

REFERENCE BOOK  
OF  
INORGANIC CHEMISTRY

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## PREFACE

This book represents the fulfillment of a plan, long cherished, of providing a volume of descriptive chemistry to complete the series begun with "Principles of Chemistry" by Hildebrand, which adheres strictly to its title, and continued with the "Course in General Chemistry" by Bray and Latimer, which presents a laboratory course. The rather radical experiment in teaching general chemistry, begun in the University of California in 1912, has been somewhat hampered by the lack of a reference book on descriptive chemistry employing the language and the point of view adopted for our instructional scheme.

This "Reference Book of Inorganic Chemistry" has been written as a reference book rather than a text. The authors have sought to present essential chemical facts briefly, clearly, and in due relation to other facts and principles. The instructor using it will have to map out his own course, following whatever order of arrangement appeals to him. The numbering of paragraphs will make it possible for him to assign for study material selected from any desired portion of the book. We feel that many teachers will welcome the greater freedom thus afforded of developing their own pedagogical methods.

Chemical properties have been widely related to atomic structures and sizes. These ideas, although new, and subject to revision, are so illuminating that they appeal strongly to the imagination. Moreover, they are not difficult to grasp; many concepts traditionally introduced into freshman courses are far more elusive.

The formulas of many compounds have been given in terms of the Lewis theory of valence, not with the idea that these formulas represent the definite locations of the electrons, but rather to call attention to the importance of considering the total number of electrons or electron pairs in a molecule.

The extensive tabulation of "half reaction" potentials, equivalent to free energy values, will enable one to predict the direction and driving force of an immense number of reactions. Many of these potentials have been calculated for this book from reaction heats and entropy values, and have not heretofore been published.

We have treated industrial processes with emphasis upon their chemistry, relation to other industries, and economic magnitude,

rather than upon their mechanical features. Illustrations\* of industrial processes, of the sort extensively used in some texts, have been left to the instructor to provide, as he can do so far more adequately, by the use of lantern slides and motion pictures. Many excellent films are now available at a nominal expense.

The book contains much more material than the average student, or even the average chemist, can assimilate. We believe, however, that students should be "exposed" to a far greater range of subject matter than is usually presented. We have found the appetite and assimilative capacity of the superior students to be almost unlimited, and we see no value in an intellectual diet list. For the average student, the presence of this extra material in the book does no more damage than the unordered articles listed on a restaurant menu.

We anticipate that this kind of a book will prove useful, not only to the freshman student, but also to the student who desires a reference book in advanced courses in chemistry and allied subjects; and further that teachers and industrial chemists will also find in it answers to many of their questions. To increase its usefulness, a large mass of data has been included in the form of tables, both in the text and in the various appendices.

In the endeavor to keep the size and cost of the book at a low figure, it was decided to omit references to the original sources of material, although in many instances such references would be of historical and scientific value. Frequent use has been made of the more comprehensive treatises, especially: Gmelin-Kraut's *Handbuch der anorganischen Chemie*; Abegg and Auerbach *Handbuch der anorganischen Chemie*; *A Text-Book of Inorganic Chemistry*, Edited by Friend; *A Comprehensive Treatise on Inorganic and Theoretical Chemistry* by Mellor; *Lexikon der anorganischen Verbindungen* by Hoffman; *Landolt-Börnstein Tabellen*; and *The International Critical Tables*.

The authors are much indebted to their colleagues in the Department of Chemistry of the University of California, especially to Professors G. N. Lewis and W. C. Bray, not only for specific criticisms and suggestions, but for many of the general ideas upon which our interpretation of the facts of inorganic chemistry has been constructed.

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# REFERENCE BOOK OF INORGANIC CHEMISTRY

## CHAPTER I

### HYDROGEN

1. **Structure of Hydrogen Atom.**—The hydrogen atom is a system composed of two corpuscles; one, the proton, is the unit charge of positive electricity and the other, the electron, is the unit charge of negative electricity. The mass of the proton is about 1,850 times that of the electron but the electrical charges, though opposite in sign, are equal in magnitude.

The atom has a large number of energy states representing different configurations of the electron and proton. The values for the energy of the atom in these different states may be expressed as a close approximation by the very simple relation,

$$E = \frac{-13.54Z^2}{N^2} \text{ volts per unit charge, where } Z \text{ is the charge on}$$

the proton (equal to unity) and  $N$ , called the **quantum number**, is any integer from 1 to  $\infty$ . The normal atom is in the first quantum state ( $N = 1$ ) and the energy in volts required to move the electron to the 2, 3, 4, 5,  $\dots$   $\infty$  quantum states is shown in Figure 1. When  $N = \infty$  the energy is zero. This corresponds to the complete separation of the electron and proton, and the total energy required per unit charge is given as 13.54 volts.

When the electron moves from a higher quantum level to a lower, the energy difference is emitted in the form of light, whose frequency,  $\nu$ , is related to the energy difference,  $\Delta E$ , by the equation,  $\Delta E = h\nu$ , where  $h$  is a constant ("Planck constant"). Likewise the atom in a lower quantum state may absorb energy in the form of light of a

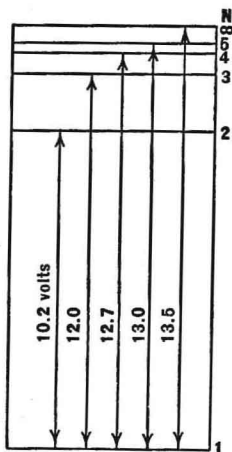


FIG. 1.—Energy levels in the hydrogen atom.



given frequency and the electron thereby move to a quantum level of correspondingly higher energy. The spectral lines arising from electrons falling from outer levels to the first quantum level are far out in the ultraviolet, but transitions from outer levels to the second quantum state give rise to the Balmer series which is in the visible spectrum. The highest frequency in the hydrogen spectrum is, of course, that corresponding to the electron falling from the infinite quantum state.

Bohr has sought to account for these quantum states by picturing the electron as revolving about the proton in some one of a number of possible orbits, which are circles or ellipses. These orbits are defined by the restriction that the momentum of the system must always be some multiple, i.e. the quantum number, of a single fundamental quantity. The total quantum number is made up of two factors,  $N = N_A + N_R$ , the one,  $N_A$ , determining the angular momentum and the other,  $N_R$ , the radial momentum, that is, momentum in the direction of the radius. These numbers fix the size of the orbits and also the ratio of the major ( $a$ ) and semi-minor ( $b$ ) axes of the orbits.

The semi-major axis of the orbit is given by  $a = \frac{0.53N^2}{Z} 10^{-8}$  cm.

For  $N = 1$ , the stable state of the atom, this gives  $a = 0.53 \cdot 10^{-8}$  cm. When  $N_R = 0$ , the orbits are ellipses whose major and minor axes are in the ratio  $N/N_A$ .

Figure 2 represents these orbits for  $N = 1, 2,$  and  $3$ . The large numbers give the values of  $N$ , the subscripts the values of  $N_A$ . While the existence of discrete energy states has been well established, we cannot regard the Bohr picture as entirely exact. Later developments by Schrödinger and others have generalized the quantum mechanics and modified somewhat Bohr's assumptions, but, as yet, they have given no detailed physical picture of the atom.

2. The same general quantum relations as outlined above hold for the other elements, complicated, however, by the facts:

(1) that the positive center is no longer a simple unit charge but a complex structure with a net positive charge equal to the

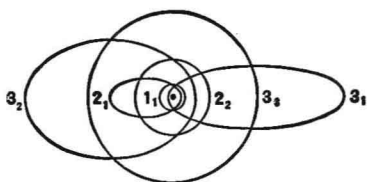


FIG. 2.—Electron orbits of hydrogen as pictured by Bohr.

atomic number, and (2) that the number of electrons is not one, but a number equal to the atomic number. It is the distribution of these electrons among the various quantum states that determines the grouping of the elements into the so-called "chemical families." The maximum number of electrons in any atom that can have the same total quantum number  $N$  is  $2N^2$ , e.g. for  $N = 1$ , the maximum number of electrons is 2; for  $N = 2$ , it is 8. Hence when the first quantum level is complete with the second element, helium, the three electrons of the third element, lithium, cannot all remain in the first level, but one of them is forced into the second. With each succeeding element of higher atomic number, the number of electrons in the second level increases until it is filled with eight electrons, i.e. in neon. Each alkali metal marks the beginning of a new quantum group and each noble gas the completion of a group. A complete table of the distribution of the electrons for all the elements is given in the appendix.

**3. Occurrence of Hydrogen.**—Only about one per cent by weight of the earth's crust (outer 10 miles) is hydrogen. However, if the composition is expressed in terms of the number of atoms, it may be stated that about sixteen per cent of all the atoms on the earth's surface are hydrogen, being second in abundance to oxygen. The major portion of the earth's hydrogen is combined with oxygen in water. It also frequently occurs combined with sulfur, carbon, nitrogen, and chlorine, and less frequently with the other halogens and phosphorus. Hydrogen is a constituent of all acids, and of all animal and vegetable tissue. Only a trace of free hydrogen is found in the atmosphere, about  $1 \times 10^{-3}$  per cent by volume. Larger quantities are sometimes found in volcanic and other natural gases. The spectrum of the sun indicates that enormous flames of incandescent hydrogen are frequently shot out distances of thousands of miles.

**4. Molecular Hydrogen.**—Atomic hydrogen combines to form the molecule  $H_2$ . Representing the proton by  $H$ , and the electron by a dot, we may write  $H:H$  as the electronic formula of the molecule. The exact arrangement of the charges in the molecule is not known so that the formula as written simply indicates that the two electrons constitute a bond holding the two protons together. The heat of formation is large, about 100,000 calories (100 kg. cal.). At temperatures of the electric arc, the molecule

is dissociated to a considerable extent into the atoms. In the absence of a catalyst the rate of combination of the atoms to form the molecule is slow.

Hydrogen has the lowest molecular weight and hence the smallest density of any substance, and, with the exception of helium, the lowest melting point and the lowest boiling point. The gas is odorless, tasteless, and colorless. The more important physical constants are collected in Table I.

TABLE I

## PHYSICAL CONSTANTS OF HYDROGEN

Melting point, ° C.....	- 259.2	Density g./liter at 0° and 760 mm.....	0.08985
° A.....	13.9		
Heat of fusion, cal. per mole	15	Density of liquid g./cc....	0.071
Boiling point, ° C.....	- 252.7	Solubility in water at 25° vol. per 100 vol. of H <sub>2</sub> O.	1.8
° A.....	20.4		
Heat of vaporization, cal. per mole.....	218	Equilibrium constant for dissociation, H <sub>2</sub> = 2H.	
Critical temperature, ° C....	- 241	At 2,000°.....	3 × 10 <sup>-4</sup>
° A....	32	3,500°.....	3.8
Critical pressure, atmos....	20		

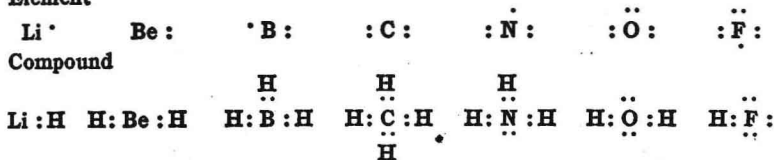
Hydrogen was first liquefied by Dewar (1898). The gas in expanding from high pressure to low pressure is heated at ordinary temperatures, but if cooled in liquid air (- 185° C.), the sign of this heat is reversed. Advantage is taken of this fact in the liquefaction process. (For further discussion of liquefaction process cf. III-6). The metals of the nickel, palladium, platinum groups occlude or dissolve hydrogen to a remarkable degree. Under certain conditions one volume of palladium will take up almost 900 volumes of hydrogen at 20° and 1 atmosphere. (Cf. Palladium, XX-27.) Molecular hydrogen has a very high relative rate of diffusion since this property is inversely proportional to the square root of the density. Thus the densities of hydrogen and oxygen are in the ratio of 1/16 and hydrogen diffuses four times as fast as oxygen.

**5. Reactions of Hydrogen.**—Hydrogen combines directly with most of the lighter elements, accompanied in the case of the

more electronegative elements with the evolution of large amount of energy; e.g. a jet of hydrogen burns readily in an atmosphere of oxygen or chlorine, and its mixtures with these gases are highly explosive.

The electron formulas of the compounds with the elements from lithium to fluorine are as follows:

**Element**



The more negative the element, the more completely does it tend to acquire the electrons of hydrogen, thus leaving the hydrogen with a valence of + 1. The more positive elements, on the other hand, tend to lose their electrons to hydrogen, giving it a valence of - 1, since, as mentioned in Paragraph 2, there is room for two electrons in the first quantum state of the hydrogen atom. In this respect hydrogen resembles the halogen family, all members of which lack one electron of completing the noble gas structure. The details of the reactions of hydrogen will be discussed under the various elements, although the general reaction of hydrogen to hydrogen ion is to be considered under the following topic.

**6. Properties of the Hydrogen Ion.**—Hydrogen ion is the substance present in all solutions of strong acids and its properties are the familiar properties common to all acids, such as sour taste, characteristic color changes with organic indicators, e.g. the change of blue litmus to red, the neutralization of bases and the solution of base metals. A complete statement of the properties of hydrogen ion would include values for the degree of dissociation, volatility, and solubility of all of its compounds, since these quantities determine the extent to which hydrogen ion will unite with negative ions. For example, the statement that the concentrations of hydrogen ion and hydroxide ion in pure water are  $10^{-7}$  moles per liter is equivalent to saying that the reaction,  $H^+ + OH^- = H_2O$ , takes place until the concentrations of the ions reach this value. Likewise the statement that the volatility of hydrogen chloride from its water solution

is high at 100° C. is equivalent to saying that the reaction,  $\text{H}^+ + \text{Cl}^- = \text{HCl}$  (gas), has a strong tendency to take place at this temperature.

7. Many of the most important reactions of hydrogen ion and hydrogen gas may be summarized in terms of the oxidation-reduction couple,  $\frac{1}{2}\text{H}_2 = \text{H}^+ + \text{E}^-$ . (The electron will be denoted by a dot in certain structural formulas, as in Paragraph 3, but in writing ordinary equations, we will use the symbol  $\text{E}^-$ .) For example, zinc will displace or liberate hydrogen from acids because the reaction,  $\text{Zn} = \text{Zn}^{++} + 2\text{E}^-$ , gives a higher "pressure" (voltage) of electrons. The total reaction,  $\text{Zn} + 2\text{H}^+ = \text{Zn}^{++} + \text{H}_2$ , is the result of the transfer of the electrons from the zinc to the hydrogen ion. On the other hand, the reaction  $\text{Ag} = \text{Ag}^+ + \text{E}^-$  has a lower voltage than hydrogen; and hydrogen reduces silver ion,  $2\text{Ag}^+ + \text{H}_2 = 2\text{Ag} + 2\text{H}^+$ , by the transfer of electrons from the hydrogen to the silver ion. Reference may be made to the table of oxidation-reduction potentials (Append. II) for the position of hydrogen in respect to a large number of oxidation-reduction couples. Mention should be made of the fact that the oxidation of metals by hydrogen ion is often a slow reaction, and that the speed depends greatly upon the nature of the surface upon which the gas deposits. Thus the action of acid upon zinc proceeds very slowly if the zinc is pure, and rapidly only when impurities are present. The power of hydrogen ion as an oxidizing agent depends, of course, upon its concentration. In normal alkaline solution, a stronger reducing agent is required to liberate hydrogen than in acid since the potential of the reaction,  $\frac{1}{2}\text{H}_2 + \text{OH}^- = \text{H}_2\text{O} + \text{E}^-$ , is 0.83 volts more positive than the potential of the acid couple.

Although the formula of hydrogen ion in water solution is written as  $\text{H}^+$ , the ion exerts such a strong attraction upon the water molecules that it might be written  $\text{H}(\text{H}_2\text{O})_n^+$ . The energy of hydration of the hydrogen ion, approximately 250,000 cal., is larger than that of any other singly charged ion.

**8. Preparation.**—Although hydrogen is liberated by the action of the electropositive metals, such as sodium, potassium, and calcium upon water, these metals are too expensive for its practical preparation. Hydrogen is sometimes prepared by passing steam over finely divided iron heated to redness.  $3\text{Fe} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 4\text{H}_2$ . The gas is conveniently prepared in

the laboratory by the action of dilute sulfuric or hydrochloric acid upon zinc or aluminum. Hydrogen so prepared usually contains small quantities of volatile hydrogen compounds resulting from the presence of impurities in the metals. These may be removed by bubbling the gas through a permanganate solution. Water vapor is conveniently removed by contact with concentrated sulfuric acid.

There are three principal sources of commercial hydrogen: the reduction of water by carbon, the destructive distillation of coal, and the electrolysis of aqueous solutions. The reduction of water by carbon involves the water gas reaction:  $\text{H}_2\text{O} + \text{C} = \text{CO} + \text{H}_2$ , and the further reaction,  $\text{H}_2\text{O} + \text{CO} = \text{H}_2 + \text{CO}_2$  (cf. XIII—6). Coke-oven hydrogen is a by-product of the destructive distillation of coal and contains large quantities of methane,  $\text{CH}_4$ , which may be removed by liquefaction. Electrolytic hydrogen is now usually prepared by the electrolysis of concentrated sodium hydroxide solutions with iron or nickel electrodes. Hydrogen is liberated at the cathode and oxygen at the anode. The gas is quite pure except for a small quantity of oxygen which is present by diffusion from the anode. This may be removed by passing the gas over a catalyst, e.g. finely divided nickel at  $250^\circ \text{C}$ ., which accelerates the combinations of hydrogen and oxygen. Large quantities of hydrogen are also formed as a by-product in the manufacture of sodium hydroxide (cf. IV—12) by the electrolysis of salt brine.

**9. Commercial Uses.**—The oxy-hydrogen flame is used in cutting and welding metals. The temperature of the flame is approximately  $2,500^\circ \text{C}$ . A special burner is employed which prevents the explosion of the gases by mixing them just before they reach the orifice. The atomic hydrogen torch, recently developed, has many advantages in welding under reducing conditions. The atomic hydrogen is formed by blowing hydrogen through a very hot electric arc. The metal surface acts as a catalyst for the union of the atomic hydrogen and is heated to a high temperature, estimated between  $4000$  and  $5000^\circ \text{C}$ , by the heat liberated through the formation of the  $\text{H}_2$  molecule.

Large quantities of hydrogen are consumed in the manufacture of synthetic ammonia by the direct union of the elements. The synthetic production of methanol,  $\text{CH}_3\text{OH}$ , and other liquid fuels by the reaction of hydrogen and carbon monoxide in the

presence of catalysts promises to become of great industrial significance. Another important use is in the hydrogenation of many oils, such as cotton-seed oil, to form solid fats.

Hydrogen is also employed as a lifting medium in balloons. Its efficiency depends upon the difference in weight of equal volumes of hydrogen and air. This is 1.2 grams per liter at 0° C. and 1 atmosphere.

**10. Analytical.**—Hydrogen is often determined by mixing with an excess of oxygen and passing the mixture over a glowing filament electrically heated. The per cent of hydrogen is calculated by the contraction in volume due to the formation of water. Hydrogen is also determined by passing the gas over hot copper oxide,  $\text{CuO} + \text{H}_2 = \text{Cu} + \text{H}_2\text{O}$ , and absorbing the water in a weighed tube of calcium chloride.

## CHAPTER II

### INERT GASES: HELIUM, NEON, ARGON, KRYPTON, XENON, RADON

1. As early as 1784, Cavendish showed that air contained a small amount of an unknown gas which was quite non-reactive, but further work on the subject was not published until 1893, when Lord Rayleigh found that the weight of 1 liter of nitrogen prepared from pure nitrogen compounds was 1.2506 g., as compared to 1.2572 g. for atmospheric nitrogen. This discrepancy led to a careful investigation of atmospheric nitrogen by Rayleigh and Ramsey and to the discovery of argon. Ramsey shortly after identified the gas given off by uranium minerals as the unknown element, helium, whose existence Lockyer had postulated in 1868 to account for a prominent yellow line in the solar spectrum. Subsequent investigation by fractional distillation of the crude argon obtained from air led to the discovery of neon, krypton and xenon, the percentage of the various gases in air being:

He	Ne	A	Kr	Xe
0.0004	0.0012	0.94	0.00005	0.000006 per cent

The natural gas fields of Texas and Kansas contain helium in small amounts, a number of these wells, high in nitrogen content, analyzing between 1 and 2 per cent of the gas.

Research on the radioactive elements (Chap. **XXI**) has shown that the so-called alpha-ray, or particle, is doubly charged helium, and that helium is thus one of the products of the decomposition of these unstable elements. It has been calculated that a gram of radium produces 0.11 cc. of helium per year, and a gram of uranium oxide,  $U_3O_8$ ,  $9.1 \times 10^{-8}$  cc. The loss of an alpha particle by radium or its isotopes results in the formation of the lowest member of the inert gas group, radon, also called niton. Radon, however, is very unstable, the average life of an atom being only a few days (Chap. **XXI**).



TABLE I  
ATOMIC AND PHYSICAL PROPERTIES

	He	Ne	A	Kr	Xe	Rn
Atomic number.....	2	10	18	36	54	86
Atomic weight.....	4.00	20.2	39.91	82.9	130.2	222
Isotopes.....	None	20, 22	36, 40	84, 86, 82 83, 80, 78	129, 132, 131 134, 136, 128 130, 126, 124	222 222 220
Electrons in various quantum levels,						
1st.....	2	2	2	2	2	2
2d.....		8	8	8	8	8
3d.....			8	18	18	18
4th.....				8	18	32
5th.....					8	18
6th.....						8
Melting point, ° C.....	-268.9 (140 atm.)	-248.7 (1 atm.)	-189.2	-169	-140	-71
Boiling point, ° A.....	4.2	24.4	83.9	104	133	202
Boiling point, ° C.....	-268.9	-245.9	-185.7	-151.8	-109.1	-61.8
Heat of vaporization, cal. per mole, at B.P.....	4.2	27.2	87.4	121.3	164.0	111.3
Critical temperature, ° C.....	25	405	1,500	2,240	3,200	3,600
Density of liquid.....	-268	-220	-117	-63	15	4.4
Potential required to ionize gas atoms, volts,	0.126	1.20	1.40	2.6	3.06	
1st electron.....	24.5	21.48	15.2	12.7	11	
2d electron.....	54.1					