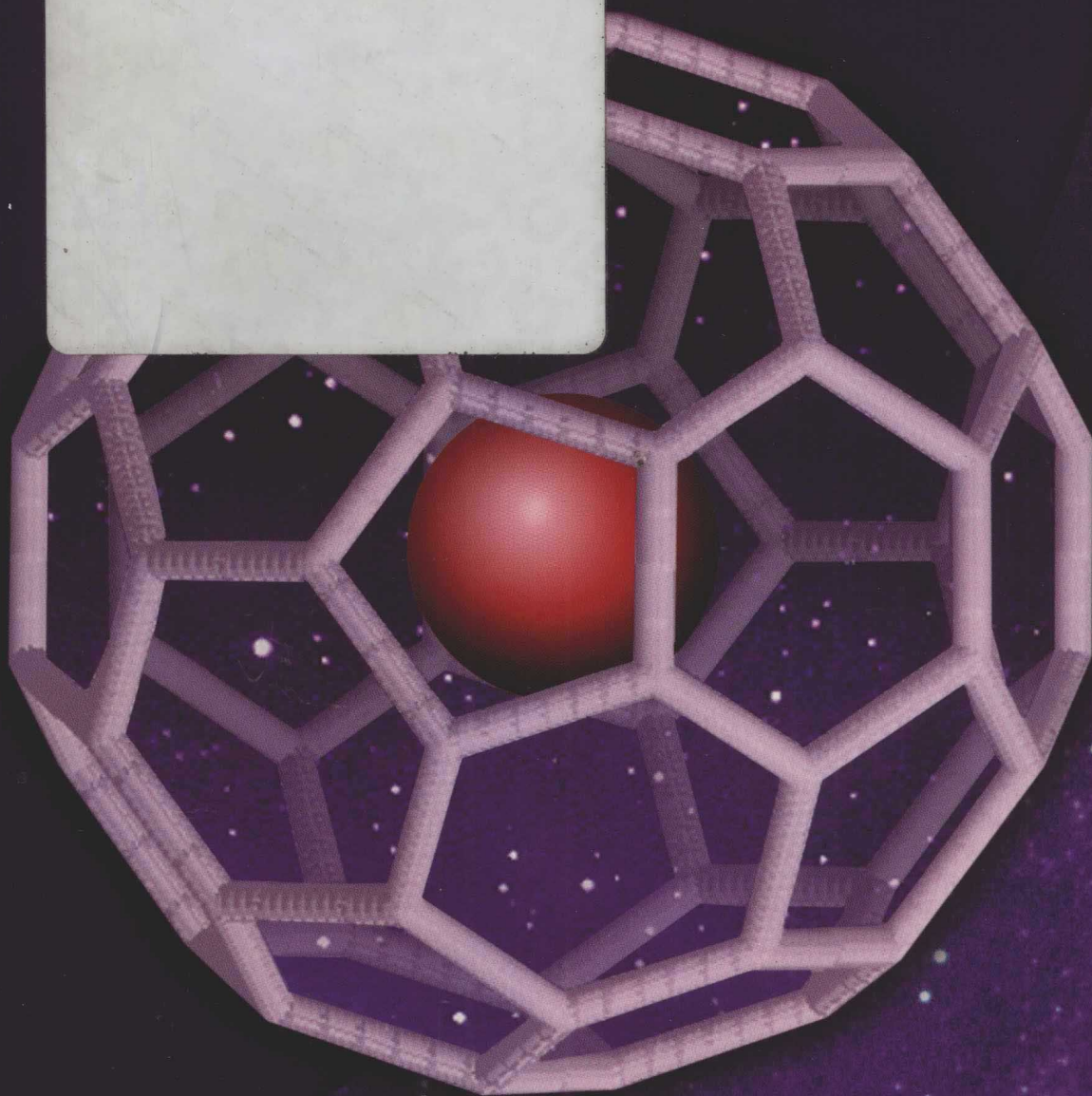


Study Solutions Manual

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ORGANIC CHEMISTRY

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Robert C. Atkins
Francis A. Carey

Student Solutions Manual
to accompany
ORGANIC CHEMISTRY

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PREFACE

It is our hope that in writing this *Solutions Manual* we will make the study of organic chemistry more meaningful and worthwhile. To be effective, a solutions manual should be more than just an answer book. What we present here was designed with that larger goal in mind.

The *Solutions Manual* contains detailed solutions to all the problems in the text. Learning how to solve a problem is, in our view, more important than merely knowing the correct answer. To that end we have included solutions sufficiently detailed to provide the student with the steps leading to the solution of each problem.

In addition, the Self-Test at the conclusion of each chapter is designed to test the student's mastery of the material. Both fill-in and multiple-choice questions have been included to truly test the student's understanding. Answers to the self-test questions may be found in the Appendix at the back of the book.

The completion of this manual was made possible through the time and talents of numerous people. Our thanks and appreciation also go to the many users of the fourth edition who provided us with helpful suggestions, comments, and corrections. We also wish to acknowledge the assistance and understanding of Kent Peterson, Shirley Oberbroeckling, and Peggy Selle of McGraw-Hill. Many thanks also go to Linda Davoli for her skillful copyediting. Last, we thank our wives and families for their understanding of the long hours invested in this work.

Robert C. Atkins
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TO THE STUDENT

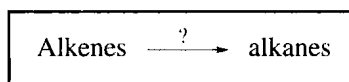
Before beginning the study of organic chemistry, a few words about “how to do it” are in order. You’ve probably heard that organic chemistry is difficult; there’s no denying that. It need not be overwhelming, though, when approached with the right frame of mind and with sustained effort.

First of all you should realize that organic chemistry tends to “build” on itself. That is, once you have learned a reaction or concept, you will find it being used again and again later on. In this way it is quite different from general chemistry, which tends to be much more compartmentalized. In organic chemistry you will continually find previously learned material cropping up and being used to explain and to help you understand new topics. Often, for example, you will see the preparation of one class of compounds using reactions of other classes of compounds studied earlier in the year.

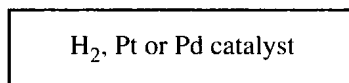
How to keep track of everything? It might be possible to memorize every bit of information presented to you, but you would still lack a fundamental understanding of the subject. It is far better to *generalize* as much as possible.

You will find that the early chapters of the text will emphasize concepts of *reaction theory*. These will be used, as the various classes of organic molecules are presented, to describe *mechanisms* of organic reactions. A relatively few fundamental mechanisms suffice to describe almost every reaction you will encounter. Once learned and understood, these mechanisms provide a valuable means of categorizing the reactions of organic molecules.

You will need to learn numerous facts in the course of the year, however. For example, chemical reagents necessary to carry out specific reactions must be learned. You might find a study aid known as *flash cards* helpful. These take many forms, but one idea is to use 3 × 5 index cards. As an example of how the cards might be used, consider the reduction of alkenes (compounds with carbon–carbon double bonds) to alkanes (compounds containing only carbon–carbon single bonds). The front of the card might look like this:



The reverse of the card would show the reagents necessary for this reaction:



The card can actually be studied in two ways. You may ask yourself: What reagents will convert alkenes into alkanes? Or, using the back of the card: What chemical reaction is carried out with hydrogen and a platinum or palladium catalyst? This is by no means the only way to use the cards—be creative! Just making up the cards will help you to study.

Although study aids such as flash cards will prove helpful, there is only one way to truly master the subject matter in organic chemistry—*do the problems!* The more you work, the more you will learn. Almost certainly the grade you receive will be a reflection of your ability to solve problems. Don’t just think over the problems, either; write them out as if you were handing them in to be graded. Also, be careful of how you use the *Solutions Manual*. The solutions contained in this book are intended to provide explanations to help you understand the problem. Be sure to write out *your* solution to the problem first and only then look it up to see if you have done it correctly.

Students frequently feel that they understand the material but don’t do as well as expected on tests. One way to overcome this is to “test” yourself. Each chapter in the *Solutions Manual* has a self-test at the end. Work the problems in these tests *without* looking up how to solve them in the text. You’ll find

it is much harder this way, but it is also a closer approximation to what will be expected of you when taking a test in class.

Success in organic chemistry depends on skills in analytical reasoning. Many of the problems you will be asked to solve require you to proceed through a series of logical steps to the correct answer. Most of the individual concepts of organic chemistry are fairly simple; stringing them together in a coherent fashion is where the challenge lies. By doing exercises conscientiously you should see a significant increase in your overall reasoning ability. Enhancement of their analytical powers is just one fringe benefit enjoyed by those students who are fully involved in the course rather than simply attending it.

Gaining a mastery of organic chemistry is hard work. We hope that the hints and suggestions outlined here will be helpful to you and that you will find your efforts rewarded with a knowledge and understanding of an important area of science.

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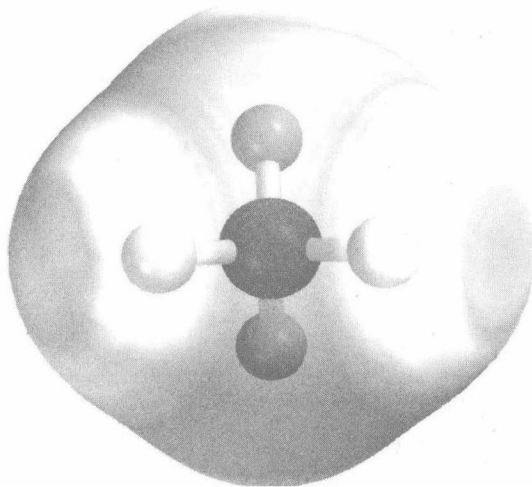
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CHAPTER 1

STRUCTURE DETERMINES PROPERTIES

SOLUTIONS TO TEXT PROBLEMS

- 1.1** The element carbon has atomic number 6, and so it has a total of six electrons. Two of these electrons are in the $1s$ level. The four electrons in the $2s$ and $2p$ levels (the valence shell) are the valence electrons. Carbon has four valence electrons.
- 1.2** Electron configurations of elements are derived by applying the following principles:
- (a) The number of electrons in a neutral atom is equal to its atomic number Z .
 - (b) The maximum number of electrons in any orbital is 2.
 - (c) Electrons are added to orbitals in order of increasing energy, filling the $1s$ orbital before any electrons occupy the $2s$ level. The $2s$ orbital is filled before any of the $2p$ orbitals, and the $3s$ orbital is filled before any of the $3p$ orbitals.
 - (d) All the $2p$ orbitals ($2p_x$, $2p_y$, $2p_z$) are of equal energy, and each is singly occupied before any is doubly occupied. The same holds for the $3p$ orbitals.
- With this as background, the electron configuration of the third-row elements is derived as follows [$2p^6 = 2p_x^2 2p_y^2 2p_z^2$]:

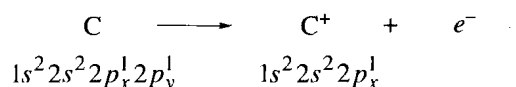
Na	($Z = 11$)	$1s^2 2s^2 2p^6 3s^1$
Mg	($Z = 12$)	$1s^2 2s^2 2p^6 3s^2$
Al	($Z = 13$)	$1s^2 2s^2 2p^6 3s^2 3p_x^1$
Si	($Z = 14$)	$1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1$
P	($Z = 15$)	$1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^1$
S	($Z = 16$)	$1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^1 3p_z^1$
Cl	($Z = 17$)	$1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^2 3p_z^1$
Ar	($Z = 18$)	$1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^2 3p_z^2$

1.3 The electron configurations of the designated ions are:

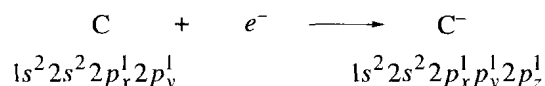
	Ion	Z	Number of Electrons in Ion	Electron Configuration of Ion
(b)	He ⁺	2	1	1s ¹
(c)	H ⁻	1	2	1s ²
(d)	O ⁻	8	9	1s ² 2s ² 2p _x ² 2p _y ² 2p _z ¹
(e)	F ⁻	9	10	1s ² 2s ² 2p ⁶
(f)	Ca ²⁺	20	18	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶

Those with a noble gas configuration are H⁻, F⁻, and Ca²⁺.

1.4 A positively charged ion is formed when an electron is removed from a neutral atom. The following equation represents the ionization of carbon and the electron configurations of the neutral atom and the ion:



A negatively charged carbon is formed when an electron is added to a carbon atom. The additional electron enters the 2p_z orbital.



Neither C⁺ nor C⁻ has a noble gas electron configuration.

1.5 Hydrogen has one valence electron, and fluorine has seven. The covalent bond in hydrogen fluoride arises by sharing the single electron of hydrogen with the unpaired electron of fluorine.

Combine H• and •F• to give the Lewis structure for hydrogen fluoride H:F•:

1.6 We are told that C₂H₆ has a carbon-carbon bond.

Thus, we combine two •C• and six H• to write the Lewis structure of ethane $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{H}:\text{C}:\text{C}:\text{H} \\ | \quad | \\ \text{H} \quad \text{H} \end{array}$

There are a total of 14 valence electrons distributed as shown. Each carbon is surrounded by eight electrons.

1.7 (b) Each carbon contributes four valence electrons, and each fluorine contributes seven. Thus, C₂F₄ has 36 valence electrons. The octet rule is satisfied for carbon only if the two carbons are attached by a double bond and there are two fluorines on each carbon. The pattern of connections shown (left) accounts for 12 electrons. The remaining 24 electrons are divided equally (six each) among the four fluorines. The complete Lewis structure is shown on the right.



(c) Because the problem states that the atoms in C₃H₃N are connected in the order CCCN and all hydrogens are bonded to carbon, the order of attachments can only be as shown (on the left) so as to have four bonds to each carbon. Three carbons contribute 12 valence electrons, three hydrogens

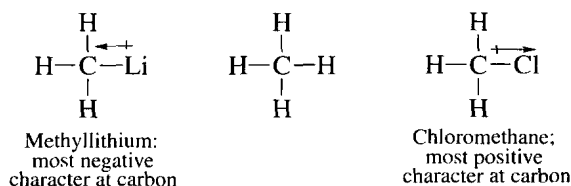
contribute 3, and nitrogen contributes 5, for a total of 20 valence electrons. The nine bonds indicated in the partial structure account for 18 electrons. Because the octet rule is satisfied for carbon, add the remaining two electrons as an unshared pair on nitrogen (on the right).



- 1.8 The degree of positive or negative character at carbon depends on the difference in electronegativity between the carbon and the atoms to which it is attached. From Table 1.2, we find the electronegativity values for the atoms contained in the molecules given in the problem are:

Li	1.0
H	2.1
C	2.5
Cl	3.0

Thus, carbon is more electronegative than hydrogen and lithium, but less electronegative than chlorine. When bonded to carbon, hydrogen and lithium bear a partial positive charge, and carbon bears a partial negative charge. Conversely, when chlorine is bonded to carbon, it bears a partial negative charge, and carbon becomes partially positive. In this group of compounds, lithium is the least electronegative element, chlorine the most electronegative.



- 1.9 (b) The formal charges in sulfuric acid are calculated as follows:

	Valence Electrons in Neutral Atom	Electron Count	Formal Charge
Hydrogen:	1	$\frac{1}{2}(2) = 1$	0
Oxygen (of OH):	6	$\frac{1}{2}(4) + 4 = 6$	0
Oxygen:	6	$\frac{1}{2}(2) + 6 = 7$	-1
Sulfur:	6	$\frac{1}{2}(8) + 0 = 4$	+2

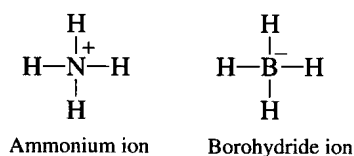
$\begin{array}{c} :\ddot{\text{O}}:^- \\ | \\ \text{H}-\ddot{\text{O}}-\text{S}^{2+}-\ddot{\text{O}}-\text{H} \\ | \\ :\ddot{\text{O}}:^- \end{array}$

(c) The formal charges in nitrous acid are calculated as follows:

	Valence Electrons in Neutral Atom	Electron Count	Formal Charge
Hydrogen:	1	$\frac{1}{2}(2) = 1$	0
Oxygen (of OH):	6	$\frac{1}{2}(4) + 4 = 6$	0
Oxygen:	6	$\frac{1}{2}(4) + 4 = 6$	0
Nitrogen	5	$\frac{1}{2}(6) + 2 = 5$	0

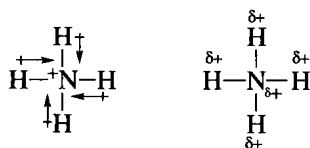
$$\text{H}-\ddot{\text{O}}-\ddot{\text{N}}=\ddot{\text{O}}:$$

- 1.10** The electron counts of nitrogen in ammonium ion and boron in borohydride ion are both four (one half of eight electrons in covalent bonds).

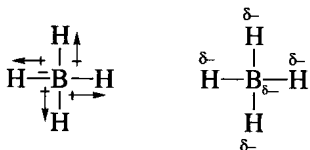


Because a neutral nitrogen has five electrons in its valence shell, an electron count of 4 gives it a formal charge of +1. A neutral boron has three valence electrons, and so an electron count of 4 in borohydride ion corresponds to a formal charge of -1.

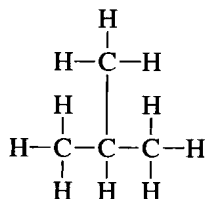
- 1.11** As shown in the text in Table 1.2, nitrogen is more electronegative than hydrogen and will draw the electrons in N—H bonds toward itself. Nitrogen with a formal charge of +1 is even more electronegative than a neutral nitrogen.



Boron (electronegativity = 2.0) is, on the other hand, slightly less electronegative than hydrogen (electronegativity = 2.1). Boron with a formal charge of -1 is less electronegative than a neutral boron. The electron density in the B—H bonds of BH_4^- is therefore drawn toward hydrogen and away from boron.

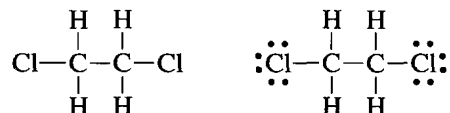


- 1.12** (b) The compound $(\text{CH}_3)_3\text{CH}$ has a central carbon to which are attached three CH_3 groups and a hydrogen.

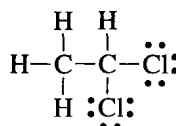


Four carbons and ten hydrogens contribute 26 valence electrons. The structure shown has 13 covalent bonds, and so all the valence electrons are accounted for. The molecule has no unshared electron pairs.

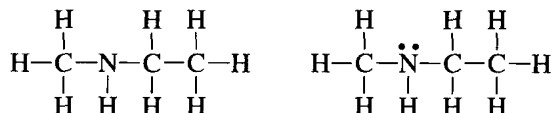
- (c) The number of valence electrons in $\text{ClCH}_2\text{CH}_2\text{Cl}$ is 26 ($2\text{Cl} = 14$; $4\text{H} = 4$; $2\text{C} = 8$). The constitution at the left shows seven covalent bonds accounting for 14 electrons. The remaining 12 electrons are divided equally between the two chlorines as unshared electron pairs. The octet rule is satisfied for both carbon and chlorine in the structure at the right.



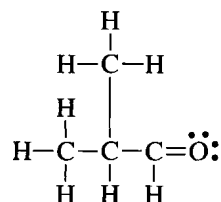
- (d) This compound has the same molecular formula as the compound in part (c), but a different structure. It, too, has 26 valence electrons, and again only chlorine has unshared pairs.



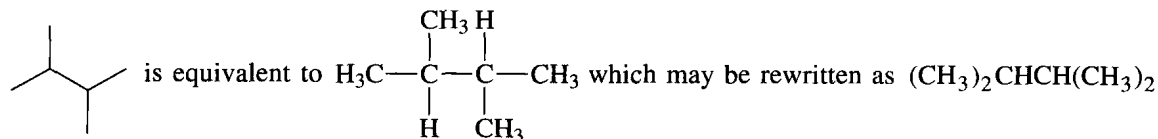
- (e) The constitution of $\text{CH}_3\text{NHCH}_2\text{CH}_3$ is shown (on the left). There are 26 valence electrons, and 24 of them are accounted for by the covalent bonds in the structural formula. The remaining two electrons complete the octet of nitrogen as an unshared pair (on the right).



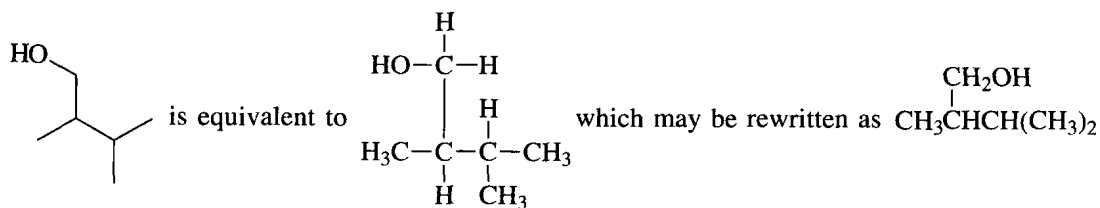
- (f) Oxygen has two unshared pairs in $(\text{CH}_3)_2\text{CHCH}=\text{O}$.



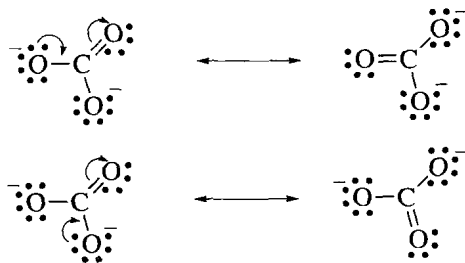
- 1.13** (b) This compound has a four-carbon chain to which two other carbons are attached.



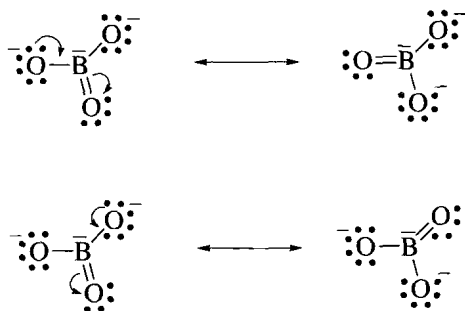
- (c) The carbon skeleton is the same as that of the compound in part (b), but one of the terminal carbons bears an OH group in place of one of its hydrogens.



- (c) All three oxygens are equivalent in carbonate ion. Either negatively charged oxygen can serve as the donor atom.



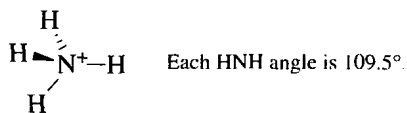
- (d) Resonance in borate ion is exactly analogous to that in carbonate.



and



- 1.17** There are four B—H bonds in BH_4^- . The four electron pairs surround boron in a tetrahedral orientation. The H—B—H angles are 109.5° .
- 1.18** (b) Nitrogen in ammonium ion is surrounded by eight electrons in four covalent bonds. These four bonds are directed toward the corners of a tetrahedron.



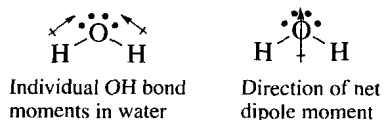
- (c) Double bonds are treated as a single unit when deducing the shape of a molecule using the VSEPR model. Thus azide ion is linear.



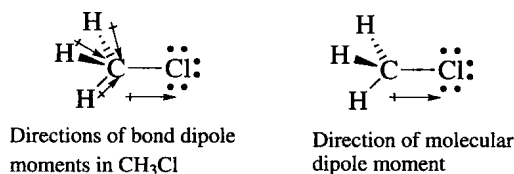
- (d) Because the double bond in carbonate ion is treated as if it were a single unit, the three sets of electrons are arranged in a trigonal planar arrangement around carbon.



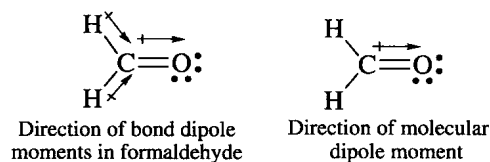
- 1.19** (b) Water is a bent molecule, and so the individual O—H bond dipole moments do not cancel. Water has a dipole moment.



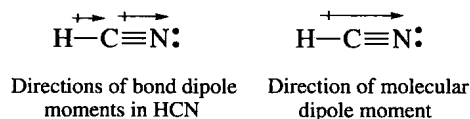
- (c) Methane, CH_4 , is perfectly tetrahedral, and so the individual (small) $\text{C}-\text{H}$ bond dipole moments cancel. Methane has no dipole moment.
- (d) Methyl chloride has a dipole moment.



- (e) Oxygen is more electronegative than carbon and attracts electrons from it. Formaldehyde has a dipole moment.



- (f) Nitrogen is more electronegative than carbon. Hydrogen cyanide has a dipole moment.



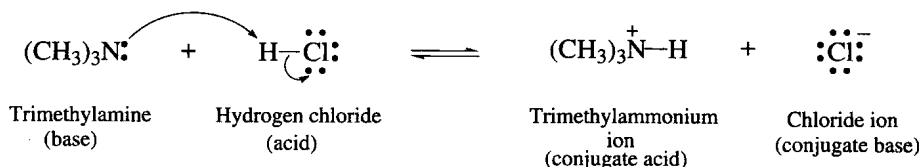
1.20 The strength of an acid can be expressed by its $\text{p}K_a$, given by the expression:

$$\text{p}K_a = -\log K_a$$

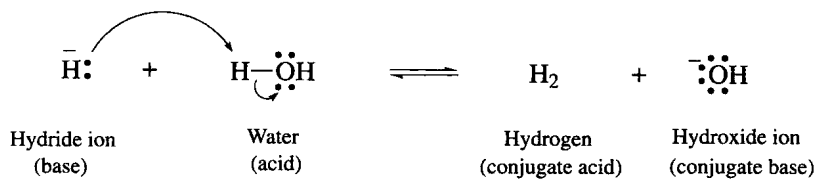
The K_a of salicylic acid is 1.06×10^{-3} ; its $\text{p}K_a$ is 2.97.

1.21 Because the $\text{p}K_a$ of HCN is given as 9.1, its $K_a = 10^{-9.1}$. In more conventional notation, $K_a = 8 \times 10^{-10}$.

1.22 (b) In an acid-base reaction, a proton is transferred from the Brønsted acid, in this case HCl , to the Brønsted base, in this case $(\text{CH}_3)_3\text{N}$. Remember to use curved arrows to track the movement of electrons, not atoms.



1.23 Hydride ion is a strong base and will remove a proton from water. The conjugate acid of hydride ion is hydrogen (H_2).



- 1.24 (b, c) You can determine the relative strength of two bases by comparing the pK_a s of their respective conjugate acids. Remember that the stronger base is derived from the weaker conjugate acid.

Base:	$\text{HC}\equiv\text{C}^-$	$\text{H}_2\ddot{\text{N}}^-$	$\text{CH}_3\text{CH}_2\ddot{\text{O}}^-$
Conjugate acid:	$\text{HC}\equiv\text{CH}$	NH_3	$\text{CH}_3\text{CH}_2\text{OH}$
pK_a of conjugate acid:	26	36	16

Recall that the smaller pK_a is associated with the stronger acid. Ammonia is a weaker acid than acetylene ($\text{HC}\equiv\text{CH}$), therefore amide ion ($\text{H}_2\ddot{\text{N}}^-$) is a stronger base than acetylide ion ($\text{HC}\equiv\text{C}^-$). Similar reasoning leads to the conclusion that because acetylene is a weaker acid than ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), acetylide ion is a stronger base than ethoxide ion ($\text{CH}_3\text{CH}_2\ddot{\text{O}}^-$).

- 1.25 Bond strength weakens going down a group in the periodic table. Because sulfur lies below oxygen, the $\text{H}-\text{S}$ bond is weaker than the $\text{H}-\text{O}$ bond. We would expect H_2S to be a stronger acid than H_2O , and this prediction is borne out by the data in Table 1.7. The relevant pK_a s are:

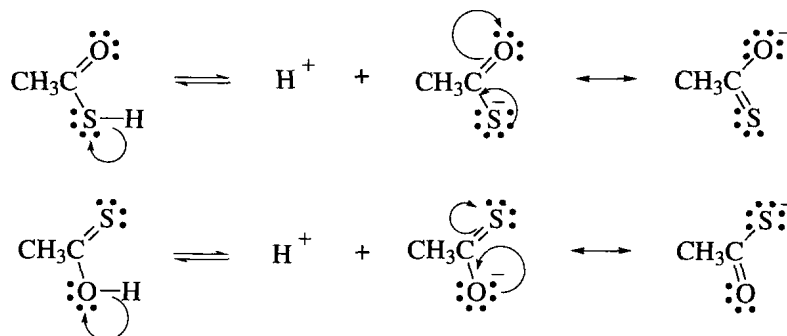
	H_2S	H_2O
pK_a	9	15.7

Because the stronger acid forms the weaker conjugate base, HS^- is a weaker base than HO^- .

- 1.26 (b) In part (a) of the problem you determined that $(\text{CH}_3)_2\ddot{\text{O}}\text{H}^+$ is a stronger acid than $(\text{CH}_3)_3\text{NH}^+$.

Recalling that the weaker acid forms the stronger conjugate base, $(\text{CH}_3)_3\text{N}^-$ is a stronger base than $(\text{CH}_3)_2\ddot{\text{O}}^-$.

- 1.27 The three oxygens in nitrate ion share a total charge of -2 . The average formal charge on each oxygen atom is -0.67 .
- 1.28 Writing the two resonance forms of each conjugate base reveals that they are equivalent.



Oxygen is more electronegative than sulfur and will bear a greater share of the negative charge.