

Inorganic Chemistry of Qualitative Analysis

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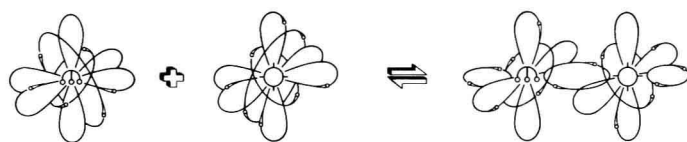
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*Inorganic Chemistry
of Qualitative Analysis*

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To
Professor Emeritus
Quaesita Cromwell Drake
of the
University of Delaware
who first inspired me
to see the meaning
in qualitative analysis

Preface

It has long been recognized by instructors of undergraduate chemistry that there is little need to teach qualitative analysis for its own sake. Actual analyses are very seldom carried out in this manner any longer. It is nevertheless true that the classical analytical scheme is one of the best vehicles ever devised for teaching the systematics of inorganic chemistry. The purpose of this book, then, is not to teach methods of analysis, but rather to give as thorough a grounding as possible in the chemical relationships in the periodic table on which the classical analytical scheme is founded. This is done in terms of trends in solubility, trends in acidity and basicity, trends in oxidizing and reducing power, and the like. In order to accomplish this intelligibly, such topics as electronegativity, oxidation potentials, and the equilibrium principle are treated, the last extensively.

The book was written for and planned around the chemistry courses 126 and 226 at Purdue University. The former is the second term freshman course for gifted students, whereas the latter is the first term sophomore course for average students which follows two semesters of general chemistry. However, although the book is planned around these courses, it is by no means limited to them and contains far more material than any but the most gifted student could be expected to absorb in one semester. This has been done on the theory that the better students should always have the opportunity to dig by themselves deeper into the subject than they can in the formal course and that the average student should be made aware that what is spooned out to him in lectures is not all that can be said.

The book is divided into sixteen chapters intended to correspond very roughly to the sixteen weeks of the semester. The material is organized insofar as possible to present new background material in the text (and lectures) at the same time as work illustrating it appears in the laboratory. For this reason, the analytical groups are considered in order of increasing complexity, and many additional illustrative experiments have been included. The laboratory procedures have been selected for their pedagogical worth rather than for their analytical utility. For example, the detection of strontium is accomplished with saturated calcium sulfate in order to demonstrate the trend of solubilities of the alkaline earth sulfates, rather than, for example, by complexing calcium with triethanolamine which,

from the analytical point of view, is more satisfactory but which teaches very little. For the same reason, the use of organic spot test reagents has been reduced to a minimum to emphasize inorganic reagents which perhaps are less satisfactory analytically but which nevertheless illustrate fundamental inorganic chemistry better. Enough organic reagents are discussed, however, to illustrate the nature of lakes (para-nitrobenzeneazoresorcinol and aluminon reagent) and chelation (dimethylglyoxime).

Several new elements have been added to the analytical scheme over the ones usually present, not because they are becoming technically important, but because they demonstrate important principles of chemistry. Thallium is added to demonstrate the principle of the chemical similarity of neighbors in the periodic table. Tungsten is added to demonstrate the existence of insoluble acids and the ambivalent nature of reagents (i.e., that addition of HCl brings both H^+ and Cl^- into the solution with the consequent effects of both). Similarly vanadium demonstrates the existence of insoluble ammonium salts as well as the ambivalence of the NH_4OH-NH_4Cl reagent and certain other points. Molybdenum is added to demonstrate the existence of amphoteric sulfides for the high oxidation states of the elements on the left-hand side of the periodic table.

In Chemistry 126 and 226 at Purdue the final unknown includes not only a selection of the elements considered in the text but also many other elements, such as Ce, Ge, In, Ta, Th, Ti, Zr, etc., for which no analytical procedures are given. Each student is told that, in addition to the elements in the regular scheme, he may have some elements from a certain specified list (different in each case). He must go to the library and devise a scheme which will accommodate these elements and no others. Thus he must actually study and compare the chemistries of these and the common elements and produce a workable analytical scheme before he goes into the laboratory to analyze the final unknown. This has proved to be one of the most popular features of the laboratory work. Besides the textbooks on qualitative analysis listed at the ends of chapters 9, 12, and 14 the following texts on inorganic chemistry may be recommended for this purpose:

GENERAL TEXTBOOKS ON INORGANIC CHEMISTRY

- Barnett, E. de Barry, and Wilson, C. L., *Inorganic Chemistry*. New York: Longmans, Green & Co., Inc., 1953.
- Hempel, C. A., *Rare Metals Handbook*. New York: Reinhold Publishing Corporation, 1954.
- Latimer, W. M., and Hildebrand, J. H., *Reference Book of Inorganic Chemistry*, 3rd ed. New York: Macmillan Company, 1951.
- Parkes, G. D., *Mellor's Modern Inorganic Chemistry*. New York: Longmans, Green & Co., Inc.
- Remy, H., *Treatise on Inorganic Chemistry*. New York: Elsevier Publishing Company, 1956.

Sidgwick, N. V., *The Chemical Elements and Their Compounds*. Oxford: The Clarendon Press, 1950.

Thorne, P. C. L., and Roberts, E. R., *Fritz Ephraim's Inorganic Chemistry*, 6th ed. New York: Interscience Publishers, Inc., 1955.

Depending on the level of the course, more or less of the textual material may be taken up in class. If it is to be used only as a laboratory manual, the experimental sections only (perhaps with the descriptive material on the individual elements) may be used.

For average students with a moderate background in general chemistry and no previous knowledge of equilibrium, the course might include:

| Week | Lecture | Laboratory |
|------|---|--|
| 1 | Chapter 1 | Check-in; Section 1-15 |
| 2 | Chapter 2 | Lecture on Section 3-6; Sections 3-12, 3-13 (known) |
| 3 | Chapter 3 | Sections 3-11, 3-13 (unknown) |
| 4 | Sections 4-1, 4-2, 4-4, 4-6, 4-7 (omit if tungsten is to be omitted), 4-8, 4-9 (omit portions on tungsten and molybdenum if desired) | Sections 4-11, 4-12 |
| 5 | Sections 5-1, 5-2, 5-12, 5-13 | Sections 4-11 (unknown), 5-14 |
| 6 | Sections 5-3, 5-4, 5-5, 5-8 | Section 5-15 (unknown) |
| 7 | Sections 7-1, 7-2, 7-3 | Sections 5-15 (unknown), 7-11 |
| 8 | Sections 7-5, 7-8, 7-9, 7-10 | Sections 7-11, 7-12 |
| 9 | Sections 9-1, 9-2, 9-4, 9-5 | Section 7-12 (unknown) |
| 10 | Sections 9-6, 9-8, 9-9 | Sections 9-17, 9-18 (unknown) |
| 11 | Sections 10-1, 10-2, 10-3, 10-5 | Section 9-18 (unknown) |
| 12 | Sections 10-6, 10-8, 10-9, 10-12, 10-13 | Sections 9-18 (unknown), 11-14, 11-15 |
| 13 | Sections 11-1 through 11-6 | Sections 11-13, 11-15, 12-9 (un- known) |
| 14 | Chapter 13 | Section 12-9 (unknown) |
| 15 | Sections 14-1 through 14-5 | Section 12-9 (unknown) |
| 16 | Sections 14-6, 14-8 | Section 12-9 (unknown); check-out |

For average students with a strong background in general chemistry but little knowledge of equilibrium, the foregoing schedule might be used with the laboratory lecture on Section 3-6 substituted for the lecture on Chapter 1. Alternatively the following schedule might be used:

| Week | Lecture | Laboratory |
|------|--|-------------------------------|
| 1 | Section 1-1, Chapter 2 | Check-in; Sections 1-15, 3-11 |
| 2 | Chapter 3 | Sections 3-12, 3-13 (known) |
| 3 | Sections 1-9, 4-1, 4-2, 4-3 | Sections 3-13 (unknown), 4-10 |
| 4 | Sections 4-4, 4-5, 4-7, etc. | Section 4-11 (unknown) |
| 5 | Sections 5-1, 5-2, 5-12, 5-13 | Sections 5-14, 5-15 |
| 6 | Sections 5-3, 5-4, 5-5, 5-8, 5-11 | Section 5-15 (unknown) |
| 7 | From this week on, the previous schedule would be followed, keeping the laboratory a half-week ahead to give one extra period for the general unknown. | |

The calendars above are set up for a four-credit course including one lecture and one recitation (or two lectures) and six hours of laboratory. The following calendar is designed for Chemistry 126 at Purdue which has students with a strong background in general chemistry and some knowledge of equilibrium. Most of the material in Chapters 1 and 2 is considered to be review for these students. The course is a five-credit course having two lectures, one recitation, and six hours of laboratory.

(In the following calendar *a* and *b* represent the first and second lectures or laboratories of the week respectively.)

| <i>Week</i> | <i>Lecture</i> | <i>Laboratory</i> |
|-------------|--------------------------------|--|
| 1a | Sections 1-1, 3-6 | Check-in; Section 1-15 |
| 1b | Chapter 3 | Sections 3-7, 3-8, 3-12 |
| 2a | Sections 1-9, 1-10, 1-11, 1-12 | Sections 3-11, 3-13 |
| 2b | Sections 4-1, 4-2, 4-3, 4-7 | Section 3-13 |
| 3a | Sections 4-4, 4-5, 4-6 | Section 3-13 (unknown) |
| 3b | Sections 4-8, 4-9 | Section 4-11 |
| 4a | Sections 5-1, 5-2 | Section 4-12 |
| 4b | Sections 5-3 through 5-6 | Section 4-12 (unknown) |
| 5a | Sections 5-7 through 5-11 | Sections 5-12, 5-13, 5-14 |
| 5b | Chapter 6 | Section 5-15 |
| 6a | Sections 7-1 through 7-5 | Section 5-15 |
| 6b | Sections 7-6 through 7-10 | Section 5-15 (unknown) |
| 7a | Sections 8-1, 8-2, 8-3 | Section 7-11 |
| 7b | Sections 8-4, 8-5, 8-6 | Section 7-12 |
| 8a | Sections 8-7, 8-8, 8-9 | Section 7-12 |
| 8b | Sections 8-10 through 8-13 | Section 7-12 (unknown) |
| 9a | Sections 9-1 through 9-7 | Section 9-17 |
| 9b | Sections 9-8, 9-9, 9-13 | Section 9-18 |
| 10a | Sections 9-14, 9-15, 9-16 | Section 9-18 |
| 10b | Sections 10-1 through 10-4 | Section 9-18 |
| 11a | Sections 10-5 through 10-8 | Section 9-18 (unknown) |
| 11b | Sections 10-9 through 10-13 | Section 11-13 |
| 12b | Sections 11-1 through 11-6 | Sections 11-14, 11-15 |
| 12a | Chapter 12 | Sections 12-9, 14-9, 14-10, 14-11 |
| 13a | Sections 13-1 through 13-6 | Section 12-9 |
| 13b | Sections 13-7 through 13-13 | Section 12-9 |
| 14a | Sections 14-1 through 14-4 | Section 12-9 |
| 14b | Sections 14-5 through 14-8 | Section 12-9 (unknown) or extra unknown |
| 15a | Sections 14-9, 14-10, 14-11 | |
| 15b | Chapter 15 or Chapter 16 | |
| 16a | Chapter 15 or Chapter 16 | |
| 16b | Examinations | Check-out. |

This volume has in large degree been a labor of love. It has had the enthusiastic support of my teaching staff. I am especially grateful to Tom Bydalek for checking the problem sets, to Pat and Ron Olsen for reading the original manuscript, and to Prof. John W. Willard of South Dakota School of Mines for reading proof. The criticisms of the reviewers, in-

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West Lafayette, Indiana

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Fig. 1-5: Pauling, Linus, *General Chemistry*, 2d ed. San Francisco: W. H. Freeman and Company, 1950.

Figs. 1-6, 1-9, 1-10, 1-11, 1-12, 1-13, 1-14, 1-16, 1-17, and 10-15: Wyckoff, R. W. G., *Crystal Structures*. New York: Interscience Publishers, Inc., 1948, 1951, 1957.

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Figs. 10-2a, 10-2b, and 10-16: Pauling, Linus, *Nature of the Chemical Bond*, 3rd ed. Ithaca, New York: Cornell University Press, 1960.

Fig. 10-2c: Pearson, R. G., "Crystal Field Explains Inorganic Behavior," *Chemical and Engineering News*, p. 72 (June 19, 1959).

Fig. 14-2: Latimer, W. M., *The Oxidation States of the Elements and their Potentials in Aqueous Solution*, 2d ed. Englewood Cliffs, N. J.: Prentice-Hall, Inc., 1952.

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