Organic Chemistry 32-235
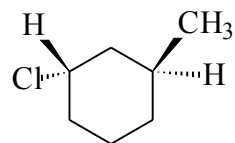## Practice Questions for Exam #2

Part 1: (Circle only **ONE** choice, circling more than one will be counted as wrong!)
   4 points each

1. The correct IUPAC name for the following compound is:

   (A) (1R, 3R)-1-chloro-3-methylcyclohexane
   (B) (1R, 3S)-1-chloro-3-methylcyclohexane
   (C) (1S, 3S)-1-chloro-3-methylcyclohexane
   (D) (1S, 3R)-1-chloro-3-methylcyclohexane
   (E) None of the above.

The Key here is to determine the configuration R or S for each chiral carbon. The answer here is 1S, 2S.

2. Consider the S_N1 reaction of tert-butyl chloride with iodide ion:

$$(CH_3)_3C-Cl \quad + \quad I^{\ominus} \longrightarrow (CH_3)_3C-I \quad + \quad Cl^{\ominus}$$
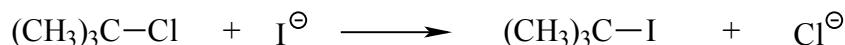
   If the concentration of iodide ion is doubled, the rate of forming tert-butyl iodide will:
   (hint: consider mechanism, i.e. how is the product formed?)

   (A) Double.   (B) Increase 4 times.   (C) Remain the same.
   (D) Decrease.   (E) None of the above.

In SN1 reaction, the rate is independent of the nucleophile involved since the nucleophile is not involved in the rate determining step. Thus the anwer is C.

3. The relationship between the following two structures is:
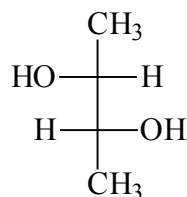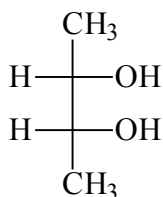
   (A) enantiomers   (B) diastereomers   (C) structural isomers
   (D) identical   (E) none of the above

The key here is to know the definition of all terms and then determine R or S configuration for each chiral carbon. The answer is (B) (by definition)

4. The specific rotation of pure (R)-2-butanol is -13.5°. What % of a mixture of the two enantiomeric forms is (S)-2-butanol if the specific rotation of this mixture is −5.4° ?

   (A) 40%   (B) 30%   (C) 60%   (D) 70%   (E) None of the above
The answer is B since e.e. is 40% favoring R. (5.4/13.5=40%)

5. Which of the following alkyl halides would undergo S_N2 reaction most rapidly?

(A) CH_3CH_2-Br   (B) CH_3CH_2- Cl   (C) CH_3CH_2-I
(D) CH_3CH_2-F   (E) they react at the same rate

In Sn2 reaction, the nucleophile attacks from the back of the leaving group. The better the leaving group, the easier it is to leave (faster rate). The answer is C since iodide ion is the best leaving group.

6. Which of the following molecules is chiral ?

(A)   (B)   (C)
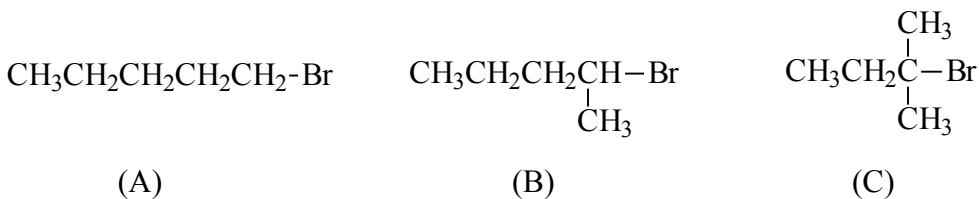

(D)   (E)
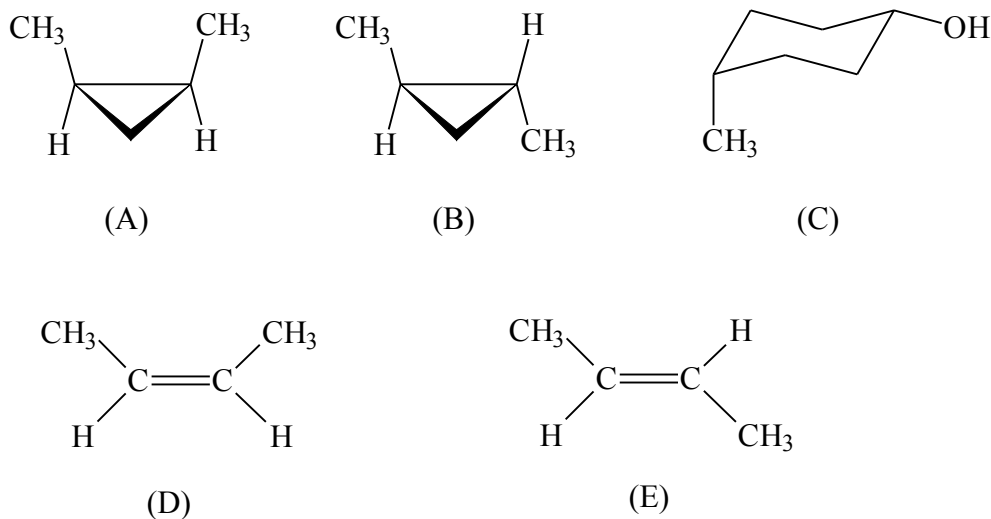
Go by definition or look for plane of symmetry/point of inversion. The answer is B.

7. The relationship between (A) and (B) structures in the previous question is:

A) identical
B) structural isomers
C) diastereomers
D) enantiomers
E) None of the above

Again need to know terms and how to apply them. The answer is C.

8. Which of the following alkyl halides would you expect to undergo S_N1 reaction most rapidly ?

$CH_3CH_2CH_2CH_2CH_2\text{-}Br$ $CH_3CH_2CH_2\overset{\displaystyle |}{\underset{\displaystyle CH_3}{CH}}\text{-}Br$ $CH_3CH_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}}\text{-}Br$

     (A)   (B)   (C)

     (D) They will not undergo S_N1 reaction

     (E) They react at the same rate

The key is to know how a Sn1 reaction proceeds (mechanism). For Sn1, the leaving group departs before bond forming happens. Therefore the intermediate is carbocation, which is the most stable on a tertiary carbon. The answer is (C). (can you explain why and how the rate depends on the stability of the intermediate?)

9. For the following reaction, the overall enthalpy change is:

$$CH_3CH_2CH_3 \;+\; Br_2 \longrightarrow CH_3CH_2CH_2Br \;+\; HBr$$

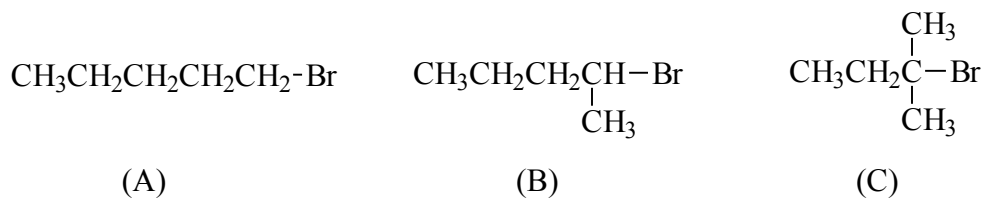(A) -12 kcal/mol   (B) +12 kcal/mol   (C) -300 kcal/mol
(D) +300 kcal/mol   (E) +15 kcal/mol

The key here is to understand how the heat of the reaction is related to bond dissociation energy (BDE) and the definition of BDE. Also it is essential to know that bond breaking requires energy. The answer is (A)

10. Which of the following alkyl halides would you expect to give the highest yield of substitution product (S_N2) with $CH_3CH_2O^-\ Na^+$?

$CH_3CH_2CH_2CH_2CH_2\text{-}Br$ $CH_3CH_2CH_2\overset{\displaystyle |}{\underset{\displaystyle CH_3}{CH}}\text{-}Br$ $CH_3CH_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}}\text{-}Br$

   (A)   (B)   (C)

     (D) They will give same yield of substitution products
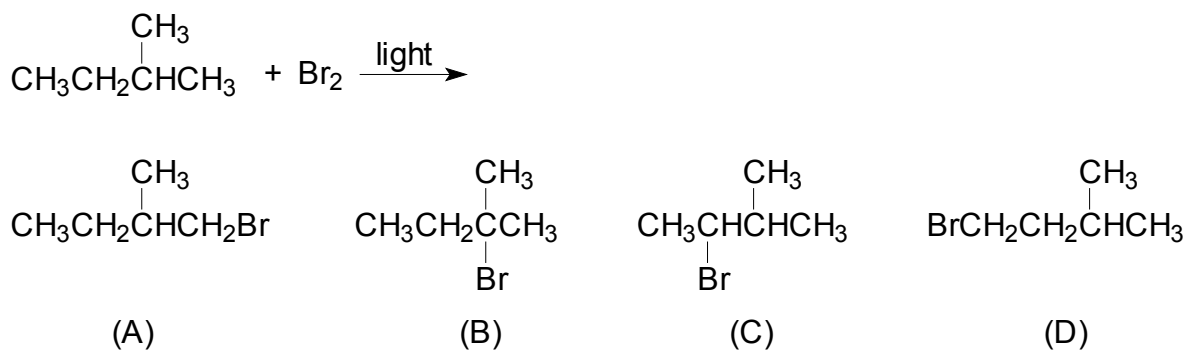
     (E) None of them gives substitution products

For SN2, the nucleophile has to attack from the back of the leaving group. Therefore the carbon being attacked must not be sterically hindered, otherwise elimination will compete. The answer here is (A) which would give the best yield of substitution product.

11. Predict which of the following carbocations has the highest energy:

$\overset{\oplus}{C}H_2$ (A) CH_3 (B) CH_3 (C) CH_3 (D)

(E) All are equally stable
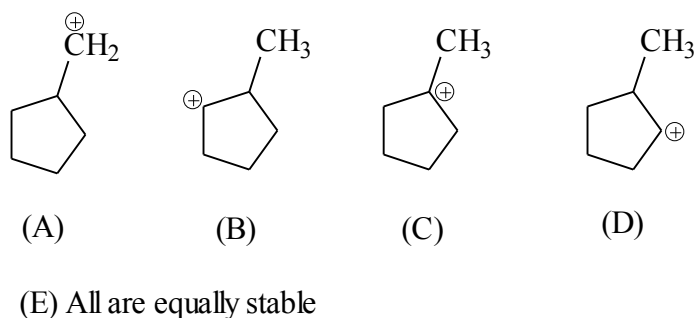
Higher energy means less stable. Stability is related to how much the charge can be spread out, which is, in this case, related to whether alkyl groups (substitution pattern) behave as electron withdrawing or donating groups. The answer is (A)

12. Bromination of alkanes is a much slower reaction than chlorination. Which of the following is expected to be the major organic product when 2-methylbutane is allowed to react with Br_2 in the presence of light or heat?

$$CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_3 \ + \ Br_2 \ \xrightarrow{\text{light}}$$

$CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2Br$ $CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}}CH_3$ $CH_3\overset{\overset{\displaystyle CH_3}{|}}{C}H\overset{\underset{\displaystyle Br}{|}}{C}HCH_3$ $BrCH_2CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_3$

(A)   (B)   (C)   (D)

The answer here is (B). How is rate of a reaction related to selectivity? Which hydrogen in the reactant is the most reactive towards radical abstraction?

13. Which of the following free radical is the most stable ?

$\bullet CH_2$ (a) CH_3 (b) CH_3 (c) CH_3 (d) CH_3 (e)
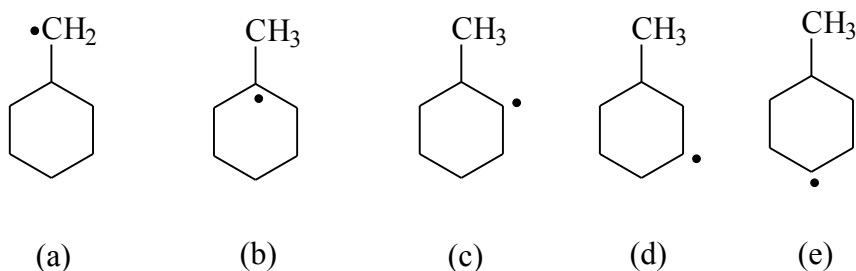
How is radical stability affected by substitution pattern? (answer is (B))

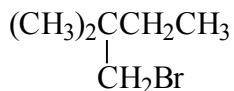14. Which of the above drawing is the most stable if the radical carbon is changed to a carbocation? (answer is B)

15. Which is the least stable in these structures if the radical carbon is changed to a carbanion?

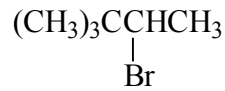(answer is A, pay attention to sign of charge!)

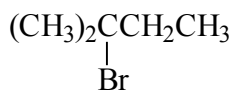*16.* The major monobromination product in the following reaction is

$$(CH_3)_3CCH_2CH_3 \ + \ Br_2 \ \xrightarrow{\ h\nu\ } \ products$$

$(CH_3)_3CCH_2CH_2Br$

(a)

$(CH_3)_2CCH_2CH_3$
|
CH_2Br

(b)

$(CH_3)_3CCHCH_3$
|
Br
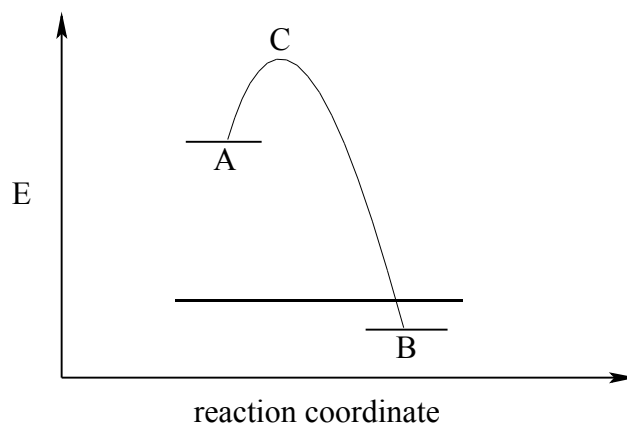
(c)

$(CH_3)_2CCH_2CH_3$
|
Br

(d)

(e) none of the above

The answer is (C) because selectivity is high for bromination which prefers to attach the weaker C-H bond.

17. According to the following energy profile, the rate of reaction from A to B is determined by

reaction coordinate

(a) the energy of A only
(b) the energy of B only
(c) the energy difference between C and A
(d) the energy difference between B and A
(e) the energy of C only

The answer is C (activation energy)

18. The bond dissociation energy is the amount of energy required to break a bond

      a)   so as to produce the more stable pair of ions
      b)   heterolytically
      c)   homolytically
      d)   via hydrogenation
      e)   none of the above

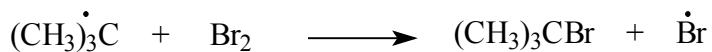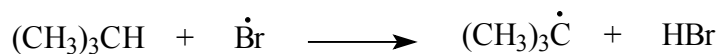Definition: homolytically

19. Given the bond dissociation energies below (in kcal/mol), calculate the overall $\Delta H°$ for the following reaction:

$$(CH_3)_3CH \ + \ Br_2 \longrightarrow (CH_3)_3CBr \ + \ HBr$$
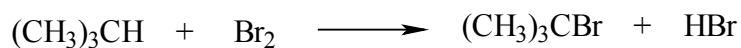
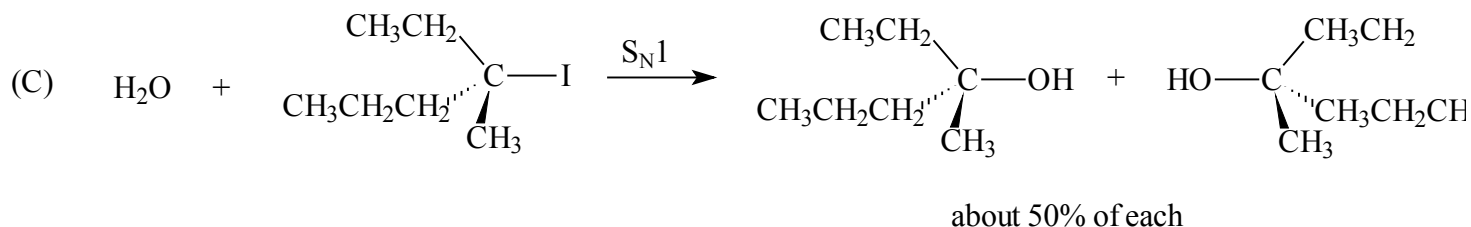|	
$(CH_3)_3C\text{-}H$	91
$(CH_3)_3C\text{-}Br$	65
Br-Br	46
H-Br	88
CH3-Br	70

$\Delta H° = \ $ -16 kcal/mol

Write chain propagation steps for the above bromination reaction.

$$(CH_3)_3CH \ + \ \dot{Br} \longrightarrow (CH_3)_3\dot{C} \ + \ HBr$$

$$(CH_3)_3\dot{C} \ + \ Br_2 \longrightarrow (CH_3)_3CBr \ + \ \dot{Br}$$
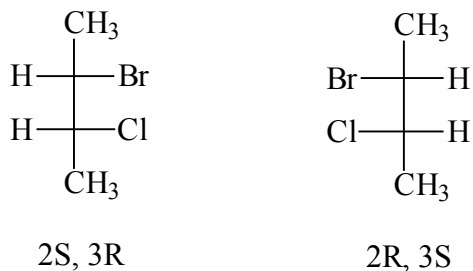
End of Part 1

Part 2:

1. (14 pt) Draw the organic product expected from each of the following reactions. Be sure to indicate stereochemistry where appropriate and to include stereoisomers if any. In case two or more stereoisomers are formed, label their relationship as diastereomers, enantiomers, structural isomers, or conformers.

(A) [cyclohexane with I substituent] + NaO—C(=O)—CH$_3$ $\xrightarrow{S_N2}$ [cyclohexane with O—C(=O)—CH$_3$ substituent]

(B) [C bonded to H, Cl, D, CH$_3$] + NaOCH$_3$ $\xrightarrow{S_N2}$ CH$_3$O—C (bonded to H, D, CH$_3$)

(C) H$_2$O + [C bonded to CH$_3$CH$_2$, I, CH$_3$CH$_2$CH$_2$, CH$_3$] $\xrightarrow{S_N1}$ [C bonded to CH$_3$CH$_2$, OH, CH$_3$CH$_2$CH$_2$, CH$_3$] + HO—C (bonded to CH$_3$CH$_2$, CH$_3$CH$_2$CH$_2$CH, CH$_3$)

about 50% of each
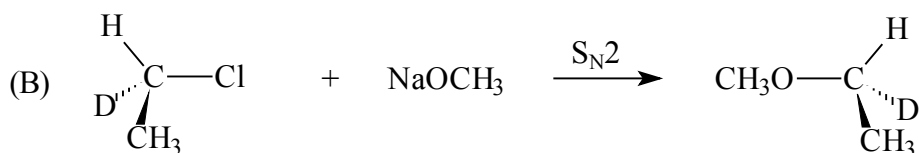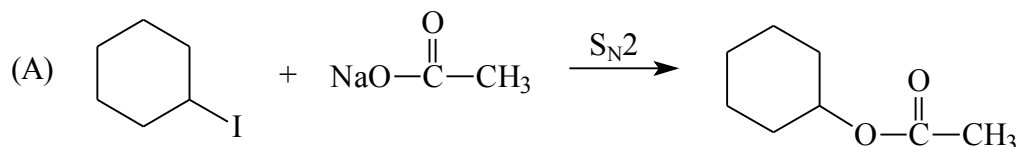
2. (10 pt) (A) Draw Fisher projections for (2R, 3S)-2-bromo-3-chlorobutane and (2S, 3R)-2-bromo-3-chlorobutane, with the carbon chain on the vertical line. Label each structure as (2R, 3S) or (2S, 3R).

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      CH3                  CH3
 H ——|—— Br          Br ——|—— H
 H ——|—— Cl          Cl ——|—— H
      CH3                  CH3

    2S, 3R               2R, 3S
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(B) Assume that you have a mixture of equal amount of each of the above compounds. Can they be separated into two containers based on physical properties such as b.p., m.p., etc.? If yes, which technique would you use? If no, briefly explain why not.

The two compounds as drawn are enantiomers which have identical b.p. and other physical properties (different only towards plane polarized light). Therefore they can't be separated based on physical properties alone.

3.(14 pt) The following equation shows the bromination of methane:

$$CH_4 \quad + \quad Br_2 \quad \xrightarrow{\text{light}} \quad CH_3Br \quad + \quad HBr$$
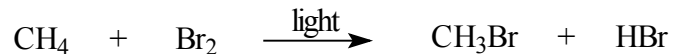
1) Propose a mechanism (initiation and propagation steps) to account for the product formation. Label the steps as A, B, C... and calculate the $\Delta H°$ for each step.

See chlorination of methane discussed in the lecture notes and textbook.
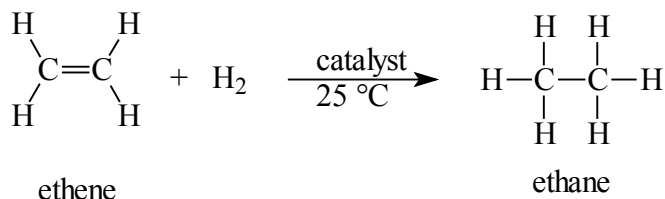
2) Draw an energy diagram (using the $\Delta H°$ for each step to set appropriate energy levels) for the two **propagation** steps, and decide which step is more likely the rate-determining step? (label this step as rds)

see the textbook for chlorination of methane and apply it to this case.

energy

reaction coordinate (progress)
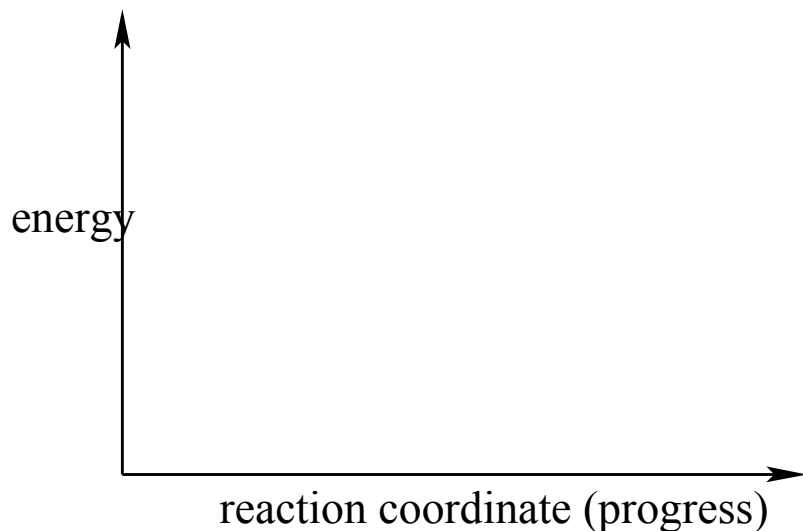
4. (14pt) At the room temperature (25 °C), ethene can be hydrogenated (add one mole of H_2 to the double bond) to give ethane in the presence of a catalyst, as shown below:

$$\underset{\text{ethene}}{\overset{\text{H}}{\underset{\text{H}}{}}\text{C}=\text{C}\overset{\text{H}}{\underset{\text{H}}{}}} \quad + \quad H_2 \quad \xrightarrow[\text{25 °C}]{\text{catalyst}} \quad \underset{\text{ethane}}{\text{H}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{H}}$$

It is known from the experiment that $\Delta G° = -30$kcal/mol. Answer the following questions:

(A) Calculate the equilibrium constant for this reaction if there is sufficient data. If there is not enough data to allow for such calculation, simply state so.

$\Delta G° = -RT\ln K$, since we know R is gas constant = 1.98 cal mol^{-1} k^{-1}, T is absolute temperature, and $\Delta G°$ is a given number, we can calculate K. It is important to pay attention to the unit here! R's unit is cal but $\Delta G°$ is usually given as kcal!

(B) Predict the sign of this $\Delta S°$ for this reaction. Briefly explain your reasoning.

Entropy measures degree of chaotic. Since two molecules combine to give one, the entropy has decreased, thus the change is negative.

(C) Predict the sign of $\Delta H°$ for this reaction. Explain briefly how you arrive at this conclusion.

$\Delta G° = \Delta H° - T\Delta S°$. It then follows that $\Delta H°$ for this reaction is negative.