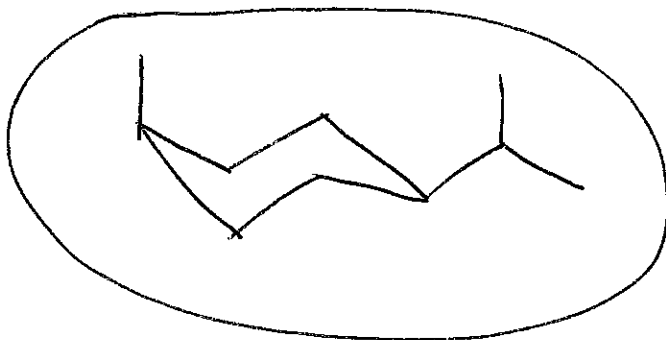
(b) In the structure of strychnine below, circle the **carbon** stereogenic (or chiral) centers.



6. [12 points] (a) Draw the structure of *cis*-1-methyl-4-isopropyl cyclohexane. Show stereochemistry clearly.



- (b) Draw the two most stable conformations of *cis*-1-methyl-4-isopropyl cyclohexane.



- (c) Circle the most stable conformer you have drawn above.

- (d) At 300 K, one conformer has a standard enthalpy that is 1.0 kJ mol^{-1} greater than the other conformer and the corresponding standard entropy difference is $10.0 \text{ J mol}^{-1} \text{ K}^{-1}$. Calculate the percentage of each conformer present at equilibrium at 300 K.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = (0 - -1.0 \frac{\text{kJ}}{\text{mol}}) - (298\text{K})(0 + 0.010 \text{ kJ/molK})$$

$$\Delta G^\circ = -2.0 \text{ kJ/mol}$$

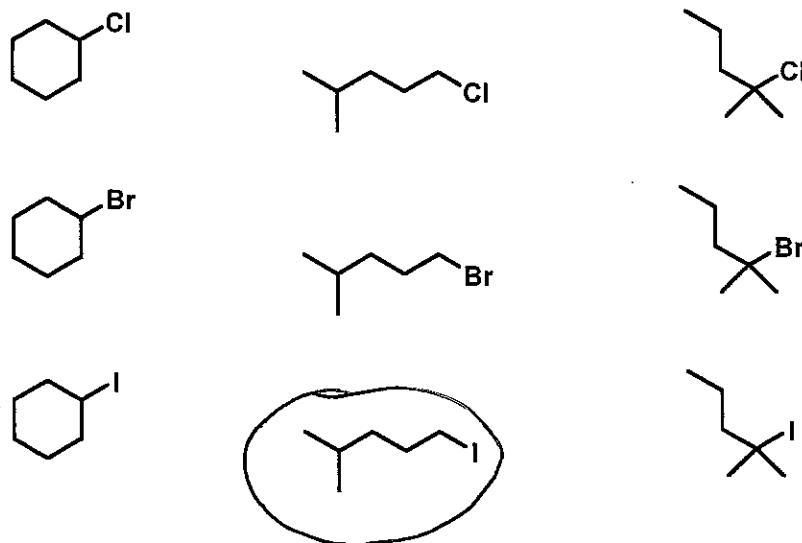
$$\Delta G^\circ = -RT \ln k = (0.008317 \text{ kJ/molK})(298\text{K})(\ln k)$$

$$-2.0 \text{ kJ/mol} = -2.5 \text{ kJ/mol} (\ln k)$$

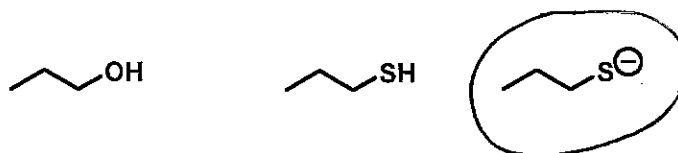
$$\ln k = 0.8 ; k = 2.2$$

$$\% \text{ conformers} = \frac{2.2}{(2.2+1)} = 69\% ; \frac{1}{3.2} = 31\%$$

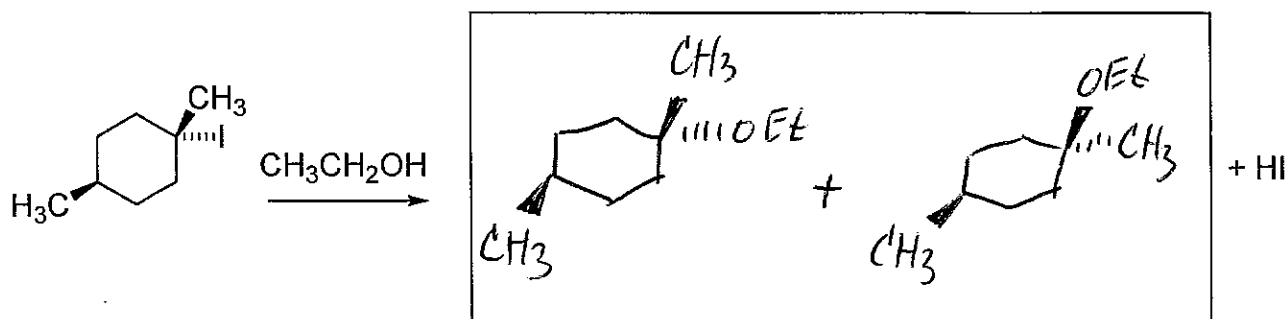
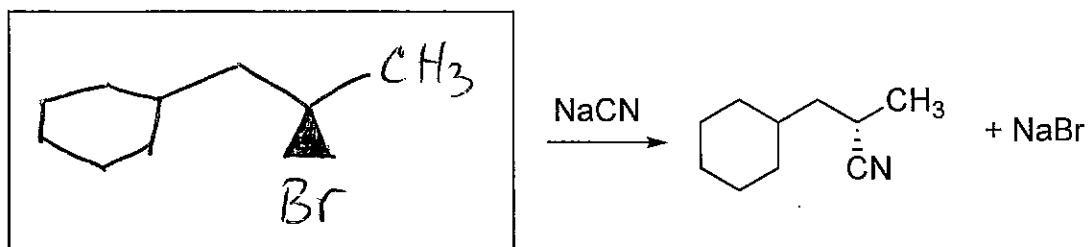
7. [12 points] (a) Circle the electrophile below that will react fastest in an S_N2 reaction.



(b) Which of the following nucleophiles will react fastest in an S_N2 reaction (circle the best answer)?

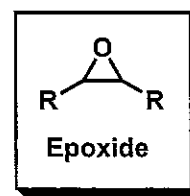


(c) Draw the appropriate reactants or products in the boxes below. Show stereochemistry where appropriate.



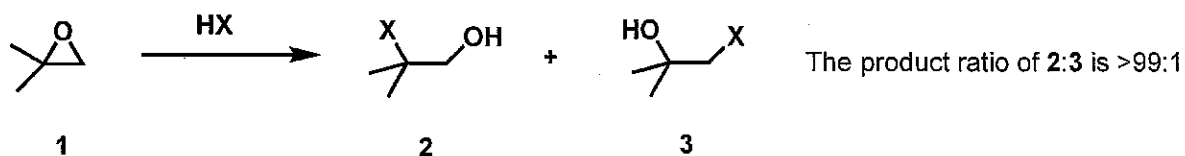
(More than one product is possible.)

8. [12 points] (a) What functional group is present in an epoxide (structure on the right)?

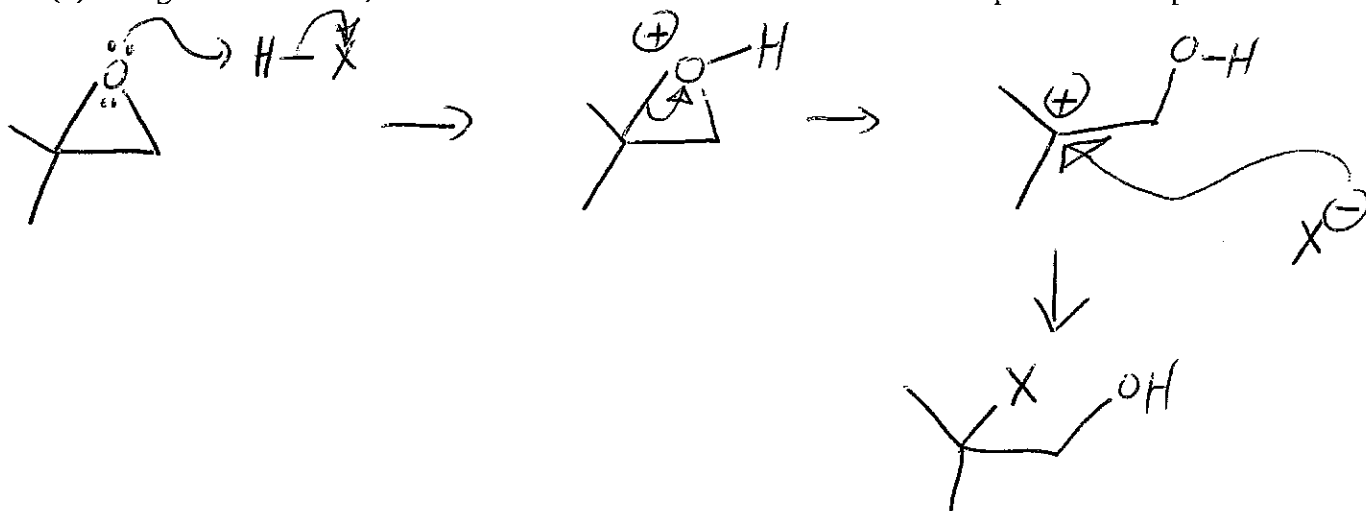


_____ (answer)

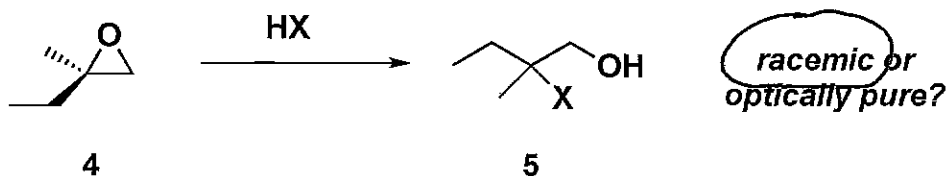
Epoxides readily react with strong acids (such as HX, where X = Cl, Br, or I) to form a ring opened product. Under strongly acidic conditions, epoxides such as compound 1 will always open to give the halogen at the more substituted position (compound 2).



- (b) Using curved arrows, draw the mechanism for the transformation of epoxide 1 into product 2.



- (c) If you treat optically pure epoxide 4 with a strong acid, would you expect the resulting ring opened product (5) to be racemic or optically pure? Provide an explanation for your answer.

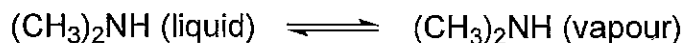


The carbocation intermediate will be attacked equally from either side.

9. [18 points] Use data for dimethylamine in the table below to answer the following questions. Assume all gases are ideal: $PV = nRT$.

Formula of dimethylamine	C_2H_7N
Molecular weight	$45.062 \text{ g mol}^{-1}$
Normal boiling point	$6.9 \text{ }^\circ\text{C}$
Standard enthalpy of vaporization	25 kJ mol^{-1}
Standard heat of formation (at 298.15 K)	$-43.9 \text{ kJ mol}^{-1}$
Standard molar entropy (at 298.15 K)	$182.3 \text{ J mol}^{-1} \text{ K}^{-1}$

- (a) Write the expression for the equilibrium constant for the vapourization reaction below in terms of activities.



$$K = \frac{a_{\text{vapor}}}{a_{\text{liquid}}}$$

- (b) Calculate the equilibrium constant for the above vapourization reaction at $6.9 \text{ }^\circ\text{C}$.

$$K = P_{\text{vapor}} = 1$$

$$a_{\text{lig}} = 1; a_{\text{vap}} = P_{\text{vap}} / 1 \text{ atm}$$

at the normal bp, $P_{\text{vap}} = 1 \text{ atm}$

- (c) Calculate the change in entropy of dimethylamine upon vaporization at its normal boiling point.

$$\Delta S_{\text{vap}}^{\circ} = \frac{\delta_{\text{rev}}}{T} = \frac{\Delta H_{\text{vap}}^{\circ}}{T} = \frac{25 \text{ kJ/mol}}{(273.15 + 6.9) \text{ K}}$$

$$= 89.27 \text{ J/molK}$$

9. (Continued)

(d) Estimate the vapour pressure of dimethylamine at 0 °C. What assumptions have you made in your estimate? and $\Delta S^\circ_{\text{vap}}$

assume $\Delta H^\circ_{\text{vap}}$ and $\Delta S^\circ_{\text{vap}}$ are independent of T:

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \left(25 \times 10^3 / 8.314\right) \left(\frac{1}{273.15} - \frac{1}{280.65}\right)$$

$$= 0.2712$$

$$k_2 = k_1 / e^{0.2712} = 0.76; \quad \boxed{P_{\text{vap}} = 0.76 \text{ atm}}$$

assuming ΔH° and ΔS° are T-independent,

$$\Delta G^\circ = -RT \ln k = \Delta H^\circ - T\Delta S^\circ = 25 - (273.15)(89)(\times 10^{-3}) = 0.6159 \text{ kJ}$$

$$\ln k = \frac{-\Delta G^\circ}{RT} = \frac{-0.6159}{(8.314)(273.15)(10^{-3})} = -0.2712$$

$$k = e^{-0.2712} = 0.76; \quad \boxed{P_v = 0.76 \text{ atm}}$$

(e) If 200 g of dimethylamine is sealed in an evacuated 400 litre drum and allowed to come to equilibrium at a temperature of 0 °C, what is the pressure inside the drum and what phases are present in equilibrium?

assume an ideal gas and ignore volume of the liquid.

$$P = \frac{nRT}{V} = \left(\frac{200}{45.06}\right) (0.0821) (273.15) / 400 = \overset{0.25}{\cancel{0.25}} \text{ atm}$$

Since $\overset{0.25}{\cancel{0.25}} < 0.76$, only vapor will be present.

10. [15 points] (a) You have a summer job in a biochemistry lab. You are given a bottle containing solid dimethylamine hydrochloride $(\text{CH}_3)_2\text{NH}_2\text{Cl}$ ($\text{p}K_a = 10.64$) and asked to prepare a buffer with a $\text{pH} = 10$. On the lab shelf, you have the following reagents: water, acetone, benzoic acid, NaOH , KCl , TiCl_4 , nitrocellulose, HCl . Which of these reagents, in addition to $(\text{CH}_3)_2\text{NH}_2\text{Cl}$, do you choose to accomplish your task? (No calculation is necessary.) Explain your answer.

Appreciable amounts of $(\text{CH}_3)_2\text{NH}_2\text{Cl}$ and $(\text{CH}_3)_2\text{NH}$ are needed.

NaOH is needed to convert some $(\text{CH}_3)_2\text{NH}_2\text{Cl}$ to $(\text{CH}_3)_2\text{NH}$.

H_2O is needed to make a solution.

Weak acid

its conjugate base

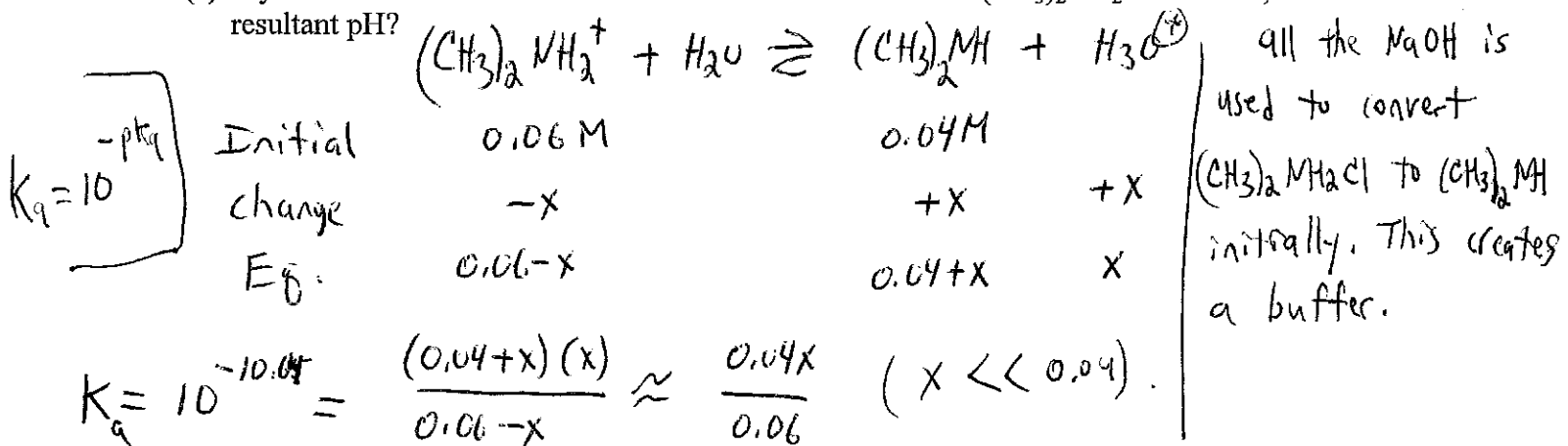
- (b) If you prepare a 0.100 M $(\text{CH}_3)_2\text{NH}_2\text{Cl}$ solution and add 0.0400 moles of HCl to 1.00 litres of the solution, what is the resultant pH ?

The pH will be far below 10.65 ; dissociation of $(\text{CH}_3)_2\text{NH}_2\text{Cl}$ can be ignored: a strong acid (HCl) is added to a weak acid, $(\text{CH}_3)_2\text{NH}_2\text{Cl}$.

$$\text{pH} = -\log\left(\frac{0.0400 \text{ mol HCl}}{1.00 \text{ L}}\right) = 1.4$$

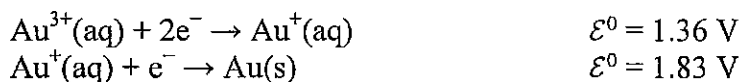
This solution is not a buffer.

- (c) If you add 0.0400 mol of NaOH to 1.00 litres of a 0.100 M $(\text{CH}_3)_2\text{NH}_2\text{Cl}$ solution, what is the resultant pH ?

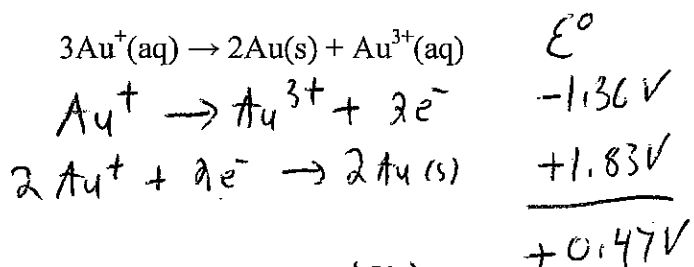


$$\text{pH} = -\log x = -\log\left[\left(\frac{0.06}{0.04}\right) \times 10^{-10.64}\right] = 10.46$$

11. [12 points] Using the following reduction potentials, at 25 °C,



(a) Calculate K for the following disproportionation reaction:

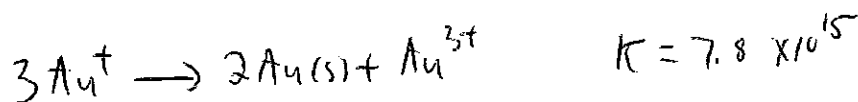


$$\ln K = \frac{nF\Delta\mathcal{E}^{\circ}}{RT} = \frac{2 \left(\frac{96.5 \text{ kJ}}{\text{V mol}} \right) (0.47 \text{ V})}{\left(\frac{0.008314 \text{ kJ}}{\text{mol K}} \right) (298 \text{ K})} = 36.6 ; \quad K = e^{+36.6}$$

$$K = 7.8 \times 10^{15}$$

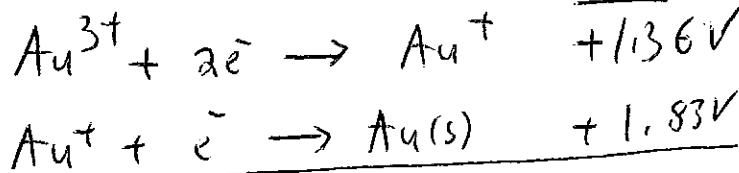
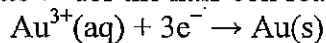
(b) If AuCl(s) is added to water, does Au(I) spontaneously disproportionate to any significant extent? Explain your answer.

If Au⁺ dissolves in water, it will disproportionate completely:



$$K \gg 1$$

(c) Calculate \mathcal{E}° for the half-cell reaction



$$\begin{array}{l} \Delta G^{\circ} = -nF\mathcal{E}^{\circ} \\ -2F(1.36) \\ -1F(1.83) \end{array}$$

$$\Delta G^{\circ} = -2F(1.36) + [-F(1.83)]$$

$$\Delta\mathcal{E}^{\circ} = -\frac{\Delta G^{\circ}}{nF} = \frac{+F(2 \times 1.36 + 1.83)}{3F} = 1.52 \text{ V}$$