

INTRODUCTION TO

Spectroscopy

Fifth Edition

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FIFTH EDITION

INTRODUCTION TO SPECTROSCOPY

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PREFACE

This is the fifth edition of a textbook in spectroscopy intended for students of organic chemistry. Our textbook can serve as a supplement for the typical organic chemistry lecture textbook or as a stand-alone textbook for an advanced undergraduate or first-year graduate course in spectroscopic methods. This book is also a useful tool for students engaged in research. Our aim is not only to teach students to interpret spectra, but also to present basic theoretical concepts. As with the previous editions, we have tried to focus on the important aspects of each spectroscopic technique without dwelling excessively on theory or complex mathematical analyses.

This book is a continuing evolution of materials that we use in our own courses, both as a supplement to our organic chemistry lecture course series and also as the principal textbook in our upper division and graduate courses in spectroscopic methods and advanced NMR techniques. Explanations and examples that we have found to be effective in our courses have been incorporated into this edition.

NEW TO THIS EDITION

This fifth edition of *Introduction to Spectroscopy* contains some important changes. The material on mass spectrometry has been moved closer to the front of the text and divided into two more easily digested chapters. Material on some newer sampling and ionization methods is included, as are additional methods of structural analysis using fragmentation patterns. All of the chapters dealing with nuclear magnetic resonance have been gathered together into sequential chapters. Expanded discussions of diastereotopic systems and heteronuclear coupling are included, as is a revised discussion of solvent effects in NMR.

Additional practice problems have been added to each of the chapters. We have included some additional solved problems, too, so that students can better develop strategies and skills for solving spectroscopy problems. The problems that are marked with an asterisk (*) have solutions included in the Answers to Selected Problems following Chapter 11.

We wish to alert persons who adopt this book that answers to all of the problems are available online from the publisher. Authorization to gain access to the website may be obtained through the local Cengage textbook representative.

ADVICE FOR STUDENTS

Success in working out the solutions to spectroscopy problems comes more easily and is more enjoyable by following some simple suggestions:

1. Carefully study the solved examples that may be found at the end of each chapter. Do not attempt to work on additional problems until you are comfortable with the approach that is being demonstrated with the solved examples.
2. There is great value to be gained in working collaboratively to solve spectroscopy problems. Try standing around a blackboard to exchange ideas. You will find it to be fun, and you will learn more!
3. Don't be afraid to struggle. It is too easy to look up the answer to a difficult problem, and you won't learn much. You need to train your brain to think like a scientist, and there is no substitute for hard work.
4. Work problems concurrently as you study each chapter. That will solidify the concepts in your mind.

Although this book concentrates on organic chemistry examples, be aware that the study of spectroscopy crosses over into many areas, including biochemistry, inorganic chemistry, physical chemistry, materials chemistry, and analytical chemistry. Spectroscopy is an indispensable tool to support all forms of laboratory research.

ACKNOWLEDGMENTS

The authors are very grateful to Mr. Charles Wandler, without whose expert help this project could not have been accomplished. We also acknowledge numerous contributions made by our students, who use the textbook and who provide us careful and thoughtful feedback.

Finally, once again we must thank our wives, Neva-Jean Pavia, Marian Lampman, and Cathy Vyvyan, for their support and patience. They endure a great deal in order to support us as we write, and they deserve to be part of the celebration when the textbook is completed! We honor the memory of Carolyn Kriz; we miss her and the love and encouragement that she provided.

Donald L. Pavia
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James R. Vyvyan

INTRO TO SPECTROSCOPY FIFTH EDITION SUMMARY OF CHANGES

The order of the chapters was rearranged to better reflect the requests and practices of our users. Mass Spectroscopy was moved to an earlier position, causing the renumbering.

Fourth edition chapter number/title	Fifth edition chapter number/title	Notes
1 Molecular Formulas and What Can Be Learned from Them	1 Molecular Formulas and What Can Be Learned from Them	Section 1.6, A Quick Look Ahead to Simple Uses of Mass Spectra, was deleted. (Mass Spectra were moved earlier into Chapters 3 and 4.) A new Section 1.6 is now titled: "The Nitrogen Rule." References were revised/updated.
2 Infrared Spectroscopy	2 Infrared Spectroscopy	Section 2.6, the solid samples subsection was updated to include ATR techniques. Several figures were revised/updated. Section 2.21, Alkyl and Aryl Halides, was revised. Section 2.23, How to Solve Infrared Spectral Problems, is a new section. The sections that followed were renumbered. Problems were revised. References were revised/updated.
3 Nuclear Magnetic Resonance Spectroscopy Part One: Basic Concepts.	5 Nuclear Magnetic Resonance Spectroscopy Part One: Basic Concepts.	New Section 5.20 References were revised/updated. New online resources were referenced and/or updated.
4 Nuclear Magnetic Resonance Spectroscopy Part Two: Carbon-13 etc.	6 Nuclear Magnetic Resonance Spectroscopy Part Two: Carbon-13 etc.	Section 6.4 introduces a new decoupling notation. New Section 6.12. Sections following 6.12 are renumbered. Several new problems were added. Some spectra replaced/improved. References were revised/updated. New online resources referenced and/or updated.
5 Nuclear Magnetic Resonance Spectroscopy Part Three: Spin-Spin Coupling	7 Nuclear Magnetic Resonance Spectroscopy Part Three: Spin-Spin Coupling	New discussion of splitting in diastereotopic systems. New discussion of heteronuclear splitting between ^1H - ^{19}F and S - ^{31}P Addition of solved example problems. New and revised end-of-chapter problems using coupling constant information and chemical shift calculations. References were revised/updated.
6 Nuclear Magnetic Resonance Spectroscopy Part Four: Other Topics in One-Dimensional NMR	8 Nuclear Magnetic Resonance Spectroscopy Part Four: Other Topics in One-Dimensional NMR	New discussion and examples of solvent effects. Addition of solved example problems. New and revised end-of-chapter problems. References were revised/updated.

(Continued)

Fourth edition chapter number/title	Fifth edition chapter number/title	Notes
7 Ultraviolet Spectroscopy	10 Ultraviolet Spectroscopy	Few changes.
8 Mass Spectrometry (first half) Chapter was split.	3 Mass Spectrometry Part One: Basic Theory, Instrumentation, and Sampling Techniques	To highlight the continued development and importance of mass spectrometry (MS) methods, we have moved this material to the early part of the text and split it into two chapters, one on theory and instrumentation (Chapter 3) and the other on detailed structural analysis using characteristic fragmentation patterns of common functional groups (Chapter 4). Expanded and refined discussion of sampling and ionization methods, including atmospheric pressure chemical ionization techniques. Examples of applications for different MS techniques and instrumentation, including pros and cons of different methods.
8 Mass Spectrometry (second half)	4 Mass Spectrometry Part Two: Fragmentation and Structural Analysis	Refined discussion of fragmentations in EI-MS for common functional groups. New examples of use of MS in structure determination. Additional solved example problems. New and revised end-of-chapter problems.
9 Combined Structure Problems	11 Combined Structure Problems	Several new problems were introduced. Two-dimensional spectra were replaced with new, improved ones. References were revised/updated. Online resources were updated.
10 Nuclear Magnetic Resonance Spectroscopy Part Five: Advanced NMR Techniques.	9 Nuclear Magnetic Resonance Spectroscopy Part Five: Advanced NMR Techniques	Sections 9.4 and 9.7 were extensively revised. Many of the two-dimensional spectra were replaced with new, improved ones.
Appendices	Appendices	Old Appendix 11 was removed. Values in some of the tables were updated or revised.

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MOLECULAR FORMULAS AND WHAT CAN BE LEARNED FROM THEM

Before attempting to deduce the structure of an unknown organic compound from an examination of its spectra, we can simplify the problem somewhat by examining the molecular formula of the substance. The purpose of this chapter is to describe how the molecular formula of a compound is determined and how structural information may be obtained from that formula. The chapter reviews both the modern and classical *quantitative methods* of determining the molecular formula. While use of the mass spectrometer (Chapter 3) can supplant many of these quantitative analytical methods, they are still in use. Many journals still require that a satisfactory quantitative elemental analysis (Section 1.1) be obtained prior to the publication of research results.

1.1 ELEMENTAL ANALYSIS AND CALCULATIONS

The classical procedure for determining the molecular formula of a substance involves three steps:

1. A **qualitative elemental analysis** to find out what types of atoms are present: C, H, N, O, S, Cl, and so on.
2. A **quantitative elemental analysis** (or **microanalysis**) to find out the relative numbers (percentages) of each distinct type of atom in the molecule.
3. A **molecular mass** (or **molecular weight**) **determination**.

The first two steps establish an **empirical formula** for the compound. When the results of the third procedure are known, a **molecular formula** is found.

Virtually all organic compounds contain carbon and hydrogen. In most cases, it is not necessary to determine whether these elements are present in a sample: their presence is assumed. However, if it should be necessary to demonstrate that either carbon or hydrogen is present in a compound, that substance may be burned in the presence of excess oxygen. If the combustion produces carbon dioxide, carbon must be present; if combustion produces water, hydrogen atoms must be present. Today, the carbon dioxide and water can be detected by gas chromatographic methods. Sulfur atoms are converted to sulfur dioxide; nitrogen atoms are often chemically reduced to nitrogen gas following their combustion to nitrogen oxides. Oxygen can be detected by the ignition of the compound in an atmosphere of hydrogen gas; the product is water. Currently, all such analyses are performed by gas chromatography, a method that can also determine the relative amounts of each of these gases. If the amount of the original sample is known, it can be entered, and the computer can calculate the **percentage composition** of the sample.

Unless you work in a large company or in one of the larger universities, it is quite rare to find a research laboratory in which elemental analyses are performed on site. It requires too much time to set up the apparatus and keep it operating within the limits of suitable accuracy and precision. Usually, samples are sent to a commercial **microanalytical laboratory** that is prepared to do this work routinely and to vouch for the accuracy of the results.

Before the advent of modern instrumentation, the combustion of the precisely weighed sample was carried out in a cylindrical glass tube, contained within a furnace. A stream of oxygen was passed through the heated tube on its way to two other sequential, unheated tubes that contained chemical substances that would absorb first water (MgClO_4) and then carbon dioxide (NaOH/silica). These preweighed absorption tubes were detachable and were removed and reweighed to determine the amounts of water and carbon dioxide formed. The percentages of carbon and hydrogen in the original sample were calculated by simple stoichiometry. Table 1.1 shows a sample calculation.

Notice in this calculation that the amount of oxygen was determined by difference, a common practice. In a sample containing only C, H, and O, one needs to determine the percentages of only C and H; oxygen is assumed to be the unaccounted-for portion. You may also apply this practice in situations involving elements other than oxygen; if all but one of the elements is determined, the last one can be determined by difference. Today, most calculations are carried out automatically by the computerized instrumentation. Nevertheless, it is often useful for a chemist to understand the fundamental principles of the calculations.

Table 1.2 shows how to determine the **empirical formula** of a compound from the percentage compositions determined in an analysis. Remember that the empirical formula expresses the simplest whole-number ratios of the elements and may need to be multiplied by an integer to obtain the true **molecular formula**. To determine the value of the multiplier, a molecular mass is required. Determination of the molecular mass is discussed in the next section.

For a totally unknown compound (unknown chemical source or history) you will have to use this type of calculation to obtain the suspected empirical formula. However, if you have prepared the compound from a known precursor by a well-known reaction, you will have an idea of the structure of the compound. In this case, you will have calculated the expected percentage composition of your

TABLE 1.1
CALCULATION OF PERCENTAGE COMPOSITION
FROM COMBUSTION DATA

$\text{C}_x\text{H}_y\text{O}_z + \text{excess O}_2 \longrightarrow x \text{CO}_2 + y/2 \text{H}_2\text{O}$
$9.83 \text{ mg} \qquad\qquad\qquad 23.26 \text{ mg} \quad 9.52 \text{ mg}$
$\text{millimoles CO}_2 = \frac{23.26 \text{ mg CO}_2}{44.01 \text{ mg/mmol}} = 0.5285 \text{ mmol CO}_2$
$\text{mmol CO}_2 = \text{mmol C in original sample}$ $(0.5285 \text{ mmol C})(12.01 \text{ mg/mmol C}) = 6.35 \text{ mg C in original sample}$
$\text{millimoles H}_2\text{O} = \frac{9.52 \text{ mg H}_2\text{O}}{18.02 \text{ mg/mmol}} = 0.528 \text{ mmol H}_2\text{O}$
$(0.528 \text{ mmol H}_2\text{O}) \left(\frac{2 \text{ mmol H}}{1 \text{ mmol H}_2\text{O}} \right) = 1.056 \text{ mmol H in original sample}$
$(1.056 \text{ mmol H})(1.008 \text{ mg/mmol H}) = 1.06 \text{ mg H in original sample}$
$\% \text{ C} = \frac{6.35 \text{ mg C}}{9.83 \text{ mg sample}} \times 100 = 64.6\%$
$\% \text{ H} = \frac{1.06 \text{ mg H}}{9.83 \text{ mg sample}} \times 100 = 10.8\%$
$\% \text{ O} = 100 - (64.6 + 10.8) = 24.6\%$

TABLE 1.2
CALCULATION OF EMPIRICAL FORMULA

Using a 100-g sample:

$$64.6\% \text{ of C} = 64.6 \text{ g}$$

$$10.8\% \text{ of H} = 10.8 \text{ g}$$

$$24.6\% \text{ of O} = \frac{24.6 \text{ g}}{100.0 \text{ g}}$$

$$\text{moles C} = \frac{64.6 \text{ g}}{12.01 \text{ g/mole}} = 5.38 \text{ moles C}$$

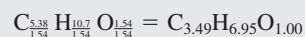
$$\text{moles H} = \frac{10.8 \text{ g}}{1.008 \text{ g/mole}} = 10.7 \text{ moles H}$$

$$\text{moles O} = \frac{24.6 \text{ g}}{16.0 \text{ g/mole}} = 1.54 \text{ moles O}$$

giving the result



Converting to the simplest ratio:



which approximates



or



sample in advance (from its postulated structure) and will use the analysis to verify your hypothesis. When you perform these calculations, be sure to use the full molecular weights as given in the periodic chart and do not round off until you have completed the calculation. The final result should be good to two decimal places: four significant figures if the percentage is between 10 and 100; three figures if it is between 0 and 10. If the analytical results do not agree with the calculation, the sample may be impure, or you may have to calculate a new empirical formula to discover the identity of the unexpected structure. To be accepted for publication, most journals require the percentages found to be *less than 0.4% off from the calculated value*. Most microanalytical laboratories can easily obtain accuracy well below this limit provided the sample is pure.

In Figure 1.1, a typical situation for the use of an analysis in research is shown. Professor Amyl Carbon, or one of his students, prepared a compound believed to be the epoxynitrile with the structure shown at the bottom of the first form. A sample of this liquid compound (25 μL) was placed in a small vial correctly labeled with the name of the submitter and an identifying code (usually one that corresponds to an entry in the research notebook). Only a small amount of the sample is required, usually a few milligrams of a solid or a few microliters of a liquid. A Request for Analysis form must be filled out and submitted along with the sample. The sample form on the left side of the figure shows the type of information that must be submitted. In this case, the professor calculated the expected results for C, H, and N and the expected formula and molecular weight. Note that the compound also contains oxygen, but that there was no request for an oxygen analysis. Two other samples were also submitted at the same time. After a short time, typically within a week, the

Microanalytical Company, Inc.

REQUEST FOR ANALYSIS FORM

Date: October 30, 2006

Report To: Professor Amyl Carbon
Department of Chemistry
Western Washington University
Bellingham, WA 98225

Sample No: PAC599A P.O. No : PO2349

Report By: AirMail Phone Email pac@www.edu
(circle one)

Elements to Analyze: C, H, N

Other Elements Present : O

Single Analysis Duplicate Analysis
 Duplicate only if results are not in range

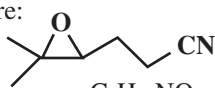
M.P. B.P. 69 °C @ 2.3 mmHg

Sensitive to : Weigh under N? Y N

Dry the Sample? Y N Details:

Hygroscopic Volatile Explosive

THEORY OR RANGE

%C <u>67.17</u>	Amount Provided <u>25 μL</u>
%H <u>8.86</u>	Structure: 
%N <u>11.19</u>	Comments: <u>C₇H₁₁NO</u>
%O <u> </u>	
%Other <u> </u>	
Mol. Wt. <u>125.17</u>	

Microanalytical Company, Inc.

November 25, 2006

Professor Amyl Carbon
 Department of Chemistry
 Western Washington University
 Bellingham, WA

RESULTS OF ANALYSIS

Sample ID	Carbon (%)	Hydrogen (%)	Nitrogen (%)
PAC599A	67.39	9.22	11.25
PAC589B	64.98	9.86	8.03
PAC603	73.77	8.20	—

Dr. B. Grant Poobah,
Ph.D.

Director of Analytical Services
 Microanalytical Company, Inc




FIGURE 1.1 Sample microanalysis forms. Shown on the left is a typical submission form that is sent with the samples. (The three shown here in labeled vials were all sent at the same time.) Each sample needs its own form. In the background on the right is the formal letter that reported the results. Were the results obtained for sample PAC599A satisfactory?

results were reported to Professor Carbon as an email (see the request on the form). At a later date, a formal letter (shown in the background on the right-hand side) is sent to verify and authenticate the results. Compare the values in the report to those calculated by Professor Carbon. Are they within the accepted range? If not, the analysis will have to be repeated with a freshly purified sample, or a new possible structure will have to be considered.

Keep in mind that in an actual laboratory situation, when you are trying to determine the molecular formula of a totally new or previously unknown compound, you will have to allow for some variance in the quantitative elemental analysis. Other data can help you in this situation since infrared (Chapter Two) and nuclear magnetic resonance (NMR) (Chapters Five to Nine) data will also suggest a possible structure or at least some of its prominent features. Many times, these other data will be less sensitive to small amounts of impurities than the microanalysis.

1.2 DETERMINATION OF MOLECULAR MASS

The next step in determining the molecular formula of a substance is to determine the weight of one mole of that substance. This may be accomplished in a variety of ways. Without knowledge of the molecular mass of the unknown, there is no way of determining whether the empirical formula, which is determined directly from elemental analysis, is the true formula of the substance or whether the empirical formula must be multiplied by some integral factor to obtain the molecular formula. In the example cited in Section 1.1, without knowledge of the molecular mass of the unknown, it is impossible to tell whether the molecular formula is $C_7H_{14}O_2$ or $C_{14}H_{28}O_4$.

In a modern laboratory, the molecular mass is determined using mass spectrometry. The details of this method and the means of determining molecular mass can be found in Chapter 3, Section 3.6. This section reviews some classical methods of obtaining the same information.

An old method that is used occasionally is the **vapor density method**. In this method, a known volume of gas is weighed at a known temperature. After converting the volume of the gas to standard temperature and pressure, we can determine what fraction of a mole that volume represents. From that fraction, we can easily calculate the molecular mass of the substance.

Another method of determining the molecular mass of a substance is to measure the freezing-point depression of a solvent that is brought about when a known quantity of test substance is added. This is known as a **cryoscopic method**. Another method, which is used occasionally, is **vapor pressure osmometry**, in which the molecular weight of a substance is determined through an examination of the change in vapor pressure of a solvent when a test substance is dissolved in it.

If the unknown substance is a carboxylic acid, it may be titrated with a standardized solution of sodium hydroxide. By use of this procedure, a **neutralization equivalent** can be determined. The neutralization equivalent is identical to the equivalent weight of the acid. If the acid has only one carboxyl group, the neutralization equivalent and the molecular mass are identical. If the acid has more than one carboxyl group, the neutralization equivalent is equal to the molecular mass of the acid divided by the number of carboxyl groups. Many phenols, especially those substituted by electron-withdrawing groups, are sufficiently acidic to be titrated by this same method, as are sulfonic acids.

1.3 MOLECULAR FORMULAS

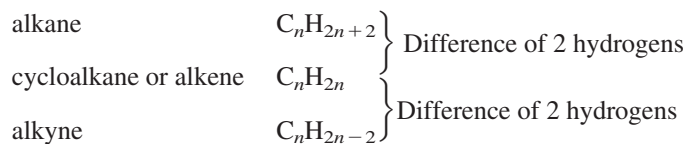
Once the molecular mass and the empirical formula are known, we may proceed directly to the **molecular formula**. Often, the empirical formula weight and the molecular mass are the same. In such cases, the empirical formula is also the molecular formula. However, in many cases, the empirical formula weight is less than the molecular mass, and it is necessary to determine how many times the empirical formula weight can be divided into the molecular mass. The factor determined in this manner is the one by which the empirical formula must be multiplied to obtain the molecular formula.

Ethane provides a simple example. After quantitative element analysis, the empirical formula for ethane is found to be CH_3 . A molecular mass of 30 is determined. The empirical formula weight of ethane, 15, is half of the molecular mass, 30. Therefore, the molecular formula of ethane must be $2(CH_3)$ or C_2H_6 .

For the sample unknown introduced earlier in this chapter, the empirical formula was found to be $C_7H_{14}O_2$. The formula weight is 130. If we assume that the molecular mass of this substance was determined to be 130, we may conclude that the empirical formula and the molecular formula are identical, and that the molecular formula must be $C_7H_{14}O_2$.

1.4 INDEX OF HYDROGEN DEFICIENCY

Frequently, a great deal can be learned about an unknown substance simply from knowledge of its molecular formula. This information is based on the following general molecular formulas:



Notice that each time a ring or π bond is introduced into a molecule, the number of hydrogens in the molecular formula is reduced by *two*. For every *triple bond* (two π bonds), the molecular formula is reduced by four. This is illustrated in Figure 1.2.

When the molecular formula for a compound contains noncarbon or nonhydrogen elements, the ratio of carbon to hydrogen may change. Following are three simple rules that may be used to predict how this ratio will change:

- To convert the formula of an open-chain, saturated hydrocarbon to a formula containing Group V elements (N, P, As, Sb, Bi), one additional hydrogen atom must be *added* to the molecular formula for each such Group V element present. In the following examples, each formula is correct for a two-carbon acyclic, saturated compound:



- To convert the formula of an open-chain, saturated hydrocarbon to a formula containing Group VI elements (O, S, Se, Te), *no change* in the number of hydrogens is required. In the following examples, each formula is correct for a two-carbon, acyclic, saturated compound:

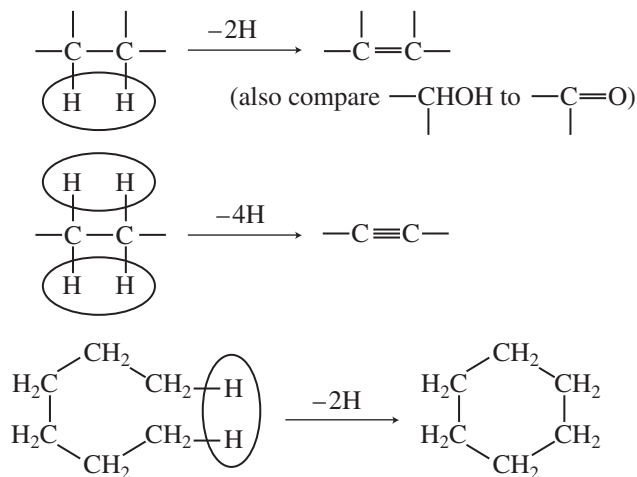


FIGURE 1.2 Formation of rings and double bonds. Formation of each ring or double bond causes the loss of 2H.

3. To convert the formula of an open-chain, saturated hydrocarbon to a formula containing Group VII elements (F, Cl, Br, I), one hydrogen must be *subtracted* from the molecular formula for each such Group VII element present. In the following examples, each formula is correct for a two-carbon, acyclic, saturated compound:



Table 1.3 presents some examples that should demonstrate how these correction numbers were determined for each of the heteroatom groups.

The **index of hydrogen deficiency** (sometimes called the **unsaturation index**) is the number of π bonds and/or rings a molecule contains. It is determined from an examination of the molecular formula of an unknown substance and from a comparison of that formula with a formula for a corresponding acyclic, saturated compound. The difference in the number of hydrogens between these formulas, when divided by 2, gives the index of hydrogen deficiency.

The index of hydrogen deficiency can be very useful in structure determination problems. A great deal of information can be obtained about a molecule before a single spectrum is examined. For example, a compound with an index of **one** must have one double bond or one ring, but it cannot have both structural features. A quick examination of the infrared spectrum could confirm the presence of a double bond. If there were no double bond, the substance would have to be cyclic and saturated. A compound with an index of **two** could have a triple bond, or it could have two double bonds, two rings, or one of each. Knowing the index of hydrogen deficiency of a substance, the chemist can proceed directly to the appropriate regions of the spectra to confirm the presence or absence of π bonds or rings. Benzene contains one ring and three “double bonds” and thus has an index of hydrogen deficiency of **four**. Any substance with an index of *four* or more may contain a benzenoid ring; a substance with an index less than *four* cannot contain such a ring.

To determine the index of hydrogen deficiency for a compound, apply the following steps:

1. Determine the formula for the saturated, acyclic hydrocarbon containing the same number of carbon atoms as the unknown substance.
2. Correct this formula for the nonhydrocarbon elements present in the unknown. Add one hydrogen atom for each Group V element present and subtract one hydrogen atom for each Group VII element present.
3. Compare this formula with the molecular formula of the unknown. Determine the number of hydrogens by which the two formulas differ.
4. Divide the difference in the number of hydrogens by **two** to obtain the index of hydrogen deficiency. This equals the number of π bonds and/or rings in the structural formula of the unknown substance.

TABLE 1.3
CORRECTIONS TO THE NUMBER OF HYDROGEN ATOMS
WHEN GROUP V AND VII HETEROATOMS ARE INTRODUCED
(GROUP VI HETEROATOMS DO NOT REQUIRE A CORRECTION)

Group	Example	Correction	Net Change
V	C—H → C—NH ₂	+1	Add nitrogen, add 1 hydrogen
VI	C—H → C—OH	0	Add oxygen (no hydrogen)
VII	C—H → C—Cl	-1	Add chlorine, lose 1 hydrogen

8 Molecular Formulas and What Can Be Learned from Them

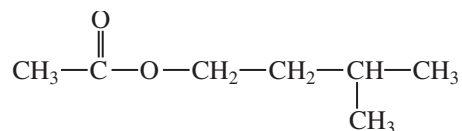
The following examples illustrate how the index of hydrogen deficiency is determined and how that information can be applied to the determination of a structure for an unknown substance.

■ EXAMPLE 1

The unknown substance introduced at the beginning of this chapter has the molecular formula $C_7H_{14}O_2$.

1. Using the general formula for a saturated, acyclic hydrocarbon (C_nH_{2n+2} , where $n = 7$), calculate the formula C_7H_{16} .
2. Correction for oxygens (no change in the number of hydrogens) gives the formula $C_7H_{16}O_2$.
3. The latter formula differs from that of the unknown by two hydrogens.
4. The index of hydrogen deficiency equals **one**. There must be one ring or one double bond in the unknown substance.

Having this information, the chemist can proceed immediately to the double-bond regions of the infrared spectrum. There, she finds evidence for a carbon–oxygen double bond (carbonyl group). At this point, the number of possible isomers that might include the unknown has been narrowed considerably. Further analysis of the spectral evidence leads to an identification of the unknown substance as **isopentyl acetate**.

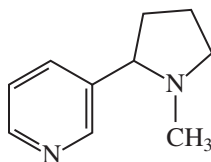


■ EXAMPLE 2

Nicotine has the molecular formula $C_{10}H_{14}N_2$.

1. The formula for a 10-carbon, saturated, acyclic hydrocarbon is $C_{10}H_{22}$.
2. Correction for the two nitrogens (add two hydrogens) gives the formula $C_{10}H_{24}N_2$.
3. The latter formula differs from that of nicotine by 10 hydrogens.
4. The index of hydrogen deficiency equals **five**. There must be some combination of five π bonds and/or rings in the molecule. Since the index is greater than *four*, a benzenoid ring could be included in the molecule.

Analysis of the spectrum quickly shows that a benzenoid ring is indeed present in nicotine. The spectral results indicate no other double bonds, suggesting that another ring, this one saturated, must be present in the molecule. More careful refinement of the spectral analysis leads to a structural formula for nicotine:

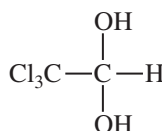


■ EXAMPLE 3

Chloral hydrate (“knockout drops”) is found to have the molecular formula $C_2H_3Cl_3O_2$.

1. The formula for a two-carbon, saturated, acyclic hydrocarbon is C_2H_6 .
2. Correction for oxygens (no additional hydrogens) gives the formula $C_2H_6O_2$.
3. Correction for chlorines (subtract three hydrogens) gives the formula $C_2H_3Cl_3O_2$.
4. This formula and the formula of chloral hydrate correspond exactly.
5. The index of hydrogen deficiency equals **zero**. Chloral hydrate cannot contain rings or double bonds.

Examination of the spectral results is limited to regions that correspond to singly bonded structural features. The correct structural formula for chloral hydrate follows. You can see that all of the bonds in the molecule are single bonds.



□ 1.5 THE RULE OF THIRTEEN

High-resolution mass spectrometry provides molecular mass information from which the user can determine the exact molecular formula directly. The discussion on exact mass determination in Chapter 3 explains this process in detail. When such molar mass information is not available, however, it is often useful to be able to generate all the possible molecular formulas for a given mass. By applying other types of spectroscopic information, it may then be possible to distinguish among these possible formulas. A useful method for generating possible molecular formulas for a given molecular mass is the **Rule of Thirteen**.¹

As a first step in the Rule of Thirteen, we generate a **base formula**, which contains only carbon and hydrogen. The base formula is found by dividing the molecular mass M by 13 (the mass of one carbon plus one hydrogen). This calculation provides a numerator n and a remainder r :

$$\frac{M}{13} = n + \frac{r}{13}$$

The base formula thus becomes



which is a combination of carbons and hydrogens that has the desired molecular mass M .

The **index of hydrogen deficiency** (unsaturation index) U that corresponds to the preceding formula is calculated easily by applying the relationship

$$U = \frac{(n - r + 2)}{2}$$

¹ Bright, J. W., and E. C. M. Chen, “Mass Spectral Interpretation Using the ‘Rule of 13,’” *Journal of Chemical Education*, 60 (1983): 557.