Therald Moeller

QUALITATIVE ANALYSIS

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An Introduction to Equilibrium
and Solution Chemistry

Preface

IN COMMON with many other teachers, I believe that no discipline in beginning chemistry is as potentially effective as qualitative analysis in giving the student an interesting and adequate integration of necessary descriptive fact with the elements of equilibrium principles and solution theory that are so essential in his subsequent courses. Furthermore, I believe that realization of this potential is determined largely by the mode of presentation employed. These beliefs have convinced me that the seemingly overworked field of qualitative analysis is still virgin as regards a textbook that can lead the student logically through the requisite theoretical concepts while simultaneously providing a background of interesting experimental work to illustrate and confirm these concepts. The present textbook is a result of this conviction.

How can presentation be tailored best to achieve this potential? Classical treatments of qualitative analysis have tended to emphasize either laboratory operations as means of determining the compositions of samples or solution theory. Emphasis on the former has often led to development of routine procedures that are carried out solely to achieve a final analytical result and are not questioned as to meaning or interpretation. Emphasis on the latter has often provided a fine introduction to physical chemistry but at the expense of showing how theory can be used as a foundation for useful and practical laboratory operations. To effect a logical combination of the two and to provide

the student adequately with both types of knowledge require that attention be paid to the following:

1. Both theory and descriptive fact must be treated logically, systematically, and comprehensively.

2. Laboratory operations must be so selected that they both illustrate the principles developed and follow logically the sequence in which those principles are discussed.

3. Laboratory operations must be approached as a series of experiments that lead to reasonable answers, rather than as a series of routine exercises.

4. The importance of laboratory technique must be given constant emphasis.

5. The quantitative aspects of both the theoretical and the practical approach must be emphasized throughout the presentation.

6. Student interest must be developed and maintained through use of the concept of continuing challenge.

Every effort has been made to employ these concepts in this textbook.

For convenience, the book has been divided mechanically into parts that treat, in order, the fundamentals of solution theory and chemical equilibrium, the chemical characteristics of selected common ionic species, and the laboratory investigation of these species. The book is so written that assignments can be made simultaneously from all three parts in order to permit maximum overlap between principle and practice. Such a procedure is recommended to anyone using the book. There is ample material for a comprehensive one-semester course dealing solely with qualitative analysis. By judicious choice of material and the elimination of certain discussions and laboratory work on some of the less important ionic species, the instructor can readily adapt the presentation to a course in which qualitative analysis is considered as a part of general chemistry.

In the part on solution chemistry, topics are introduced in a logical order of generally increasing difficulty. By judicious cross-referencing and constant review, each topic is related to those already considered and to the practical operations in the laboratory. Much emphasis is placed upon the solving of numerical problems to implement the thesis that the student can appreciate the fundamentally quantitative nature of chemistry adequately only if he can solve problems which illustrate the concepts under consideration. His confidence in the validity of these concepts increases in direct proportion to his facility in performing mathematical operations. To this end, many illustrative numeri-

cal examples are included, in addition to the usual exercises at the ends of chapters. The logical dimensional approach to problem solving is emphasized throughout as a means of aiding mathematical thought and of providing the student with a key to the reasonableness of his calculations.

In its treatment of laboratory study, this textbook departs extensively from what has become common practice in the field. The laboratory studies are introduced by a series of exercises on techniques and useful operations. These are designed to acquaint the student with the approaches he will find necessary in subsequent operations and thereby to emphasize the importance of correct technique and to improve his confidence in his ability to solve laboratory problems. These exercises also provide laboratory experience during the period in which fundamental theory is being presented. The anions are then considered prior to the cations and in extensive detail. This presentation is based upon the following theses:

1. The useful chemistry of the cations is often dependent upon the anions present. It is logical, therefore, that the student have prior knowledge of the anions.
2. The laboratory investigation of the anions is less readily reduced to routine than that of the cations and thus requires that the student develop a reasoning and logical experimental approach and that he learn to interpret all his observations. This training is invaluable in his subsequent study of the cations.
3. The chemistry of the anions is less amenable to illustrating the principles of solution chemistry than that of the cations. The student can thus develop a background of principles before it is necessary to apply them for maximum understanding of the laboratory work.

The somewhat unconventional order of cation presentation which then follows is designed to carry the student slowly and logically from a rather simple chemistry to one that is complicated by variations in the more involved properties of amphoterism, complex-ion formation, and oxidation-reduction.

Throughout the laboratory work, the investigative approach is stressed as important in maintaining student interest and in providing training for more advanced study. Each exercise is considered as one to be investigated and interpreted, rather than as a routine that needs only to be repeated for confirmation. Additional challenge is provided by required analyses of "known" and "unknown" samples. Constant attention to points of cleanliness, orderliness, and correctness of manipulation is a reflection of my feeling that the sooner such

habits are developed the sooner the student will enjoy success in chemistry.   All work is on the semimicro scale.

Compilation of this book would have been impossible without the assistance given, consciously or unconsciously, by many of my colleagues and students over an extended period.   To acknowledge adequately the contribution of each would be highly desirable but clearly impossible.   To express general gratitude to all is the very least that I can do.   It is my hope that those who use this textbook will offer freely their opinions and suggestions as to means for its future improvement.

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PART

I

Principles of
Solution Chemistry

1

Introduction

CHEMISTRY has been properly defined as a science dealing with matter, with the changes which matter undergoes, and with the laws which govern these changes. It is apparent that any study embracing what is covered in this definition can be either experimental or theoretical in nature. Historically, all chemical studies were essentially experimental, but as experiments became more and more systematic, theoretical approaches developed and increased in usefulness and importance. The result is that modern chemistry is now a combination of laboratory and theoretical work, each being used to supplement and aid in the explanation of the other. This is as it should be, provided proper emphasis is placed upon each phase. One must remember, however, that a true appreciation of the scope and importance of chemistry can come only through a careful combining of the practical and theoretical phases and that overemphasis upon either can give only a distorted picture of the true subject.

Many phases of chemistry lend themselves to such combinations of factual and theoretical material. Few, however, can be handled more usefully than an investigation of the properties of the ions which the elements form. Such a combined study can be made through what is called *qualitative analysis*.

QUALITATIVE ANALYSIS

In the nineteenth century, a major field in inorganic chemistry involved the study and analysis of minerals. There developed, as a

result, a series of systematic procedures for the detection of the metallic and nonmetallic components of these minerals. Because of the importance of this general field, these procedures were combined into courses of instruction known as qualitative analysis. Such courses became standard requirements in all curricula in chemistry and were very useful in providing students with the methods of finding out what substances were present both in minerals and in a variety of other materials.

Emphasis has of course changed in subsequent years, and it is now true that the detection of inorganic components is much more successfully effected by instrumental techniques than by the classical procedures of qualitative analysis. Yet qualitative analysis remains as an important subject. This is because it offers an excellent means for the comparative study of the properties of ions in a fashion which avoids the routine of preparing innumerable individual compounds. Furthermore, it provides an early introduction to solution chemistry, and it acquaints the student with many theoretical principles which can be tested readily in the laboratory. The primary objective of qualitative analysis is thus an elucidation of the properties of ions through a combination of experiment and theory. No longer does the subject exist as a training for analysts. Indeed, few analysts will ever find it necessary to resort to the systematic approaches developed in qualitative analysis for the solving of any practical problem.

The Scope of Qualitative Analysis. Qualitative analysis embraces the behavior of the ions formed by the various elements. For simplification, the majority of the carbon-containing ions are excluded. These are better considered in their relationship to other organic substances and are treated in organic chemistry. The multitude of remaining cations and anions would require so much time for complete characterization that it is customary to select a limited number of the more common species for thorough investigation and as a place to illustrate theoretical principles. The behavior of other related species can then be handled on comparative bases and by reference to what is known about those studied. This is the same device used in studying the chemical elements as a whole and is an application of periodic-group and other similarities and differences relating to atomic structures. Thus, to cite an example, rubidium ion is so closely similar to potassium ion that its detection and general chemical behavior can be inferred logically from the known chemistry of the latter species. The same is true in many other instances.

Properly, qualitative analysis may employ any type or combination

of properties for the detection of a given species. Occasionally, mere visual examination or an evaluation of such obvious properties as color or solubility may suffice, but in a more practical sense one resorts to chemical reactions. These may occur in the solid, liquid, or gaseous states, but the most useful reactions which permit a combination of experimental and theoretical approaches are those which take place in solution. These are reactions of dissolution, precipitation, complex-ion formation, oxidation-reduction, etc., which are characteristic of the species in question. When carried out in proper sequence and with due regard for interferences and theoretical interpretations, they constitute the procedures of separation and identification of qualitative analysis. Because they are necessarily systematic, these procedures then yield logical classifications of the species being studied.

Typical classifications of common ionic species are outlined in Chap. 11. Many of the properties of individual species which are essential to the development and understanding of such classifications are summarized in Chaps. 12 and 13. Laboratory work which is designed to provide the necessary experimental background is introduced in Chap. 14. The student should refer to these chapters for a general indication of the scope of qualitative analysis.

CHEMICAL BONDING AND VALENCY TYPES

Inasmuch as the bulk of the chemistry to be considered relates to ionic species, it is essential to review briefly the general subjects of chemical bonding and valency to provide the necessary background. It will be recalled that atoms of the various elements differ from each other in the number of neutrons, protons, and electrons present and in the arrangement of the electrons. Of these particles, only the electrons are responsible for the chemical behaviour of an atom and thus for the chemical characteristics of the element in question. Specifically, of the electrons, only those in the outermost shells (highest energy levels) are directly involved when atoms participate in chemical reactions. These are the so-called *valence electrons*.

It is convenient, therefore, to designate as the *kernel* of an atom that part which remains unchanged in chemical reaction, i.e., the nucleus and all the electrons except those of the valence type. By convention, the symbol for the element is used to describe the kernel of an atom of that element, and an appropriate number of dots, crosses, etc., is employed to indicate the number of valence electrons. Thus, the sodium atom, which is given in detail as

$$\begin{pmatrix} 11p \\ 12n \end{pmatrix} \quad 2e^- \quad 8e^- \quad 1e^-$$

(nucleus)　　(electron shells)
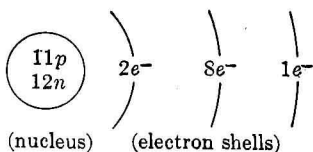
can be abbreviated in the kernel notation as

$$Na\cdot$$

By the same token, the elments in the first two rows of the periodic table are then designated as

I	II	III	IV	V	VI	VII	O
Li $\cdot$	$\cdot$ Be $\cdot$	$\cdot$ B $\cdot$	$\cdot$ C $\cdot$	$\cdot$ N $\cdot$	$\cdot$ O $\cdot$	: F $\cdot$	: Ne :
Na $\cdot$	$\cdot$ Mg $\cdot$	$\cdot$ Al $\cdot$	$\cdot$ Si $\cdot$	$\cdot$ P $\cdot$	$\cdot$ S $\cdot$	: Cl $\cdot$	: Ar :

If the valence electrons are responsible for chemical characteristics, how can one relate them to observed chemical behavior? It appears that in chemical reactions rearrangements of valence electrons occur to give electronic structures of enhanced stabilities. If then there is any regularity in the chemical behavior of the elements, certain types of stable electronic arrangements must exist and be attained. An examination of the properties of all the elements reveals immediately that the inert gas elements are unique in their inability to combine with other species.[1] It is reasonable to conclude, therefore, that the electronic structures of the atoms of these elements are structures of chemical stability. These electronic structures, as summarized in Table 1-1, suggest that a heliumlike structure with only two electrons or a structure with eight valence electrons and the underlying shells effectively completely occupied is a stable structure which might be approached by other atoms through appropriate gain or loss of sufficient electrons.

The elements in the first two rows of the periodic table (see above) form compounds which agree in composition with tendencies on the parts of the reacting atoms to achieve these inert-gas-atom structures. Thus, lithium fluoride, LiF, may be considered to result from the transfer of the single valence electron of the lithium atom to the outer shell

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[1] It should be noted that so-called "compounds" of certain of the inert gas elements have been obtained. However, all such combinations result under conditions different from those characteristic of compound formation in the chemical sense and are comparatively unstable. Apparently in such unions attractive forces are operative which differ from those in materials such as hydrogen chloride, potassium nitrate, etc.

of the fluorine atom. This leaves residues with the same numbers of electrons as, respectively, atoms of the inert gases helium and neon. The same reasoning can be applied to other combinations of the elements of low atomic number. Indeed, it can be extended to so many combinations of the other elements that it is often concluded that configurations of the inert-gas-atom type are always approached in chemical combination. Such is actually the case only for elements of atomic numbers less than 22 and for other elements which differ in atomic numbers from inert gas elements by no more than 3 or 4 units. For
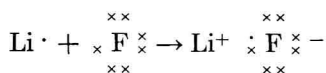
Table 1-1
Electronic Arrangements in Inert Gas Atoms

Symbol	Electron distribution by shells						Kernel designation
	K	L	M	N	O	P	
He	2						He :
Ne	2	8					: Ne :
Ar	2	8	8				: Ar :
Kr	2	8	18	8			: Kr :
Xe	2	8	18	18	8		: Xe :
Rn	2	8	18	32	18	8	: Rn :

other elements, other stable structures must be sought. Among these are 18-electron and 18 plus 2-electron arrangements. The 18-electron (pseudo inert gas or nickel group) structures are roughly those of the nickel-palladium family and are approached in compounds formed by the elements that immediately follow this family in atomic number. The 18 plus 2-electron (zinc group) structures are those of the zinc-mercury family and are approached in compounds formed by elements which immediately follow that family in atomic number. There are, in addition, structures of complete irregularity among the transition and inner transition (rare earth type) series. Regular arrangements are summarized in Table 1-2.

Approaches to Stable Structures. Stable structures are achieved as a result of either *electron transfer* or *electron sharing*. These are discussed as follows:

1. *Electron Transfer.* This amounts to the loss of electrons by atoms of one element and gain of those electrons by atoms of the other element. When this occurs, the material losing electrons is left with an excess of protons over electrons and becomes a positive ion, or *cation*. Correspondingly, the material gaining electrons has more electrons than protons and becomes a negative ion, or *anion*. Such a process can be formulated in a specific case as

$$\text{Li} \cdot + \overset{\times\times}{\underset{\times\times}{\times}}\text{F}\overset{\times}{\underset{}{\times}} \rightarrow \text{Li}^+ \quad \overset{\times\times}{\underset{\times\times}{\times}}\text{F}\overset{\times}{\underset{}{\times}}{}^-$$

Electron transfer thus leads to the formation of *ions* or of *ionic compounds*. The valency exhibited in such compounds is termed *electrovalence*. It is apparent that in an ionic compound the more metallic

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Table 1-2
Regular Structures of Chemical Stability

I. Helium structure (2 electrons):
    $H^- \rightarrow He \leftarrow Li^+, Be^{2+}$

II. Inert gas structures (8 electrons):
    $O^{2-}, F^- \rightarrow Ne \leftarrow Na^+, Mg^{2+}, Al^{3+}$
    $S^{2-}, Cl^- \rightarrow A \leftarrow K^+, Ca^{2+}, Sc^{3+}$
    $Se^{2-}, Br^- \rightarrow Kr \leftarrow Rb^+, Sr^{2+}, Y^{3+}$
    $Te^{2-}, I^- \rightarrow Xe \leftarrow Cs^+, Ba^{2+}, La^{3+}$
    $At^- \rightarrow Rn \leftarrow Fr^+, Ra^{2+}, Ac^{3+}$

III. Pseudo inert gas structures (18 electrons):
    $Ni \leftarrow Cu^+, Zn^{2+}, Ga^{3+}$
    $Pd \leftarrow Ag^+, Cd^{2+}, In^{3+}$
    $Pt \leftarrow Au^+, Hg^{2+}, Tl^{3+}$

IV. Zinc group structures (18 + 2 electrons):
    $Zn \leftarrow Ga^+, Ge^{2+}, As^{3+}$
    $Cd \leftarrow In^+, Sn^{2+}, Sb^{3+}$
    $Hg \leftarrow Tl^+, Pb^{2+}, Bi^{3+}$

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element has lost its valence electrons completely to the more nonmetallic element and that the resulting particles are held together by electrostatic attractions.

Actually, compound formation by electron transfer is not a particularly common phenomenon. The removal of a single valence electron may not be extremely difficult to bring about, but the removal of a second or a third electron from an already positively charged ion becomes more difficult because of the electrostatic attraction which must be overcome. Correspondingly, although the addition of one electron to a neutral atom may proceed readily enough, the addition of