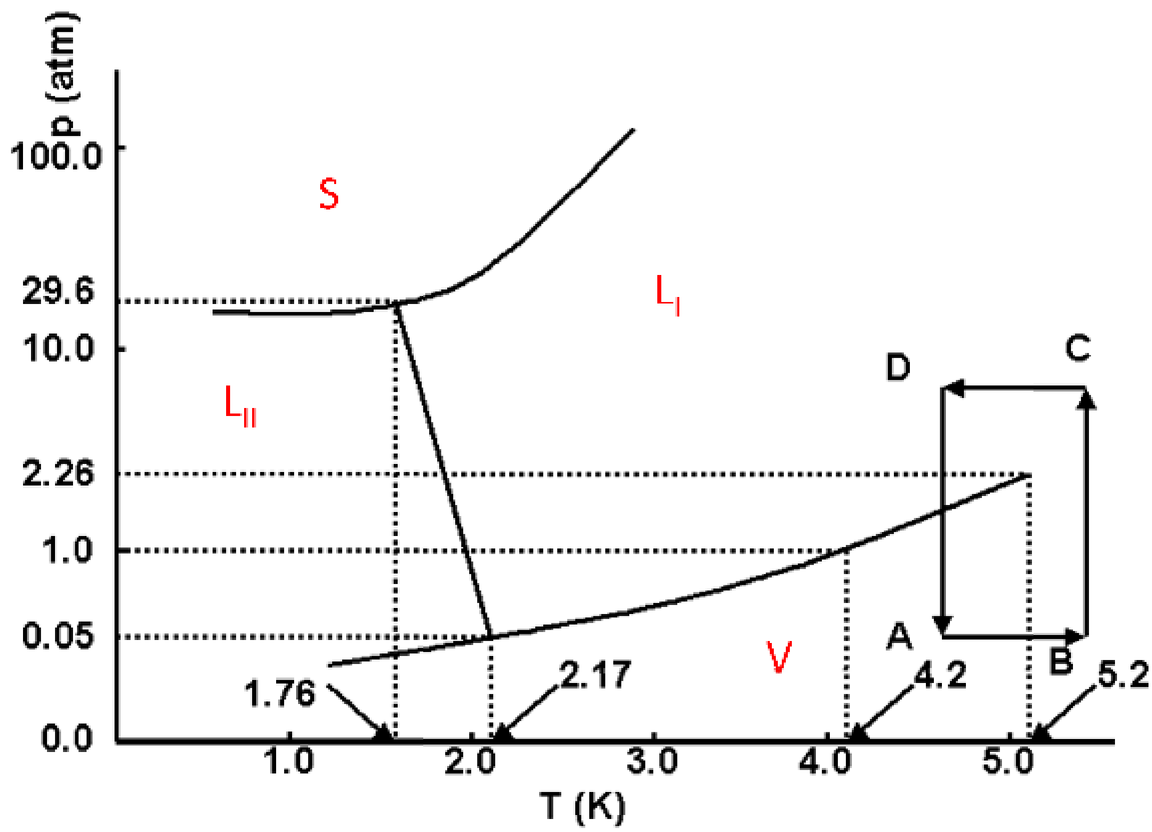
Q 1 The phase diagram for helium is shown below; the diagram is not to scale. This is a system which has two liquid phases ($L_I$ and $L_{II}$) in addition to solid (S) and vapour (V) phases. The transition from liquid phase $L_{II}$ to $L_I$ is endothermic, and both liquid phases are less dense than the solid.




(a) Label the regions of the diagram according to the phases which are stable in each region.

(b) Give the appropriate value of the
 (i) normal boiling point 4.2
 (ii) critical temperature 5.2
 (iii) critical pressure 2.26

(c) Is the density of phase $L_I$ greater than, equal to, or less than the density of phase $L_{II}$ at 2 K?

Density $L_{II}$ < Density $L_I$

(d) Identify any triple points and specify what phases are in equilibrium at them.
TP at 0.05 atm and 2.17K and $L_I$, $L_{II}$ and V in eq.
TP at 29.6 atm and 1.76K and S $L_I$ and $L_{II}$

(e) Samples of solid helium are transferred to two evacuated containers (i.e. at zero pressure), one at 2 K and one at 3 K. What phases are present at equilibrium in the two containers?

(i) at 2 K Providing the pressure>0.05 atm $L_{II}$ present_

(ii) at 3 K Providing the pressure>0.05 atm $L_{I}$ present_

(f) Describe the phase changes that occur when a sample of He initially at 0.05 atm and 4.5 K (point A) is taken along the path indicated on the diagram.

| | |
|---|---|
| A to B | gas becomes critical fluid__________ |
| B to C | critical fluid becomes denser |
| C to D | critical fluid becomes a liquid____________ |
| D to A | liquid vaporises________________________ |

(g) What is the sign (< 0 or > 0 or = 0 ) of $\Delta S_{universe}$ for the change

$$He(l) \rightarrow He(g)$$

at 4K and 1 atm pressure. Briefly (two sentences) explain your answer.

At 4K and 1 atm $L_I$ the most stable phase so the transition from Liquid to gas is NOT spontaneous therefore $\Delta S_{universe}$ <0

Q.2. Carbon dioxide and ammonia can react to form urea, $CO(NH_2)_2(s)$, according to the equation:

$$CO_2\,(g) + 2\,NH_3(g) \rightleftharpoons H_2O(l) + CO(NH_2)_2(s)$$

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

NOTE: ΔE° ≡ ΔU°

| | $\Delta G_f°$ (kJ mol$^{-1}$) | S° (J K$^{-1}$ mol$^{-1}$) |
|---|---|---|
| $CO_2(g)$ | -394.4 | 213.6 |
| $NH_3(g)$ | -16.7 | 192.5 |
| $H_2O(l)$ | -237.2 | 69.9 |
| $CO(NH_2)_2(s)$ | -197.2 | 110.0 |

$$\Delta G^\circ = -237.2 - 197.2 - (-394.4 + 2(-16.7)) = -6.6 = -6600J$$

$$\Delta S^\circ = 69.9 + 110.0 - (213.6 + 2(192.5)) = -421.7JK^{-1}$$

**Calculate** $\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ = -6600 + 298 \times (-421.7) = -132.3kJ$

**Calculate** $\Delta E^\circ = \Delta H^\circ - \Delta(pV) = -132.3 - \left(-3 \times 8.314 \times 298\right) = -132.3 + 7.4 = 124.9kJ$

**Calculate** $\Delta(pV) = (pV)_{product} - (pV)_{reactant} = n_{product}RT - n_{reactant}RT = -3RT$

Assume gases ideal

ΔG° = ____________________ ΔS° = ___________________________

ΔH° = ____________________ ΔE° = ___________________________

(b) Calculate the equilibrium constant at 25 °C.

$$K = e^{-\Delta G^\circ/RT} = e^{6600/(8.314\times 298)} = e^{2.6639} = 14.35$$

(c) At what temperature is the value of the equilibrium constant equal to one (1)?

$$1 = K = e^{-\Delta G^\circ/RT} = e^{-\Delta H^\circ/RT} \times e^{\Delta S^\circ/R}$$

**solve for T**

$$e^{-\Delta H^\circ/RT} = e^{-\Delta S^\circ/R}$$

$$\frac{-\Delta H^\circ}{RT} = \frac{-\Delta S^\circ}{R}$$

***OR***

$$-RT\ln K = \Delta H^\circ - T\Delta S^\circ = 0$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-132300}{-421.7} = 313.7$$

(d) Write the equilibrium expression in terms of activities.

$$K = \frac{a_{H_2O(l)} a_{CO(NH_2)_2(s)}}{a_{CO_2(g)} a^2_{NH_3(g)}}$$

(e) Liquid water, solid urea, carbon dioxide gas and ammonia gas are contained in a closed vessel. What is the value of ΔG when partial pressure of carbon dioxide is 0.5 atm and the partial pressure of ammonia is 0.5 atm? Carry your calculations to three significant figures.

$$\Delta G = \Delta G^{\circ} + RT \ln Q = \Delta G^{\circ} + RT \ln \frac{a_{H_2O(l)} a_{CO(NH_2)_2(s)}}{a_{CO_2(g)} a^2_{NH_3(g)}}$$

**Set activities of solids and liquids=1 and activites of gases=pressures**

$$\Delta G = \Delta G^{\circ} + RT \ln \frac{1}{p_{CO_2} p^2_{NH_3}} = -6600 + 8.314 \times 298 \times \ln(1/(0.5) \times (0.5)^2) = -6600 + 5152 = -1448 J$$

Calculate ΔG

(f) In which direction does the reaction proceed under the conditions described in part(e)?

Is ΔG <0 or =0 or >0??? Reaction proceeds towards products because ΔG <0!

(g) What are the equilibrium partial pressures of $CO_2$ and $NH_3$?

| | $P(CO_2)$ | $P(NH_3)$ |
|---|---|---|
| I | 0.5 | 0.5 |
| C | -x | -2x |
| E | (0.5-x) | (0.5-2x) |

$$K = 14 = \frac{1}{p_{CO_2} p^2_{NH_3}} = \frac{1}{(0.5 - x)(0.5 - 2x)^2}$$

How do we solve this??? No approximation possible!!!! YOU WILL NOT GET ONE THIS HARD!!!

The best answer is x = 0.05, to solve this put

$$(0.5 - 2x)^2 = \frac{1}{14(0.5 - x)} \approx \frac{1}{14(0.5)} = \frac{1}{7}$$

$$0.5 - 2x = 0.38$$

$$2x = 0.5 - 0.38 = 0.12$$

$$x = 0.06$$

(h) If the reaction mixture in part (e) is allowed to come to equilibrium, in which direction will the reaction proceed if solid urea is added to the equilibrium mixture? Assume that there are no volume changes.

No change!

Q.3. Consider the galvanic cell based on the following half-reactions

$Au^{3+} + 3e^{-} \rightarrow Au$ $E° = 1.50$ V

$Tl^{+} + e^{-} \rightarrow Tl$ $E° = -0.34$ V

(a) Write the overall cell reaction in the direction of spontaneous change.

The direction of spontaneous change needs $E°_{cell} > 0$ so that the $Au^{3+}$ is reduced

$3Tl + Au^{3+} \rightarrow Au + 3Tl^{+}$ $E°_{cell} = E°_{R} - E°_{L} = 1.50-(-0.34)V = 1.84$

(b) Calculate $E°_{cell}$ and $\Delta G°$

$\Delta G° = -nF\, E°_{cell}$

$E°_{cell}$ = ____________________ $\Delta G°$ = ____________________

(c) If the cell is operated with the $[Au^{3+}]$ concentration at the gold (Au) electrode set at $1 \times 10^{-2}$ M, what concentration of $Tl^{3+}$ is required in the thallium (Tl) electrode so that the direction of spontaneous change is for $Tl^{+}$ to be reduced?

Use Nernst equation $\boldsymbol{E = E^{\circ} - \frac{RT}{nF}\ln\frac{[Tl^{+}]^{3}}{[Au^{3+}]}}$

**Calculate $[Tl^{+}]$ needed to make** $E_{cell} < 0$ (not $E°_{cell}$ )

**Find $[Tl^{+}]$ that makes E=0, that is**

$$\frac{nFE^{\circ}}{RT} = \ln\frac{[Tl^{+}]}{[Au^{3+}]}$$

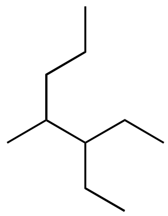
$$\frac{[Tl^{+}]}{[Au^{3+}]} = e^{3FE^{\circ}/RT}$$

$$[Tl^{+}] = [Au^{3+}]e^{3FE^{\circ}/RT} = 1\times10^{-2}e^{3\times96500\times1.84/8.314\times298} = 1\times10^{-2}e^{532680/2478} = 3\times10^{91}\,!!!$$

**Enormous! Not practical! Check my arithmetic!!!!!**

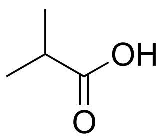
**4.** [9 points] Name the following compounds according to IUPAC nomenclature:

(a)



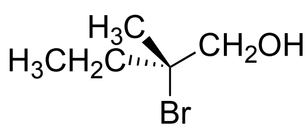
3-ethyl-4-methylheptane

(b)




2-methylpropanoic acid

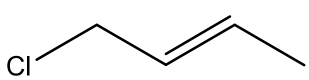
(c)




must provide stereochem!!

(R)-2-bromo-2-methyl-butan-1-ol

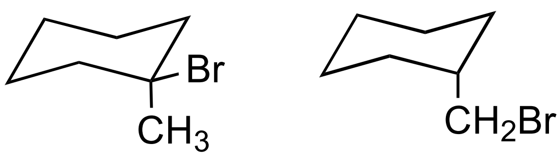
**5.** [3 points] Draw the structure of (*E*)-1-chloro-2-butene.



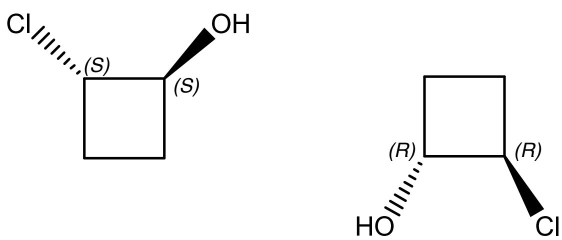

(E)-1-chloro-2-butene.

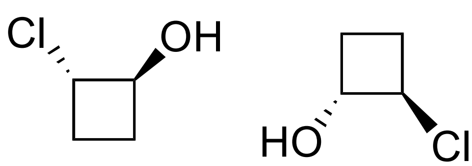
**6.** [16 points] Below are eight pairs of structural formulas. In the box to the right of each pair, place the number (from the six terms listed below) that BEST describes the relationship between the two structures. NOTE: Each term may be used more than once and not all terms need be used.

| | |
|---|---|
| 1. Identical | 4. Constitutional isomers |
| 2. Diastereomers | 5. Enantiomers |
| 3. Conformers | 6. None of the above relationships |

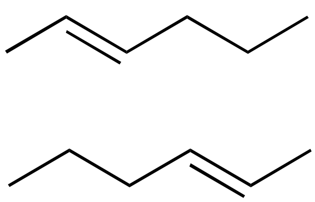
**(a)** 


4



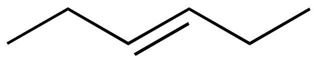

**(b)** 


5

**(c)** 

1

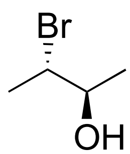
**(d)**

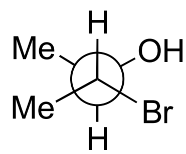


4

**6. (Continued)**

**(e)**

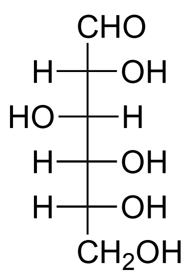


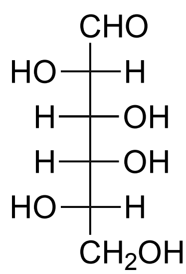




3

3-bromobutan-2-ol both are this!

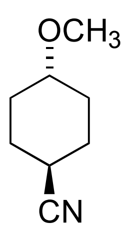
**(f)**

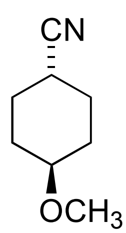



2

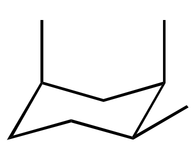
**(g)**

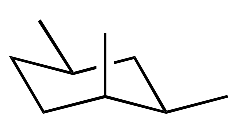



1

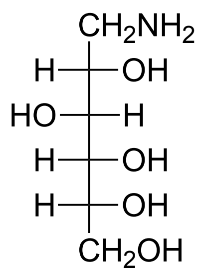
**(h)**





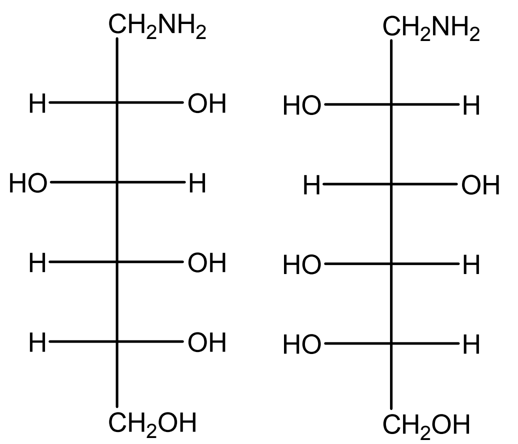
**Conformers 2,4ax 1eq goes 2,4eq 1ax**

**7.** [11 points] (–)-Glucamine, shown below, has a specific rotation of –7.95°.




(Š)-Glucamine

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




ENANTIOMER!

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

(1) +7.95°

(2) –7.95°

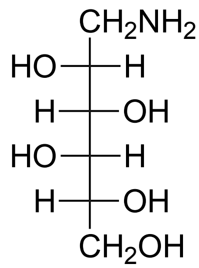
(3) positive, but can't determine the exact rotation based on the given information

(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

**7. (Continued)**

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




(1) +7.95°

(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

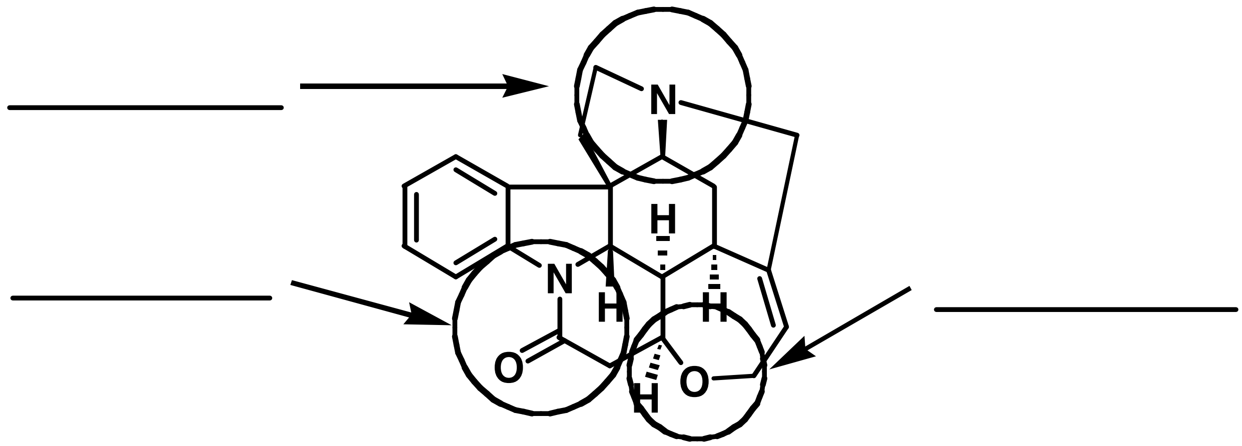
(5) can't determine the sign or the exact rotation based on the given information

This is a diastereomer therefore cannot tell!

**8.** [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:

amine

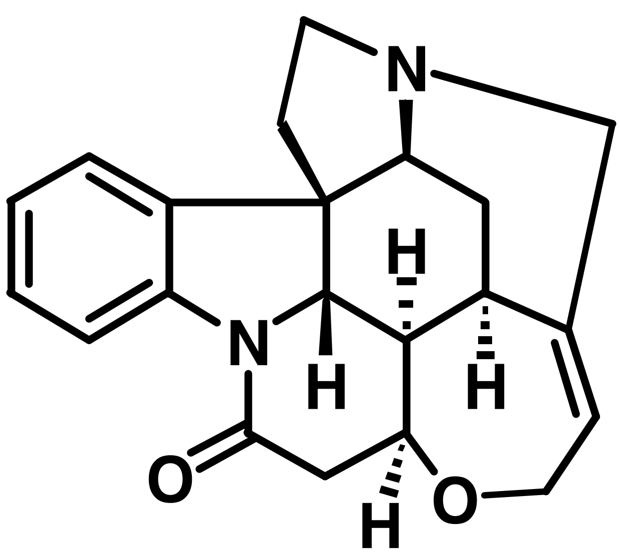


**Strychnine**

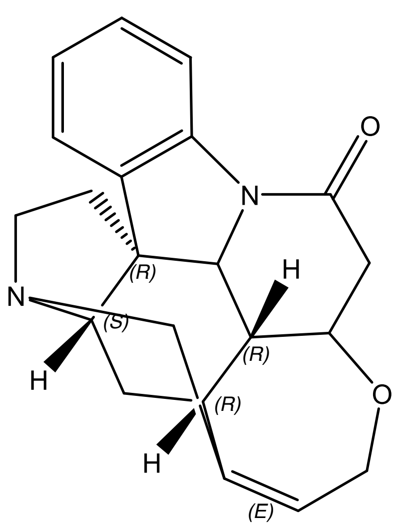
amide

ether

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

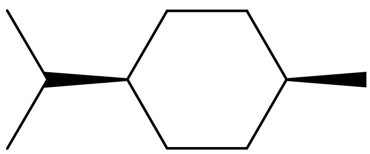


**Strychnine**



strychnine

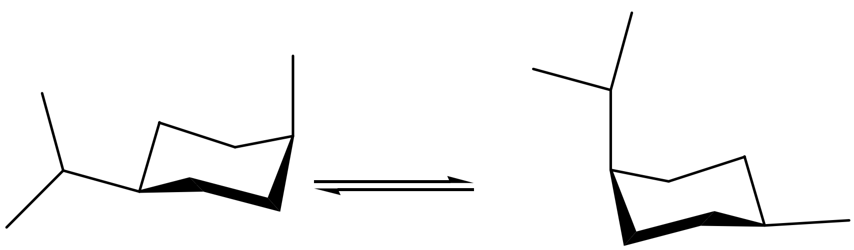
**9**. [12 points] **(a)** Draw the structure of *cis*-1-methyl-4-isopropyl cyclohexane. Show stereochemistry clearly.

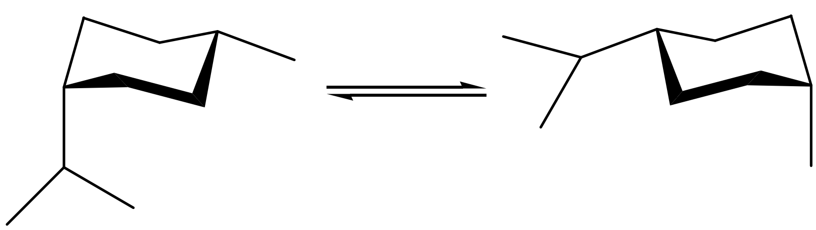


cis-1-methyl-4-isopropyl cyclohexane

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

Draw eq isopropyl and ax methyl





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

Eq(isopropyl) ax (methyl) most stable

**(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 J $mol^{-1}$ $K^{-1}$. Calculate the percentage of each conformer present at equilibrium at 300 K.

Calculate K, then do the ice table starting with100% of one conformer.

The equilibrium is

Eq(isopropyl)-ax(methyl)    Ax(isopropyl)-Eq(methyl)

Call this A B

$\Delta H° = 1000J$ and $\Delta S° = 10JK^{-1}$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = 1000 - 300 \times 10 = -2000$$

$$K = e^{-\Delta G^{\circ}/RT} = e^{-2000/(8.314 \times 300)} = e^{-0.802} = 0.448$$

**ICE TABLE**

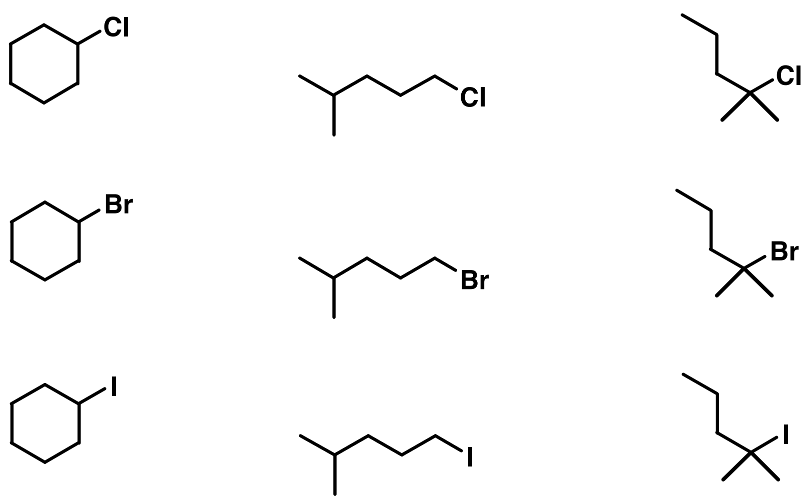
| | A | B |
|---|---|---|
| **I** | **100** | **0** |
| **C** | **-x** | **+x** |
| **E** | **100-x** | **+x** |

$$K = \frac{B}{A} = \frac{x}{100 - x}$$

$$x = \frac{K \times 100}{1 + K} = \frac{0.45 \times 100}{1.45} = 31\%$$

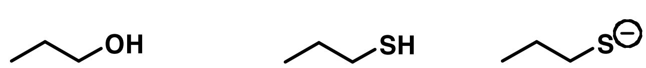
**31% of least stable conformer and 69% of most stable.**

**10.** [12 points] **(a)** Circle the electrophile below that will react fastest in an $S_N2$ reaction.



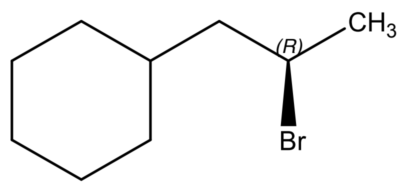

Primary iodide!

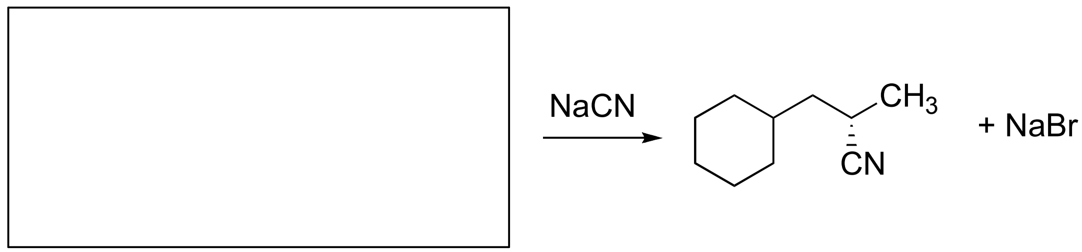
**(b)** Which of the following nucleophiles will react fastest in an $S_N2$ reaction (circle the best answer)?



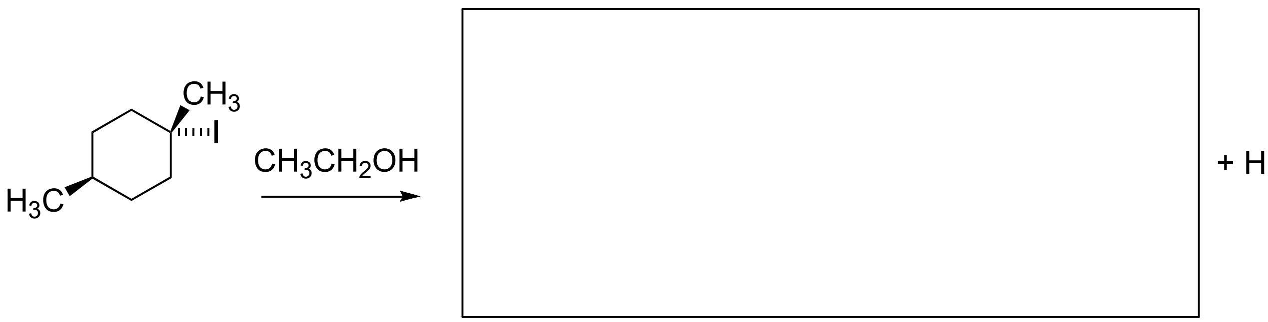

**Thiolate**

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

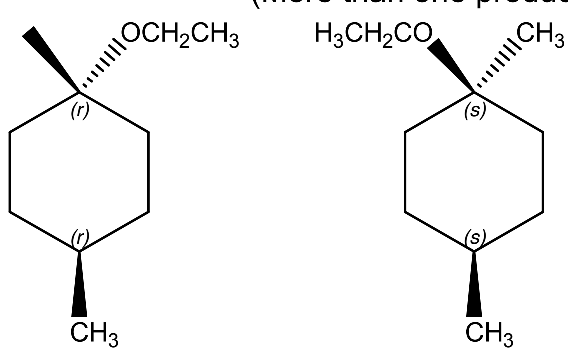



Secondary carbon giving stereo specific product, therefore $S_N2$!



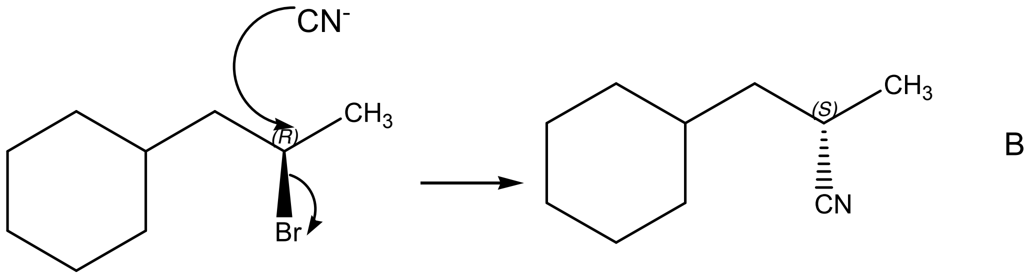

(More than one product is possible.)

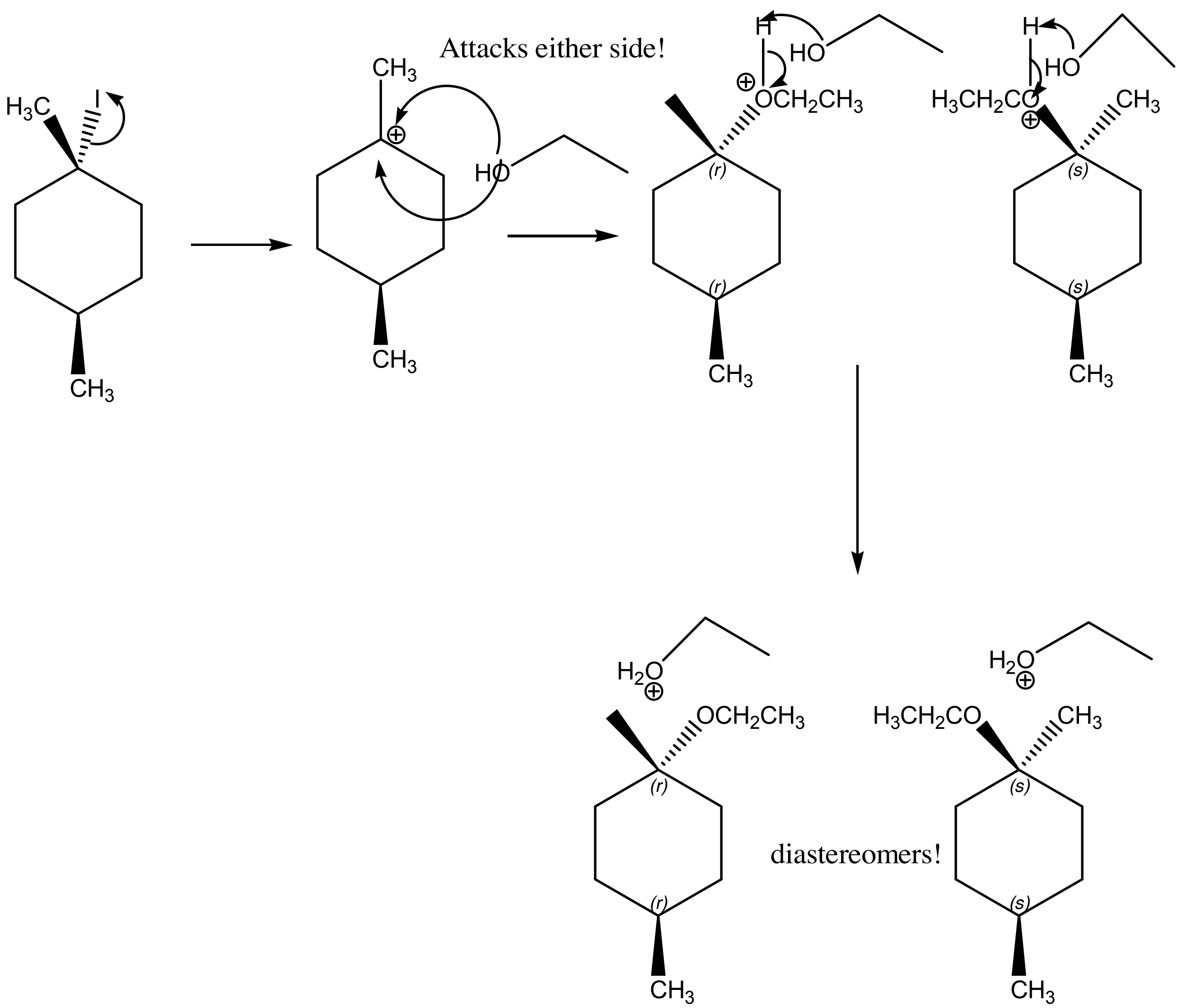



Tertiary carbon therefore $S_N1$, therefore 2 products. CIS and Trans!!!!!

**10 Continued**

**(d)** Using curved arrows, draw the mechanism for the transformations in part(c)




(1*r*,4*r*)-1-ethoxy-1,4-dimethylcyclohexane

The little r tells you the orientation of groups in a achiral molecule and cis/trans designation is ambiguous!

**11**. [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 g $mol^{-1}$ |
| Normal boiling point | 6.9 °C |
| Standard enthalpy of vaporization | 25 kJ $mol^{-1}$ |
| Standard heat of formation (at 298.15 K) | −43.9 kJ $mol^{-1}$ |
| Standard molar entropy (at 298.15 K) | 182.3 J $mol^{-1}$ $K^{-1}$ |

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

$$(CH_3)_2NH \text{ (liquid)} \rightleftharpoons (CH_3)_2NH \text{ (vapour)}$$

$$K = \frac{a_{(CH_3)_2NH(v)}}{a_{(CH_3)_2NH(l)}} = p_{(CH_3)_2NH(v)}$$

**(b)** Calculate the equilibrium constant for the above vapourization reaction at 6.9 °C.

The important point here is the normal boiling point is at 1 atm, therefore standard state!

Therefore at normal boiling point $p_{dimethylamine} = 1$

Therefore K = 1, therefore $\Delta G^o = 0$ and $\Delta G=0$ (at equilibrium)

Therefore $\Delta G^o=0=\Delta H^o-T_{bp}\Delta S^o$

$\Delta S^o=\Delta H^o/T_{bp}$

Can calculate $\Delta S^o$ if needed!

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

$\Delta S^o$ if needed!!!!!!

**(d)** Estimate the vapour pressure of dimethylamine at 0 °C. What assumptions have you made in your estimate?

Use van't hoff equation $\ln\left(\frac{K_1}{K_2}\right) = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \ln\left(\frac{p(\text{at } T_1)}{p(\text{at } T_2)}\right)$

Put $T_1$=6.9+273 and $p_1$=1 and solve for $p_2$ with $T_2$ = 0 +273. And $\Delta H^\circ$= 25 kJ

**(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?

**The point here is if the pressure generated by the dimethylamine is greater than the pressure calculated in part (e) then liquid will form! So calculate the pressure generated by 200 g using the ideal gas equation**

**p= nRT/V**

**12**. [15 points] **(a)** You have a summer job in a biochemistry lab. You are given a bottle containing solid dimethylamine hydrochloride $(CH_3)_2NH_2Cl$ (p$K_a$= 10.64) and asked to prepare a buffer with a 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 $(CH_3)_2NH_2Cl$, do you choose to accomplish your task? (No calculation is necessary.) Explain your answer.

dimethylamine hydrochloride is acidic

$(CH_3)_2NH_2Cl$ when dissolved in water produces $(CH_3)_2NH_2^+$

$$(CH_3)_2NH_2^+ + H_2O \qquad (CH_3)_2NH + H_3O^+$$

To create a buffer you need a mixture of an acid and its conjugate base. We have only the acid so we need NaOH to convert the dimethylammonium ion to the base

$(CH_3)_2NH_2^+ + OH^- \rightarrow H_2O + (CH_3)_2NH$

**(b)** If you prepare a 0.100 M $(CH_3)_2NH_2Cl$ solution and add 0.0400 moles of HCl to 1.00 litres of the solution, what is the resultant pH?

p$K_a$ of HCl is -7, this is a very strong acid and completely swamps dissociation of $(CH_3)_2NH_2^+$

Calculate concentration of HCl then calculate pH =$-\log_{10}$[HCl] none from equilibrium!

**(c)** If you add 0.0200 mol of $Ba(OH)_2$ to 1.00 litres of a 0.100 M $(CH_3)_2NH_2Cl$ solution, what is the resultant pH?

The addition of $Ba(OH)_2$ generates 0.04 mole of $OH^-$ which reacts with $(CH_3)_2NH_2^+$ to produce base. Therefore 0.04 mole base and 0.06 mole acid in one litre. Calculate pH.

# Equations Sheet

1. $\Delta E = q + w$
2. $H = E + PV$
3. $G = H - TS$
4. $\Delta G_{\text{reaction}} = \Delta G^0_{\text{reaction}} + RT \ln Q$
5. $\Delta G^0_{\text{reaction}} = -RT \ln K$
6. $\ln\left(\frac{K_1}{K_2}\right) = \frac{\Delta H^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$
7. $\Delta G = w_{\text{el}} = -nF\Delta\mathcal{E}$
8. $\Delta\mathcal{E} = \Delta\mathcal{E}^0 - \frac{RT}{nF} \ln Q$
9. $\Delta\mathcal{E}^0 = \frac{RT}{nF} \ln K$
10. $R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1} = 0.0821\ \text{L atm K}^{-1}\ \text{mol}^{-1}$
11. $1\ \text{L atm} = 101.3\ \text{J}$
12. $F = 96,500\ \text{coulombs mol}^{-1}$
13. $1\ \text{J} = 1\ \text{volt coulomb}$
14. $K_w = 1.00 \times 10^{-14}$ at $25°C$ ($298.15°K$)
15. Kelvins $=$ degrees Celsius $+ 273.15$

# PERIODIC TABLE OF THE ELEMENTS

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 H 1.008 | | | | | | | | | | | | | | | | | 2 He 4.003 |
| 3 Li 6.941 | 4 Be 9.012 | | | | | | | | | | | 5 B 10.811 | 6 C 12.011 | 7 N 14.007 | 8 O 15.999 | 9 F 18.998 | 10 Ne 20.180 |
| 11 Na 22.990 | 12 Mg 24.305 | | | | | | | | | | | 13 Al 26.982 | 14 Si 28.086 | 15 P 30.974 | 16 S 32.07 | 17 Cl 35.453 | 18 Ar 39.948 |
| 19 K 39.098 | 20 Ca 40.08 | 21 Sc 44.956 | 22 Ti 47.88 | 23 V 50.942 | 24 Cr 51.996 | 25 Mn 54.938 | 26 Fe 55.847 | 27 Co 58.93 | 28 Ni 58.69 | 29 Cu 63.55 | 30 Zn 65.39 | 31 Ga 69.72 | 32 Ge 72.61 | 33 As 74.922 | 34 Se 78.96 | 35 Br 79.904 | 36 Kr 83.80 |
| 37 Rb 85.468 | 38 Sr 87.62 | 39 Y 88.906 | 40 Zr 91.22 | 41 Nb 92.906 | 42 Mo 95.94 | 43 Tc (98) | 44 Ru 101.07 | 45 Rh 102.906 | 46 Pd 106.42 | 47 Ag 107.87 | 48 Cd 112.41 | 49 In 114.82 | 50 Sn 118.71 | 51 Sb 121.76 | 52 Te 127.60 | 53 I 126.90 | 54 Xe 131.29 |
| 55 Cs 132.905 | 56 Ba 137.33 | 57 La 138.91 | 72 Hf 178.49 | 73 Ta 180.948 | 74 W 183.85 | 75 Re 186.2 | 76 Os 190.2 | 77 Ir 192.2 | 78 Pt 195.08 | 79 Au 196.967 | 80 Hg 200.59 | 81 Tl 204.37 | 82 Pb 207.2 | 83 Bi 208.980 | 84 Po (209) | 85 At (210) | 86 Rn (222) |
| 87 Fr (223) | 88 Ra 226.03 | 89 Ac 227.03 | 104 Rf (261) | 105 Db (262) | 106 Sg (263) | 107 Bh (262) | 108 Hs | 109 Mt | 110 Ds | | | | | | | | |
| | | | 58 Ce 140.12 | 59 Pr 140.91 | 60 Nd 144.24 | 61 Pm (145) | 62 Sm 150.4 | 63 Eu 151.97 | 64 Gd 157.25 | 65 Tb 158.93 | 66 Dy 162.50 | 67 Ho 164.930 | 68 Er 167.26 | 69 Tm 168.934 | 70 Yb 173.04 | 71 Lu 174.97 | |
| | | | 90 Th 232.038 | 91 Pa 231.04 | 92 U 238.03 | 93 Np 237.05 | 94 Pu (244) | 95 Am (243) | 96 Cm (247) | 97 Bk (247) | 98 Cf (251) | 99 Es (252) | 100 Fm (257) | 101 Md (258) | 102 No (259) | 103 Lr (260) | |