Student Solution Supplement for
INTRODUCTION TO ORGANIC CHEMISTRY

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University of California, Berkeley

Macmillan Publishing Co., Inc.

NEW YORK

Collier Macmillan Publishers

LONDON

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CONTENTS

Organic Chemistry generally has the reputation of being one of the most difficult courses on campus. It contains a great deal of material, including many names and facts, together with theoretical principles and examples of inductive and deductive logic. Learning organic chemistry requires both the memorizing aspects of a language course and the problem-solving examples of a mathematics course. Many students dread the prospect or necessity of taking organic chemistry. Yet, countless thousands of students have learned the subject and many have thoroughly enjoyed it. Learning organic chemistry is work, but so are many other skills worth knowing and doing. The time and effort required provide their reward in that unique joy of accomplishment that is among life's greatest pleasures.

Learning anything requires the reinforcement not just of repetition, but of repetition in different contexts. In the typical college or university chemistry course, such reiteration is provided in several different ways in order to involve the whole brain. The following techniques are used generally.

Lectures. The lecture is often underrated or misunderstood in the learning process, but it is especially important for a subject as large and complex as organic chemistry. Modern textbooks in organic chemistry, including ours, contain a great deal of material, more than can be memorized by the average student. However, much of this material provides the factual and historical justification for generalizations presented and does not need to be learned specifically. Reactions, for example, can be divided into important and less important categories, with a broad intermediate range depending on

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individual interests and abilities. In this text, the most important
reactions are clearly distinguished by the experimental details and
examples given. A further guide is provided by the frequency with
which a given reaction is exampled in the text, as summarized in
Appendix VIII. In addition, most lecturers provide further guides to
the relative importance of different topics. Moreover, we *listen*
to a lecturer and learn with our ears, using a different part of the
brain from that used in reading. Some persons learn better by having
material presented aurally, others learn more through visual experience
Most of us learn best by a combination of both.

Lecture Notes. Taking lecture notes helps in several ways. It
is difficult to pay continuous attention to any lecture for an entire
period, particularly if the lecturer is not having one of his best
days. Taking lecture notes helps to focus concentration and minimize
that lapse of attention and drifting into fantasies which is all too
human. Even though the material in lecture notes is already mostly
given in the textbook, the act of writing uses a different brain
function and provides a further reinforcement for learning. Lecture
notes are generally hurried and often contain typographical errors.
It is important to transcribe the rough notes into legible and organ-
ized form as soon as possible after the lecture. This should be done
while the lecture is still fresh in the memory and before this short-
term memory has started to fade. Many students in our modern world
use tape recorders in class. Tape recorders can be useful to cover
those inevitable attention lapses, but they are not a substitute for
lecture notes. Remember that a principal function of the lecture
notes is to involve one more and different brain function in the
learning experience.

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Laboratory. Most introductory organic chemistry courses have an associated laboratory. The primary purpose of the laboratory is to learn the experimental operations of organic chemistry and to gain facility in the associated physical manipulations. It takes actual practice to set up experimental apparatus and carry out a preparation, just as it takes manipulative skills and practice to play the piano or make a béarnaise. However, the laboratory experience provides still another reinforcement route to learning the organic chemistry in lecture and text. Furthermore, organic compounds are stuff that melts, boils, smells, has colors and crystalline form. Modern organic chemistry has lots of abstract theories and principles, but they apply to real physical substances. This character of organic compounds is emphasized in the text, but is reinforced by the laboratory work.

Textbook Study. Mere reading is not study. Study requires reading with concentration and thought. It is work and requires self-discipline. It may help to constantly formulate examples. In studying a new reaction, run through specific examples in your mind, using the examples provided in the text as a guide. In the examples of nomenclature given, provide further examples of your own by adding or taking away one or more carbons. Most reactions fall into a very few categories such as displacement, proton or hydrogen atom transfer, bond dissociation, etc. In studying each new reaction, see how these categories apply. The most important thing to remember about any given reaction is that it exists; that is, that a given functional group transformation or interconversion can be accomplished. It is secondarily useful, although still important, to know the overall reaction conditions and reagents required and any structural limitations involved. It is generally sufficient to know these aspects

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in general terms, such as heating the reaction mixture or keeping it
cold, having acid or base present, etc., rather than memorizing a
host of specific details. Remember that when a chemist actually runs
a given preparation in the laboratory, he first looks up specific
related examples in the literature in order to provide specific
experimental details.

   Problems Sets. Except for the first and final two chapters,
each chapter in this text is followed by a number of problems. *Working
problems is as important in organic chemistry as in mathematics.*
It is not sufficient with respect to each problem to thumb back through
the chapter to find the answer, or to read the answer in this answer
book. In principle, the student should learn the material in each
chapter sufficiently well to be able to answer all of the questions
without such reference, and to use the answer book only as a check.
In practice, however, the working out of problems is still another
path to reinforcement and learning, and many of the answers, especially
for the early chapters, contain explanations as to how the problem
was solved. Multi-step syntheses provide an excellent test of know-
ledge. It is necessary but not sufficient to know each reaction; a
multi-step synthesis requires that the correct reactions be put
together in the proper sequence. Many students find it useful to
construct "flash cards" for learning reactions. If you use this
technique, be sure to make your own. Remember that the process of
writing out the flash cards helps one to learn what's on them.

   The answers to the problems should be consulted only after a
serious attempt has been made to solve each problem. If the answer
given is not clear or understandable, check back through the textbook

and your lecture notes. If confusion still exists, by all means see your professor and/or teaching assistant. That is what they are paid for, and most organic chemistry classes are too large for the instructor to come to you. Most instructors like to teach, and by using their office hours judiciously, you give them the opportunity to derive additional pleasure from their profession. Finally, but most important, study should be frequent and in continuous pieces. The student who limits his study to "cramming" for examinations will not learn organic chemistry. There is a great deal of structural hierarchy in the science, and a given level must be thoroughly understood in order to learn what comes next.

With these guides, we hope that you will be one of the many students who enjoy organic chemistry.

1. (a) $H:\overset{..}{\underset{..}{O}}:\overset{:\overset{..}{O}:^-}{\underset{:\overset{..}{O}:_-}{S}}^{++}:\overset{..}{\underset{..}{O}}:^- \longleftrightarrow H:\overset{..}{\underset{..}{O}}:\overset{:O:}{\underset{:O:}{S}}:\overset{..}{\underset{..}{O}}:^-$

(b) $H:\overset{..}{N}:^-H$

(c) $\overset{\overline{:\overset{..}{O}}:N::\overset{..}{O}:}{\underset{:\overset{..}{O}::\overset{..}{N}:\overset{..}{O}:^-}{\uparrow}}$

(d) $:\overset{..}{\underset{..}{Cl}}:\overset{..}{\underset{..}{O}}:^-$

(e) $H:\overset{..}{\underset{..}{O}}:\overset{..}{\underset{H}{N}}:H$

(f) $^-:\overset{..}{\underset{..}{O}}:\overset{..}{\underset{H}{N}}:H$

(g) $:\overset{..}{\underset{..}{O}}::\overset{+}{N}::\overset{..}{\underset{..}{O}}:$

(h) $^-:\overset{..}{\underset{..}{O}}:\overset{+}{\overset{..}{O}}:\overset{..}{O}: \longleftrightarrow :\overset{..}{\underset{..}{O}}:\overset{+}{\overset{..}{O}}:\overset{..}{\underset{..}{O}}:^-$

(i) $H:\overset{\overset{+}{\cdot\cdot}}{\underset{H}{O}}:H$

(j) $:N:::\overset{+}{\underset{..}{O}}:$

(k) $H:C:::\overset{+}{\underset{..}{O}}: \longleftrightarrow H:\overset{+}{C}::\overset{..}{\underset{..}{O}}:$

(l) $^-:\overset{..}{N}::\overset{+}{N}::\overset{..}{N}:^-$

(m) $^-:\overset{..}{\underset{:\overset{..}{O}:}{O}}:C:\overset{..}{\underset{..}{O}}:^- \longleftrightarrow :\overset{..}{\underset{:\overset{..}{O}:_-}{O}}::C:\overset{..}{\underset{..}{O}}:^- \longleftrightarrow ^-:\overset{..}{\underset{:\overset{..}{O}:_-}{O}}:C::\overset{..}{\underset{..}{O}}:$

(n) $H:\overset{..}{N}::C::\overset{..}{\underset{..}{O}}:$

2. (a) $H:\overset{..}{\underset{H\cdot}{C}}:^- \equiv H-\overset{\overset{..}{|}}{\underset{|}{\underset{H}{C}}}$

(b) $H:\overset{H}{\underset{H}{C}}:\overset{+}{\underset{H}{C}} \equiv H-\overset{H}{\underset{H}{C}}-\overset{+}{\underset{H}{C}}$

(c) $H:\overset{H}{\underset{H}{C}}:\overset{H}{\underset{H}{C}}\cdot \equiv H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}$

(d) $H:\overset{..}{\underset{H}{C}}:C:::C:H \equiv H-\overset{H}{\underset{H}{C}}-C\equiv C-H$

(e) $H:\overset{H}{\underset{H}{C}}:\overset{\overset{..\cdot}{O}}{C}:\overset{H}{\underset{H}{C}}:\overset{H}{\underset{H}{C}}:H \equiv H-\overset{H}{\underset{H}{C}}-\overset{O}{\underset{}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$

(f) $H:\overset{H}{\underset{H}{C}}:\overset{..}{\underset{..}{O}}:\overset{H}{\underset{H}{C}}:H \equiv H-\overset{H}{\underset{H}{C}}-O-\overset{H}{\underset{H}{C}}-H$

(g) $H:\overset{H}{\underset{H}{C}}:\overset{..}{\underset{H}{N}}:H \equiv H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{}{N}}-H$

(h) $H:\overset{H}{\underset{H}{C}}:\overset{+}{\underset{H}{N}}:H \equiv H-\overset{H}{\underset{H}{C}}-\overset{+}{\underset{H}{N}}-H$

(i) $H:\overset{H}{\underset{H}{C}}:\overset{..}{\underset{..}{O}}:^- \equiv H-\overset{H}{\underset{H}{C}}-O^-$

(j) $H:\overset{H}{\underset{H}{C}}:\overset{+}{\underset{..}{O}}:H \equiv H-\overset{H}{\underset{H}{C}}-\overset{+}{\underset{}{O}}-H$

(k) $H:\overset{H}{C}::\overset{H}{C}:\overset{..}{\underset{..}{Cl}}: \equiv H-\overset{H}{C}=\overset{H}{C}-Cl$
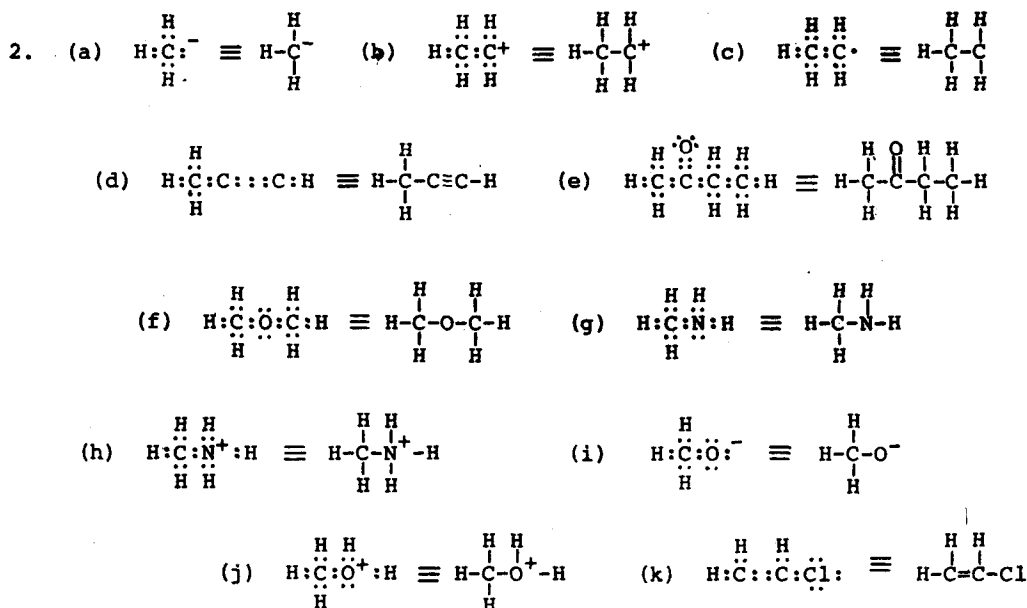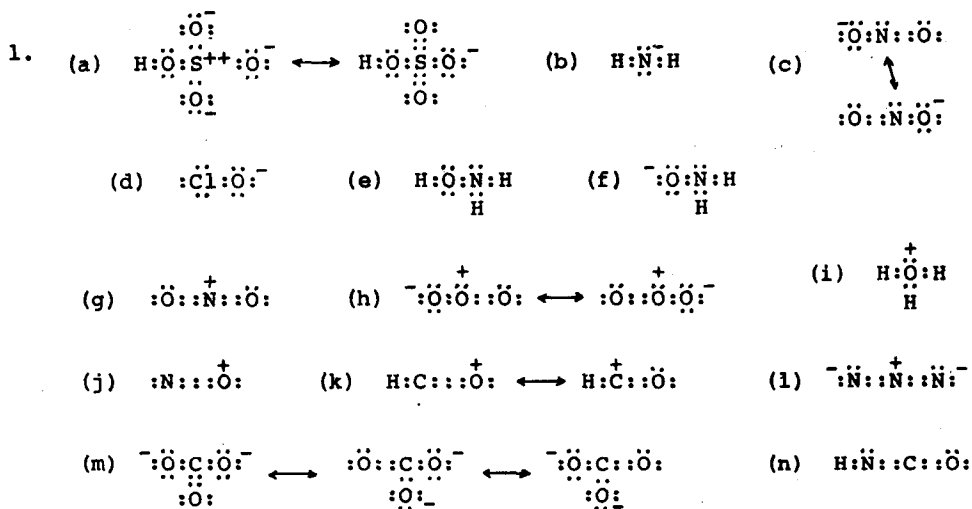
Note that in many applications it is useful to combine these symbols
by using lines to represent electron-pair bonds and retaining dots
to represent lone pairs. Examples:

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(a) $H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}:^-$ (g) $H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle \ddot{}}{}}{N}}-H$ (i) $H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\ddot{\underset{\cdot\cdot}{O}}:^-$ (j) $H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{+}{\underset{\cdot\cdot}{O}}-H$

3. (a)   (d)

   (b)

                             (e)

   (c)

4. (a) $H:\overset{\overset{\displaystyle H}{}}{\underset{\underset{\displaystyle H}{}}{C}}:\ddot{O}:H \;\rightleftharpoons\; H^+ \;+\; H:\overset{\overset{\displaystyle H}{}}{\underset{\underset{\displaystyle H}{}}{C}}:\ddot{\underset{\cdot\cdot}{O}}:^-$

   (b) $H:\overset{\overset{\displaystyle H}{}}{\underset{\underset{\displaystyle H}{}}{C}}:\ddot{O}:H \;+\; H^+ \;\rightleftharpoons\; H:\overset{\overset{\displaystyle H}{}}{\underset{\underset{\displaystyle H}{}}{C}}:\overset{\overset{\displaystyle H}{}}{\underset{\cdot\cdot}{O}}:H$
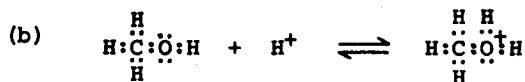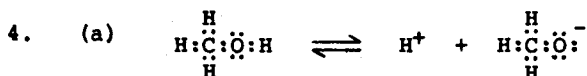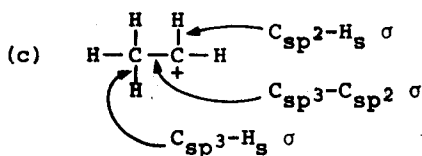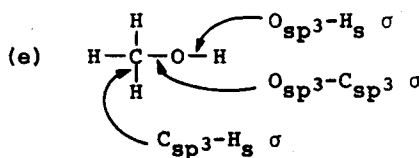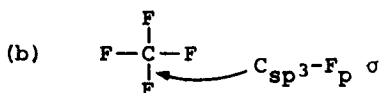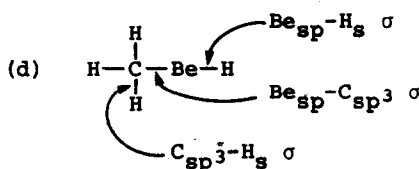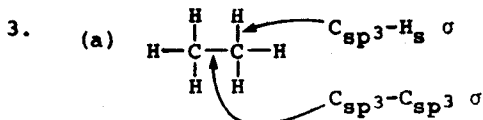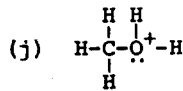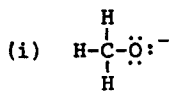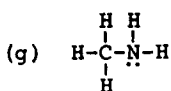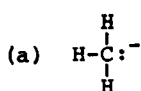
5. Resonance structures involve changes only in electronic positions or configurations; they do not involve changes in nuclear positions. The following pairs involve changes in the positions of one or more atoms and are <u>not</u> resonance structures: (b),(c), (f), (g), (j), (k).

6. (a) $H-\overset{\overset{\displaystyle O^-}{|}}{C}=\overset{+}{N}H_2$ is less important (higher energy) because of charge separation.

   (b) $H-\overset{\overset{\displaystyle O^-}{|}}{C}=CH_2$ is more important (lower energy) because the negative charge is on a more electronegative element (O rather than C).

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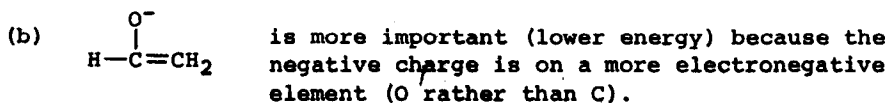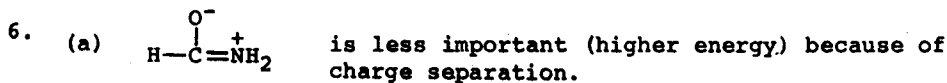
(c)
$$\begin{array}{c} O^- \\ \big| \\ H\!-\!C\!\equiv\!NH \end{array}$$
is more important because O is a more electronegative element than N.

(d) The first structure is most important because of the absence of charge separation. The second structure is next in stability, because the negative charge is associated with the more electronegative element (oxygen) and the positive charge with the more electropositive element (carbon).

(e) These structures are exactly equivalent and contribute equally to the resonance hybrid.

(f) These two structures are also equivalent.

(g) $CH_3\!-\!\overset{+}{N}\!\equiv\!C\!-\!O^-$ is more important than $CH_3\!-\!\overset{-}{N}\!-\!C\!\equiv\!O^+$ because O is more electronegative than N. Note that the most important resonance structure for this compound is $CH_3\!-\!N\!=\!C\!=\!O$, in which charge separation is absent.

(h) $\overset{-}{O}\!-\!\overset{+}{O}\!=\!O$ is more important because each atom has a complete octet. If we include all of the electrons, the second structure is $:\!\ddot{O}\!=\!\ddot{O}\!=\!\ddot{O}:$ in which the central oxygen has an expanded octet or ten electrons, a particularly unfavorable configuration for first-row elements. Note that no octet structure can be written for ozone without charge separation.

7. (a) The remaining percentage is assumed to be oxygen; hence,
70.4% C, 13.9% H, 15.7% O.

The following steps are used:

(i) Divide the weight percents by the appropriate atomic weights to derive relative numbers of atoms:

$$C, \quad \frac{70.4}{12.01} = 5.86$$

$$H, \quad \frac{13.9}{1.008} = 13.8$$

$$O, \quad \frac{15.7}{16.0} = 0.98$$

(ii) Divide by the lowest common denominator to convert to ratios of integers.

$$C, \quad \frac{5.86}{0.98} = 5.98 \cong 6$$

$$H, \quad \frac{13.8}{0.98} = 14.08 \cong 14$$

$$O, \quad \frac{0.98}{0.98} = 1$$

The formula is $C_6H_{14}O$.

Note that because of experimental errors in actual analyses, the numbers rarely come out as true integers, and some rounding off is required.

(b) CH. This is the empirical formula. To determine the molecular formula (C_2H_2, C_3H_3, etc.) additional information, such as the molecular weight, is required.

(c) C_4H_5N (d) $C_{17}H_{19}NO_3$ (e) $C_{10}H_{12}NO$
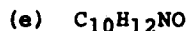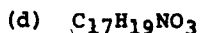
8. This problem illustrates the actual results of combustion analyses. First convert to percent compositions, then proceed as in problem #7.

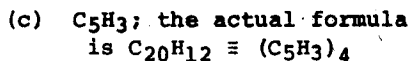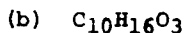(a) 0.0382 g of CO_2 contains $\frac{12.01}{44.01} \times 0.0382 = 0.0104$ g of C

$$\frac{0.0104}{0.0132} = 0.788 \quad \text{The compound contains } 78.8\% \text{ C.}$$

0.0126 g of H_2O contains $\frac{2.016}{18.016} \times 0.0126 = 0.00141$ g of H

$$\frac{0.00141}{0.0132} = 0.107 \quad \text{The compound contains } 10.7\% \text{ H.}$$

Continuing as in problem #7, we find that the empirical formula for camphor is $C_{10}H_{16}O$.

(b) $C_{10}H_{16}O_3$ (c) C_5H_3; the actual formula is $C_{20}H_{12} \equiv (C_5H_3)_4$

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9. (a) alkene   (f) ketone
   (b) ether   (g) aldehyde   (k) aromatic ring
   (c) alcohol   (h) disulfide   (l) primary amine
   (d) alkyl chloride (i) thiol   (m) alkyne
   (e) carboxylic acid (j) sulfide   (n) organometallic

10. The numbers in parentheses give the number of each functional
    group present if greater than one.

    (a) alkene, alcohol
    (b) alkene, alcohol (4), ester
    (c) tertiary amine, primary amine, ester, aromatic ring
    (d) sulfide, carboxylic acid, amide (2), ether, aromatic ring
    (e) ketone
    (f) sulfide, primary amine, carboxylic acid
    (g) alcohol (2), alkene, aromatic ring, ether, tertiary amine
    (h) organometallic
    (i) sulfide, halide (2)
    (j) none (alkane)
    (k) ether (3), primary amine, aromatic ring
    (l) alkene (5), alcohol
    (m) aromatic ring, amide, tertiary amine, alkene, ether
    (n) ester (2), tertiary amine
    (o) thiol, primary amine, amide, carboxylic acid
    (p) ketone, alkene, alcohol, alkyne

<u>Chapter 3</u>: ORGANIC REACTIONS

1. (a) $\Delta G° = \Delta H° - T\Delta S° = 7.3 - \dfrac{(298)(0.3)}{1000} = 7.21$ kcal mole^{-1}

Remember that e.u. (entropy unit) is equivalent to cal deg^{-1}
(calories, not kilocalories!); hence, the second term is divided
by 1000 to convert both enthalpy and entropy parts to the same units.

(b) $\Delta G° = -RT \ln K$ or $-2.303RT \log K$
$R \equiv 1.987$ cal deg^{-1} (again, note the difference between cal and kcal)

$$-\frac{7210}{(2.303)(1.987)(298)} = \log K = -5.29$$

$$K = 5.16 \times 10^{-6}$$

(c) No; it actually "goes to completion" in the opposite direction.

2. At 25° C, $\Delta G° = 12.22$ kcal mole^{-1} and the equilibrium lies to the left.
At 800° K, $\Delta G° = -4.6$ kcal mole^{-1} and the equilibrium lies to the
right. In this reaction, note that $\Delta H°$ controls the position of equi-
librium at low temperature, while $\Delta S°$ controls it at high temperature.
Because the entropy term is temperature-dependent, its effect is more
important at high temperatures.

3. (a) $\Delta G° = -RT \ln K$. If $K = 10$, $\Delta G° = -1.36$ kcal mole^{-1}. If $K = 100$,
$\Delta G° = -2.72$ kcal mole^{-1}. The number 1.4 is a convenient number to
remember to help put energy quantities into proper perspective.
That is, 1.4 kcal mole^{-1} corresponds approximately to an equilibrium
constant of 10; 14 kcal mole^{-1} corresponds approximately to $K = 10^{10}$.

(b) $\Delta G° = \Delta H° - T\Delta S°$. If $\Delta G° = -1.36$ kcal mole^{-1} and $\Delta S° = 0$ at 25°C,
then $\Delta H° = -1.36$ kcal mole^{-1}. If $\Delta G° = -1.36$ kcal mole^{-1} and
$\Delta H° = 0$ at 25° C, then $\Delta S° = 4.56$ e.u.

4. (a) rate $= (6 \times 10^{-6}$ M^{-1}sec$^{-1})(0.05$M$)(0.10$M$) = 3 \times 10^{-8}$ M sec^{-1}

(b) At 10% reaction, 0.005M CH$_3$Cl or OH$^-$ will have reacted. Thus,

$$\frac{(0.005\text{M})}{(3 \times 10^{-8}\text{ M sec}^{-1})} = 167,000 \text{ sec}$$

The reaction rate at 10% reaction $= (6 \times 10^{-6})(0.045)(0.095) =$
2.57×10^{-8} M sec^{-1}