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NAVAL SHIPS' TECHNICAL MANUAL

CHAPTER 220
VOLUME 1

BOILER WATER AND FEEDWATER WATER CHEMISTRY

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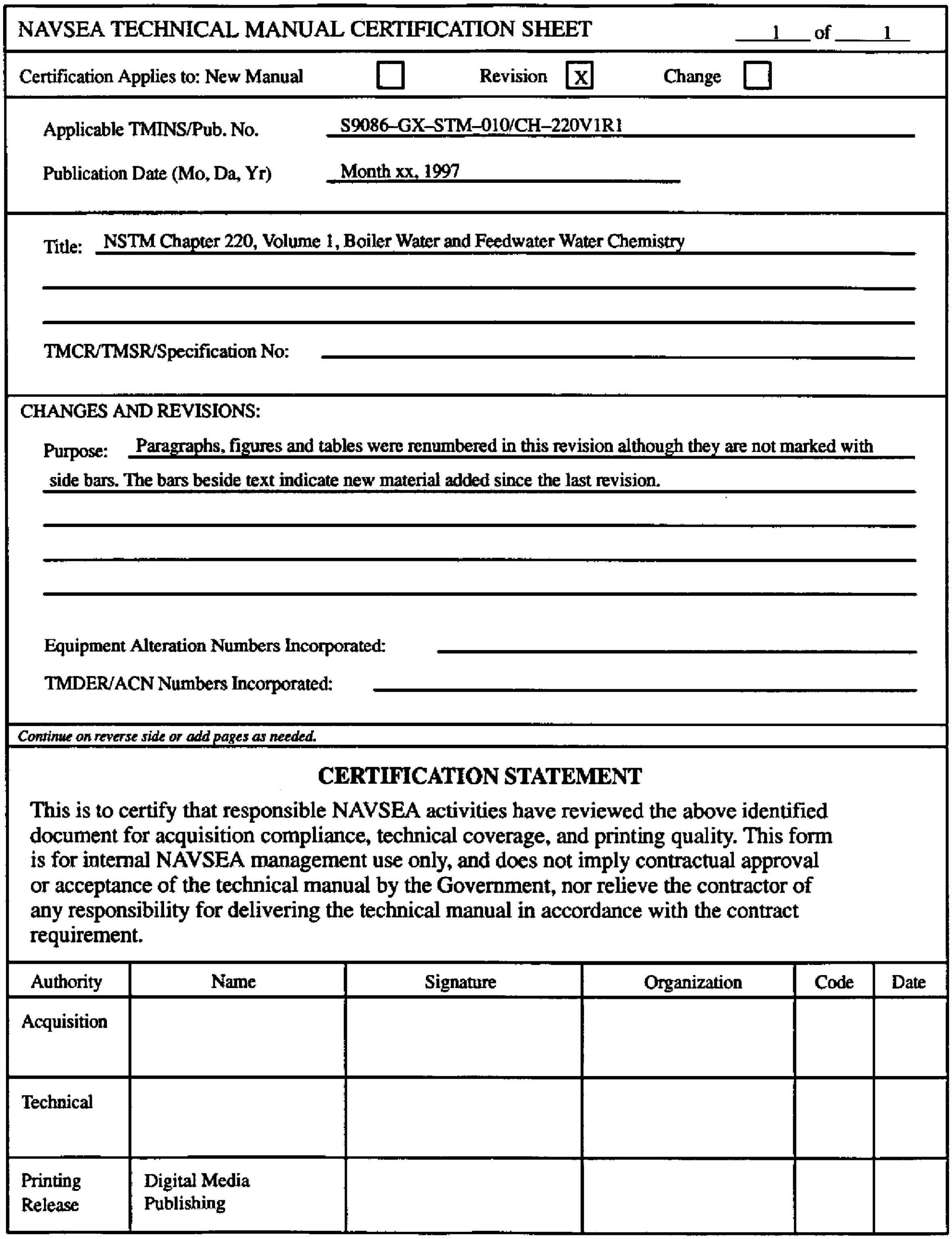

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NOTE

THIS CHAPTER HAS BEEN REFORMATTED FROM DOUBLE COLUMN TO SINGLE COLUMN TO SUPPORT THE NSTM DATABASE. THE CONTENT OF THIS CHAPTER HAS NOT BEEN CHANGED.

CHAPTER 220

BOILER WATER AND FEEDWATER
VOLUME 1 - WATER CHEMISTRY

SECTION 1.

INTRODUCTION

220-1.1 PURPOSE

220-1.1.1 This volume is intended for use as a text for teaching water chemistry in steam propulsion plants (non-nuclear). Thus, it is aimed at readers with a wide variety of backgrounds and goals. For this reason, the text presupposes no prior chemistry study although some knowledge of elementary algebra is assumed. After a brief introduction, many fundamentals of chemistry are developed in the initial sections, although the coverage is not complete. Succeeding sections become more practically oriented to the operation of naval steam propulsion plants.

220-1.2 DEFINITIONS

220-1.2.1 By the briefest definition, **chemistry is the study of matter and the changes which matter undergoes.** This study includes the description, composition, and classification of the vast number of natural and man-made substances. Since chemistry is involved with the fundamental properties of matter, it is an essential supporting science for many other fields of science and engineering.

220-1.2.2 The changes of matter with which chemistry is concerned are chiefly of two types: **physical changes and chemical changes.** A physical change does not alter the basic identity of a substance. The melting of ice and the vaporization of liquid water into steam (a gas) are examples of physical changes. In both these examples the substance undergoing the change retains its basic chemical identity, water, which has the chemical formula, H_2O. In general, **changes of a given substance from one state of matter (gas, solid, and liquid) to another are physical changes.**

220-1.2.3 In contrast to physical changes, chemical changes do involve a change in the identity of substances. For example, water can be decomposed into its constituent parts, hydrogen and oxygen, and this is a chemical change. **Chemical changes are those changes in which one or more substances disappear and one or more new substances are formed.**

220-1.3 WATER CHEMISTRY IN STEAM PROPULSION PLANTS (NON-NUCLEAR)

220-1.3.1 Water is the most abundant substance on the surface of the earth and is most familiar in its liquid state. It also has the ability to dissolve a wide variety of substances. Thus, a great volume of fundamental chemical knowledge has been developed from the study of the reactions between substances dissolved in water or the reaction of various substances with water. Water chemistry, therefore, is the study of those reactions which occur in a water environment (aqueous environment).

220-1.3.2 In addition to its abundance, some of the physical properties of water have led to its widespread use as a heat transfer fluid in power generation systems. These properties include a large heat capacity, which is the amount of heat required to raise the temperature of a given amount of water, usually expressed in BTU's per pound-mass per degree Fahrenheit or calories per gram per degree Celsius. A large heat capacity means that water is an efficient carrier of heat and makes it useful for either heating or cooling. Also, water has a high heat of vaporization, which is the amount of heat required to change a given amount of liquid at its boiling point to steam. The opposite side of the same coin is the condensation of a given amount of steam to liquid at its boiling point which releases the same amount of heat as that absorbed upon vaporization.

220-1.3.3 In a steam cycle, water at a relatively low temperature is heated to the boiling point; vaporized by absorbing heat from some source; moved to another location where it performs work such as turning a turbine generator; and finally condensed as it cools in the heat rejection process. The large heat capacity and heat of vaporization of water mean that, for each cycle, water transfers a larger amount of heat than most other fluids.

220-1.3.4 Water used in naval steam propulsion plants is relatively pure. However, it is in contact with several metals at high temperature and pressure. These conditions promote several chemical reactions and certain chemicals are added to prevent or control these reactions. The goal of this text is to develop the fundamental principles needed to understand the nature, consequences, and control of the water chemistry involved with naval steam propulsion plants.

SECTION 2.

ATOMIC THEORY AND THE PERIODIC TABLE

220-2.1 INTRODUCTION

220-2.1.1 Man is intimately familiar with all three physical states of matter (gas, liquid, and solid). His body is composed of matter; he eats, drinks, and breathes matter. He shapes it to wear, to live in, to carry him beneath the ocean or to the moon. These and all other forms of matter have one thing in common. They can all be broken down into fundamental units called atoms. This section describes atoms and the atomic theory.

220-2.2 GLOSSARY OF TERMS

220-2.2.1 Terms used in this section are defined as follows:

1. **Atom:** An extremely small particle consisting of a positively charged nucleus surrounded by negatively charged electrons.
2. **Atomic Mass Number (A):** The sum of the number of protons, Z, and the number of neutrons, N, in a nucleus. A = N + Z.
3. **Atomic Mass Unit (AMU):** One AMU is 1/12 the mass of ^{12} C atom and equals 1.66 x 10^{-24} gm.
4. **Atomic Number (Z):** The number of protons in the nucleus of an atom.
5. **Atomic Weight:** The weighted average of the masses (in AMU) of all stable isotopes of an element.
6. **Electron Shell:** A major energy state of electrons in atoms. Each shell is composed of one or more orbitals with slightly different energies.
7. **Element:** All atoms having the same atomic number.

8. **Group:** A vertical column in the periodic table.
9. **Inert Gas Configuration:** The arrangement of electrons in an atom such that there are 8 electrons in the outermost shell.
10. **Isotopes:** Those atoms having the same atomic number but different atomic mass numbers.
11. **Nucleus:** The central core of an atom. It consists of neutrons and protons and has a positive charge.
12. **Orbital:** A minor energy state within an electron shell.
13. **Period:** A horizontal row in the periodic table.
14. **Periodic Table:** A table or chart of the elements in order of their atomic number and grouped by chemical properties.

220-2.3 THE ATOM

220-2.3.1 GENERAL. According to the atomic theory, all matter is composed of atoms existing individually or in combination with each other. An **atom** is an extremely small, electrically neutral particle and is the smallest unit involved in chemical changes of matter. Atoms have dimensions on the order of 10^{-8} cm. They can be treated as distinct particles because they behave as such chemically, but it is now known that atoms themselves are composed of even smaller particles. The understanding of many aspects of chemistry requires a knowledge of the structure of the atom.

220-2.3.2 GENERAL FEATURES. All atoms consist of a central, positively charged core which is orbited by one or more negatively charged particles. Figure 220-2-1 is a highly simplified schematic representation of this arrangement. The atomic core is called the **nucleus.** It is roughly spherical and is composed of two types of particles - **neutrons** and **protons.** These particles are relatively massive and are essentially equal in weight. Their most apparent difference is electrical charge. Neutrons are electrically neutral (uncharged) and protons carry a positive charge. Atoms are identified by the number of neutrons and protons in their nuclei, as will be discussed in paragraphs 220-2.3.4 through 220-2.3.5.4. Together, the neutrons and protons give the nucleus its mass, but the protons alone account for the positive charge.

220-2.3.2.1 The charge of a single proton has the value 1.6×10^{-19} coulomb, but this number is seldom used in chemistry. It is much simpler to treat the proton’s charge as a unit. In this way, a nucleus which contains one proton is said to have a charge of +1 or simply 1, since it is understood that the charge on a nucleus is positive. A nucleus with two protons has a charge of 2, and so on.

220-2.3.2.2 The particles which orbit the nucleus are **electrons.** They are very light in weight, with a mass only 1/1837 the mass of a proton or neutron. Each electron is negatively charged and the charge on one electron is equal in magnitude (but opposite in sign) to the charge on one proton. The number of electrons orbiting a nucleus is exactly equal to the number of protons contained in that nucleus, so the equal and opposite charges cancel each other and the atom as a whole is neutral. The electrons are bound in the atom by electrostatic attraction, so the atom remains neutral unless some external force causes a change in the number of electrons.

220-2.3.3 ATOMIC DIMENSIONS. The diameter of the atom is determined by the range of the electrons in their travels around the nucleus and is on the order of 10^{-8} cm. The diameter of the nucleus is roughly 10,000 times smaller, and is on the order of 10^{-13} to 10^{-12} cm. Since the nucleus is composed of neutrons and protons which are about 1837 times heavier than an electron, the nucleus contains practically all the mass of the atom but constitutes a very small fraction of the volume. Although electrons are individually very small, the volume in which they move around the nucleus constitutes by far the largest part of the atomic volume. On a relative scale, if the nucleus were the size of a pea, the nearest electron would be found about 10 to 20 yards away. Figure 220-2-1 illustrates these size relationships, but not to scale. If the nucleus were really the size shown, the electrons would be several hundred feet away.

220-2.3.3.1 Some of the properties of the atom and its component parts are summarized in Table 220-2-1. The masses listed in this table are in atomic mass units (AMU's) which is a relative scale on which the mass of a proton is about 1.0. A more precise definition is deferred until the necessary concepts and definition have been discussed. Numerically, one AMU is equal to 1.66 x 10^{-24} grams.

Example 2-1: A lead nucleus has a mass of 207 AMU's and a diameter of 2.0 x 10^{-12} cm. Calculate its density in grams/cc and in tons/cc. Density = mass/volume.

Question: In nature, the density of substances never even comes close to the tremendously high value calculated in the previous problem. How is this observation related to what you have learned about atomic theory up to this point?

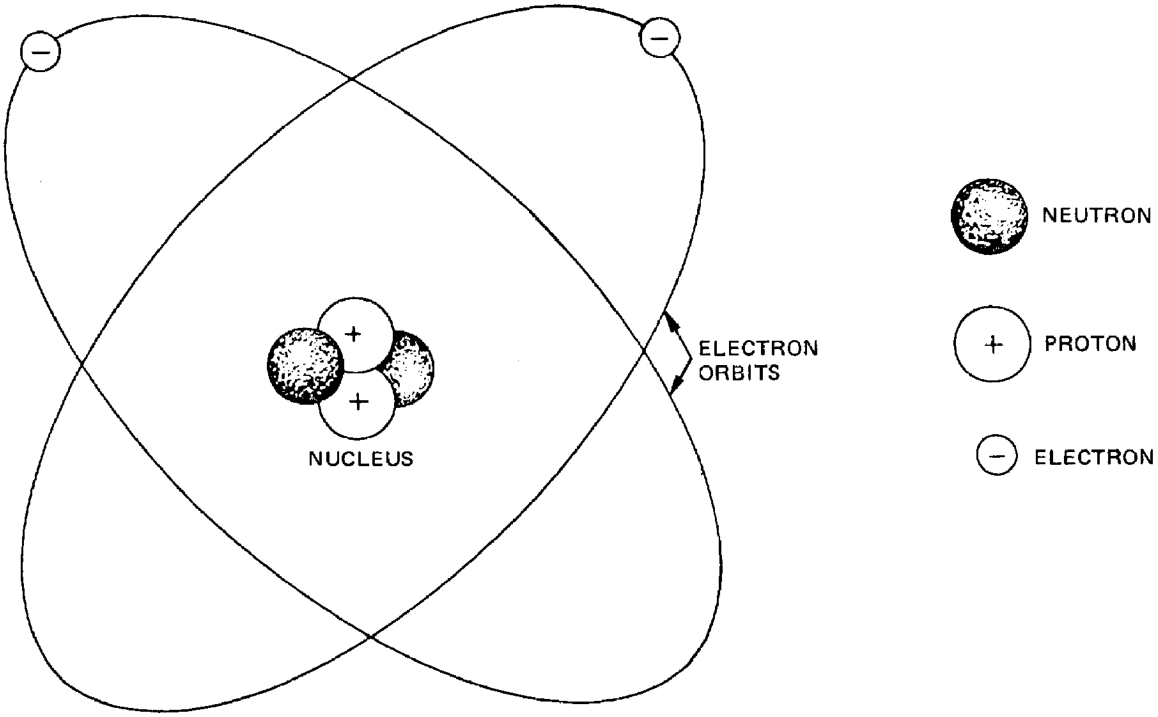


Figure 220-2-1 Schematic Diagram of a Simple Atom (Helium)

Solution 2-1: ***First, calculate the volume of the nucleus in cc and its mass in grams and in tons, then calculate the density.***

$$\text{Volume} = 4/3\,\pi r^3 = 4.20\ \frac{2.0 \times 10^{-12}}{2}\ cm^3$$

$$= 4.20 \times 10^{-36} cc$$

$$\text{Mass (grams)} = 207\ AMU \times 1.66 \times 10^{-24}\ gm/AMU$$

$$= 3.44 \times 10^{-22}\ gm$$

$$\text{Mass (tons)} = 3.44 \times 10^{-22}\ gm \times 2.2 \times 10^{-3}\ lb/gm \times \frac{1T}{2000\ lb}$$

$$= 3.78 \times 10^{-28}\ T$$

$$\text{Density (gm/cc)} = \frac{3.44 \times 10^{-22}\ gm}{4.2 \times 10^{-36}\ cc} = 8.2 \times 10^{13}\ gm/cc$$

$$\text{Density (tons/cc)} = \frac{3.78 \times 10^{-28}\ T}{4.2 \times 10^{-36} cc}$$

$$= 9 \times 10^{7}\ T/cc$$

Table 220-2-1 ATOMIC PROPERTIES

Name	Relative Mass, AMU*	Relative Charge (Based on the Charge of a Proton)	Location in the Atom	Magnitude of Diameter, cm
Atom	1.0 to about 260	0	-	10^{-8}
Electron	0.00055 or 1/1837	-1	Outside the nucleus	-
Nucleus	1.0 to 260	1 to about 105	-	10^{-12}
Proton	1.0	+1	Inside the nucleus	Less than 10^{-12}
Neutron	1.0	0	Inside the nucleus	Less than 10^{-12}
* 1 AMU -= 1.66 x 10^{-24} grams.				

220-2.3.4 CHEMICAL ELEMENTS. An atom is classified chemically by the number of protons in its nucleus. All atoms having the same number of protons in their nuclei have the same chemical behavior and collectively they constitute a **chemical element.** At present, 103 elements are known. The number of protons in the nuclei of atoms of these elements forms a continuous series from 1 (the element hydrogen) to 103 (the element lawrencium). The first 92 elements are found in nature. All others are man-made. Also, several isotopes of elements 104 and 105 have been reported, but the names of these elements have not been assigned yet.

220-2.3.4.1 The number of protons in the nucleus plays such an important role in identifying the atom it is given a special name, **atomic number.** The symbol Z is often used for atomic number (or number of protons). Using the examples above, hydrogen has atomic number 1 and lawrencium has atomic number 103.

220-2.3.4.2 Each chemical element has been assigned a special one- or two-letter **symbol.** The symbols for all the elements are listed in Table 220-2-2, with the elements in alphabetical order. The first 15 elements and their symbols are given in order of their atomic number in Table 220-2-3. The first letter of a chemical symbol is always capitalized no matter where or how the symbol is used. If the symbol has two letters, the second letter is never capitalized. Some of the symbols are derived from the Latin name of the element and bear no apparent relationship to the English name of the element. For example, the symbol for sodium, Na, is from the Latin name, natrium. Other examples in this category are potassium (K), iron (Fe), silver (Ag), antimony (Sb), tin (Sn), tungsten (W), gold (Au), and lead (Pb).

220-2.3.5 OTHER FEATURES OF ATOMS AND ELEMENTS. **Atomic Mass Number** , A, is the sum of the number of protons, Z, and the number of neutrons, N, in a nucleus. That is, $A = Z + N$. Since Z and N are always integers (whole numbers), A is also an integer.

220-2.3.5.1 Isotopes. Isotopes are those atoms in which Z is the same but N and, thus A, are different. If Z is the same then all these atoms belong to the same chemical element. Only their masses differ. An example is oxygen ($Z = 8$). If the mass numbers of all the atoms in a sample of pure oxygen were determined, it would be found that 99.75 percent of the atoms have $A = 16$ (8 protons and 8 neutrons), 0.037 percent have $A = 17$ (8 protons and 9 neutrons), and 0.204 percent have $A = 18$ (8 protons and 10 neutrons). Every element has more than one isotope, but usually most, and in some cases all the isotopes are radioactive. Most of these radioactive isotopes do not occur in nature but are man-made. Although there are only about 100 elements, there are more than 1200 isotopes known at this time.

220-2.3.5.2 Designating Isotopes. A shorthand notation is used for the purpose of designating a particular isotope. For the hypothetical atom X having Z protons and mass number A, the notation is $^{A}_{Z}X$. The stable oxygen isotopes are written:

$$^{16}_{8}O,\quad ^{17}_{8}O,\quad \text{and}\ ^{18}_{8}O$$

Table 220-2-2 ELEMENTS, SYMBOLS, ATOMIC NUMBERS, AND ATOMIC WEIGHTS

Element	Symbol	Atomic Number (Z)	Atomic Weight (AMU)
Actinium	Ac	89	[227]*
Aluminum	Al	13	26.982
Americium	Am	95	[243]
Antimony	Sb	51	121.750
Argon	Ar	18	39.948
Arsenic	As	33	74.922
Astatine	At	85	[210]
Barium	Ba	56	137.340
Berkelium	Bk	97	[247]
Beryllium	Be	4	9.012
Bismuth	Bi	83	208.980

Table 220-2-2 ELEMENTS, SYMBOLS, ATOMIC NUMBERS, AND ATOMIC WEIGHTS - Continued

Element	**Symbol**	**Atomic Number (Z)**	**Atomic Weight (AMU)**
Boron	B	5	10.811
Bromine	Br	35	79.909
Cadmium	Cd	48	112.400
Calcium	Ca	20	40.080
Californium	Cf	98	[249]
Carbon	C	6	12.011
Cerium	Ce	58	140.120
Cesium	Cs	55	132.905
Chlorine	Cl	17	35.453
Chromium	Cr	24	51.996
Cobalt	Co	27	58.933
Copper	Cu	29	63.540
Curium	Cm	96	[247]
Dysprosium	Dy	66	162.500
Einsteinium	Es	99	[254]
Erbium	Er	68	167.260
Europium	Eu	63	151.960
Fermium	Fm	100	[253]
Fluorine	F	9	18.998
Francium	Fr	87	[223]
Gadolinium	Gd	64	157.250
Gallium	Ga	31	69.720
Germanium	Ge	32	72.590
Gold	Au	79	196.967
Hafnium	Hf	72	178.490
Helium	He	2	4.003
Holmium	Ho	67	164.930
Hydrogen	H	1	1.008
Indium	In	49	114.820
Iodine	I	53	126.904
Iridium	Ir	77	192.200
Iron	Fe	26	55.847
Krypton	Kr	36	83.800
Lanthanum	La	57	138.910
Lawrencium	Lw	103	[257]
Lead	Pb	82	207.190
Lithium	Li	3	6.939
Lutetium	Lu	71	174.970
Magnesium	Mg	12	24.312
Manganese	Mn	25	54.938
Mendelevium	Md	101	[256]
Mercury	Hg	80	200.590
Molybdenum	Mo	42	95.940

Table 220-2-2 ELEMENTS, SYMBOLS, ATOMIC NUMBERS, AND ATOMIC WEIGHTS - Continued

Element	Symbol	Atomic Number (Z)	Atomic Weight (AMU)
Neodymium	Nd	60	144.240
Neon	Ne	10	20.183
Neptunium	Np	93	[237]
Nickel	Ni	28	58.710
Niobium	Nb	41	92.906
Nitrogen	N	7	14.007
Nobelium	No	102	[254]
Osmium	Os	76	190.200
Oxygen	O	8	15.999
Palladium	Pd	46	106.400
Phosphorus	P	15	30.974
Platinum	Pt	78	195.090
Plutonium	Pu	94	[242]
Polonium	Po	84	[210]
Potassium	K	19	39.102
Praseodynium	Pr	59	140.907
Promethium	Pm	61	[147]
Protactinium	Pa	91	[231]
Radium	Ra	88	[226]
Radon	Rn	86	[222]
Rhenium	Re	75	186.200
Rhodium	Rh	45	102.905
Rubidium	Rb	37	85.470
Ruthenium	Ru	44	101.070
Samarium	Sm	62	150.350
Scandium	Sc	21	44.956
Selenium	Se	34	78.960
Silicon	Si	14	28.086
Silver	Ag	47	107.870
Sodium	Na	11	22.990
Strontium	Sr	38	87.620
Sulfur	S	16	32.064
Tantalum	Ta	73	180.948
Technetium	Tc	43	[98]
Tellurium	Te	52	127.600
Terbium	Tb	65	158.924
Thallium	Tl	81	204.370
Thorium	Th	90	232.038
Thulium	Tm	69	168.934
Tin	Sn	50	118.690
Titanium	Ti	22	47.900
Tungsten	W	74	183.850
Uranium	U	92	238.030

Table 220-2-2 ELEMENTS, SYMBOLS, ATOMIC NUMBERS, AND ATOMIC WEIGHTS - Continued

Element	**Symbol**	**Atomic Number (Z)**	**Atomic Weight (AMU)**
Vanadium	V	23	50.942
Xenon	Xe	54	131.300
Ytterbium	Yb	70	173.040
Yttrium	Y	39	88.905
Zinc	Zn	30	65.370
Zirconium	Zr	40	91.220
* Numbers in brackets represent the atmonic mass number of the most stable known isotope of the element.			

Table 220-2-3 PROPERTIES OF THE FIRST FIFTEEN ELEMENTS

Element	**Symbol**	**Atomic Number (Z)**	**Atomic Weight (AMU)**	**Description of Properties**
Hydrogen	H	1	1.008	Colorless gas, burns readily with oxygen to form $H_2 O$; forms HCI with chlorine
Helium	He	2	4.003	Colorless gas, very non-reactive chemically
Lithium	Li	3	6.939	Silvery white, soft metal, very reactive chemically, forms $Li_2 O$ and LiCl readily.
Beryllium	Be	4	9.012	Grey metal, much harder than lithium, fairly reactive chemically, forms BeO and $BeCl_2$ easily.
Boron	B	5	10.811	Yellow or brown non-metal, very hard element, not very reactive, but will form $B_2 O_3$, and BCl_3 .
Carbon	C	6	12.011	Black non-metal, brittle, non-reactive at room temperature. Forms CO_2 and CCl_4 .
Nitrogen	N	7	14.007	Colorless gas, not very reactive, will form $N_2 O_5$ and NH_3 .
Oxygen	O	8	15.999	Colorless gas, moderately reactive, will combine with most elements, forms CO_2 , MgO, etc.
Flourine	F	9	18.998	Green-yellow gas, extremely reactive, irritating to smell, forms NaF, MgF_2 .
Neon	Ne	10	20.183	Colorless gas, very non-reactive chemically.
Sodium	Na	11	22.990	Silvery soft metal, very reactive chemically, forms $Na_2 O$ and NaCl.
Magnesium	Mg	12	24.312	Silvery white metal, much harder than sodium. Fairly reactive, forms MgO and $MgCl_2$.

Table 220-2-3 PROPERTIES OF THE FIRST FIFTEEN ELEMENTS -

Continued

Element	**Symbol**	**Atomic Number (Z)**	**Atomic Weight (AMU)**	**Description of Properties**
Aluminum	Al	13	26.982	Silvery white metal, like magnesium but not as reactive. Forms $Al_2 O_3$ and $SiCl_4$.
Silicon	Si	14	28.086	Grey non-metallic, brittle and non-reactive at room temperature. Forms SiO_2 and $SiCl_4$.
Phosphorus	P	15	30.974	Black, red, violet, or yellow solid, low melting point, quite reactive, forms $P_2 O_5$ and PCl_3 .

(This is the most common notation, but some books use the older convention of writing the mass number on the right instead of the left, for example, ${}_8 O^{17}$.) Z may be omitted because it is determined by the symbol X. Thus ${}^{16}O$ is sufficient to fully describe the oxygen isotope with the mass number 16 composed of 8 protons and 8 neutrons. The notation O-16 is also used occasionally.

220-2.3.5.3 Atomic Mass Units. In Table 220-2-1, the masses of atomic particles are given in atomic mass units (AMUs). These units are a relative weight scale on which the mass of the isotope ${}^{12}_{6}C$ is used as a standard and all others are related to it. Specifically, 1 AMU is defined as 1/12 the mass of the ${}^{12}_{6}C$ atom. In grams 1 AMU = 1.66 x 10^{-24} gram. Since the mass of a proton or neutron is approximately 1 AMU, the mass of any particular atom is approximately equal to its atomic mass number.

220-2.3.5.4 Atomic Weight of Elements. Chemists usually find that the atomic weight of an element is more useful than isotopic masses. The rest of this text frequently refers to atomic weight. The **atomic weight** of an element is defined as the weighted average of the masses of all its naturally occurring isotopes. The atomic weight of the elements are listed in Table 220-2-4.

Example 2-2: The masses and percentage abundances of the stable isotopes of oxygen are (exact masses are given here to obtain an answer which agrees with values given elsewhere in the text):

Isotope	**Mass, AMU**	**Abundance in Nature, percent**
${}^{16}O$	15.995	99.759
${}^{17}O$	16.999	0.037
${}^{18}O$	17.999	0.204

Calculate the atomic weight of oxygen.

Solution 2-2: Since the atomic weight of an element is the weighted average of the masses of its stable isotopes, proceed as follows:

15.995 x 0.99759 = 15.956
16.999 x 0.00037 = 0.006
17.999 x 0.00204 = 0.037
Atomic weight of oxygen = 15.999 AMU

In this text, atomic weight always refers to an element, not an individual atom.

Question: Can you clearly distinguish among atomic number, atomic mass number, and atomic weight? If not, read this section again.

220-2.4 THE PERIODIC TABLE

220-2.4.1 GENERAL. Over many years of chemical investigation, a remarkable feature of the elements emerged. It was observed that if the elements are arranged in order of their atomic numbers, the chemical properties are repeated somewhat regularly. To a lesser extent, the physical properties are also repeated periodically. This periodic repetition can be seen in Table 220-2-4. Compare the properties of lithium (Li), sodium (Na), and potassium (K), and also those of beryllium (Be), magnesium (Mg), and calcium (Ca). In the list of elements shown in this table, the properties are repeated every eighth element.

220-2.4.2 DESCRIPTION OF THE TABLE. The arrangement of the elements in the form of a table in which elements with similar chemical properties are grouped together is called a periodic table. One of the most common versions is given as Figure 220-2-2. In this table, elements are arranged in order of increasing atomic number in succeeding rows. Each row is called a **period.** Note that some periods are longer than others. Elements with generally similar chemical properties appear in vertical columns called **groups.** Each group is designated by a Roman numeral and a capital letter, except the one on the extreme right-hand side, Group O. At the bottom of the periodic table are two long rows of elements identified as the lanthanide series and the actinide series. They are separated from the table primarily to keep it from becoming unmanageably wide. Also, the elements within each of these two series show similar chemical properties. The number directly above each element is its atomic number and below each element is its atomic weight. In several cases, the atomic weights are in parentheses. This method is used to indicate that these elements have no stable isotopes, that is, they are all radioactive. The value enclosed in parentheses and used for the atomic weight is the atomic mass number of the most stable known isotope as indicated by the longest half-life.

220-2.4.3 CLASSES OF ELEMENTS. There are three broad classes of elements. These are the metals, the **non-metals,** and the **semi-metals.**

220-2.4.3.1 Metals. The metals constitute the largest class of elements and are located on the left and toward the center of the periodic table. In Figure 220-2-2, the heavy line running step-wise from boron (B) to astatine (At) generally separates the metals from the rest of the elements. (Elements in the actinide and lanthanide series are metals.)

220-2.4.3.1.1 Metals are familiar to most people by their physical properties. They are usually thought of as being hard and strong, capable of being shaped mechanically (malleable and ductile), good conductors of heat and electricity, and having lustrous surfaces when fresh and clean. More important for chemical classification are the chemical properties of metals. Thus, mercury (Hg) is a metal, although it is a liquid at room temperature and sodium is a metal although it is not at all hard or strong.

220-2.4.3.1.2 Chemical compounds are covered in a later chapter, but it can be noted here that metals cover a wide range chemically. The reaction with water ranges from violent with sodium and potassium to imperceptible with gold and platinum. Metals are divided into two categories:

1. The light metals which are soft, have a low density, are very reactive chemically, and are unsatisfactory as structural materials; and
2. The transition metals which are hard, have a high density, do not react readily, and are useful structural materials.

NOTE

The metals in category 1 are located at the far left of the table (Groups IA and IIA). The metals in category 2 are located in the middle of the table (the B groups).

220-2.4.3.2 Non-Metals. This class of elements occupies the part of the periodic table to the right of the heavy, step-like line. The physical properties of the non-metals in general are just the opposite of those attributed to metals. Non-metals are often gases at room temperature, the ones which are solids are not lustrous, are not malleable or ductile, and are poor conductors of heat and electricity. Some non-metals are very reactive but the nature of the reactions is different from that of metals.

220-2.4.3.2.1 The six elements in Group O represent a special sub-class of non-metals. They are all gases and are very unreactive so they are called the **inert gases.** For many years, it was believed that the inert gases would not and could not participate in chemical reactions. In 1962, the first true compounds of an inert gas, XeF_4 and $XePtF_6$, were positively identified. Since that time, several other compounds have been prepared. The preparation of these compounds requires rather special conditions, so under ordinary conditions, the inert gases may be considered unreactive.

220-2.4.3.3 Semi-Metals. The obvious trend in the periodic table is that from left to right across any period, the elements change from distinctly metallic (Group IA) to distinctly non-metallic (Group VIIA). This change in character is not sharply defined but is rather gradual. Generally, elements well to the left of the heavy diagonal line are metals and those well to the right are non-metals. Some of the elements near the line, however, exhibit properties of metals under some conditions and properties of non-metals under other conditions. These elements are called the semi-metals and include boron (B), silicon (Si), germanium (Ge), arsenic (As), and tellurium (Te). They are usually classed as semi-conductors of electricity and are widely used in electrical components such as transistors.

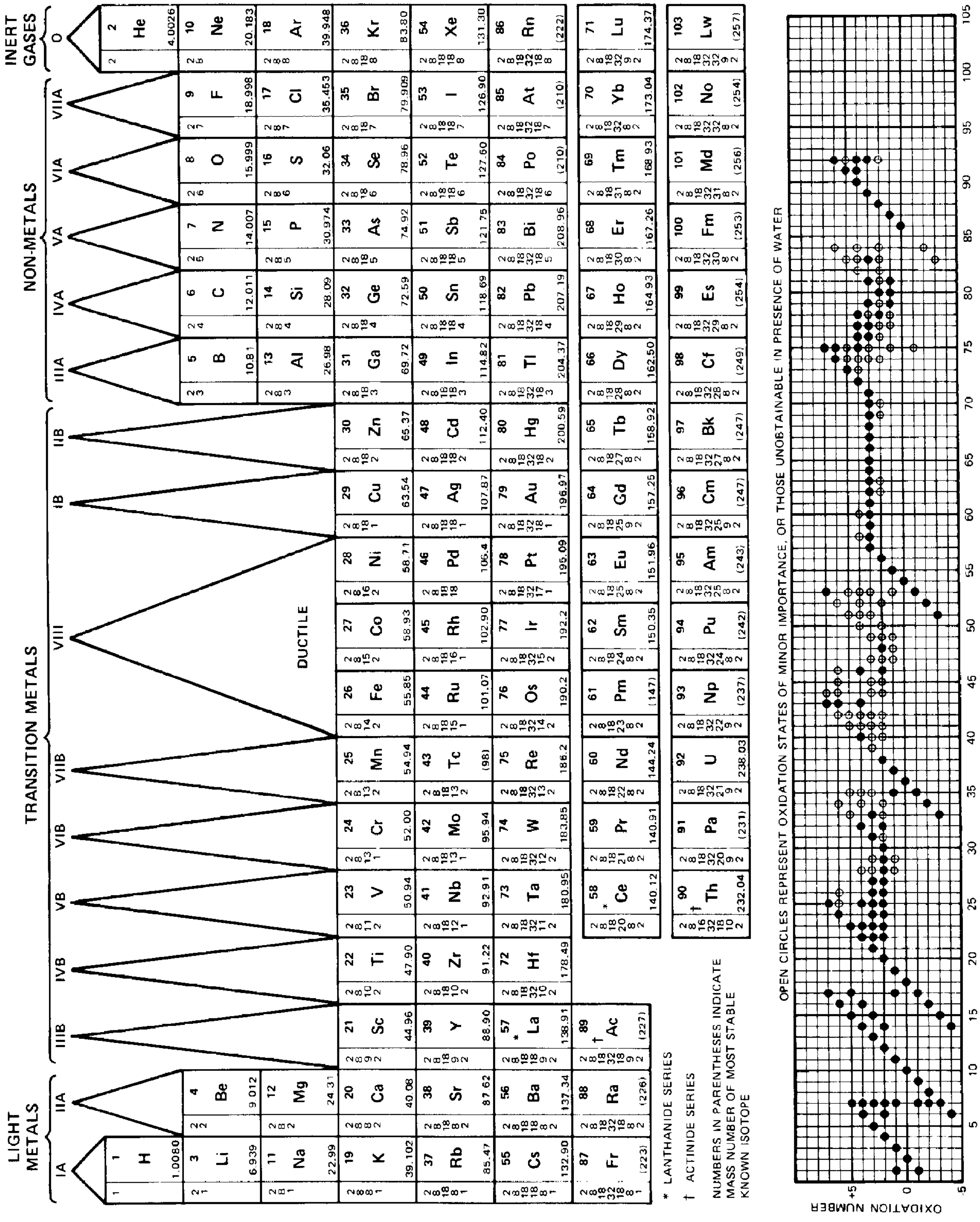


Figure 220-2-2 Periodic Table

220-2.4.4 TRENDS WITHIN GROUPS. As shown in the previous section, there are some exceptions to even the broadest generalizations concerning chemical properties and the periodic table. When more detailed observations are attempted, other exceptions can be expected. The usefulness of such observations, however, far outweighs the inconvenience of the exceptions. The simplest and most important observation is: **all elements within a particular group have similar physical and chemical properties.**

220-2.4.4.1 This rule holds best at the extreme sides of the table. All elements in Group O are unreactive gases; all in Group VIIA have similar chemical properties although there is a gradual change in physical properties. Fluorine (F) is a gas while iodine (I) is a solid at room temperature.

220-2.4.4.1.1 On the left side of the table all Group IA elements (except hydrogen) are soft metals which undergo similar chemical reactions. Hydrogen is somewhat of a maverick because it has some properties similar to Group IA elements and some similar to Group VIIA elements. The elements in Group IIA form similar compounds and are much harder than their neighbors in Group IA.

220-2.4.4.1.2 In the region of the table labeled Transition Metals, the exceptions begin to appear. Within any group in this region, all the elements are metals, but their chemical properties may differ. In some cases, an element may be more similar to neighbors within its period than it is to elements directly below it. Iron (Fe) is more similar to cobalt (Co) and nickel (Ni) than it is to ruthenium (Ru) and osmium (0s).

220-2.4.4.1.3 The line separating metals from non-metals cuts across several groups, as seen in Figure A-1. In this region of the table the rule of group similarities loses much of its usefulness. In Group IVA, for example, carbon (C) is a non-metal, silicon (Si) and germanium (Ge) are semi-metals, and tin (Sn) and lead (Pb) are metals. Even in this region, however, a more detailed inspection of chemical properties than is presented here would reveal some similarities.

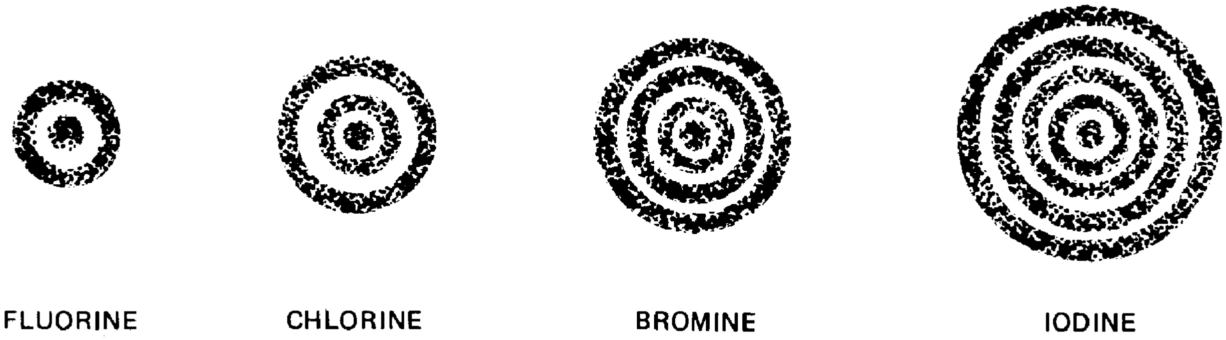
220-2.4.5 EXPLANATION OF THE PERIODIC TABLE. Based on a wealth of experimental data, it is now known that **chemical reactions involve only the electrons** in atoms. In fact, only some of the electrons are involved. Since chemical properties are periodic, then something about electrons must be periodic also. This something is the manner in which electrons are arranged in the atom.

220-2.4.5.1 Atomic Structure. Electrons are in constant motion around the nucleus. They have both kinetic and potential energy and their total energy is the sum of the two. This total energy is quantized; that is, there are definite, discrete values of total energy which atomic electrons can possess. These energy states can be visualized as spherical shells around the nucleus separated by forbidden areas where electrons cannot exist in a stable state. This sort of arrangement is illustrated in Figure 220-2-3.

220-2.4.5.1.1 It is customary, then, to speak of electron shells around the nucleus, and these shells are referred to by number. The first or No. 1 shell is the one nearest the nucleus; the second or No. 2 shell is next, then the third or No. 3 shell, and so on in numerical order. **Atomic electrons always seek the lowest energy state available. In general, electrons closer to the nucleus have a lower energy state.**

220-2.4.5.1.2 The electron shells represent major energy states of electrons. Each shell contains one or more **subshells** called **orbitals,** each with a slightly different energy. In order of increasing energy, the orbitals are designated by the small letters s, p, d, f, g, h, etc. The first four were named for historical reasons: all others are in alphabetical order.

220-2.4.5.1.3 No two shells consist of the same number of orbitals. The first shell contains only one orbital - an s orbital. The second shell contains an s and a p orbital. In general, each higher shell contains a new type of orbital: the first shell contains an s orbital, the second shell contains s and p orbitals, the third shell contains s, p, and d orbitals, the fourth shell contains s, p, d, and f orbitals, and so on.



FLUORINE CHLORINE BROMINE IODINE

NOTE: THE DARK AREAS REPRESENT THE ELECTRON CLOUDS OR SHELLS. THE NUCLEI OF THE ATOMS HAVE NOT BEEN SHOWN. THE DARK AREAS IN THE CENTER REPRESENT THE INNERMOST SHELL.

Figure 220-2-3 Electron Shells of Atoms

220-2.4.5.1.4 Each orbital can hold a definite maximum number of electrons. It follows then, that there is also a limit to the number of electrons in each shell and that this limit increases as one goes to higher shells. The numbers of electrons which can occupy the different orbitals and shells are shown in Table 220-2-4.

Table 220-2-4 ELECTRON, ORBITAL, AND SHELL RELATIONSHIPS IN ATOMIC STRUCTURE

Shell Number	**Type of Orbitals**	**Maximum Number of Electrons in each Orbital**	**Maximum Total Electrons in Shell**
1	s	2	2
2	s	2	
	P	6	8
3	s	2	
	P	6	
	d	10	18
4	s	2	
	p	6	
	d	10	
	f	14	32
5	s	6	
	p	6	
	d	10	
	f	14	
	g	18	50

220-2.4.5.2 Relation of Atomic Structure to the Periodic Table. A more specific statement can now be made about which electrons are involved in chemical reactions: **chemical reactions involve primarily the electrons in the outermost shell of an atom.** The term **outermost shell** refers to the shell farthest from the nucleus which has part or all of its allotted number of electrons. Some atoms have more than one partially filled shell. All such partially filled shells have some effect on chemical behavior, but the outermost one has the greatest effect.

220-2.4.5.2.1 In Figure 220-2-2, the column of numbers immediately to the left of each element gives the number of electrons in each partially or completely filled shell. Comparing these numbers for all elements in a particular group leads to the following important conclusion. **All elements with the same number of electrons in their outermost shell (or shells, above argon) possess similar chemical properties.**

220-2.4.5.2.2 Referring again to Figure 220-2-2, it is seen that all the Group IA elements have 1 electron in their outermost shell: all in Group IIA have 2 electrons in their outermost shell. All the transition metals have a partially filled inner shell. All Group IIIA elements have 3 electrons in their outermost shell, and so on, through Group VIIA with 7 electrons. Note that all inert gases except He have 8 electrons in their outermost shell. For He, the outermost shell is the first shell which can hold a maximum of only two electrons. **This arrangement in which the outermost shell is either completely filled** (as with He and Ne) **or contains eight electrons** (as with Ne, Ar, Kr, Xe, Rn) **is called the inert gas configuration.** The inert gas configuration is exceptionally stable energetically since these inert gases are the least reactive of all the elements. The inert gas configuration and its chemical importance are discussed further in Section 3.

220-2.5 SUMMARY

220-2.5.1 The atomic theory postulates that all matter is composed of atoms. Atoms themselves are composed of neutrons and protons in a nucleus, and electrons around the nucleus. These electrons exist in definite discrete energy states called orbitals. Atoms interact chemically through a process involving their outermost electrons. The configuration of atomic electrons and, thus, chemical properties, recur periodically throughout all elements.

SECTION 2 PROBLEMS

1.
   (a) The isotope ^{24}Mg has how many protons in its nucleus?
   (b) How many neutrons?
   (c) How many electrons around the nucleus?
   (d) What shells would these electrons occupy?

2. Supply the missing information in the table below. (Do not write in the book.)

Notation	Element	No. of Neutrons	No. of Protons	Atomic Mass No.
^{12}C	carbon	6	6	____
^{1}H	hydrogen	____	____	____
____	iron	29	26	____
____	____	11	11	____
____	oxygen	____	____	17

3. Explain why elements in a vertical column (a group) of the periodic table generally exhibit similar chemical properties.

4. Several elements have only one stable isotope in nature. Examples are: ^{9} Be, ^{19} F, ^{23} Na, ^{27} Ai, ^{59} CO. Without referring to the periodic table, estimate the atomic weights of the above elements, then compare your estimate with the value given in Figure 220-2-2.

5. Calculate the atomic weight of the hypothetical element erinium (En), given the following information:

^{290} En	23.46	289.80
^{292} En	76.54	291.90

6. Suppose the element En has atomic number 115. To what group would it belong? Would you expect it to be a metal or a non-metal?

SECTION 2 PROBLEM ANSWERS

1.
   - (a) 12 protons
   - (b) 12 neutrons
   - (c) 12 electrons
   - (d) 2 electrons in the first shell, 8 in the second shell, 2 in the third shell

2.

Notation	Element	No. of Neutrons	No. of Protons	Atomic Mass No.
^{12} C	carbon	6	6	12
^{1} H	hydrogen	0	1	1
^{55} **Fe**	iron	29	26	55
^{22} Na	sodium	11	11	22
^{17} O	oxygen	9	8	17

3. All elements in a vertical column (or group) have the same number of electrons in their outermost shell. Since chemical reactions primarily involve these outer shell electrons the chemical properties are similar.

4.

Element	Estimated Atomic Weight (AMU)	Actual Atomic Weight Element (AMU)
beryllium	9	9.01
fluorine	19	18.998
sodium	23	22.99
aluminum	27	26.98
cobalt	59	58.93

5. 291.41 AMU

6. Element number 115 would belong to Group VA and would be a metal with chemical properties similar to bismuth.

SECTION 3.

COMPOUNDS AND CHEMICAL REACTIONS

220-3.1 INTRODUCTION

220-3.1.1 Most elements do not exist in nature in a free state. Rather, they are usually combined with other elements. These combinations, called compounds, and mixtures of these compounds make up the familiar world.

220-3.2 GLOSSARY OF TERMS

220-3.2.1 Terms used in this section are defined as follows:

a. **Anion:** A negative ion.

b. **Avogadro's Number:** 6.02×10^{23} , the number of units in a mole of any pure substance.

c. **Cation:** A positive ion.

d. **Chemical Bond:** The force holding atoms together in a compound.

e. **Compound:** A distinct substance composed of two or more elements combined in a fixed, definite ratio.

f. **Chemical Equation:** A shorthand method of representing a chemical reaction. When balanced, an equation shows the reactants, products, and the proportions involved in the reaction.

g. **Chemical Formula:** The symbolic representation of a chemical compound showing the elements which compose the compound and the ratio in which they are combined.

h. **Chemical Reaction:** A process in which the original chemicals (reactants) are converted into new chemicals (products).

i. **Crystal (ionic):** The ordered arrangement of ions in ionic compounds whereby each anion is surrounded by several cations, and vice versa.

j. **Covalent Bond:** The type of chemical bond formed by the approximately equal sharing of electrons between two or more atoms.

k. **Electron-Dot Notation:** A symbolic representation of atoms using chemical symbols and dots for the outer shell electrons.

l. **Electronegativity:** A measure of the strength with which an atom (or element) attracts electrons.

m. **Endothermic Reaction:** A chemical reaction which consumes energy.

n. **Exothermic Reaction:** A chemical reaction which releases energy.

o. **Formula Weight:** The sum of the atomic weights of all the atoms in the formula of a compound.

p. **Gram Atomic Weight:** The number of grams of an element numerically equal to its atomic weight. The number of grams in a mole of an element.

q. **Gram Formula Weight:** The number of grams of a compound numerically equal to its formula weight. The number of grams in a mole of a compound.

r. **Ion:** An atom or group of atoms which has an excess or deficiency of electrons and behaves as a unit in chemical reaction.

s. **Ionic Bond:** The type of chemical bond which results from the complete transfer of one or more electrons from one atom to another.

t. **Law of Conservation of Mass (atoms):** The total mass (total number of atoms of each element) must be the same on both sides of a chemical equation.

u. **Law of Definite Proportions:** Two or more elements combine chemically in a definite proportion by weight when forming a compound.

v. **Mole:** Avogadro's number (6.02×10^{23}) of units of any pure substance. A mole of an element contains 6.02×10^{23} atoms of that element and weighs one gram atomic weight. A mole of a compound contains 6.02×10^{23} molecules (or units) of that compound and weighs one gram formula weight.

w. **Molecule:** The smallest entity of a covalent compound.

x. **Octet Rule:** Elements combine to form compounds in such a way that they will have 8 (an octet) electrons in their outermost shell (or two electrons if the outermost shell is the 1st electron shell).

y. **Oxidation Numbers:** Numbers assigned to atoms to keep track of electrons exchanged or shared in chemical reactions. For ions, the oxidation number is equal in sign and magnitude to the ionic charge.

z. **Products:** Chemicals which are formed in a chemical reaction.

aa. **Polyatomic Ion:** An ion composed of two or more atoms and which behaves as a unit in chemical reactions.

ab. **Reactants:** Chemicals which are used up in a chemical reaction.

ac. **Stoichiometry:** The weight relations in chemical reactions based on the Laws of definite proportions and conservation of mass.

ad. **Weight Fraction:** The ratio of the total weight of an element (or group of elements) in a compound to the gram formula weight of the compound.

220-3.3 COMPOUNDS

220-3.3.1 GENERAL. A **compound** is a distinct substance composed of two or more elements combined chemically in a definite, fixed ratio. Each pure compound exhibits a unique set of physical and chemical properties, such as melting point, boiling point, color, density, and chemical interaction with other substances. A compound can be broken down by chemical means into the two or more elements of which it is composed. Elements cannot be broken down further by chemical means.

220-3.3.1.1 The properties of a compound do not usually bear any resemblance to those of its constituent elements. Common table salt, for example, is composed of sodium (Na) and chlorine (Cl). This familiar compound is nothing like the soft silvery metal, sodium, or the greenish-yellow , deadly gas, chlorine.

220-3.3.2 CHEMICAL FORMULAS. Just as symbols are used to denote elements, there is a symbolic method of representing compounds. These symbolic representations are called **formulas** and consist of the symbols for the elements which make up the compound. Numerical subscripts indicate the fixed, whole-number ratio in which atoms of the respective elements combine to form the compound. The formula for sodium chloride is $NaCl$ and indicates this compound is composed of sodium and chlorine atoms in a ratio of 1:1. The compound, carbon dioxide, is composed of carbon and oxygen in a ratio of 1:2 and its formula is CO_2 . Similarly, water consists of hydrogen and oxygen in a 2:1 ratio; thus, its formula is H_2O. If no subscript is specified in a formula, it is understood to be one.

220-3.3.3 THE MOLECULE AS THE FUNDAMENTAL UNIT OF COMPOUNDS. A **molecule** is the smallest particle into which a compound can be divided without changing its chemical identity. A visible amount of water (H_2O), for example, is composed of a tremendously large number of molecules, each of which consists of one oxygen atom and two hydrogen atoms bound together. Similarly, carbon dioxide (CO_2) is made up of many molecules containing two oxygen atoms bound to one carbon atom.

220-3.3.3.1 Although the concept of the molecule is useful in visualizing compounds, there are some compounds to which it cannot be applied strictly. These are the ionic compounds discussed in paragraph 220-3.3.5 through 220-3.3.5.7.

220-3.3.4 CHEMICAL BONDING. The forces which hold atoms together in a compound are called **chemical bonds** . In the discussion of chemical bonding, it is convenient to use a method of representing elements and compounds which shows more than the symbols or formulas alone. One such method is the **electron-dot notation.** In this notation, the symbol for an element represents the nucleus and all electron shells except the outermost. The number of electrons in the outermost shell is indicated by an appropriate number of dots around the symbol. The electron-dot notations for several elements are shown in Figure 220-3-1.

220-3.3.4.1 The Octet Rule. Atoms combine to form compounds because by doing so their outermost electrons are rearranged into a more stable (lower energy) state. What then constitutes a stable electron configuration? The answer lies in an observation made in paragraphs 220-2.4.5 through 220-2.5. There it is noted that the inert gases are the most stable elements chemically. It is also pointed out that in every inert gas the outermost electron shell is either completely filled (He and Ne) or contains 8 electrons (Ne, Ar, Kr, and Xe). These configurations are referred to as the inert gas configuration. **Atoms** of other elements **gain stability by acquiring the inert gas configuration.** An atom acquires this configuration by interacting with other atoms.

220-3.3.4.1.1 This process is described in general terms by the **Octet Rule.**

In forming compounds, atoms share or transfer electrons in such a way that each atom in the compound attains the inert gas configuration. (The name, Octet Rule, is derived from the fact that each inert gas, except He, has an octet of electrons (8) in its outermost shell.)

220-3.3.4.2 Electronegativity. In the following discussion of chemical bonding, two extremes (equal sharing and complete transfer of electrons) are used as models. The bonds in a few compounds fit one or the other of these models very closely, but most chemical bonds are intermediate between the two extremes. The exact nature of the bond formed between two atoms is highly dependent on the relative attraction of the atoms for electrons. A measure of this relative attraction is called **electronegativity.** Table 220-3-1 gives the electronegativities of the elements. With only a few exceptions, electronegativity increases from left to right across any row and from bottom to top in any particular column.

220-3.3.5 IONIC BONDING. The model of **ionic bonding** is the complete transfer of one or more electrons from one atom to one or more other atoms. This transfer results in an imbalance of electrostatic charges in these atoms. An atom which has either an excess or deficiency of electrons relative to the charge on its nucleus (or atomic number) is called an **ion.** The net charge on the ion is equal in magnitude to the number of electrons lost or gained in the transfer process described by the Octet Rule. The charge is positive if electrons are given up (deficiency) or negative if electrons are gained (excess). The general term, ion, refers to both positive and negative ions. More specifically, negative ions are called **anions** and positive ions are **cations.**

Question: In some versions of the periodic table (other than Figure 220-2-2), hydrogen is listed at the top of both Groups IA and VII.A. Using the Octet Rule (and Figure 220-3-1) can you offer an explanation of why hydrogen has some properties similar to both groups?

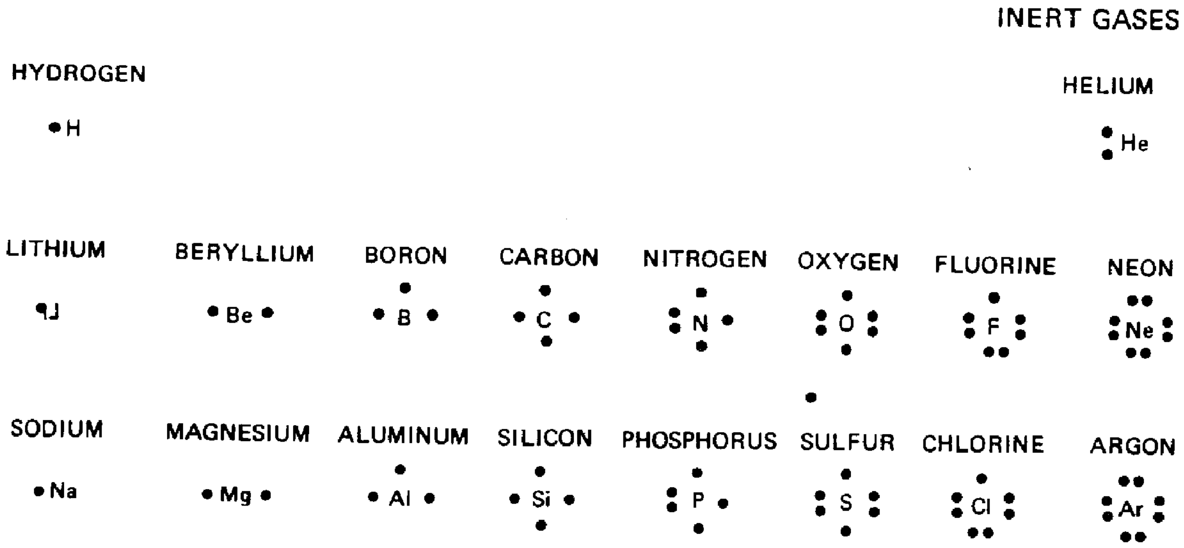


Figure 220-3-1 Electron-Dot Notations

220-3.3.5.1 Compounds which are formed by the complete transfer of electrons are ionic compounds. The bonding in ionic compounds can be considered to be simple electrostatic attraction between oppositely charged spheres.

220-3.3.5.2 Consider sodium chloride, NaCl as an example. Reference to the periodic table (Figure 220-2-2) or Figure 220-3-1 shows that sodium has one 3rd shell electron and chlorine has 7. If sodium were to give up one electron and chlorine were to gain one, each would attain the inert gas configuration. Sodium would acquire the electron configuration of neon and chlorine would acquire the electron configuration of argon. As a result, sodium would be left with a net +1 charge and chlorine would have a - 1 charge.

220-3.3.5.3 The electron-dot notation for NaCl is

For purposes of illustration, an asterisk (*) is used to represent the transferred electron. Actually, electrons are indistinguishable regardless of their source.

220-3.3.5.4 There are no discrete molecules in ionic compounds. In solid NaCl, for example, the Na+ and Cl- ions are arranged in a three-dimensional network in which all the nearest neighbors of each Cl- ion are Na+ ions. Similarly, all the nearest neighbors of each Na+ ion are Cl- ions. This arrangement is called a crystal and is illustrated schematically in Figure 220-3-2.

220-3.3.5.5 In a visible grain of NaCl, the structure shown in Figure 220-3-2 (b) is repeated again in all directions. In a crystal of any ionic compound the total positive charge is equal to the total negative-charge, so the net charge on the crystal is zero. The formulas of ionic compounds express the requirement of charge neutrality by showing the smallest whole-number ratio of ions that has a net charge of zero.

Table 220-3-1 ELECTRONEGATIVITIES OF ELEMENTS

	H																	He
	2.1																	
	Li	Be											B	C	N	O	F	Ne
	0.97	1.47											2.01	2.50	3.07	3.50	4.10	
	Na	Mg											Al	Si	P	S	Cl	Ar
	1.01	1.23											1.47	1.74	2.06	2.44	2.83	
	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
	0.91	1.04	1.20	1.32	1.45	1.56	1.60	1.64	1.70	1.75	1.75	1.66	1.82	2.02	2.20	2.48	2.74	
	Rb	Sr	Y	Zr	Nb	Mo	(Tc)	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
	0.89	0.99	1.11	1.22	1.23	1.30	1.36	1.42	1.45	1.35	1.42	1.46	1.49	1.72	1.82	2.01	2.21	
	Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	(Po)	(At)	(Rn)
	0.86	0.97		1.23	1.33	1.40	1.46	1.52	1.55	1.44	1.42	1.44	1.44	1.55	1.67	1.76	1.90	
	(Fr)	(Ra)	**							←~1.2(estimated)→								
	0.86	0.97																
*	La	Ce	Pr	Nd	(Pm)	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			
	1.08	1.08	1.07	1.07	1.07	1.07	1.01	1.11	1.10	1.10	1.10	1.11	1.11	1.06	1.14			
**	(Ac)	Th	(Pa)	U	(Np)	(Pu)	(Am)	(Cm)	(Bk)	(Cf)	(Es)	(Fm)	(Md)	(No)				
	1.00	1.11	1.14	1.22	1.22	1.22												

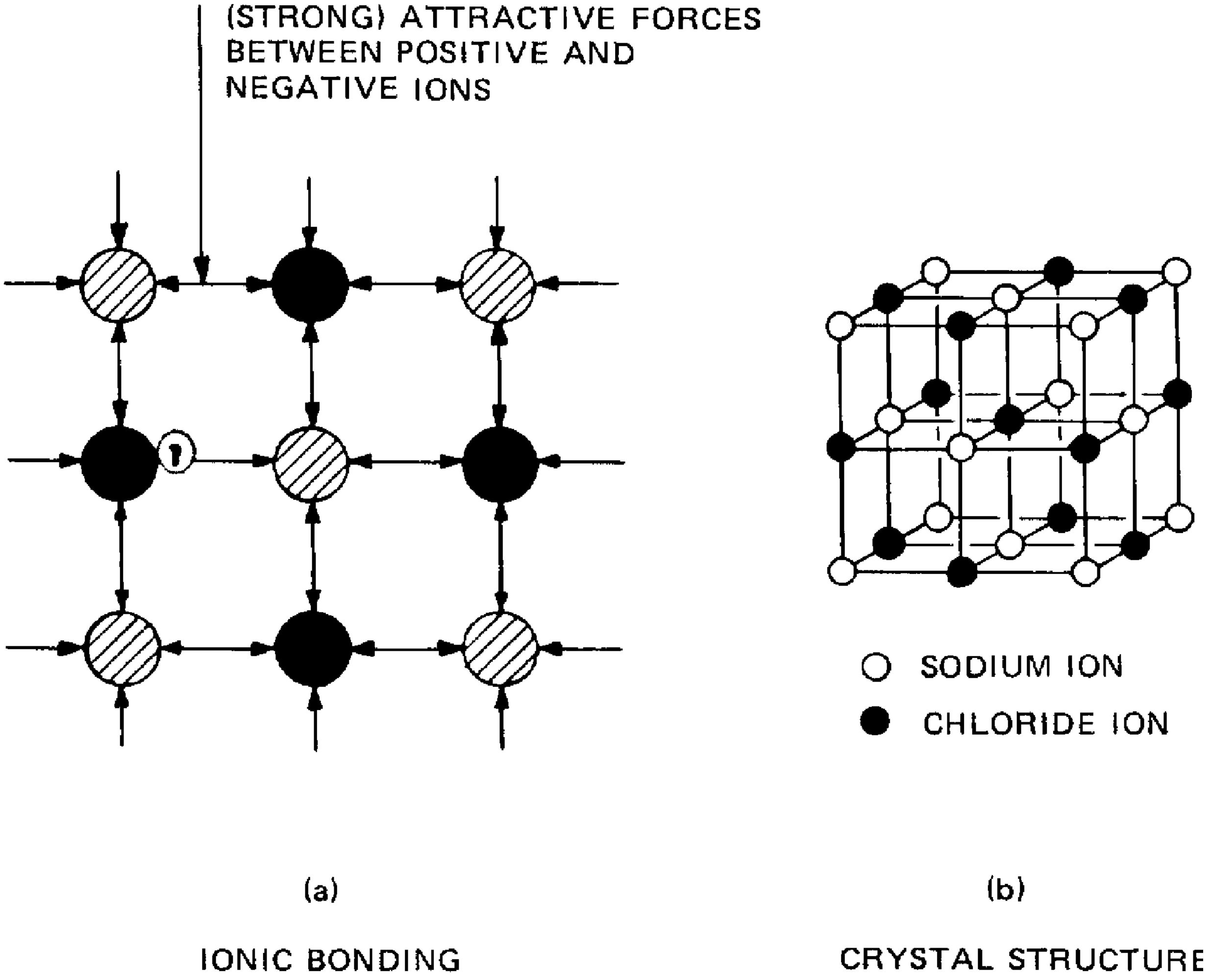
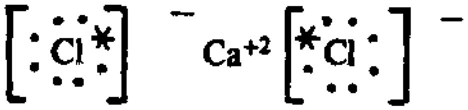


Figure 220-3-2 Ionic Bonding and Crystal Structure of Sodium Chloride

220-3.3.5.6 Another example of an ionic compound is calcium chloride, $CaCl_2$. The calcium atom has two electrons in its outermost (4th) shell. By giving up both electrons, it becomes a Ca^{+2} ion with the electron configuration of argon. Two chlorine atoms accept one electron each and become Cl^- ions also with the argon configuration. The electron-dot notation is:



To satisfy the requirement of charge neutrality, there must be twice as many Cl^- ions as there are Ca^{+2} ions in the compound as shown by the formula, $CaCl_2$.

220-3.3.5.7 Compounds which best fit the ionic model are those which contain elements with very different electronegativities. Although there is no hard and fast rule, if the difference in electronegativity between two elements is greater than about 1.5 and if these elements form a compound, it is expected to be ionic. The elements on opposite sides of the periodic table best meet these requirements. In general, ionic compounds result from the combination of distinctly metallic elements with distinctly nonmetallic elements.

220-3.3.6 COVALENT BONDING. The model of **covalent bonding** is the arrangement in which two atoms share one or more electrons equally. Covalent bonds result from the simultaneous attraction of two nuclei for one or more electrons situated between the two nuclei. In most cases, there are 2, 4, or 6 electrons in a covalent bond. A two-electron bond is most common and is called a single bond. A four-electron bond is a double bond and a six-electron bond is a triple bond.

220-3.3.6.1 General. The best examples of covalent bonding are found in combinations of atoms of the same element. These combinations are diatomic molecules, for example, H_2 , N_2 , O_2 , F_2 , Cl_2 , and the other Group VIIA elements. The electron-dot notations for individual atoms of several of these elements are given in Figure 220-3-1. Two atoms of each of these elements achieve the stable inert gas configuration by sharing their electrons as shown in Figure 220-3-3. This figure also illustrates that, in applying the Octet Rule, all the electrons in a covalent bond are considered to belong to both atoms simultaneously.

Figure 220-3-3 Diatomic Molecules of Some Elements

220-3.3.6.1.1 Consider the Octet Rule and the formation of ammonia, NH_3 . Hydrogen has one electron in its 1st electron shell. By acquiring one additional electron, hydrogen can attain the electron configuration of the inert gas, helium. Nitrogen has five electrons in its outermost (2nd) electron shell, and by acquiring 3 additional electrons, it can attain the inert gas configuration of neon. The requirements of both hydrogen and nitrogen can be satisfied by the arrangement shown for ammonia in Figure 220-3-4.

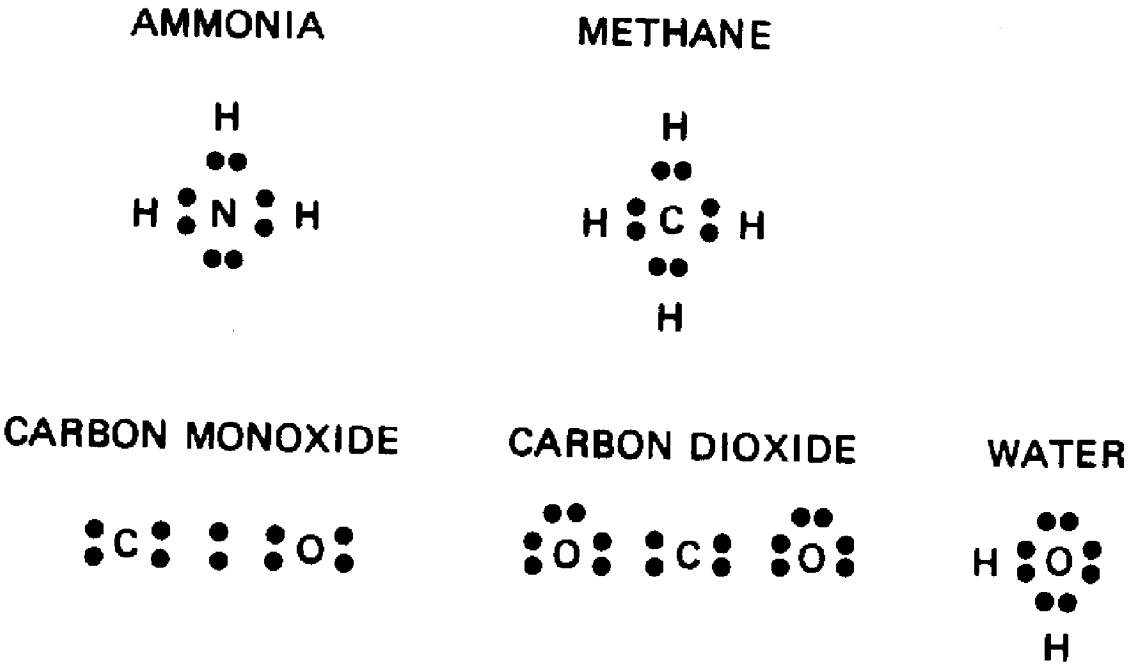


Figure 220-3-4 Electron-Dot Notations for Some Covalent Compounds

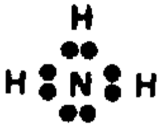
220-3.3.6.1.2 Other examples of covalent compounds also are shown in Figure 220-3-4. For each of these compounds, there exist individual molecules made up of atoms as shown in the figure. For clarity, the molecules are depicted as being flat. Most molecules are not flat, but have a definite, three-dimensional orientation. Whenever the shape of the molecules of a compound is important to the discussion, it will be noted in the text.

220-3.3.6.2 General Rule Relating Electronegativity and Covalent Compounds. The general rule relating electronegativity and covalent compounds is: If the difference in electronegativity of two elements is less than about 1.5 and if these elements form a compound, it will be covalent. The elements which best satisfy these requirements are the nonmetals, many of which combine with each other and have electronegativities such that most of the compounds are covalent.

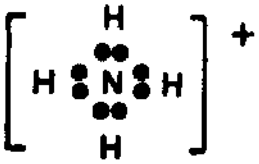
220-3.3.6.2.1 Only in the diatomic molecules of elements such as N_2 , O_2 , F_2 are the electronegativities exactly equal. In all other cases, there is always some difference in electronegativity. The greater this difference, the more unequal is the sharing of electrons and the more ionic is the nature of the bond. For a particular compound, Table 220-3-1 shows which element has the greater influence on the electrons.

220-3.3.6.3 Intermolecular Attractions. In solid covalent compounds, the molecules are held together by intermolecular attractions called **van der Waals forces.** These forces arise from the attraction of the atomic nuclei in one molecule for electrons in another molecule. The van der Waals forces are roughly 100 times weaker than covalent or ionic bonds, which are approximately equal. Because of the weakness of the van der Waals forces, covalent compounds have lower melting points than do ionic compounds. Many covalent compounds are liquids or gases at room temperature, while most ionic compounds melt at several hundred degrees Celsius.

220-3.3.6.4 Compounds with Both Ionic and Covalent Bonds. In Figure 220-3-4, the electron-dot notation for ammonia is given as:



The unused pair of electrons on the N atom can participate in forming another covalent bond, for example, with another hydrogen atom. The hydrogen atom already has one electron and nitrogen has the unused pair, so if another N-H single bond is formed, one electron must be given up. It is immaterial whether hydrogen or nitrogen gives up the electron; the result is:



Here, the brackets are used to indicate that the positive charge applies to the entire group, NH_4^+ (ammonium). Each N-H bond in this species is covalent, equivalent, and indistinguishable from all others. The entire group, NH_4^+, now behaves as a unit and participates in ionic bonding in compounds such as ammonium chloride, NH_4Cl. In this ionic compound, the NH_4^+ ion is held together by covalent bonds and is bound ionically to Cl- ions.

220-3.3.6.4.1 A **general definition of an ion** is any atom or group of atoms which has an excess or deficiency of electrons and which behaves as a unit in ordinary chemical reactions. Ions which consist of more than one atom are called **polyatomic ions.** Some common polyatomic ions are listed in Table 220-3-2.

Table 220-3-2 COMMON POLYATOMIC IONS AND FORMULAS

Name	Formula
Ammonium	NH_4^+
Acetate	$C_2H_3O_2^-$
Carbonate	CO_3^{-2}
Chromate	CrO_4^{-2}
Hydronium	H_3O^+
Hydroxyl	OH^-
Nitrate	NO_3^-
Phosphate	PO_4^{-3}
Monohydrogen phosphate	HPO_4^{-2}
Dihydrogen phosphate	$H_2PO_4^-$
Sulfate	SO_4^{-2}
Sulfite	SO_3^{-2}

220-3.3.7 OXIDATION NUMBERS. In discussing the ability of atoms to combine with each other, the term **valence** has been used for many years. Originally, valence was defined as the number of hydrogen atoms a particular atom can combine with or release in chemical reactions. Through years of use (and overuse), the term also acquired the meanings: (1) the charge on an ion, and (2) the total number of atoms with which a particular am will form chemical bonds. Because of these several meanings, this text does not use the term valence at all.

220-3.3.7.1 The preferred term used to describe the bonding capacity or combining power of elements is **oxidation number** (or **oxidation state**). The system of oxidation numbers is essentially a bookkeeping device to keep track of the electrons of atoms in compounds. In the case of ionic compounds, this bookkeeping is fairly straight forward since the oxidation number of an ion is the same as its ionic charge. In a covalent bond between two different atoms, the more electronegative atom attracts the electrons more strongly than does the less electronegative atom. The **stronger** atom is usually assigned a negative oxidation number as if it had completely captured the electron. The **weaker** atom is assigned a positive oxidation number as if it had lost the electrons.

220-3.3.7.2 The following rules govern the assignment of oxidation numbers.

a. The oxidation number of an element in ionic form is the same as the charge on the ion. Thus,
   1 Group IA elements almost always have a +1 oxidation number
   2 Group IIA elements almost always have a +2 oxidation number
   3 Group VIIA elements almost always have a -1 oxidation number

b. The oxidation number of all pure elements is zero. This includes elements which exist as diatomic molecules such as H_2 , O_2 , Cl_2 .

c. The oxidation number of hydrogen is +1 in all its compounds except metal hydrides, such as NaH and CaH_2 , in which it is -1.

d. The oxidation number of oxygen is -2 in all its compounds, except peroxides such as H_2O_2 , in which it is -1.

e. The sum of the oxidation numbers of all the elements in a neutral compound is zero.

f. The sum of the oxidation numbers of all the elements in a polyatomic ion is equal to the charge of the ion.

220-3.3.7.3 Many elements have different oxidation numbers in different compounds. In such cases, the formula of the compound must be known to determine the oxidation number. The examples in paragraphs 220-3.3.7.4 through 220-3.3.7.6 illustrate the foregoing rules. The oxidation numbers of sodium and chlorine in NaCl can be determined using Rule 1. Sodium belongs to Group IA and chlorine to Group VIIA; thus, the oxidation number of sodium in NaCl is +1 and that of chlorine is -1, the same as their ionic charges.

220-3.3.7.4 In the compound calcium bromide, by Rule 1, calcium has an oxidation number of +2 and bromine has an oxidation number of -1. Rule 5 requires that the sum of all the oxidation numbers in the compound be zero, so there must be two Br- ions for each Ca^{+2} ion. The formula for the compound must be $CaBr_2$.

220-3.3.7.5 Carbon and oxygen form two compounds: carbon monoxide (CO) and carbon dioxide (CO^2). (The $CO_3{}^{-2}$ ion alone is not a compound.) By Rule 4, the oxidation number of oxygen is -2 in both compounds. For Rule 5 to hold, carbon must have different oxidation numbers in the two compounds. In CO, carbon has an oxidation number of +2 and in CO_2 , it has +4. In this case, the formulas for the two compounds had to be known to determine the oxidation number of carbon.

220-3.3.7.6 Suppose one wishes to predict the formula of the compound between sodium and the PO_4^{-3} ion. By Rule 1, the oxidation number of Na is + 1 and that of PO_4^{-3} is -3. To satisfy Rule 5, the formula must be Na_3PO_4 .

220-3.4 CHEMICAL REACTIONS

220-3.4.1 **A chemical reaction is the conversion of one or more original substances (reactants) into one or more different substances (products).** The substances may be elements or compounds, with the exception that the conversion of one element into a different element is a nuclear reaction, not a chemical reaction. There is always some energy change, often in the form of heat, associated with chemical reactions. If energy is liberated by a reaction, the reaction is said to be **exothermic.** If energy is taken up by a reaction the reaction is said to be **endothermic.** Chemical reactions are highly dependent on the conditions of temperature and pressure and the stable form of substances often varies with these conditions.

220-3.4.2 Even though a particular reaction may be possible on the basis of energy, it may not occur spontaneously. Very often, some amount of energy, called **activation energy,** must be supplied to cause the reaction to take place. For example, the compound H_2O is more stable than the individual free elements, H_2 and O_2 . At room temperature and atmospheric pressure, however, a mixture of 2 parts H_2 to one part O_2 does not react noticeably. If sufficient energy is supplied to the mixture, even by a spark, the reaction occurs explosively. Once the reaction starts, the energy liberated by the process is more than enough to activate the remaining reactants, so the reaction proceeds until one or both of the reactants are consumed. The excess energy is given off as heat and light.

220-3.4.3 **A chemical equation is a shorthand method of describing a chemical reaction.** For example, the equation

$$2H_2 + O_2 \rightarrow 2H_2O \quad (3\text{-}1)$$

can be expressed in words as, two molecules of hydrogen react with one molecule of oxygen to form two molecules of water. Obviously, the equation is faster and easier than the word description. Equation 3-1 also illustrates a fundamental law, the **Law of Conservation of Atoms,** which states: **Atoms are conserved in a chemical reaction.** Consider a slightly different form of the equation:

$$H_2 + O_2 \rightarrow H_2O \text{ (Incomplete) } (3\text{-}2)$$

There are two atoms of oxygen on the left side of equation 3-2 and one atom of oxygen on the right. This equation indicates that one oxygen atom disappears. Since **atoms** do not change their identity in chemical reactions, equation 3-2 is a false statement and an invalid equation. An equation is said to be **balanced** if the total number of atoms of each element is the same on both sides of the equation. Balancing is accomplished by appropriate adjustment of the numerical coefficients of the terms (symbols and formulas) in the equation. By convention, the smallest whole numbers which accomplish the balancing are used.

220-3.4.4 In writing equations, three general steps are required:

1. Write (at least mentally) a word equation:
   carbon plus oxygen yields carbon monoxide
2. Substitute the appropriate symbols and formulas

$C + O_2 \rightarrow CO$ (Incomplete)

3. Balance the equation by adding whole numbers in front of the symbols and formulas, as necessary.

$2C + O_2 \rightarrow 2CO$

The products and formulas required in steps 1 and 2 ultimately depend on experimental evidence, but with practice many equations can be inferred from a knowledge of general chemical properties. For simple reactions such as the one above, step 3 can be performed easily by inspection. Note that the equation

$4C + 2O_2 \rightarrow 4CO$

is also balanced but the coefficients are not the smallest whole numbers possible.

Example 3-2: Write a balanced equation for the formation of ammonia from hydrogen and nitrogen.

Solution 3-2: Step 1 is given.
Hydrogen plus nitrogen yields ammonia.
Step 2: $H_2 + N_2 + NH_3$ (Incomplete)
Step 3: By inspection, the equation is unbalanced with respect to both nitrogen and hydrogen. First, balance the equation with respect to one of these, say nitrogen. This can be done by:
$H_2 + N_2 \rightarrow 2NH_3$, (Incomplete)
but the hydrogen atoms are still unbalanced. There are six hydrogen atoms on the right and two on the left. All that is needed is to multiply H_2 on the left by three:
$3H_2 + N_2 \rightarrow 2NH_3$
The Law of Conservation of Atoms is actually a consequence of the more general Law of Conservation of Mass, which requires that the total mass of products be equal to the total mass of reactants in a chemical reaction.

220-3.5 WEIGHT RELATIONS IN COMPOUNDS AND REACTIONS

220-3.5.1 GENERAL. Historically, chemistry has relied on weight as a convenient measure of amount. The following paragraphs show there is a very definite relation between weight and number of particles (atoms, molecules, ions).

220-3.5.2 FORMULA WEIGHT. The **formula weight** (sometimes abbreviated FW) of a compound is the sum of the atomic weights of all the atoms in the formula for the compound. Unless stated otherwise, the units of formula weights are atomic mass units (AMU's), the same as for atomic weights. Some examples are:

H_2 O; Formula weight
= 2(atomic weight of hydrogen) + (atomic weight of oxygen)
= 2(1) + 16 = 18 AMU

NaCl; Formula weight
= (atomic weight of Na) + (atomic weight of chloride)
= (23) + (35.5) = 58.5 AMU

Al_2 O_3 ; Formula weight
= 2(atomic weight of Al) + 3(atomic weight of oxygen)
= 2(27) + 3(16) = 102 AMU

H_3 PO_4 ; Formula weight
= 3(atomic weight of hydrogen) + (atomic weight of P) + 4(atomic weight of oxygen)
= 3(1) + (31) + 4(16)
= 3 + 31 + 64 = 98 AMU

NOTE

The atomic weight of each element in a compound must be multiplied by the number of such atoms in the formula.

220-3.5.2.1 Some texts use **molecular weight** and **formula weight** interchangeably. Perhaps, in the case of covalent compounds, molecular weight is more descriptive because it can be thought of as the weight of one molecule. In ionic compounds, however, there are no discrete molecules so molecular weight is somewhat misleading. For that reason, this text uses the general term formula weight, which is equally valid for both ionic and covalent compounds.

220-3.5.3 THE LAW OF DEFINITE PROPORTIONS. Previous paragraphs presented the idea that a compound consists of atoms in a fixed ratio. The **Law of Definite Proportions** extends that idea to a weight basis instead of an atom basis. The law is stated: **A given compound always consists of the same elements combined in the same proportions by weight, no matter where the compound originated or how it was prepared.** Suppose samples of pure water are collected from locations scattered throughout the world. Further suppose that each sample is decomposed into its constituent elements. In all cases only hydrogen and oxygen will be found. If the weight of each element is determined, in every case the weight ratio, hydrogen: oxygen, is 1:8.

220-3.5.3.1 These results are easily understood by considering the formula of water, H_2O. The formula weight of water is 18. There are two atoms of hydrogen and one atom of oxygen, so their weight ratio is

2(atomic weight of hydrogen):(atomic weight of oxygen)

= 2(1):16

= 1:8

Even though the atomic weights are in AMU's, the factor for converting AMU's to any other weight units is a constant, so the ratio will be the same whether the weights are in AMU's, grams, pounds, or tons.

220-3.5.3.2 A quantity closely related to weight ratio, is **weight fraction** (or percent). The weight fraction of a particular element in a given compound is the total weight of that element in the formula divided by the formula weight. In the case of water,

$$\text{weight fraction of hydrogen} = \frac{\text{weight of hydrogen}}{\text{formula weight}}$$

$$= \frac{2(\text{atomic weight of hydrogen})}{\text{formula weight}}$$

$$= \frac{2}{18} = \frac{1}{9} = 0.11 \text{ or } 11 \text{ percent}$$

The remaining 89 percent is oxygen, as shown by:

$$\text{weight fraction of oxygen} = \frac{\text{atomic weight of oxygen}}{\text{formula weight}}$$

$$= \frac{16}{18} = 0.89 \text{ or } 89 \text{ percent}$$

220-3.5.4 WEIGHTS IN EQUATIONS. Recall that the equation, $2H_2 + O_2 \rightarrow 2H_2O$ can be expressed as: Two molecules of hydrogen react with one molecule of oxygen to form two molecules of water. If an experimenter wished to verify that statement, he would face a dilemma. Practically, it is impossible to work with one or two molecules, and a visible amount of any substance contains billions of billions of molecules or atoms. The experimenter requires that the equation be restated in terms of measurable amounts of the substances rather than molecules.

220-3.5.4.1 One of the most convenient measures of amount is weight and, since atomic weight and formula weight are defined in atomic mass units, the equation can be restated in AMU's as follows:

$$\begin{array}{ccccc} 2H_2 & + & O_2 & \longrightarrow & 2H_2O \\ 4(\text{At. Wt. of hydrogen}) & + & 2(\text{At. Wt. of oxygen}) & \longrightarrow & 2(\text{Formula Wt. of } H_2O) \\ 4(1 \text{ AMU}) & & 2(16 \text{ AMU}) & & 2(18) \text{ AMU} \\ 4 \text{ AMU} & & 32 \text{ AMU} & & 36 \text{ AMU} \end{array} \quad (3\text{-}3)$$

220-3.5.4.2 Thus, 4 AMU's of hydrogen react with 32 AMU's of oxygen to form 36 AMU's of water. This, however, does not help the experimenter very much, because 1 AMU = 1.67×10^{-24} grams, so even 1000 AMU cannot be weighed directly.

220-3.5.4.3 Chemical equations, like algebraic equations, can be multiplied by a constant factor without changing the validity of the statement. Thus,

$$2(2H_2 + O_2 \rightarrow 2H_2O)$$

$$4H_2 + 2O_2 \rightarrow 4H_2O$$

is a true statement, because the *ratio* of the numerical coefficients is unchanged.

Now multiply Equation 3-3 by the huge number, 6.02×10^{23}.

$$6.02 \times 10^{23} \left(\begin{array}{c} 2H_2 + O_2 \rightarrow 2H_2O \\ 4 \text{ AMU} + 32 \text{ AMU} \rightarrow 36 \text{ AMU} \end{array} \right)$$

The reason for choosing this number becomes apparent after a few mathematical manipulations.

220-3.5.4.4 Convert AMU's to grams, using 1 AMU = 1.67×10^{-24} gram

$$6.02 \times 10^{23} \left(\begin{array}{ccccc} 2H_2 & + & O_2 & \longrightarrow & 2H_2O \\ 6.68 \times 10^{-24} \text{ gram} & + & 53.44 \times 10^{-24} \text{ gram} & \rightarrow & 60.12 \times 10^{-24} \text{ gram} \end{array} \right)$$

Now multiply through by 6.02×10^{23}.

$$\begin{array}{ccccc} 2(6.02 \times 10^{23})\ H_2 & + & (6.02 \times 10^{23})\ O_2 & \rightarrow & 2(6.02 \times 10^{23})\ H_2O \\ 4 \text{ grams} & + & 32 \text{ grams} & \longrightarrow & 36 \text{ grams} \end{array} \qquad (3\text{-}4)$$

It can now be stated that 4 grams of hydrogen react with 32 grams of oxygen to form 36 grams of water. All these quantities can be determined easily. Notice also that the number of grams of each substance in equation (3-4) is the same as the number of AMU's of the substances in equation (3-3).

220-3.5.4.5 Several very important conclusions can be drawn from the above process.

a. The weight in grams of 6.02×10^{23} atoms of hydrogen is the same as the atomic weight (in AMU's) of hydrogen. In equation 3-4,

$6.02 \times 10^{23}\ (2H_2) = 6.02 \times 10^{23}\ (4H) = 4$ grams of hydrogen or

$6.02 \times 10^{23}\ (H) = 1$ gram of hydrogen

b. The weight in grams of 6.02×10^{23} atoms of oxygen is the same as the atomic weight (in AMU's) of oxygen.

c. The weight in grams of 6.02×10^{23} molecules of water is the same as the formula weight (in AMU's) of water.

These conclusions and some related definitions find wide applicability throughout chemistry. The number 6.02×10^{23} is called **Avogadro's Number** in honor of Amedeo Avogadro who first proposed how to obtain equal numbers of molecules of different substances. A term more frequently used in chemistry is the mole. **A mole of any element or compound is Avogadro's Number of units of that element or compound.**

220-3.5.4.6 The unit of covalent compounds is the molecule. The unit of ionic compounds is the combination represented by the formula, for example, NaCl. The unit of elements is the atom, or the molecule in cases such as N_2 , O_2 , H_2 , etc. It is equally valid to refer to a mole of an ion, say Na+, or even a mole of electrons. In all these cases, the meaning is 6.02 x 10^{23} units of the species under discussion. One mole (Avogadro's Number, 6.02 x 10^{23} units) of any compound has a weight in grams equal to its formula weight. One mole of CH_4 (formula weight = 12 + 4(1) = 16) contains 6.02 x 10^{23} molecules with the composition CH_4 and weighs 16 grams. One mole of NaCl (formula weight = 58.5) contains 6.02 x 10^{23} units of the combination NaCl and weighs 58.5 grams.

220-3.5.4.7 In extending this to elements, care must be taken to specify what is meant, that is, whether the element is in the form of individual atoms or in the form of molecules such as H_2 , O_2 , Cl_2 , etc. One mole of any element in the form of individual atoms has a weight in grams equal to its atomic weight. One mole of any element in molecular form has a weight in grams equal to its formula weight. To illustrate, one mole of sodium (atomic weight = 23) consists of 6.02 x 10^{23} Na atoms and weighs ^{23} grams. One mole of H_2 (formula weight = 2) consists of 6.02 x 10^{23} H_2 molecules and weighs 2 grams, while one mole of H (atomic weight = 1) consists of 6.02 x 10^{23} H **atoms** and weighs 1 gram.

Question:	Conversion factors are often used to change one set of units to another set of units. Can you show that Avogadro's number is the conversion factor for changing grams to atomic mass units?

220-3.5.4.8 Two additional terms often are used in chemistry. The **gram atomic weight** of any element is that number of grams of the element equal to its atomic weight. For example, a gram atomic weight of sodium is 23 grams of sodium. In the case of compounds, a **gram formula weight** is that number of grams of the compound equal to its formula weight. One gram formula weight of NaCl is 58.5 grams.

NOTE

> One gram formula weight of a compound is the actual weight in grams of one mole of the compound and one gram atomic weight of any element is the actual weight in grams of one mole of the element.

220-3.5.4.9 The following relationship is offered to help clarify this possibly confusing abundance of terms having similar or the same meanings.

$$\left.\begin{array}{l}\textit{Atomic weight in grams} \equiv \textit{1 gram atomic weight} \\ \textit{Formula weight in grams} \equiv \textit{1 gram formula weight}\end{array}\right\} \equiv \textit{1 mole} \equiv \left\{\begin{array}{l}\textit{Avogadro's Number of units} \\ \textit{6.02 x } 10^{23} \textit{ units}\end{array}\right.$$

The important point is that one mole is always 6.02 x 10^{23} units of something. The weight of this one mole varies depending on precisely what that something is. A common analogy with the term, mole, is the term, dozen. Dozen is the particular name given to a collection of 12 units of something, for example, a dozen apples, donuts, or ships. Mole is just an extension of the same concept to a larger scale. Mole is simply the name given to a certain large number (6.02 x 10^{23}) of units of something. There are, of course, subtle differences between the two terms. For example, one is seldom concerned with the mass of a dozen apples, donuts, or ships, because it is more convenient to count the units. Since it is extremely difficult to count atoms and molecules, mass is used as a convenient substitute and, due to Avogadro's relation, serves the same purpose as counting units. This leads to another statement regarding balanced equations. The numerical coefficients tell the number of moles of each reactant and product in the reaction. To summarize:

$$\begin{array}{ccccc}
2H_2 & + & O_2 & \rightarrow & 2H_2O \\
\text{12 molecules} & + & \text{11 molecules} & \rightarrow & \text{12 molecules} \\
\text{(4 AMU's)} & & \text{(32 AMU's)} & & \text{(36 AMU's)} \\
\text{2 moles} & + & \text{1 mole} & \rightarrow & \text{2 moles} \\
\text{(4 grams)} & & \text{(32 grams)} & & \text{(36 grams)}
\end{array}$$

220-3.5.5 CHEMICAL CALCULATIONS. The ultimate objective in dealing with weight relations in chemistry is to acquire the capability of performing calculations involving exact amounts of the reactants and products in chemical reactions. Such calculations are called **stoichiometric calculations.** The name is derived from the word stoichiometry which means the study of the weight relationships in a chemical reaction.

220-3.5.5.1 Stoichiometric Calculation. It is very important to remember that a stoichiometric calculation can be performed only in conjunction with a balanced equation. Further, the statement of a chemical equation is in terms of molecules or moles, so the calculations must be in the same terms. In practice, amounts of substances are usually expressed in weights, such as grams. The relationship between grams and moles is expressed by the following equations.

$$\text{number of moles of a compound} = \frac{\text{grams of the compound}}{\text{formula weight of the compound (grams per mole)}} \qquad (3\text{-}5)$$

$$\text{number of moles of an element} = \frac{\text{grams of the element}}{\text{atomic weight of the element (grams per mole)}} \qquad (3\text{-}6)$$

Also,

$$\text{number of atoms (or molecules)} = \frac{\text{AMU's of the element (or compound)}}{\text{atomic (or formula) weight in AMU's}} \qquad (3\text{-}7)$$

However, it is usually more convenient to calculate the number of atoms or molecules using the number of moles and Avogadro's number:

number of atoms (or molecules) = number of moles x Avogadro's number (3-8)

220-3.5.5.1.1 All stoichiometric calculations can be performed in a logical sequence of steps.

1. Write and balance the equation (if not given).
2. Clearly establish what information is given and what is wanted.
3. Inspect the units of the given information. If not in moles, convert to moles using equations (3-5) and (3-6).

4. Using the relationship expressed in the balanced equation, calculate the number of moles of the substance of interest.

5. If the answer is wanted in units other than moles, perform the necessary conversion by rearranging equations (3-5) and (3-6), for example, grams of the compound = (number of moles of the compound) (formula weight of the compound).

220-3.5.5.1.2 No amount of explanation can provide proficiency in solving stoichiometric problems. The reader is encouraged to study the following examples carefully. Problems at the end of the chapter provide additional practice.

Example 3-3: *Calculate the number of moles in 75 grams of*

(a) $NaCl$

(b) Pb

(c) NH_3

Solution 3-3: *(a) Use Equation (3-5)*

$$\text{number of moles NaCl} = \frac{\text{grams of NaCl}}{\text{formula weight of NaCl}}$$

$$\begin{aligned}\text{Formula weight of NaCl} &= \text{At. Wt. Na} + \text{At. Wt. Cl}\\ &= 23. + 35.5\\ &= 58.5\end{aligned}$$

$$\text{number of moles NaCl} = \frac{75.0}{58.5} = 1.28 \text{ moles}$$

(b) Use Equation (3-6)

$$\text{number of moles of Pb} = \frac{\text{grams of Pb}}{\text{atomic weight of Pb}}$$

$$\text{Atomic weight of Pb} = 207.19$$

$$\text{number of moles of Pb} = \frac{75.0}{207.19} = .36 \text{ moles}$$

(c) Again use Equation (3-5)

$$\begin{aligned}\text{Formula weight of } NH_3 &= (\text{at. wt. N}) + 3(\text{at. wt. H})\\ &= 14 + 3(1) = 17\end{aligned}$$

$$\text{number of moles of } NH_3 = \frac{75}{17} = 4.41 \text{ moles}$$

Example 3-4: Calculate the number of units in:
(a) 1.28 moles of NaCl
(b) 0.36 moles of Pb
(c) 4.41 moles of NH_3

Solution 3-4: Recall that 1 mole of any substance always contains 6.02×10^{23} units of that substance. Thus:

(a) 1.28 moles NaCl x 6.02×10^{23} units/mole = 7.71×10^{23} units (NaCl pairs)

(b) 0.36 moles Pb x 6.02×10^{23} units/mole = 2.17×10^{23} units (atoms of Pb)

(c) 4.41 moles NH_3 x 6.02×10^{23} units/mole = 26.5×10^{23} units (molecules of NH_3)

Example 3-5: In the reaction of nitrogen with hydrogen to form ammonia, how many grams of nitrogen will react completely with 10.00 grams of hydrogen, and how many grams of ammonia will be produced?

Solution 3-5: (1) First, write the balanced equation

$$N_2 + 3H_2 \rightarrow 2NH_3$$

(2) The amount (in grams) of hydrogen is given. The amounts of N_2 and NH_3 are to be calculated.

(3) Convert 10 grams of H_2 to moles of H_2

$$\text{number of moles of } H_2 = \frac{\text{grams of } H_2}{\text{formula weight of } H_2}$$

$$= 10/2 = 5 \text{ moles of } H_2$$

(4) The equation states that 3 moles of H_2 react with 1 mole of N_2. Then 5 moles of H_2 must react with:

$$5 \text{ moles } H_2 \times \frac{1 \text{ mole } N_2}{3 \text{ moles } H_2} = 1.67 \text{ moles of } N_2.$$

The equation also states that for every 3 moles of H_2 which react completely with N_2, 2 moles of NH_3 are formed. If 5 moles of H_2 react completely, then:

$$5 \text{ moles } H_2 \times \frac{2 \text{ moles } NH_3}{3 \text{ moles } H_2} = 3.33 \text{ moles of } NH_3 \text{ formed}$$

(5) Convert moles of N_2 and NH_3 to grams

Rearranging Equations (3-5) and (3-6) gives

$$\begin{aligned}\text{grams of } N_2 &= (\text{no. of moles of } N_2)\ (\text{formula wt of } N_2)\\ &= 1.67\ (28)\\ &= 46.8 \text{ grams}\end{aligned}$$

$$\begin{aligned}\text{grams of } NH_3 &= (\text{no. of moles of } NH_3)\ (\text{formula wt of } NH_3)\\ &= 3.33\ (17)\\ &= 56.6 \text{ grams}\end{aligned}$$

NOTE: The apparent violation of the Law of Conservation Of Mass ($46.8 + 10.0 \neq 56.6$) is due to round-off errors in the calculations.

Example 3-6: Iron reacts with oxygen to form the oxide, Fe_2O_3. If 500 grams of Fe_2O_3 are formed by this reaction, how many grams of iron would be consumed?

Solution 3-6: A balanced equation is required. The word equation is given above. Substituting symbols and formulas gives,

$$Fe + O_2 \rightarrow Fe_2O_3 \qquad \text{(Incomplete)}$$

Balance the equation by adjusting the coefficients.

$$4Fe + 3O_2 \rightarrow 2Fe_2O_3$$

Convert 500 grams of Fe_2O_3 to moles of Fe_2O_3 by:

$$\begin{aligned}\text{moles } Fe_2O_3 &= \frac{\text{grams } Fe_2O_3}{\text{formula weight of } Fe_2O_3}\\ &= \frac{500}{2(55.8) + 3(16)} = \frac{500}{160}\\ &= 3.12 \text{ moles}\end{aligned}$$

The balanced equation states that the mole ratio of Fe to Fe_2O_3 is 4:2 = 2:1, or that for each mole of Fe_2O_3 formed, 2 moles of Fe are consumed.

If 3.12 moles of Fe_2O_3 are formed, then:

$$3.12 \text{ moles } F_2O_3 \times \frac{4 \text{ moles Fe}}{2 \text{ moles } Fe_2O_3} = 6.24 \text{ moles of Fe consumed}$$

The problem asked for the amount of Fe in grams, so convert to grams using,

$$\begin{aligned} \text{grams of Fe} &= \text{moles of Fe} \times \text{gram atomic weight of Fe} \\ &= 6.24 \times 55.8 \\ &= 348 \text{ grams} \end{aligned}$$

220-3.5.6 THE LIMITING REACTANT. Very often in stoichiometric calculations, the amounts of two or more reactants may be given for the purpose of calculating the amount of one or more products formed. In such cases, care must be exercised because one reactant may be entirely consumed before another, and will thus limit the amount of product formed.

Example 3-7: *How many moles of water would be formed from 6 moles of hydrogen and 12 moles of oxygen?*

Solution 3-7: *From previous discussions the balanced equation is:*

$$2H_2 + O_2 \rightarrow 2H_2O$$

It is seen that 2 moles of hydrogen are required to react with each mole of oxygen, or the ratio hydrogen: oxygen is 2:1. From this ratio, it is apparent that all of the oxygen in this problem cannot be used up because that would require 2 x 12 (moles O_2*) = 24 (moles* H_2*) but there are only 6 moles of* H_2 *present. Hydrogen must be the limiting reactant. Again using the above ratio of 2 moles* H_2*:1 mole* O_2*, 6 moles of* H_2 *will react with 3 moles of* O_2*. Also from the equation, for each mole of* H_2 *which reacts, 1 mole of water is formed, so 6 moles of* H_2 *will form 6 moles of water. (Note that 9 moles of* O_2 *will be left over.)*

Example 3-8: *Sodium hydroxide (NaOH) reacts with hydrochloric acid (HCl) to form water and sodium chloride. Starting with 50 grams of each reactant how much of each product will be formed?*

Solution 3-8: *Substituting appropriate formulas into the word equation gives:*

$$NaOH + HCl \rightarrow H_2O + NaCl$$

and inspection shows the equation is balanced.

Now convert the given quantities of reactants to moles:

$$\text{Moles NaOH} = \frac{\text{grams NaOH}}{\text{formula weight NaOH}} = \frac{50}{(23 + 17)} = \frac{50}{40}$$

$$= 1.25 \text{ moles}$$

$$\text{Moles HCl} = \frac{\text{grams HCl}}{\text{formula weight HCl}} = \frac{50}{(1 + 35.5)}$$

$$= \frac{50}{36.5} = 1{,}37 \text{ moles}$$

The equation shows that HCl and NaOH react in a ratio of 1 mole:1 mole. Obviously, then, NaOH is the limiting reactant and 1.25 moles of each reactant will be consumed.

Further inspection of the equation shows that 1.25 moles of each of the products will be formed. Finally, convert moles of products to grams of products.

$$\begin{aligned} \text{grams } H_2O &= \text{moles of } H_2O \text{ x formula weight of } H_2O \\ &= 1.25 \text{ x } (2 + 16) \\ &= 1.25 \text{ x } 18 \\ &= 22.5 \text{ grams} \end{aligned}$$

$$\begin{aligned} \text{grams NaCl} &= \text{moles of NaCl x formula weight of NaCl} \\ &= 1.25 \text{ x } (25 + 35.5) \\ &= 1.25 \text{ x } 58.5 \\ &= 73.1 \text{ grams} \end{aligned}$$

SECTION 3 PROBLEMS

1. Using the Octet Rule, predict the formula for the compound formed by:
    - a calcium and chlorine
    - b cesium and bromine
    - c hydrogen and fluorine
    - d magnesium and fluorine
    - e magnesium and oxygen
2. Write the formula for:
    - a sodium sulfate
    - b barium carbonate
    - c potassium chromate
3. Calculate the formula weights of trisodium phosphate (Na3PO4), sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3).
4. Calculate the weight percent of each element in:
    - a Na_3PO_4

  - b NaOH
  - c $Na_2 CO_3$

5. How many moles are there in 100 grams of NaOH (sodium hydroxide)?

6. Calculate the number of moles in 225 grams of:
   - a $Na_3 PO_4$
   - b $CA(OH)_2$

7. How many molecules are there in 3.5 moles of:
   - a NH_3
   - b CO_2
   - c CH_4

8. Calcium and oxygen react as follows to produce calcium oxide:
   $2\ Ca + O_2 \rightarrow CaO$ How many grams of oxygen are required to react with 10 grams of calcium?

9. Sodium sulfite reacts with oxygen to form sodium sulfate. Five hundred grams of $Na_2 SO_3$ will react with how many grams of O_2 ? How much $Na_2 SO_4$ will be formed?

10. The reaction between sodium hydroxide and carbon dioxide produces sodium carbonate and water. If 12 grams of sodium hydroxide and 50 grams of carbon dioxide are available for reaction, how much sodium carbonate will be formed? How much of each reactant will be left after the reaction?

SECTION 3 PROBLEM ANSWERS

1.
   - a $CaCl_2$
   - b CsBr
   - c HF
   - d MgF_2
   - e MgO

2.
   - a $Na_2 SO_4$
   - b $BaCO_3$
   - c $K_2 CrO_4$

3. $Na_3 PO_4 = 164$, $NaOH = 39.8$, $Na_2 CO_3 = 106$

4.
   - a Na = 42.1 percent, P = 18.9 percent, O = 39.0 percent
   - b Na = 57.5 percent, O = 39.9 percent, H = 2.6 percent
   - c Na = 43.4 percent, C = 11.3 percent, O = 45.3 percent

5. 2.5 moles

6.
   - a 1.37 moles
   - b 3.04 moles

7.
   - a 21.1×10^{23} molecules
   - b 21.1×10^{23} molecules
   - c 21.1×10^{23} molecules
8. 4.0 grams O_2
9. 63.5 grams O_2 , 563.5 grams $Na_2 SO_4$
10. 15.9 grams $Na_2 CO_3$ formed, 0 grams NaOH left, 43.4 grams CO_2 left.

SECTION 4.

WATER

220-4.1 INTRODUCTION

220-4.1.1 Water is the most abundant chemical compound and is familiar in all three physical states. Because of its great abundance, water originally served as the reference standard for several physical measurements such as temperature, volume, mass, and energy. Some of these, for example the unit of mass, have been redefined as more precise methods of measurement were developed. The abundance of water, its innumerable uses, and the existence of most forms of life on this planet are due to some unusual properties of this compound.

220-4.2 GLOSSARY OF TERMS

220-4.2.1 Terms used in this section are defined as follows:

1. **Boiling Point:** The temperature at which the physical state of a substance changes from liquid to gas.
2. **Charge Separation:** A non-homogeneous distribution of charge in a molecule due to (a) the structure of the molecule and (b) the unequal attraction of the electrons by the atoms in the molecule.
3. **Heat Capacity:** The amount of heat required to raise the temperature of a substance one degree, cal/C or BTU/F.
4. **Heat of Fusion:** The amount of heat required to change a substance at its melting point from a solid to a liquid.
5. **Heat of Vaporization:** The amount of heat required to change a substance at its boiling point from a liquid to a gas.
6. **Hydrate:** A type of compound formed by water molecules with some ionic compounds.
7. **Hydrogen Bond:** A chemical bond formed between molecules containing hydrogen covalently bonded to O, N, or F atoms. The hydrogen bond is formed between the partially positive hydrogen atom of one molecule and the partially negative O, N, or F atom of another molecule.
8. **Melting Point:** The temperature at which the physical state of a substance changes from solid to liquid.
9. **Polar Compounds:** Those covalent compounds in which the molecules exhibit a net separation of charge.
10. **Specific Heat:** The amount of heat required to raise the temperature of 1 unit mass of a substance 1 degree, cal/gram-C or BTU/lbm-F.

11. **Water of Hydration:** The water molecules in hydrates.

220-4.3 UNUSUAL PROPERTIES OF WATER

220-4.3.1 GENERAL. The unusual behavior of water is best illustrated by comparing its properties to those of similar compounds. Table 220-4-1 gives some of the physical properties of the compounds of hydrogen with the Group VIA elements: O_2 , S, Se, and Te.

Table 220-4-1 PHYSICAL PROPERTIES OF GROUP VIA COMPOUNDS WITH HYDROGEN

Compound	Formula Weight	Melting Point, C	Boiling Point, C	Heat of Vaporization cal/gm
H_2 Te	128.6	-48.9	-2.2	36
H_2 Se	81.0	-64.0	-41.3	60
H_2 S	34.1	-85.5	60.3	132
H_2 O	18.0	0	100	540

220-4.3.1.1 Consider first the property of boiling point. These values are shown graphically in Figure 220-4-1 along with the boiling points of the inert gases and the hydrogen compounds of Group IVA elements. The values for the inert gases show a smoothly decreasing trend as the atomic weight decreases. The hydrogen compounds of the Group IVA elements show a similar variation with formula weight. The compounds H_2 Te, H_2 Se, and H_2 S also show this variation, but H_2 O is very much out of line. Its boiling point is roughly 200 Celsius degrees higher than would be expected on the basis of other data in Figure 220-4-1. Inspection of Table 220-4-1 shows that for each property listed, the value for H_2 O is much larger than expected compared to the properties of the other Group VIA compounds. The unusual behavior of water is due to the structure of water molecules and the difference in electronegativity between hydrogen and oxygen.

220-4.3.2 POLARITY AND HYDROGEN BONDING. Water is a covalent compound. As noted in Section 3, the sharing of electrons in covalent bonds usually is not equal. The more electronegative of the two atoms attracts the electrons more than does the less electronegative atom. In effect, the electrons are pulled closer to the more electronegative atom. The result is a partial negative -(δ) charge on the more electronegative atom and a partial positive +(δ) charge on the other atom. The symbol, δ, (delta) for **partial** is used to emphasize that neither atom completely captures the electron and thus, does not have a full unit of charge. Some of the consequences of these partial charges in covalent molecules depend on the structure of the molecule. The compound carbon monoxide, CO, consists of a carbon atom bonded to an oxygen atom by a triple covalent bond. Reference to Table 220-3-1 shows that oxygen is more electronegative than carbon, so oxygen acquires a partial negative charge and carbon acquires a partial positive charge. This is illustrated schematically in Figure 220-4-2 (a). The result is a **net** separation (i.e., unequal distribution) of positive and negative charge, although the molecule as a whole is neutral. Covalent compounds in which there is a **net** separation of positive and negative charge are called **polar** compounds.

220-4.3.2.1 The importance of the emphasis on **net** separation of charge on the whole molecule is illustrated by carbon dioxide. Each CO_2 molecule is linear, as shown in Figure 220-4-2(b). In Figure 220-4-2 a single dash (H-O) represents a single, two electron covalent bond; a double dash (=) represents a double bond, and (≡) a triple bond. As in carbon monoxide each C-O bond is polar, but in CO_2 the polarities of the two bonds are in opposite directions and cancel each other. Overall, the CO_2 molecule is nonpolar.

220-4.3.2.2 Contrast CO_2 with H_2 O shown in Figure 220-4-2(c). The H_2 O molecule is nonlinear. The angle between the two H-O bonds is about 105°. In this case, the polarities of the two bonds do not cancel and there is a net polarity in the H_2 O molecule.

220-4.3.2.3 The small size of hydrogen and the large electronegativity of oxygen lead to an interaction between H_2 O molecules. The +δ, hydrogen atom of one molecule is electrostatically attracted to the -δ, oxygen atom of a different molecule. This attractive force is called a **hydrogen bond** and is illustrated in Figure 220-4-3.

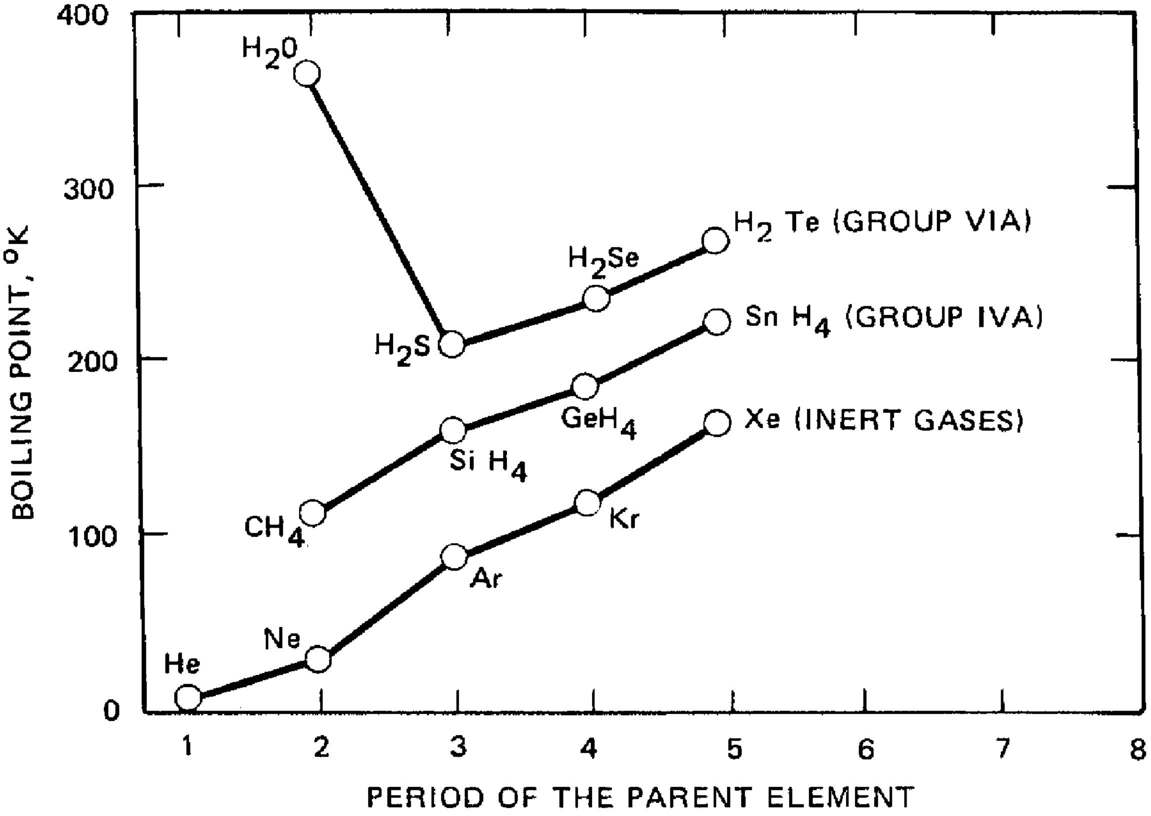


Figure 220-4-1 Boiling Points of Inert Gases and Compounds of Hydrogen with Elements in Groups IVA and VIA

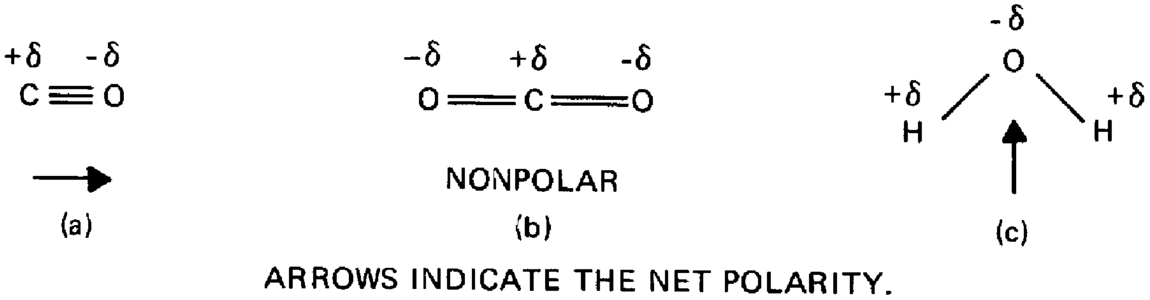


Figure 220-4-2 Polar and Nonpolar Molecules

220-4.3.2.4 Hydrogen bonds are weaker than normal covalent or ionic bonds, but are stronger than the van der Waals forces which result from the attraction of the atomic nuclei of one molecule for the electrons of another molecule. The approximate relative strengths of these forces are as follows:

van der Waals	Hydrogen Bond	Covalent/Ionic Bond
1	10	100

220-4.3.2.5 It is the formation of hydrogen bonds that gives water its unique properties. Hydrogen bonding also occurs in other compounds, most noticeably those which contain hydrogen bonded covalently to the most electronegative atoms, N, O, and F. These include many complex biological compounds and the more familiar compounds, HF, and NH_3 .

220-4.3.3 EFFECTS OF HYDROGEN BONDING IN WATER. All the physical properties treated in paragraphs 220-4.3.3 through 220-4.3.3.11 involve the strength of attraction between molecules and the motion of the molecules. Heat is a form of energy and when heat is added to a substance, the basic effect is an increase in the kinetic energy of the fundamental particles of that substance. Except as noted below, this increase in the kinetic energy is reflected as an increase in temperature.

220-4.3.3.1 Beginning with ice, let us trace water through its physical states. Although the discussion is limited to water, the general concepts, except those involving hydrogen bonding, apply to all pure covalent compounds. In ice, the water molecules are in a very orderly arrangement similar to the arrangement of ions in an ionic crystal. The crystalline state of water is illustrated in Figure 220-4-4. Each water molecule is hydrogen-bonded to four other water molecules. Although the general position of water molecules in the crystal is fixed, the molecules are not absolutely motionless. They can oscillate back and forth similar to a three-dimensional series of steel balls all interconnected by springs. The oscillations are more energetic at high temperatures and less energetic at low temperatures.

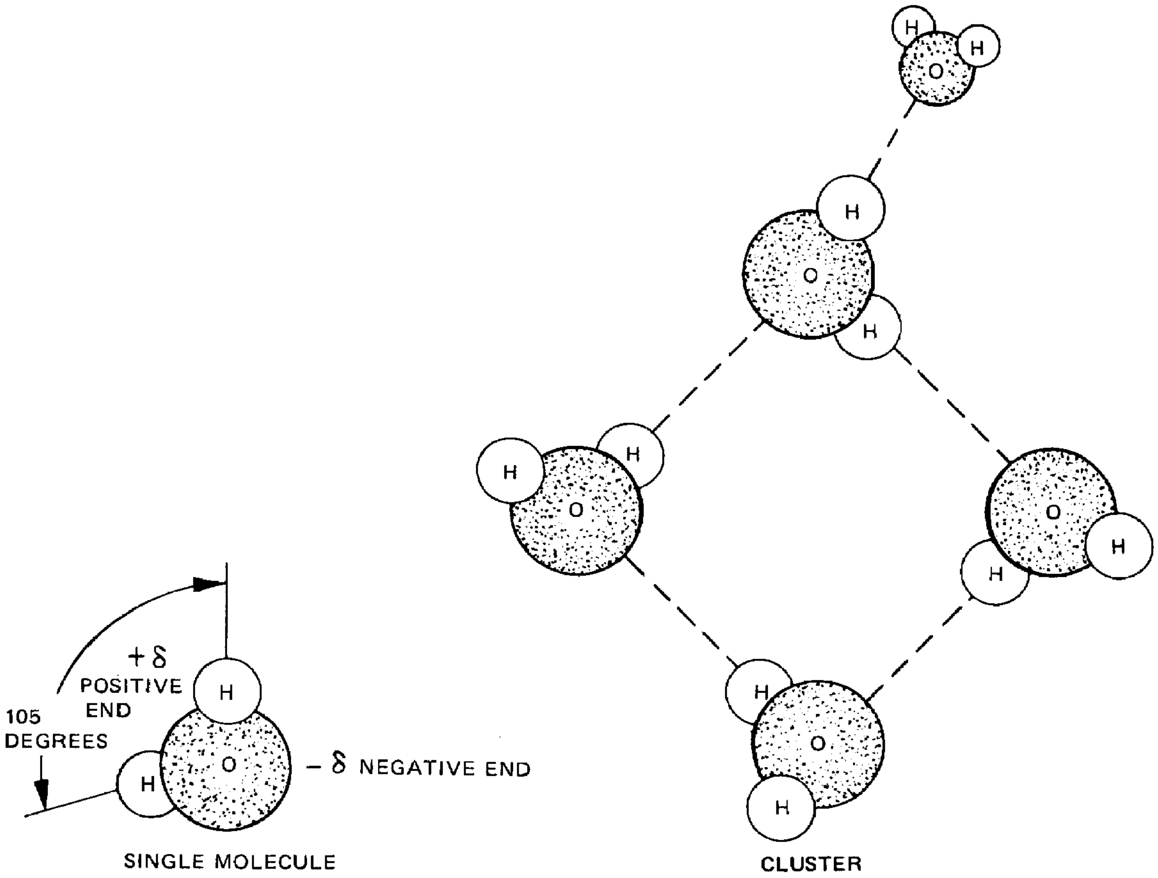


Figure 220-4-3 Hydrogen Bonding Cluster

220-4.3.3.2 The temperature at which the physical state of a substance changes from solid to liquid is the **melting point** of that substance. The melting point of ice is defined to be 0°C. Defining the boiling point of water to be 100°C thus establishes the centigrade temperature scale. At the melting point, the molecular oscillations become sufficiently energetic to overcome some of the intermolecular bonds. Melting of ice can be pictured as the process of breaking enough of the hydrogen bonds to cause the crystal to collapse.

220-4.3.3.3 There is a certain amount of heat required to change 1 gram of ice at 0°C to 1 gram of water at 0°C. That is, starting with ice at 0°C, any added heat goes into breaking apart the crystal and does not cause a rise in temperature. The amount of heat required to transform a given amount of a pure substance at its melting point from solid to liquid is called the **heat of fusion,** ΔH_f , of that substance. For ice, ΔH_f = 80 cal/gm or 144 BTU/lbm. Although the crystal structure collapses when ice melts, the destruction is not complete. There remain fragments of the crystal (or clusters) in which several water molecules are held together by hydrogen bonds. The liquid is sometimes described as being semi-ordered.

220-4.3.3.4 Although paragraph 220-4.3.3.5 briefly describes the **structure** of semi-ordered liquid water, it should be borne in mind that the situation is very dynamic. Clusters of molecules and individual molecules have much more freedom of movement than in the solid state and intermolecular bonds are constantly being formed and broken. Thus, any attempt at defining a structure for such a system must deal with average effects.

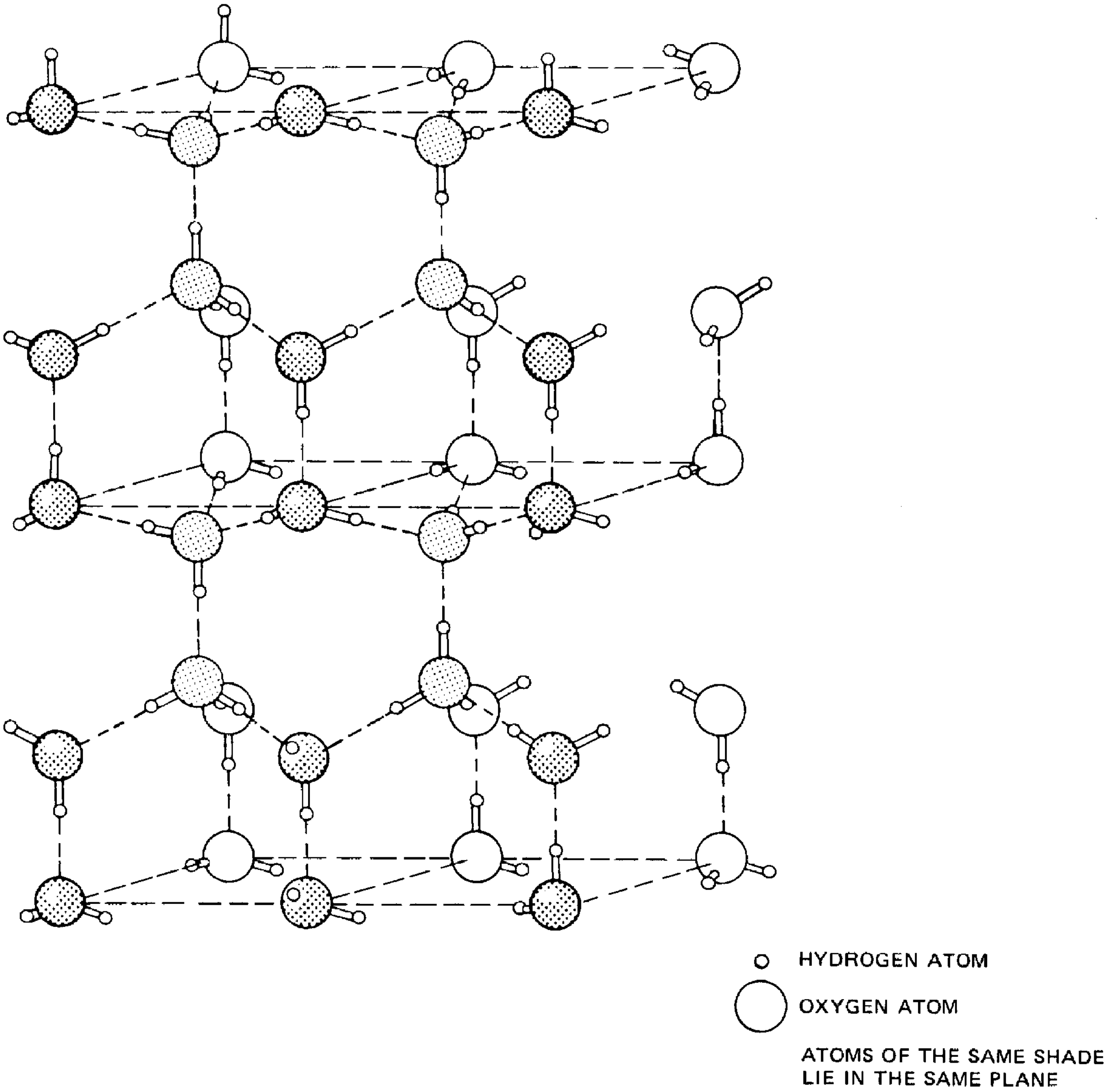


Figure 220-4-4 Ice Crystal Molecule Arrangement

220-4.3.3.5 Note in Figure 220-4-4 , the open spaces in the crystal network. On melting, the crystal structure is retained by fragments of the crystal, but now there are individual water molecules that can fit into the open spaces of the clusters. Thus, there is an increase in density when ice melts. As the temperature increases, more molecules exist individually, but the network of the clusters expands. The combined result of these two effects is that water has its highest density at 4°C. Above this temperature, network expansion causes the density to decrease; below 4°C, the smaller number of molecules in the open spaces causes the density to decrease. If ice were more dense than cold water, most of the world’s bodies of water (including the oceans) would be mostly solid ice with a few feet of water on the surface.

220-4.3.3.6 As heat is added to liquid water, the motion of individual molecules and clusters increases and the temperature rises. The amount of heat required to raise the temperature of a substance 1 degree is the **heat capacity** of that substance. The heat capacity per unit mass is called **specific heat.** The specific heat of liquid water varies with temperature, but between 0°C and 100°C it is about 1 cal/gram-C or 1 BTU/lbm-F.

220-4.3.3.7 At one atmosphere pressure, water boils at 100°C (by definition). In general, the **boiling point** is that temperature at which the physical state of a substance changes from liquid to gas. The addition of heat to water at its boiling point does not cause a rise in temperature. All the added energy goes into breaking the intermolecular bonds and allowing the molecules to escape into the vapor. The amount of heat required to change a substance at its boiling point from a liquid to a gas is the **heat of vaporization,** ΔH_v , of that substance. For water, ΔH_v = 540 cal/gram or 972 BTU/lbm.

220-4.3.3.8 The gaseous state is highly disordered. Compared to solid and liquid water, there is relatively little intermolecular interaction in water vapor. The molecules are in rapid, random motion, constantly colliding with each other and the walls of any container. Collectively, these collisions with the container are measurable as pressure. As heat is added to water vapor, or any gas, the speed of the molecules and the temperature increase. If the volume is fixed, the pressure also increases. The relationship between temperature, pressure, and volume of gases is discussed in more detail in Section 6.

220-4.3.3.9 Figure 220-4-5 summarizes the process of melting 1 gram of ice, heating the water to 100°C, and vaporizing (or boiling) it to steam. The reverse process, of course, is condensing 1 gram of steam, cooling the water to 0°C, and solidifying (or freezing) it.

220-4.3.3.10 The preceding discussion noted several instances in which hydrogen bonding plays a role in the behavior of water. Among these are melting ice, and heating and vaporizing the liquid. In most other covalent compounds the intermolecular forces involved in these processes are van der Waals forces which are about ten times weaker than hydrogen bonds. For that reason, the energies required to produce the physical changes in water are much greater than the amount required for the same change in a compound which does not form hydrogen bonds. The energies are not just 10 times greater because each water molecule may be hydrogen-bonded to as many as four other molecules.

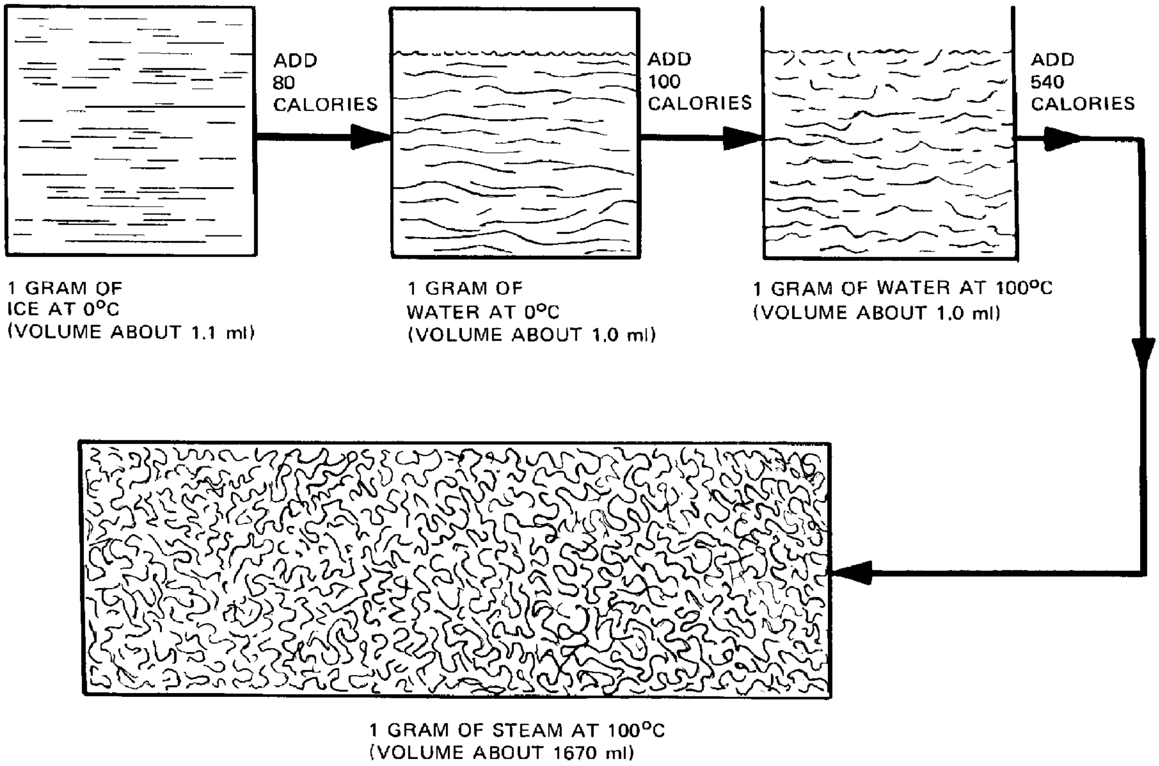


Figure 220-4-5 Changes of State of Water at 1 Atmosphere

220-4.3.3.11 It is interesting to speculate about what the behavior of water would be if hydrogen bonding did not occur. Without this extra bonding, water would be expected to freeze at roughly -100°C and boil at about -80°C. The consequences are immediately obvious: there would be no solid or liquid water on the earth's surface, no oceans, rivers, glaciers, nor polar ice caps. The familiar forms of life, including man, could not exist.

220-4.3.4 CHEMICAL PROPERTIES OF WATER. Water is a very stable compound, but this does not mean that it is chemically unreactive. Many of the specifics of the chemistry of water are described in subsequent sections. In this section, only a few types of reactions and a type of compound are introduced.

220-4.3.4.1 Reactions. Under normal pressure and at room temperature, water reacts directly with the active metals and non-metals, such as:

$2Na + 2H_2O \rightarrow 2NaOH + H_2$

$2F2 + 2H_2O \rightarrow 4HF + O_2$

It also reacts readily with many oxides of metals and non-metals.

$CaO + H_2O \rightarrow Ca(OH)_2$

$CO_2 + H_2O \rightarrow H_2CO_3$

As discussed in Section 8, one of the properties which distinguishes metals from non-metals is the manner in which the elements and their oxides react with water.

220-4.3.4.2 Hydrates. Many ionic compounds form definite compounds with water. These compounds are called **hydrates** and occur most readily when water is present during the formation of the ionic compound. For example, if $CuSO_4$ (copper sulfate) is prepared in the presence of water, the compound $CuSO_4 \bullet 5H_2 O$ is formed. The formula with the dot (•) between $CuSO_4$ and $H_2 O$ indicates that these two distinct compounds are chemically combined in the ratio of 1 mole of $CuSO_4$ to 5 moles of $H_2 O$ to form a different compound. Hydrates result from the interaction of the positive ion (Cu++ in the above case) and the oxygen end of the water molecule which has a partial negative charge. Since the oxygen atom has less than a full unit of charge, the bonding in hydrates is weaker than a normal bond.

220-4.3.4.2.1 Most hydrates are easily (and sometimes visibly) decomposed by mild heat. Thus:

$$\underset{\text{(blue)}}{CuSO_4 \cdot 5H_2O} \xrightarrow{\text{heat}} \underset{\text{(white)}}{CuSO_4} + 5H_2O$$

In many cases, the hydrate is reformed if the ionic compound is exposed to moisture.

$$\underset{\text{(white)}}{CuSO_4} + 5H_2O \longrightarrow \underset{\text{(blue)}}{CuSO_4 \cdot 5H_2O}$$

220-4.3.4.2.2 The water in hydrates is called the **water of hydration** and usually does not participate in chemical reactions that the ionic part of the compound undergoes. Consider the reaction:

$$2Na_3 PO_4 \bullet 12H_2 O + 3CaCl_2 \rightarrow 6NaCl + Ca_3 (PO_4)_2 + 24H_2 O$$

It is apparent that the water molecules do not react at all and the equation can be written:

$$2Na_3 PO_4 + 3CaCl_2 \rightarrow 6NaCl + Ca_3 (PO_4)_2$$

The following example illustrates, however, that the water of hydration must be taken into account in practical applications.

Example 4-1: Trisodium phosphate is available as the hydrate, Na_3 PO4 • $12H_2$ O. How much of the hydrate must be weighed out to obtain 100 grams of $Na_3 PO_4$?

Solution 4-1: There are two equally valid methods of solving this problem.
a. The weight fraction method: One can determine the weight fraction of $Na_3 PO_4$ in $Na_3 PO_4 \bullet 12H_2 O$ and then determine how much of the hydrate is needed to give 100 grams of $Na_3 PO_4$.

$$\begin{aligned}
\text{Formula weight (FW) of } Na_3PO_4 &= 3\ (Na) + P + 4\ (0)\\
&+ 3\ (23) + 31 + 4\ (16)\\
&= 164 \text{ grams}\\
\text{FW of } Na_3PO_4 \cdot 12H_2O &= \text{FW of } Na_3PO_4\\
&+ 12\ (\text{FW of } H_2O)\\
&= 164 + 12[2(H) + 0]\\
&= 164 + 216\\
&= 380 \text{ grams}
\end{aligned}$$

$$\text{Fraction of } Na_3PO_4 = \frac{164}{380} = 0.43 \text{ or } 43 \text{ percent}$$

Let the amount of $Na_3PO_4 \cdot 12H_2O$ *needed to give 100 grams of* Na_3PO_4 *be X. Then,*

$$0.43\ X = 100$$

$$X = \frac{100}{0.43} = 232 \text{ grams } Na_3PO_4 \cdot 12H_2O \text{ required}$$

b. *The mole method:*

Inspection of the formula $Na_3PO_4 \cdot 12H_2O$ *shows that 1 mole of* $Na_3PO_4 \cdot 12H_2O$ *contains 1 mole of* Na_3PO_4 *and 12 moles of water. From method a., FW of* $Na_3PO_4 = 164$*, so the number of moles in 100g* Na_3PO_4 *is:*

$$\text{moles } Na_3PO_4 = \frac{\text{grams of } Na_3PO_4}{\text{FW of } Na_3PO_4} = \frac{100}{164} = 0.61 \text{ mole}$$

So 0.61 mole Na_3PO_4 *would be contained in 0.61 mole* $Na_3PO_4 \cdot 12H_2O$.

Also, from method a.,

$$\text{FW of } Na_3PO_4 \cdot 12H_2O = 380 \text{ grams.}$$

$$\begin{aligned}
\text{So, grams } Na_3PO_4 \cdot 12H_2O \text{ required} &= \text{moles } Na_3PO_4 \cdot 12H_2O\\
&= 0.61 \times 380\\
&= 232 \text{ grams } Na_3PO_4 \cdot 12H_2O \text{ required.}
\end{aligned}$$

220-4.4 SUMMARY

220-4.4.1 The usefulness of water in many of its applications is due to the formation of hydrogen bonds. Hydrogen bonding results in strong intermolecular interactions and requires relatively large amounts of heat to produce changes in the temperature and physical state of water. The polarity of the water molecule leads to the formation of compounds called hydrates and also plays a role in other chemical properties of water.

SECTION 5.

SOLUTIONS

220-5.1 INTRODUCTION

220-5.1.1 As noted in the introduction to Section 3, elements rarely exist in the pure form in nature, but rather as chemical compounds. These compounds also are seldom found in a pure form. Most of the physical world, from seawater to granite, is composed of mixtures. A special class of mixtures, called solutions, is the subject of this section.

220-5.2 GLOSSARY OF TERMS

220-5.2.1 Terms used in this section are defined as follows:

a. **Aqueous Solution:** Any solution in which water is the solvent.

b. **Concentration:** The amount of solute contained in a specific amount (volume or weight) of a solution.

c. **Conductivity:** A measure of the ability of a liquid or solution to conduct electricity; proportional to the concentration of electrolytes.

d. **Electrolyte:** Any compound which forms ions when dissolved and thus forms solutions which conduct an electric current.

e. **Equivalents-per-Million:** A chemical concentration term for dissolved material used in reporting sample test results. It expresses the chemical equivalent unit weight of material dissolved in a million unit weights of solution.

f. **Heterogeneous:** Non-uniform; having parts with distinctly different characteristics.

g. **Homogeneous:** Uniform; having no discernible difference between various parts.

h. **Inverse Solubility:** The property of being less soluble at higher temperatures.

i. **Ionic Equation:** A type of chemical equation which includes only those ions directly involved in a chemical reaction.

j. **Mixture:** A combination of two or more substances capable of being separated by some physical process.

k. **Molarity:** Concentration units which express the number of moles of solute per liter of solution.

l. **Molar Ionic Conductivity:** The conductivity due to a particular ion in a l$\underline{M}$ solution.

m. **Parts-per-Million:** Concentration units which express the weight of solute in a given weight of solution, that is, the parts by weight of solute in 1 million parts by weight of solution.

n. **Precipitation:** The process by which a pure substance separates from a solution; for example, rain precipitates from the atmosphere, solid AgCl precipitates from a solution of NaCl and $AgNO_3$.

o. **Saturated Solution:** A solution which contains as much of a particular solute as will dissolve at a given temperature and pressure.

p. **Solubility:** The maximum amount of a substance which will dissolve in a given amount of solvent at a specific temperature.

q. **Solute:** A component of a solution; usually the component present in smallest amount.

r. **Solution:** Any homogeneous mixture on a molecular level.

s. **Solvent:** A component of a solution; usually the component present in greatest amount.

t. **Suspension:** A heterogeneous mixture of a finely divided substance in another, less dense substance. Examples are mud in water and soot in air.

220-5.3 MIXTURES AND SOLUTIONS

220-5.3.1 MIXTURES. A **mixture** is a combination of two or more substances which can be separated by some physical process. For example, a mixture of sawdust and iron filings can be separated by passing a magnet back and forth through the mixture. The iron filings will be collected on the magnet while the sawdust is left behind.

220-5.3.1.1 There are two broad categories of mixtures: heterogeneous and homogeneous. **Heterogeneous mixtures** are those in which there is a discernible difference in composition between different parts of the mixture. In the mixture of sawdust and iron filings, the parts which are iron can be differentiated from those which are wood. The ease of differentiation depends somewhat on how finely divided the particles are; the distinction can be made under a microscope if necessary.

220-5.3.1.2 **Homogeneous mixtures** are those in which there is no difference in composition throughout the mixture. Such a mixture is salt water, in which no difference can be discerned even under the most powerful microscope. **Homogeneous mixtures of two or more substances are called solutions.**

220-5.3.2 SOLUTIONS. Solutions are well-known in all three physical states. Most alloys are solid solutions, the atmosphere is a gaseous solution, and carbonated beverages are solutions of a gas (carbon dioxide) in a liquid. The most familiar solutions are liquids, and most of these are solutions of a solid in a liquid.

220-5.3.2.1 The reader may already be familiar with several terms associated with solutions. One substance is said to dissolve in, or be dissolved by, another substance. The substance present in smaller amount is usually thought of as the one which is dissolved and is usually called the **solute** . The other substance, present in greater amount, is the one that does the dissolving and is usually called the **solvent** . In some cases, this distinction between solvent and solute is vague. For example, in the case of a solution composed of equal parts of water and alcohol, it is, in most respects, immaterial which substance is called the solute and which the solvent.

220-5.3.2.2 Some mixtures such as muddy water and smoke may appear to be solutions, but are really heterogeneous mixtures called suspensions. The mud will eventually settle out of muddy water and soot will settle out of black smoke.

220-5.3.2.3 In this section, major attention is given to solutions of solids in liquids, particularly water. Section 6 discusses solutions of gases in water. Solutions in which water is the solvent are called **aqueous solutions.**

220-5.4 WHY SUBSTANCES DISSOLVE

220-5.4.1 GENERAL. It is well known that NaCl (table salt) dissolves in water. Perhaps not so well-known, but easily verified, is the fact that salt will not dissolve in ordinary rubbing alcohol. The full explanation of why a particular compound will dissolve in one substance but not in another is very complex. Many of the fundamentals, however, can be understood on the basis of previous discussions of chemical bonding and intermolecular interactions. Three types of attractive forces are to be considered:

a. Forces between solute molecules or ions

b. Forces between solvent molecules

c. Forces between solute molecules or ions and solvent molecules

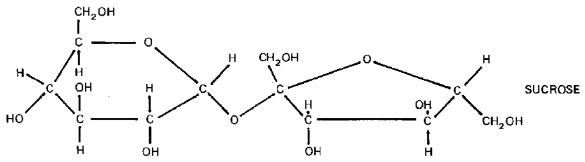
220-5.4.1.1 A general requirement for the formation of a solution is that the forces of 3 must be stronger than or approximately equal to the forces of 1 and 2. The examples in paragraphs 220-5.4.2 through 220-5.4.7 illustrate these interactions.

220-5.4.2 IONIC SOLUTE - POLAR COVALENT SOLVENT. Consider NaCl and water again. Sodium chloride is an ionic compound, and water is a polar covalent compound which exhibits hydrogen bonding between molecules. If solid NaCl is placed in water, the Na^+ ions in the crystal are attracted by the negative end of the polar water molecules and the Cl- ions are attracted by the positive end of the water molecules. This is shown schematically in Figure 220-5-1. Note that in this two-dimensional representation of the NaCl crystal, a Na^+ ion on the edge of the crystal is not completely surrounded by Cl^- ions. Such Na^+ ions are thus not held in the crystal by the full ionic attraction experienced by an Na^+ ion inside the crystal and completely surrounded by Cl^- ions. The same reasoning applies to Cl^- ions on the edge of the crystal.

220-5.4.2.1 The ends of a water molecule have less than a full unit of charge, but several water molecules act on any particular Na^+ or Cl^- ion on the edge of the crystal. The sum of these forces is greater than the ionic attraction holding the ion in the crystal and the ion is pulled into the water. When the ions originally on the edge of the crystal dissolve, other ions then become the edge of the crystal and the process continues.

220-5.4.2.2 As shown in Figure 220-5-1 , each ion in solution is surrounded by water molecules oriented such that the end of the molecule nearer the ion has a partial charge opposite in sign to that of the ion. The maximum number of water molecules which can fit around any particular ion is determined by the relative sizes of the ion and the water molecule. The exact number is of little practical importance and at any given instant, a particular ion may have less than its maximum number of water molecules due to the rapid movement of the ions and molecules in solution. For simplicity, Figure 220-5-1 shows all dissolved ions as being surrounded by the same number of water molecules.

220-5.4.3 POLAR COVALENT SOLUTE - POLAR COVALENT SOLVENT. A solid need not be ionic to dissolve in a polar solvent such as water. Sugar (sucrose) is a polar covalent compound with the formula $C_{12}H_{22}O_{11}$ and the structure:



220-5.4.3.1 The interaction of polar water molecules with polar sugar molecules is strong enough to pull the entire sugar molecule into the liquid. A factor contributing to the strength of this interaction is the existence of H-O bonds in sugar molecules. This indicates that these molecules are capable of engaging in hydrogen bonding with water molecules. Each sugar molecule contains eight H-O bonds so each of these molecules may be hydrogen-bonded to as many as eight water molecules.

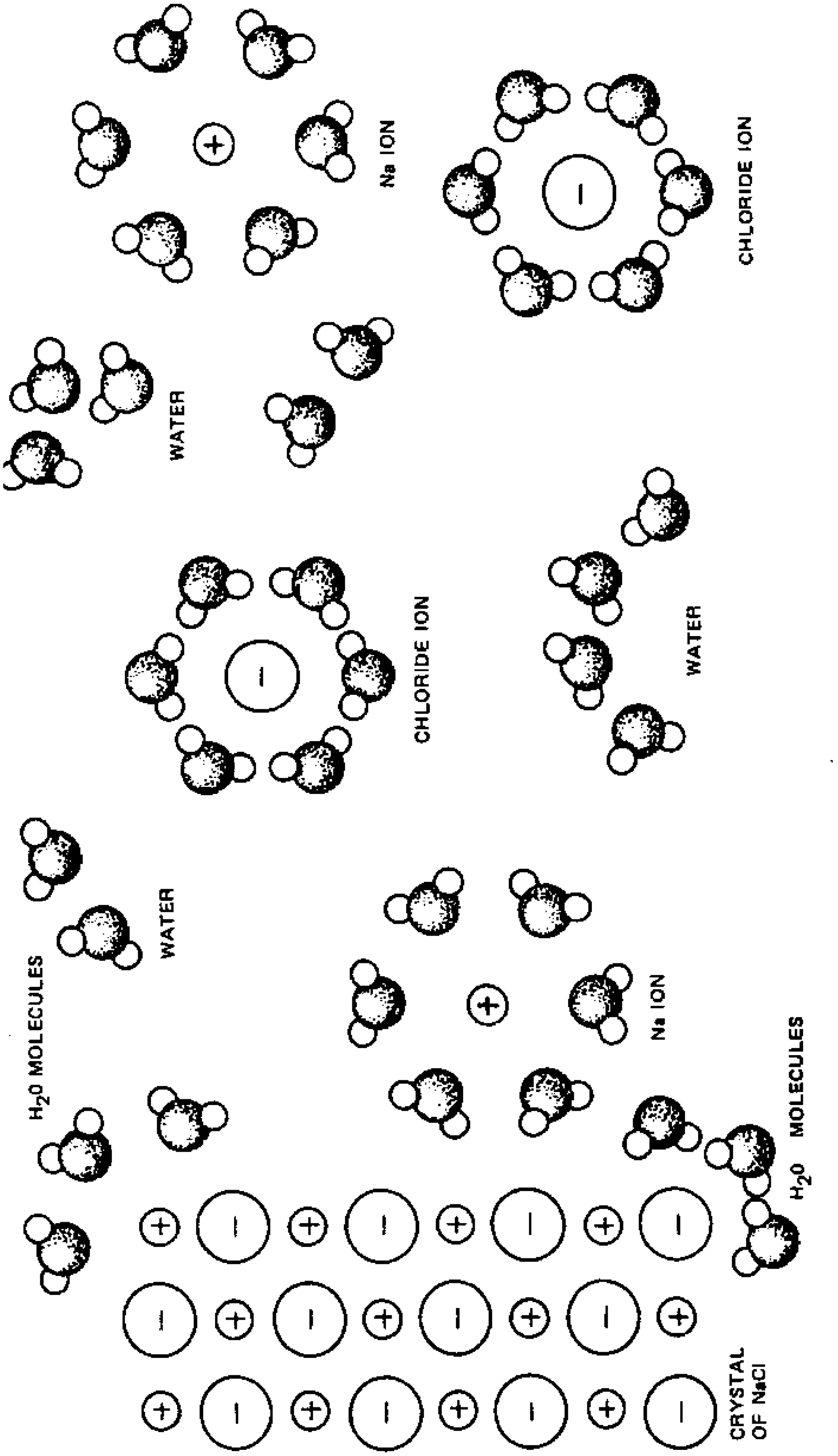
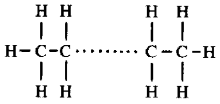


Figure 220-5-1 Sodium Chloride Dissolving to Form an Electrolytic Solution

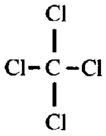
220-5.4.4 NONPOLAR COVALENT SOLUTE - POLAR COVALENT SOLVENT. The commercial product, paraffin, the major component of candles, is a mixture of compounds all having the general formula, $C_n\ H_{2n}$ +2 where n = 20 to 30, and the straight-chain structure:



Paraffin
(total of n C atoms)

Since these molecules are non-polar and incapable of forming hydrogen bonds, the only interactions between these and water molecules are van der Waals forces. These forces are much weaker than the hydrogen bonds between water molecules, so paraffin does not dissolve in water.

220-5.4.5 NONPOLAR COVALENT SOLUTE - NONPOLAR COVALENT SOLVENT. Carbon tetrachloride, CCl_4 , is a nonpolar covalent liquid with the structure:



Carbon Tetrachloride

Carbon tetrachloride readily dissolves paraffin. The van der Waals attractions between carbon tetrachloride and paraffin molecules are stronger than those between carbon tetrachloride molecules and those between paraffin molecules.

220-5.4.6 IONIC SOLUTE - NONPOLAR COVALENT SOLVENT. As a final example, consider NaCl in carbon tetrachloride. The Na^+ and Cl^- ions are held in the crystal by ionic bonds. Since carbon tetrachloride molecules are nonpolar the only interaction between these molecules and the ions is of the van der Waals type. As seen before, van der Waals forces are much weaker than ionic bonds and therefore are not sufficient to pull the ions out of the crystal. Thus, NaCl does not dissolve in carbon tetrachloride.

220-5.4.7 GENERAL SOLUBILITY RULE. The preceding examples can be summarized with the following conclusions. Polar covalent solvents dissolve ionic and polar covalent compounds but not nonpolar covalent compounds. Further, nonpolar covalent liquids dissolve nonpolar covalent solids but not ionic or polar covalent solids. These conclusions are stated very briefly as the general rule: **Like substances tend to dissolve one another, unlike substances do not** . This rule is certainly not universally true, but considering the complexities involved, it is surprisingly accurate.

220-5.5 CONCENTRATION UNITS

220-5.5.1 GENERAL. Any amount of water containing any amount of NaCl may be described as **salt water or an aqueous NaCl solution** . In order to describe solutions definitively, a system of expressing the amount of solute in a certain amount of solvent or solution is needed. Such a system is called **concentration** . Just as there are different units of length such as inch, meter, and light-year, there are different units of concentration. The units chosen for a particular solution or application are largely a matter of convenience. Although some concentration units express the amount of solute in a given amount of solvent, **in this text concentration is expressed only as the amount of solute in a given amount of solution** . Four types of such concentration units will be used: parts per million, molarity, normality, and cc/kg. The first two types are discussed in the following paragraphs. The other two are developed as needed in Section 6 and Section 8.

220-5.5.2 PARTS-PER-MILLION (PPM). The parts-per-million units of concentration express the weight of solute in a fixed weight of solution. **A concentration of 1 ppm is defined as one part by weight of solute in one million (10^6) parts by weight of solution** . Thus, a 1 ppm NaCl solution could contain 1 gram of NaCl in 10^6 grams of solution, or 1 pound of NaCl in 10^6 pounds of solution. The parts may be expressed in any weight units so long as when both solute and solution are in the same units the ratio between them is $1:10^6$ (for a 1 ppm solution). For a 2 ppm solution the ratio is $2:10^6$, and so on. The ppm units are normally used to describe dilute solutions.

220-5.5.2.1 At room temperature, the density of water is about 1 gram/milliliter, so a liter of water weighs about 1000 grams. At this temperature, a 1 ppm solution contains about 1 milligram (1 mg = 10^{-3} g) of solute per liter of solution (10^3 g or 10^6 mg). Note that the amount of solute is so small that it does not significantly contribute to the weight of the solution. Thus, the approximation is good only for dilute aqueous solutions near room temperature.

220-5.5.3 MOLES/LITER OR MOLARITY. Molarity is a system of expressing the number of moles of a solute contained in one liter of solution. **A 1 molar solution contains one mole (or 1 gram formula weight) of solute in each liter of solution.** Such a concentration is indicated by $1\underline{M}$ where M means moles/liter or molar. Similarly, the designations $0.5\underline{M}$ and $5\underline{M}$ describe solutions containing 1/2 and 5 moles of solute per liter of solution.

220-5.5.3.1 From the discussion of the mole in Section 3, one mole of a pure substance always contains 6.02 x 10^{23} molecular or ionic units. A $1\underline{M}$ solution of a compound which does not form ions when it dissolves, such as sugar, contains 6.02 x 10^{23} molecules per liter of solution. If a compound forms ions on dissolving, the chemical formula indicates the relative number of ions of each type. For example, a $1\underline{M}$ NaCl solution contains 6.02 x 10^{23} Na^+ ions and 6.02 x 10^{23} Cl^- ions per liter of solution.

220-5.5.4 EQUIVALENTS-PER-MILLION (EPM). Data for this paragraph will be provided in a future change to this volume.

Example 5-1: *How many grams of NaCl must be added to 5 liters of water at room temperature to prepare a 200 ppm NaCl solution?*

Solution 5-1: *A 200 ppm NaCl solution contains*

$$\frac{200 \text{ grams NaCl}}{10^6 \text{ grams solution}}$$

Assume the solution weighs 10^3 grams/liter.

Calculate NaCl to be added to 5 liters:

$$\frac{200 \text{ grams NaCl}}{10^6 \text{ grams solution}} \times 5 \text{ liters} \times \frac{10^3 \text{ grams of solution}}{\text{liter solution}} = 1 \text{ gram}$$

Example 5-2: *How much NaOH is required to prepare 5 liters of 0.5$\underline{M}$ NaOH? What will be the concentration of NaOH in ppm?*

Solution 5-2: *A 0.5$\underline{M}$ solution contains 0.5 moles NaOH per liter. To calculate grams NaOH we need formula weight:*

FW of NaOH = 23 + 16.0 + 1.0 = 40 grams/mole

To prepare 5 liters of 0.5$\underline{M}$ NaOH: 0.5 moles NaOH 1 liter x 5 liters x 40 grams/mole = 100 grams NaOH are required.

To calculate ppm NaOH, divide grams of NaOH by grams of solution and convert to ppm (assume the solution weighs 1000 grams/liter).

$$\frac{100 \text{ grams NaOH}}{5 \text{ liters solution}} \times \frac{1 \text{ liter}}{10^3 \text{ grams solution}}$$

$$\times \quad \frac{1 \text{ ppm}}{10^{-6} \text{ gram solute/gram solution}} = 2 \times 10^4 \text{ ppm NaOH}$$

Alternatively, using the approximation that ppm = milligrams/liter,

$100 \text{ grams}/5 \text{ liters} \times 10^3 \text{ milligrams}/1 \text{ gram} = 2 \times 10^4 \text{ milligrams/liter} = 2 \times 10^4 \text{ ppm}$

Example 5-3: Suppose a boiler water solution contains 100 ppm of sodium sulfite (Na_2SO_3). Express the Na_2SO_3 concentration in moles/liter.

Solution 5-3: A 100 ppm solution contains

$100 \text{ parts by weight } Na_2SO_3/10^6 \text{ parts by weight of solution}$

Consider one liter of solution:

At room temperature, 1 liter of solution weighs about 1000 grams.

Calculate the weight of solute in 1 liter of a 100 ppm solution

$100 \text{ grams } Na_2SO_3/10^6 \text{ grams solution} \times 1000 \text{ grams solution/liter} = 0.1 \text{ gram } Na_2SO_3\text{/liter}$

To calculate moles/liter, we need formula weight of Na_2SO_3

$$\text{FW of } Na_2SO_3 = 2 \times 23.0 + 32.1 + 3 \times 16.0$$

$$= 126.1 \text{ grams/mole}$$

$$\text{Concentration, moles/liter} = 0.1 \text{ gram } Na_2SO_3\text{/liter} \times 1 \text{ mole}/126.1 \text{ grams}$$

$$= 7.93 \times 10^{-4} \text{ moles/liter}$$

220-5.6 SOLUBILITY

220-5.6.1 There is a limit to the amount of a solid which will dissolve in a certain amount of water. If more and more NaCl is added to a given amount of water, eventually a point will be reached after which no more salt will dissolve. At this point, the solution is said to be **saturated.** The term **solubility** is used to describe the amount of a substance which will dissolve in a given amount of solvent. The term is often used in both a qualitative (relative or inexact) sense and a quantitative (absolute or exact) sense. Qualitatively, a substance which dissolves in relatively large amounts in a particular solvent is said to have a high solubility or to be highly soluble. Conversely, if a relatively small amount of a substance will dissolve in a solvent, the substance is said to have a low solubility or to be slightly soluble. In the quantitative sense, **the solubility of a solid compound is the maximum amount of the compound which will dissolve in a specified amount of solvent at a particular temperature.**

220-5.6.2 Some substances have such a low solubility that they are described as being insoluble. Usually, however, a small amount of the substance does dissolve. Barium sulfate ($BaSO_4$), for example, dissolves in water only to the extent of 0.004 gram in 1 liter of water at 100°C. For most practical purposes, then, $BaSO_4$ is insoluble in water. For comparison, the solubility of $K_2 SO_4$ is 241 grams in 1 liter of water at 100°C.

220-5.6.3 Two other relative terms are used frequently in describing solutions. These are **concentrated** and **dilute.** Since these are relative terms, it is difficult to set down precise definitions for them, but a distinction can often be made as follows. A dilute solution is one in which the amount of solute is so low that the density of the solvent is not changed significantly. A concentrated solution is one in which the density of the solution is appreciably different from the density of the pure solvent.

220-5.7 FACTORS AFFECTING SOLUBILITY

220-5.7.1 The single most important physical factor which affects the solubility of solids is temperature. The solubility of most compounds increases significantly as the temperature of the solution increases, up to 100 to 200°C, and then decreases at high temperatures. Although most compounds exhibit such behavior, there are many which do not. Some, such as NaCl, show little variation in solubility as the temperature changes. Others such as sodium sulfate ($Na_2 SO_4$) reach a maximum solubility at a relatively low temperature, and above or below this temperature, the solubility decreases. Examples of these types of solubility changes are shown in Figure 220-5-2.

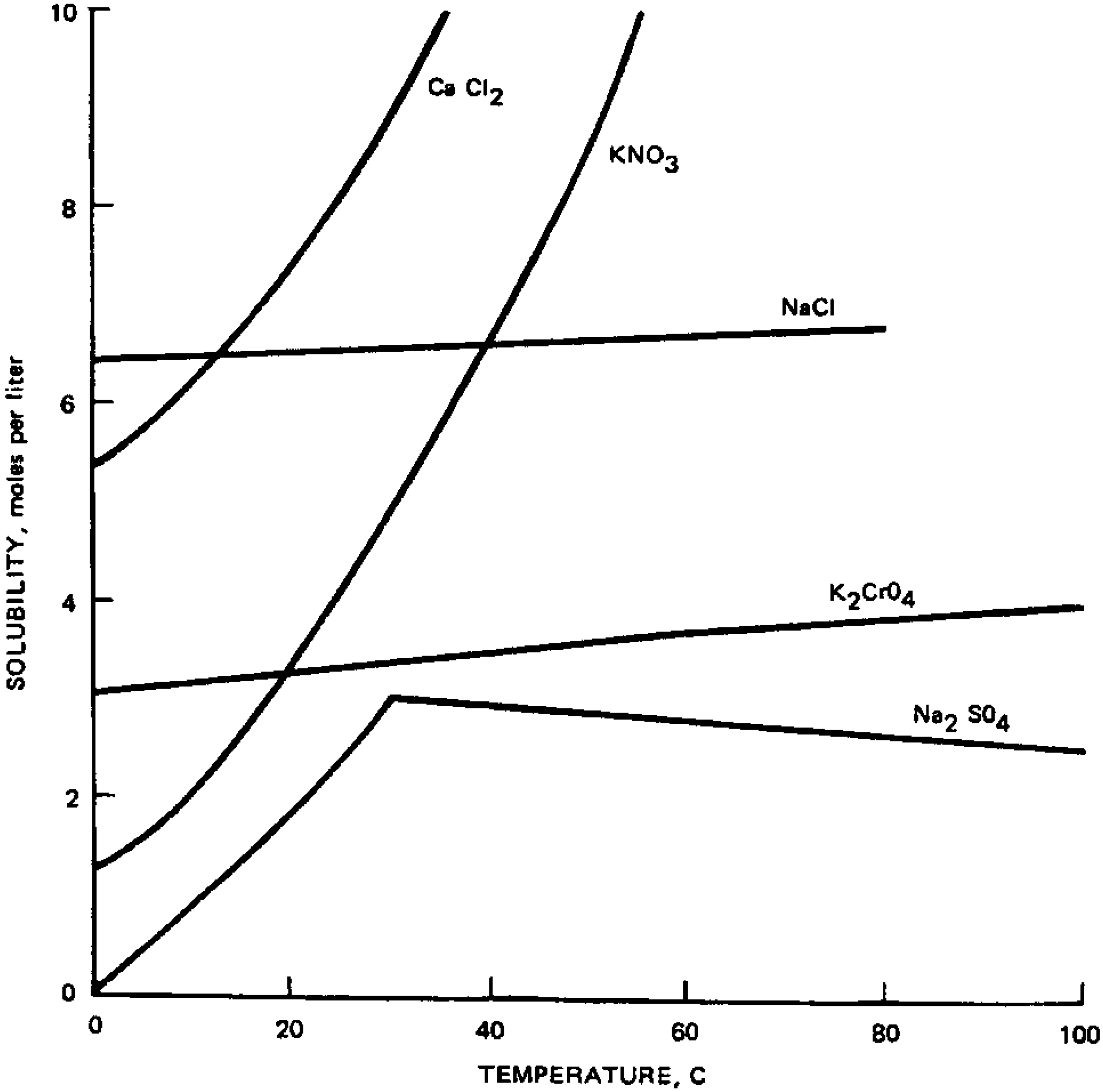


Figure 220-5-2 Solubility vs Temperature

220-5.7.2 **The property of decreasing solubility with increasing temperature is called inverse solubility** . Thus, $Na_2 SO_4$ is said to have an inverse solubility above about 30°C. If a $Na_2 SO_4$ solution is saturated at 30°C and the temperature is increased, the solubility will be exceeded and some of the $Na_2 SO_4$ will come out of solution. Such a process in which a solid separates from a solution is called **precipitation.**

220-5.7.3 If a compound used in a heat transfer system such as a marine boiler has an inverse solubility in the normal operating temperature range, the concentration of the compound must be carefully controlled. Otherwise, the high temperatures near heat transfer surfaces may cause the solubility to be exceeded and the compound will precipitate on hot surfaces. Such deposits would then reduce the heat transfer capability of the system.

220-5.7.4 Pressure has an insignificant effect on the solubility of solids in a liquid. The solubility of gases in a liquid, however, depends very strongly on both the temperature of the solution and the pressure of the gas. The solubility of gases is inversely proportional to the temperature of the solution (over the range 0 to 100°C) and directly proportional to the pressure of the gas. This behavior is treated in more detail in Section 6.

220-5.8 WATER AS A MEDIUM FOR CHEMICAL REACTIONS

220-5.8.1 Solid Na_2SO_3 reacts very slowly with oxygen in the atmosphere. If both are dissolved in water, the reaction takes place much more rapidly. This and countless other examples illustrate the ability of water to facilitate chemical reactions.

220-5.8.2 There are several reasons for the ability of aqueous solutions of compounds to react more readily than the solid compounds. One of the most fundamental reasons is the mobility of solute ions or molecules. For a chemical reaction to occur, the atoms, ions, or molecules of the reactants must come within a certain distance of each other. In solution, the solute ions or molecules are highly mobile and easily approach each other, whereas in the solid form, the molecules or ions are in relatively fixed positions. The water does not usually participate directly in the reaction. It simply provides a medium or environment in which the reaction takes place. For that reason, water is not shown in the chemical equations for such reactions.

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4 \quad (5\text{-}1)$$

This equation may be simplified even further. Sodium sulfite and sodium sulfate are ionic compounds and produce ions in solution, so the equation may be written:

$$4Na^{+} + 2SO_3^{-2} + O_2 \rightarrow 4Na^{+} + 2SO_4^{-2} \quad (5\text{-}2)$$

Since the Na^{+} ions do not participate in the reaction and are unchanged by it, they may be deleted.

$$2SO_3^{-2} + O_2 \rightarrow 2SO_4^{-2} \quad (5\text{-}3)$$

Such equations show only the ions and molecules directly involved in a chemical reaction and are called **ionic equations.**

220-5.9 ELECTRICAL PROPERTIES OF WATER AND AQUEOUS SOLUTIONS

220-5.9.1 To illustrate some of the important electrical properties of water and solutions, consider a simple electrical circuit (Figure 220-5-3) which includes an ordinary light bulb to indicate current flow and a container of pure water as part of the circuit. When a voltage is applied to this circuit by the battery, negligible current flows and the bulb does not glow. If sugar is added to the water, the bulb still does not glow (no current flow). If a small amount of NaCl is added to the water, the bulb glows dimly, and as more NaCl is added, the bulb glows more brightly. From this observation, it is concluded that neither pure water nor an aqueous sugar solution conducts electricity. An aqueous NaCl solution does conduct electricity and the amount of current flow is directly proportional to the concentration of NaCl in the solution.

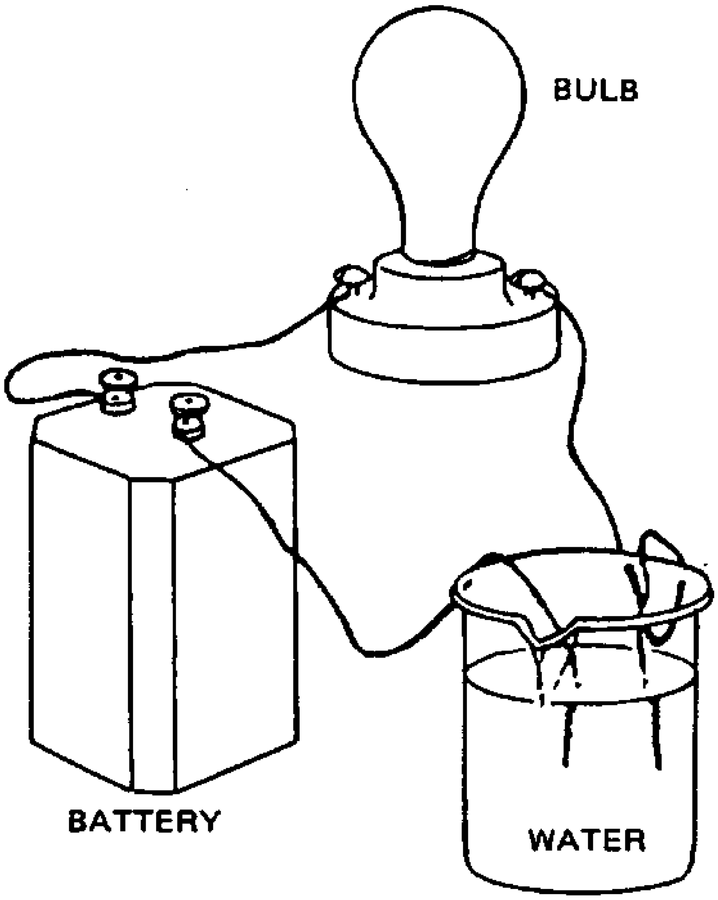


Figure 220-5-3 Current Flow Through Liquid

220-5.9.2 For current to flow through a liquid there must be ions in the liquid. Water is very slightly ionized but to such a small extent that the amount of current flow is insignificant. Sugar retains its molecular identity when dissolved in water, but NaCl dissociates entirely into Na^+ and Cl^- ions. The ions are free to move throughout the solution and, under the influence of an applied electrical potential, this movement constitutes a flow of electric current.

220-5.9.3 Compounds which form ions in aqueous solution and, thus, conduct electricity are called electrolytes. **All ionic compounds and some covalent compounds, such as HCl, are electrolytes** . Nonelectrolytes do not form ions in solution but exist as individual molecules.

220-5.9.4 As noted previously, the amount of current which a solution of an electrolyte is able to conduct is directly proportional to the concentration of ions. Since pure water is essentially nonconducting, a quantitative measurement of the ability of an aqueous solution to conduct electricity, conductivity, is an indication of the amount of ionic impurities (or solute) in the water. Before defining conductivity, first consider the more familiar concept of electrical resistance. For a particular solid conductor of length d and cross sectional area A, the resistance R is given by:

$$R \quad \rho d/A \qquad (5\text{-}4)$$

where ρ is a characteristic proportionality constant called resistivity.

220-5.9.5 The most convenient way of measuring the resistance of liquids is to construct a rigid cell having flat metallic plates (of surface area A) parallel to each other and held at some fixed distance, d, apart. A cell of this type measures the resistance of a section of liquid of length, d, and cross sectional area, A. For any particular cell, d and A are constant. The term d/A is called the cell constant and can be determined experimentally. If the same cell is used to measure the resistance of various solutions, the measured values of R will be directly proportional to the resistivity ρ.

220-5.9.6 Electrical resistance is inversely proportional to current flow. For solutions, this means that resistance is inversely proportional to concentration of electrolyte. It is conceptually simpler to use a quantity which is directly proportional to concentration, so**we define conductivity, L, as the reciprocal of resistivity** .

$L = l/\rho = d/RA$ (5-5)

Resistance, R, has the units ohms. If d is in cm and A is in cm^2 , L has the units:

$$\frac{\text{cmn}}{\text{ohm–cm}^2} = \frac{1}{\text{ohm . cm}}$$

The unit 1/ohm is called a mho, so conductivity has the units mho/cm. For very low values of conductivity, the units micromho/cm are frequently used. l µmho = 10^{-6} mho.

220-5.9.7 For any particular ion at a given ionic concentration, the conductivity due to that ion is independent of the source of the ion. That is, the contribution of Cl- ions to conductivity is the same in a 1M NaCl solution as it is in a 1M KCl solution. Let us define **molar ionic conductivity** , *l* , of a particular ion as the conductivity due to that ion in a solution containing one mole of that ion per liter. Table 220-5-1 lists the molar ionic conductivities of several ions. Thus, if the concentrations of all the ions in a solution are known, the total conductivity of the solution can be calculated. In general, **the conductivity, L, of a solution containing i different ions is:**

Table 220-5-1 MOLAR IONIC CONDUCTIVITIES

Ion	**mho/cm *l* , mole/liter**	**Ion**	**mho/cm *l* , mole/liter**
H_3O^+	0.350	PO_4^{-3}	0.303 (estimated)
B_a^{+2}	0.127	OH^-	0.198
Ca^{+2}	0.119	SO_4^{-2}	0.160
K^+	0.074	CO_3^{-2}	0.138
NH_4^+	0.073	HPO_4^{-2}	0.114
Ag^+	0.062	Cl^-	0.076
Na^+	0.050	NO3-	0.071
Li+	0.039	HCO_3^-	0.044
		$H_2PO_4^-$	0.033
where: L is in µmmho/cm *l* $_i$ is the molar ionic conductivity in the ith ion in c_i is the concentration of the ith ion in moles/liter			$\frac{\text{Mho/cm}}{\text{mole/liter}}$

Table 220-5-1 MOLAR IONIC CONDUCTIVITIES - Continued

Ion	**mho/cm** *l* **, mole/liter**	**Ion**	**mho/cm** *l* **, mole/liter**
10^6 is the factor for converting mhos to µmho. The summation sign, Σ means that the terms *l* c for all the ions are to be summed.			

Example 5-4: *Calculate the conductivity of:* (1) a 0.01 $\underline{M}$ NaOH solution,
(2) a 1 ppm NaCl solution,
(3) a solution which is 10^{-4} $\underline{M}$ in a Na_2SO_4 and 10^{-5} $\underline{M}$ in KCl.

Solution 5-4: *All parts use Equation (5-6) and data from Table 5-1*

(1) 0.01 $\underline{M}$ NaOH

$$L = 10^6 \, \Sigma \lambda_i c_i$$

$$= 10^6 \, (\lambda_{Li} c_{Li} + \lambda_{OH} c_{OH})$$

$$= 10^6 \, (0.05 \text{ x } 0.01 + 0.198 \text{ x } 0.01)$$

$$= 10^6 \, (5 \text{ x } 10^{-4} + 1.98 \text{ x } 10^{-3})$$

$$= 10^6 \, (2.48 \text{ x } 10^{-3})$$

$$= 2.48 \text{ x } 10^3 \ \mu\text{mho/cm}$$

(2) 1 ppm NaCl

Before Equation (5-6) can be used, the concentration must be converted to moles/liter.

1 ppm NaCl = 1 mg NaCl/liter of solution.

Convert 1 mg NaCl to moles of NaCl.

Formula weight of NaCl = 23 + 35.5 = 58.5 grams/mole

1 mg = 10^{-3} gram so,

$$\text{moles NaCl} = \frac{10^{-3} \text{ gram}}{58.5 \text{ grams/mole}} = 1.71 \text{ x } 10^{-5} \text{ mole.}$$

If $1.71 \text{ x } 10^{-5}$ *mole of NaCl dissolves,* $1.71 \text{ x } 10^{-5}$ *mole of* Na^+ *ions and* $1.71 \text{ x } 10^{-5}$ *mole of* Cl^- *ions are formed*

$$L = 10^6 \, (\lambda_{Na} c_{Na} + \lambda_{Cl} c_{Cl})$$

$$= 10^6 \, (0.050 \text{ x } 1.71 \text{ x } 10^{-5} + 0.076 \text{ x } 1.71 \text{ x } 10^{-5})$$

$$= 10^6 \, (8.55 \text{ x } 10^{-7} + 1.30 \text{ x } 10^{-6})$$

$$= 10^6 \, (2.16 \text{ x } 10^{-6})$$

$$= 2.16 \ \mu\text{mho/cm}$$

(3) 10^{-4} $\underline{M}$ Na_2SO_4 and 10^{-5} $\underline{M}$ KCl

In this case, we must note that if 10^{-4} *mole of* Na_2SO_4 *dis-*

solves, the concentration of Na^+ ions is 2×10^{-4} $\underline{M}$ and the concentration of SO_4^{-2} ions is 1×10^{-4} $\underline{M}$. Thus,

$$L = 10^6 (\ell_{Na} c_{Na} + \ell_{SO4} \; c_{SO4} + \ell_K c_K + \ell_{Cl} c_{Cl})$$

$$= 10^6 (0.050 \times 2 \times 10^{-4} + 0.160 \times 10^{-4}$$

$$+ 0.074 \times 10^{-5} + 0.076 \times 10^{-5})$$

$$= 10^6 (1 \times 10^{-5} + 1.60 \times 10^{-5} + 0.074 \times 10^{-5}$$

$$+ 0.076 \times 10^{-5})$$

$$= 10^6 (2.75 \times 10^{-5})$$

$$= 27.5 \; \mu mho/cm$$

220-5.9.8 Actually, equation (5-6) is true only for very dilute (less than ~ 0.001M) solutions. Above this concentration there is a small but detectable interaction between ions in a solution, and the molar ionic conductivities are not exactly constant with increasing concentration. For simplicity and because these ionic interactions are usually small, this text assumes that the ions are independent and that equation (5-6) is true at all concentrations.

220-5.9.9 Conductivity alone does not indicate which ions are in a solution, it only provides an indication of the total amount of all ionic substances in a solution. In Example 5-4 it was shown that 1 ppm NaCl solution has a conductivity of about 2.2 µmho/cm. A 1 ppm solution of most ionic compounds will have a conductivity in the range 2 to 12 mmho/cm. Pure water has a conductivity of 0.05 µmho/cm. Table 220-5-2 lists typical conductivities for various types of water.

Table 220-5-2 TYPICAL CONDUCTIVITIES OF WATER

Source of Water	L, µmho/cm
Steam plant condensate	1 to 2
Distilled water	1 to 5
Typical tap water	500 to 1000
Boiler water	430 to 930
Seawater	70,000 to 80,000

220-5.10 SUMMARY

220-5.10.1 The general solubility rule, **like dissolves like** , indicates that polar liquids usually dissolve ionic and polar solids, and nonpolar liquids usually dissolve nonpolar solids. The solubility of most solids increases as the temperature of the solvent increases, but some solids have an inverse solubility. Ionic compounds and some covalent compounds form ions when they dissolve. Such compounds are called electrolytes and their solutions are conductors of electricity. The conductivity of a solution is a measure of the total amount of electrolytes contained in the solution.

SECTION 5 PROBLEMS

1. How many grams of NaCl must be added to 5 liters of water to prepare a 0.02$\underline{M}$ solution?
2. Calculate the concentration in ppm of Cl- ion in a 0.05$\underline{M}$ NaCl solution and a 0.05$\underline{M}$ $CaCl_2$ solution.
3. If 200 ml of a 0.5$\underline{M}$ NH_4 Cl solution are mixed with 600 ml of a 1.5$\underline{M}$ NH_4 Cl solution, what is the molar concentration of NH_4 Cl in the final solution?
4. A solution which contains 1 mole/liter of $AgNO_3$ is added to 500 ml of a NaCl solution until no more precipitate forms. The precipitate is collected, dried, and weighed. If the weight of the precipitate is 3.15 grams, what was the molar concentration of NaCl in the initial solution? (Assume AgCl is completely insoluble.)
5. Calculate the conductivity of a 0.5$\underline{M}$ K_2 SO_4 solution.
6. Three-hundred milliliters of a 2 x 10-3$\underline{M}$ LiCl solution are added to 200 ml of a 1 X 10-3$\underline{M}$ NH_4 NO_3 solution. What is the conductivity of the final solution?
7. Calculate the conductivities of all the solutions described in Problem 3, i.e., before and after mixing.

SECTION 5 PROBLEM ANSWERS

1. 5.85 grams NaCl.
2. 1770 ppm Cl^- in a 0.05$\underline{M}$ NaCl solution. 3550 ppm Cl^- in a 0.05$\underline{M}$ $CaCl_2$ solution.
3. 1.25$\underline{M}$ NH_4 Cl.
4. Initial solution is 0.044$\underline{M}$ NaCl.
5. 1.54×10^5 µmho/cm.
6. 1.96×10^2 µmho/cm.
7. 0.5$\underline{M}$ NH_4 Cl solution: L = 7.45×10^4 µmho/cm. 1.5$\underline{M}$ NH_4 Cl solution: L = 2.24×10^5 µmho/cm. 1.25$\underline{M}$ NH_4 Cl solution: L = 1.86×10^5 µmho/cm.

SECTION 6.

GASES AND THEIR AQUEOUS SOLUTIONS

220-6.1 INTRODUCTION

220-6.1.1 The historical development of many of the fundamental principles of chemistry was either based on or supported by direct experimental observations on gases. Among these principles are the law of definite proportions, the law of conservation of atoms in chemical reactions, Avogadro's number, and the atomic theory of matter.

220-6.1.2 The reason for the fundamental role of gases in the development of chemistry is the great similarity in the physical behavior of all gases. This chapter reviews the laws which describe the interrelationships among pressure, volume, temperature, and quantity of gases. The factors which affect the solubilities of gases in water are also discussed.

220-6.2 GLOSSARY OF TERMS

220-6.2.1 Terms used in this section are defined as follows:

a. **Absolute Pressure:** The actual pressure on a system, as opposed to gage pressure which is usually the difference between actual pressure and atmospheric pressure.

b. **Absolute Temperature:** Any temperature expressed on a scale on which zero corresponds to the lowest temperature theoretically possible. The most common absolute scales are Kelvin and Rankine.

c. **Avogadro's Law:** Equal volumes of gases measured at the same temperature and pressure contain the same number of molecules or moles.

d. **Boyle's Law:** The volume occupied by a given amount of a gas is inversely proportional to absolute pressure at constant temperature.

e. **Charles' Law:** The volume occupied by a given amount of a gas is directly proportional to absolute temperature at constant pressure.

f. **Dalton's Law of Partial Pressures:** The partial pressure of any component of a mixture of gases is the pressure which that component would exhibit if it were the only gas at the same temperature and confined in the same volume. Further, the total pressure of a mixture of gases is the sum of the partial pressures of all the components.

g. **Henry's Law:** At a given temperature, the solubility of a gas in water is directly proportional to the partial pressure of the gas above the surface of the water.

h. **Ideal Gas:** A hypothetical gas which is described exactly by the kinetic theory of gases and obeys the ideal gas law.

i. **Ideal Gas Law:** $PV = nRT$; Exactly describes the physical behavior of an ideal gas and approximately describes the behavior of real gases under ordinary conditions of temperature and pressure.

j. **Kinetic Theory of Gases:** A theory which describes a gas as being composed of rigid, spherical molecules or atoms in constant motion with no forces of attraction between molecules or atoms.

k. **Molar Gas Volume:** The volume occupied by one mole of a gas at standard temperature and pressure (22.4 liters/mole).

l. **Standard Temperature and Pressure:** 0°C (32°F) and 1 atmosphere (14.7 psia or 760 mm Hg) pressure.

m. **Vapor Pressure of Water:** The partial pressure due to water vapor which is always present in the gas phase above the surface of water.

220-6.3 THE GAS STATE

220-6.3.1 GENERAL. A classical theory concerning gases was developed more than 100 years ago and is called the **kinetic theory of gases** . This theory provides a general description of the gas state and from this theory most of the laws which describe the physical behavior of gases can be derived. Although the theory and derivations are not considered in detail in this text, the broad features of the kinetic theory are useful in understanding the relations which are discussed.

220-6.3.1.1 The kinetic theory treats the molecules or atoms of a gas as rigid spheres of negligible volume which are in constant rapid motion and, on the average, relatively far apart. The average distance between molecules depends on the total number of molecules and the volume in which they are confined. The only interactions between molecules are assumed to be elastic collisions such as those between billiard balls, i.e., it is assumed that there are no forces of attraction (such as chemical bonding or van der Waals forces) between molecules. As a result of these assumptions it can be shown that the average kinetic energy of the molecules is proportional to the temperature of the system and that pressure is the average force exerted on the walls of the container by the collisions of the gas molecules with the walls.

220-6.3.1.2 In reality, no gas behaves exactly as described by the kinetic theory, although all gases approach such behavior at high temperatures and low pressures. Thus, the kinetic theory is said to describe the behavior of an ideal gas. The laws described in the following paragraphs apply strictly only to an ideal gas, but paragraphs 220-6.3.6 through 220-6.3.6.2 present evidence that they often closely approximate the behavior of real gases.

220-6.3.2 ABSOLUTE TEMPERATURE AND PRESSURE. As noted in paragraphs 220-6.3 through 220-6.3.1.2, the kinetic energy of gas molecules is proportional to temperature. This proportionality and others in subsequent sections assume their simplest form if temperature is expressed on an absolute scale. An absolute temperature scale is one on which zero corresponds to the lowest temperature theoretically possible. Thus there cannot be negative temperatures on an absolute scale. The most common absolute temperature scale is the Kelvin scale, although the Rankine scale is often used in engineering in the United States.

220-6.3.2.1 Divisions on the Kelvin (K) scale are the same as those on the Celsius scale. Zero on the Celsius scale corresponds to 273°K, so temperatures on either of these scales are easily converted to the other scale by the general relationship:

$K = C + 273$ (6-1)

220-6.3.2.2 Divisions on the Rankine (K) scale are the same as those on the Fahrenheit scale. Zero degrees Fahrenheit corresponds to 460°R, so the general relationship between these scales is:

$R = F + 460$ (6-2) For converting between Celsius and Fahrenheit scales, the relationship is:

$F = 9/5C + 32$ (6-3) The physical significance of absolute temperature is that at absolute zero, all molecular motion ceases. Although temperatures as low as 0.001°K have been reached, there are good theoretical reasons for believing that absolute zero can never be attained.

220-6.3.2.3 Expressing pressure on an absolute basis does not require a new pressure scale. It does require recognition of what a pressure gage measures. A pressure gage indicates the difference in pressure between two different systems. Most commonly, one of the systems is the atmosphere, so the gage indicates the difference between atmospheric pressure (14.7 psi at sea level, on the average) and the pressure of the system of interest. For instance, if the gage on a cylinder of gas indicates zero (0 psig), the actual or absolute pressure (psia) inside the cylinder is the same as the external atmospheric pressure. Should the pressure in the cylinder drop below the external atmospheric pressure, the internal pressure is referred to as a vacuum pressure. In general:

Absolute pressure (psia) = gage pressure (psig) + atmospheric pressure (6-4) The more common units of pressure are psi, atmospheres (atm.), and millimeters of mercury (mmHg) for which the following identities are applicable.

14.7 psia = I atm. = 760 mmHg

220-6.3.3 THE GAS LAWS. In describing the physical behavior of gases there are four variables to be considered: (1) **the amount of gas, usually expressed as the number of moles, n, (2) temperature, T, (3) pressure, P** , and **(4) volume, V** , occupied by the gas. Paragraphs 220-6.3.3.1 through 220-6.3.3.4 first present the law which relates all four variables and then show how more limited, simpler laws result from the general law if some of the variables are constant.

220-6.3.3.1 The Ideal Gas Law. The ideal gas law is a general description of the physical behavior of an ideal gas and is stated mathematically as:

$$PV = nRT \quad (6\text{-}5)$$

where:

P	is absolute pressure
V	is volume
n	is the number of moles of gas
T	is the absolute temperature
R	is a constant The constant R is called the ideal or universal gas constant because it is independent of the variables P, V, T, and n. Values of R in various units are given in Table 220-6-1. If three of the variables in equation (6-5) are fixed, the fourth can be determined using this equation.

Table 220-6-1 VALUE OF THE UNIVERSAL GAS CONSTANT, R

Value	**Units**
0.08206	(liter-atm)/(mole-°K)
0.0456	(liter-atm)/(mole-°R)
82.06	(ml-atm)/(mole-°K)
62.4	(liter-mm Hg)/(mole-°K)
1.61×10^{-3}	(ft^3 -atm)/(mole-°K)
0.67	(liter-atm)/(mole-°K)
2.37×10^{-2}	

220-6.3.3.1.1 A useful form of the ideal gas law is obtained by considering an ideal gas at the initial conditions n_1 , P_1 , V_1 , and T_1 . Thus,

$$\frac{P_1V_1}{n_1T_1} = R$$

If the conditions are changed to n_2, P_2, V_2, and T_2, then:

$$\frac{P_2V_2}{n_2T_2} = R$$

Since R is constant,

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

Example 6-1: *Consider a 0.9-cubic-foot tank containing oxygen. The pressure exerted by the gas is 875 psia at 70°F. Calculate the number of moles and the grams of oxygen in the tank.*

Solution 6-1: *Apply the ideal gas law to estimate the number of moles of oxygen.*

$$PV = nRT$$

$$P = 875 \text{ psia}$$

$$V = 0.9 \text{ ft}^3$$

$$T = (F + 460)R = (70 + 460)R = 530°R$$

$$R = 1.61 \text{ x } 10^3 \text{ (ft}^3\text{-atm)/(mole-°R) (table 220-10)}$$

$$n = ?$$

To use R in (ft^3-atm)/(mole-°R), P must be in atmospheres

$$P = (875 \text{ psia}) \frac{(1 \text{ atm})}{(14.7 \text{ psia})} = 59.6 \text{ atmospheres}$$

$$PV = nRT \text{ or } n = \frac{PV}{RT}$$

$$n = \frac{(59.6 \text{ atm}) \; 0.9\text{ft}^3}{(1.61 \text{ x } 10^{-3} \text{ ft}^3 \text{ atm/mole °R}) \; (530°\text{R})}$$

$$= \frac{(59.6) \; (0.9)}{(530) \; (1.61 \text{ x } 10^{-3})} \text{ moles} = 62.8 \text{ moles}$$

To calculate grams, we need the formula weight for O_2.

formula weight O_2 = 32.0 grams/mole

Weight O_2 = (62.8 moles) (32.0 grams/mole) = 2010 grams.

220-6.3.3.2 Boyle's Law: **Constant Temperature and Amount** . Suppose the amount of gas, n, and the temperature, T, are held constant and V and P are allowed to change. Then, in equation (6-6), $n_1 T_1 = n_2 T_2$ so these terms cancel and the equation becomes:

$$P_1V_1 = P_2V_2 \text{ (at constant n and T)}$$

In order for Equation (6-6) to be true, both sides must equal a constant:

$$P_1V_1 = P_2V_2 = \text{a constant, } k(n, T)$$

or more generally;

$$PV = k(n, T)$$

$$V = \frac{k(n, T)}{P}$$

NOTE

The constant is written in the form k(n, T) to emphasize that it is truly constant only if n and T are constant.

220-6.3.3.2.1 Equations (6-7) and (6-8) are mathematical expressions of Boyle's law which states: **The volume occupied by a given amount of gas is inversely proportional to the pressure applied to the gas if the temperature is constant** . Equation (6-7) is usually the most useful form of Boyle's law because it does not require a specific value for the constant k (n, T).

220-6.3.3.2.2 A familiar example of the relationship expressed by Boyle's law is a hand-operated air pump. As the plunger is forced down, the volume of the trapped gas (air) decreases and pressure increases until the pressure in the pump exceeds the pressure inside the object being inflated. Since pressure is the result of collisions of gas molecules with the walls of the container, the kinetic theory explanation of Boyle's law is as follows. A decrease in the volume in which a gas is confined reduces the free space in which the gas molecules travel. Thus, the frequency of gas molecules colliding with the walls of the container increases and this is observed as an increase in pressure.

Example 6-2: A 10-cubic-foot tank contains nitrogen at a pressure of 100 psig.

Example 6–2: A 10–cubic–foot tank contains nitrogen at a pressure of 100 psig.

This tank is valve-connected to another tank with a volume of 30-cubic-feet, and initially under a vacuum (0 psia). The valve is opened and the gas is allowed to expand into the 30-cubic-foot tank at constant temperature. (It may be noted that to maintain constant temperature, some amount of heat must be added to the system during the expansion process.) Calculate the new pressure gage reading.

Solution 6-2: *Boyle's law applies because temperature is constant and the amount of gas in the total system (10 cu ft + 30 cu ft = 40 cu ft) has not changed. Thus,*

$$P_1V_1 = P_2V_2$$

Note that P_1 is given as a gage pressure and the equation requires absolute pressure.

$$P_1 \text{ (absolute)} = P_1 \text{ (gage)} + 14.7 \text{ psia}$$

$$= 100 \text{ psig} = 14.7 \text{ psia}$$

$$P_1 = 114.7 \text{ psia}$$

From the other information given:

$$V_1 = 10 \text{ cu ft}$$

$$V_2 = 40 \text{ cu ft}$$

P_2 *unknown*

$$P_2 = \frac{P_1 V_1}{V_2}$$

$$= \frac{114.7 \text{ psia x } 10 \text{ cu ft}}{40 \text{ cu ft}}$$

$$= 28.68 \text{ psia}$$

To convert this to a gage pressure:

$$P_2 \text{ (gage)} = P_2 \text{ (absolute)} - 14.7 \text{ psia}$$

$$= 28.68 \text{ psia} - 14.70$$

$$P_2 = 13.98 \text{ psig}$$

220-6.3.3.3 Charles' Law: Constant Pressure and Amount. Again consider the ideal gas law, equation (6-6), and suppose that n and P are constant. Thus,
and the result is:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ (at constant n and P)} \qquad (6\text{-}9)$$

Since both sides of this equation must equal a constant, the general expression is:

V = k(n, P)T (6-10) Equations (6-9) and (6-10) are forms of Charles' law: **The volume occupied by a given amount of gas is directly proportional to absolute temperature if pressure is constant** .

220-6.3.3.3.1 This relationship between volume and temperature of a gas at constant pressure is illustrated in Figure 220-6-1. A drop of mercury is placed in a small-bore glass tube closed at one end. The mercury plugs the tube and falls, trapping a quantity of air in the tube. As the tube is alternately placed in ice-water and boiling water the trapped air contracts and expands. The mercury plug moves up and down the tube exerting a constant pressure on the trapped air. In terms of the kinetic theory, the temperature-volume relationship is due to the direct proportionality between temperature and the velocity of gas molecules. Thus, if temperature increases, the gas molecules travel more rapidly and collide with the restraining boundaries more frequently and with greater force. In the example above, one boundary (the mercury plug) is movable and exerts a constant pressure, so the plug is forced upward by the increased force and frequency of the collisions.

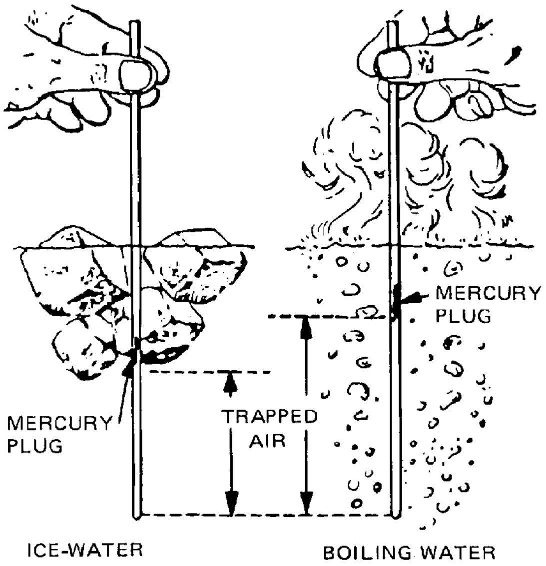


Figure 220-6-1 Demonstrating Effect of Temperature on Volume of a Gas

Example 6-3: An upright cylinder is closed at the bottom and open at the top. The cylinder is located in a room containing a pure N_2 atmosphere. An air-tight, frictionless piston is allowed to drop into the cylinder and falls until the trapped gas supports the weight of the piston. The volume of the trapped gas is 5 liters at 25°C. If the temperature of the gas in the cylinder is then increased to 120°C, calculate the volume of the trapped gas.

Solution 6-3: Since the piston is an air-tight, frictionless fit, it rides on the gas exerting a constant pressure and preventing any gas from escaping. Thus, Charles' law applies:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_1 = 5 \text{ liters}$$

$$T_1 = 25°C = (25 + 273)K = 298°K$$

$$T_2 = 120°C = (120 + 273)K = 393°K$$

$$V_2 = V_1 \frac{T_2}{T_1}$$

$$= 5 \text{ liters} \quad \frac{393°K}{298°K}$$

$$= 6.60 \text{ liters}$$

220-6.3.3.4 Avogadro’s Law: Constant Temperature and Pressure. As a final special case of the ideal gas law, consider temperature and pressure constant. Equation 6-6 then becomes:

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} \text{ (at constant P and T)}$$

or, in general,

$$V = n\, k(T, P)$$

where k (T, P) is a constant dependent on temperature and pressure. This may be considered a form of Avogadro’s law and means that the volume occupied by a gas is directly proportional to the amount of gas at constant temperature and pressure.

220-6.3.3.4.1 This relationship is illustrated by inflating an air-mattress, for example. If the mattress is completely deflated initially, the volume of gas inside is zero. As air is added, the volume increases and the mattress inflates. Neglecting the weight of the mattress material, the pressure of the gas inside is the same as the external atmospheric pressure and remains so until the mattress is just filled. (Usually, more air is added to pressure the mattress and provide the cushioning effect.) The kinetic theory explanation of the relationship is just a numbers effect. Temperature does not change so the molecules do not move faster or slower, but as more molecules are added, the greater the frequency of molecule-wall collisions and the extra force pushes back any movable, constant-pressure restraint. (Actually, the temperature would change because the gas must perform work to move the restraint, but this can be compensated for by adding heat to the system.)

Question: Avogadro originally stated his relationship as the hypothesis (now accepted as a law): Equal volume of different gases measured at the same temperature and pressure contain equal numbers of molecules (or atoms). Is equation (6-11) consistent with this statement?

220-6.3.4 STANDARD TEMPERATURE AND PRESSURE. Avogadro’s law states that equal volumes of gases measured at the same temperature and pressure contain equal numbers of moles of gas. To provide a common basis for comparing many different measurements, one particular temperature and one particular pressure are selected as Standard Temperature and Pressure (STP). **The exact values of STP agreed upon by convention are 0°C (273°K, 32°F, or 492°R) and 1 atmosphere (760 mm Hg or 14.7 psia) pressure** . The actual measurement of the volume of a gas may be performed at any temperature and pressure. Then the volume at STP can be calculated using the ideal gas law.

220-6.3.5 MOLAR GAS VOLUME. An important feature of Avogadro's law becomes more apparent when the law is stated: equal numbers of moles of different gases occupy the same volume when measured at the same temperature and pressure. This means that the **volume of one mole of any gas at STP is a constant** . The value of the constant can be calculated by substituting values of STP, n and R in equation (6-5).

$$PV = nRT \qquad (6\text{-}13)$$

$$V = \frac{nRT}{P}$$

$$= \frac{1 \text{ mole} \times 0.082 \ \frac{\text{liter atmosphere}}{\text{mole-°K}} \times 273\text{°K}}{1 \text{ atmosphere}}$$

$$= 22.4 \text{ liters}$$

Thus, one mole of a gas at STP occupies 22.4 liters. This value is called the molar gas volume.

220-6.3.5.1 The observation that the molar gas volume is a constant provides another way of viewing the chemical equations for reactions which involve gases. Consider the reaction of nitrogen and hydrogen to form ammonia:

$N_2 + 3H_2 \rightarrow 2NH_3$ (6-14) All the reactants and the product are gases at ordinary temperatures and pressures. As discussed in Section 3, the relative numbers of molecules or moles of reactants and products are the same as the ratios of the numerical coefficients in the balanced equation. For gases this statement can be expanded to: The relative volumes of reactants and products at the same temperature and pressure are the same as the ratios of the numerical coefficients in the balanced equation. Thus, for the reaction described by equation (6-14), 1 liter of N_2 reacts with 3 liters of H_2 to form 2 liters of NH_3 (all at the same temperature and pressure). This statement could also be in units of cubic feet or gallons, or the generalized term volume. One volume of N_2 reacts with 3 volumes of H_2 to form 2 volumes of NH_3 . The only conditions are that the volumes be in the same units and that all be at the same temperature and pressure.

220-6.3.6 IDEAL VERSUS REAL GASES. An ideal gas may be defined as one which behaves according to the ideal gas law or one which is described exactly by the kinetic theory of gases. Real gases deviate from the kinetic theory assumption that no forces of attraction exist between gas molecules (or atoms). Real gas molecules do experience such forces, the theory of which was first proposed by van der Waals to account for the deviation of real gases from ideal behavior.

Question: All real gases condense to liquids at some temperature and pressure. Does this experimental observation argue for the existence of attractive forces between gas molecules?

220-6.3.6.1 Real gases approach ideal behavior most closely under conditions which reduce the effects of the van der Waals forces. In general, these conditions are low pressure and high temperature. Even at STP, however, it is found that most gases obey the ideal gas law fairly well. One measure of this approach to ideal behavior is the molar gas volume. Experimental values of molar gas volume for several gases are given in Table 220-6-2. (Values in the table are given to three decimal places to allow precise comparisons between ideal and real gases.)

Table 220-6-2 MOLAR VOLUMES OF SOME GASES AT STP

Gas	Formula	Molar Volume at STP (liters)
Hydrogen	H_2	22.430
Helium	He	22.426
Ideal gas	—	22.414
Nitrogen	N_2	22.402
Carbon monoxide	CO	22.402
Oxygen	O_2	22.393
Methane	CH_4	22.360
Carbon dioxide	CO_2	22.262
Hydrogen chloride	HCl	22.248
Ammonia	NH_3	22.094
Chlorine	Cl_2	22.063
Sulfur dioxide	SO_2	21.888

220-6.3.6.2 Note that all the experimental values listed in the table are within 2 percent of the ideal gas value. In most calculations then, it is valid to assume that real gases obey the ideal gas law. Unless specifically stated otherwise, that assumption is used throughout this text, with the following important exception. Steam does not approach ideal behavior at ordinary temperatures and pressures. To illustrate this deviation of steam from ideal gas behavior, saturated steam at 425°F and 323.5 psia has a molar volume of 1.60 filters/mole. For the same conditions, the molar volume of an ideal gas is 1.83 liters/mole. The molar volume of steam is about 15 percent lower than the ideal gas value. This is largely due to hydrogen bonding between H_2 O molecules (Section 3). The properties of steam should be obtained from steam tables rather than by application of the ideal gas law.

220-6.3.7 DALTON’S LAW OF PARTIAL PRESSURES. Previous paragraphs describe the behavior of pure gases. Paragraph 220-6.3.7.1 deals with mixtures of gases. (All mixtures of gases are gaseous solutions because they are completely homogeneous; however, they are commonly referred to as mixtures.)

220-6.3.7.1 Similar to a pure gas, a mixture of gases confined in a volume V at a temperature T will exert some pressure P on the container. The contribution of a particular component of the mixture to the total pressure is called the partial pressure, p, of that component. Dalton’s law of partial pressures states that the partial pressure of each component of a mixture of gases is just the pressure which that gas would exhibit if it were the only gas in the container at the specified temperature. This means that the total pressure, P_t , is simply the sum of the partial pressures of all components of the mixture, i.e.:

The term n_i /n_t is called the mole fraction of component i. equation (6-20) means that the partial pressure of

$$P_t = p_1 + p_2 + p_3 + \ldots \qquad (6\text{-}15)$$

For any component, i, the partial pressure can be expressed in terms of the ideal gas law as:

$$p_i = \frac{n_i R T_i}{V_i} \qquad (6\text{-}16)$$

Thus,

$$P_t = \frac{n_1 R T_1}{V_1} + \frac{n_2 R T_2}{V_2} + \frac{n_3 R T_3}{V_3} + \ldots \qquad (6\text{-}17)$$

Because of the entire volume, V, of the container is available to each component and temperature T is uniform throughout the mixture, all the T's and V's in Equation (6-17) are the same and the equation can be written:

$$P_t = (n_1 + n_2 + n_3 + \ldots)\frac{RT}{V} \qquad (6\text{-}18)$$

or,

$$P_t = n_t \frac{RT}{V} \qquad (6\text{-}19)$$

when n_t is the total number of moles of all gases in the mixture.

Equation (6-16) can be divided by Equation (6-19) to give:

$$\frac{p_i}{P_t} = \frac{n_i \frac{RT}{V}}{n_t \frac{RT}{V}} = \frac{n_i}{n_t}$$

or,

$$p_i = \frac{n_i}{n_t} P_t \qquad (6\text{-}20)$$

component i is the product of the mole fraction of i and the total pressure.

Example 6-4: The composition of air is given in Table 220-6-3. Estimate the partial pressures of N_2 , 0_2 , and Ar in a sample of air at atmospheric pressure.

Table 220-6-3 AVERAGE COMPOSITION OF DRY AIR AT SEA LEVEL

Component	**Percent (by volume)**
Nitrogen (N_2)	78.1
Oxygen (O_2)	21.0
Argon (Ar)	0.93
Carbon dioxide (CO_2)	0.033
Neon (Ne)	0.002

Solution 6-4: *The solution to this problem becomes very simple if the relationship between volume fraction (or percent) and mole fraction is recognized.*

$$\text{Volume fraction of component } i = \frac{V_i}{V\ total} = X_i$$

$$(\text{Volume \% of } i = X_i \times 100)$$

where V_i *is the volume which* n_i *moles of pure i would occupy if subjected to the same temperature and total pressure as the mixture, that is, if* $p_i = P_t$

Now solve the ideal gas law for V and substitute into the above expression for volume fraction.

$$V = \frac{nRT}{P}$$

$$\frac{V_i}{V_t} = \frac{n_i \frac{RT}{p_i}}{n_t \frac{RT}{P_t}}$$

By the definition of V_i , $p_i = P_t$, *so*

$$\frac{V_i}{V_t} = \frac{n_i}{n_t} = X_i$$

Thus, volume fraction (or volume % 100) is numerically equal to mole fraction, and the problem can be solved using Equation (6-20), substituting the volume fraction (X_i) *for the mole fraction* (n_i/n_t).

$$p_i = \frac{n_i}{n_t} P_t$$

For N_2

$$p_{N_2} = (\text{volume fraction})\ P_t$$

$$= (0.781)\ 14.7\ \text{psia} = 11.48\ \text{psia}$$

For O_2

$$p_{O_2} = (\text{volume fraction})\ P_t$$

$$= (0.21)\ 14.7\ \text{psia} = 3.09\ \text{psia}$$

For Ar

$$p_{Ar} = (\text{volume fraction})\ P_t$$

$$= (0.0093)\ 14.7\ \text{psia} = 0.14\ \text{psia}$$

220-6.4 AQUEOUS SOLUTIONS OF GASES

220-6.4.1 GENERAL. All gases dissolve in water to some extent. In general, the solubility of a gas increases with increasing pressure of the gas. In order to dissolve, a gas molecule must strike the surface of the water. An increase in pressure implies either an increase in gas concentration (by reducing the volume or increasing the amount) or an increase in the velocity of the gas molecules (increase in temperature at constant volume). Either effect results in a greater number of gas molecules striking the liquid surface per unit time and thus a greater number of molecules are dissolved.

220-6.4.1.1 In addition, the solubility of a gas in water generally decreases with increasing temperature of the solution over the range of temperatures from 32°F to about 200°F. Dissolved gas molecules are also in constant motion although movement is more restricted in the liquid than in the gaseous state. Thus, there is always a chance that the motion of a dissolved molecule will carry it to the liquid surface and out of solution again. As the temperature of the liquid increases the velocity of dissolved molecules also increases and so does the probability that a molecule will escape from the solution.

220-6.4.1.2 Under ordinary temperatures (0-100°C) and pressures (0-10 atm) the solubility of most gases in water is low. For example, the solubility of oxygen at 1 atmosphere in water at 0°C is 6.98×10^{-2} gram/liter or 2.18×10^{-3} mole/liter. To avoid working with such small numbers, the concentrations of gases in aqueous solutions are usually expressed in units of cubic centimeters (cc) of gas, at STP, per kilogram (kg) of solution, cc (STP)/kg. In practice, the concentration of a gas can be determined by stripping the gas from a known weight of solution and measuring the volume of gas at any known temperature and pressure. The volume can then be corrected to STP using the ideal gas law in the form given by equation 6-6. This volume in cc, divided by the weight of the original solution, in kg, gives the concentration in units of cc (STP)/kg. This is often written as just cc/kg but it must be understood that the volume is always referred to STP unless other conditions are specifically stated.

220-6.4.2 HENRY’S LAW. The effect of pressure on the solubility of a gas in water is described quantitatively by Henry’s law. For a pressure, P, of a pure gas in direct contact with water at a temperature, T, the maximum concentration (solubility) of gas in the water is given by:

$C = H(T)P$ (6-21) where H(T) is the Henry's law constant for that particular gas and that temperature T of the solution. If P is in atm and C is in cc/kg, then H(T) has the units atm/cc/kg.

NOTE

Some texts state Henry's law in the form:

$$C = \frac{P}{H(T)}$$

Thus, the constant H(T) as used in this text is the reciprocal of the constant in the alternate form:

$$H(T) = \frac{1}{H(T)}$$

The form used here was chosen for its simplicity and ease of use.

In the case of a mixture of gases, rather than a pure gas, in contact with the water, the partial pressure of each component of the mixture must be used in equation (6-21). Thus, for component, i:

$C_i = H_i\ (T)p_i$ (6-22)

220-6.4.2.1 Henry's Law Statement. **In effect, Henry's law says that the solubility of a gas in water is directly proportional to the partial pressure of the gas above the surface of the water.** If the concentration of a gas in water is at its maximum value for a given partial pressure and the partial pressure is then increased, more of the gas will dissolve. If the partial pressure is reduced, some of the gas will come out of solution, often with the formation of bubbles in the water. For a given amount of gas in a pressurized water system, if the pressure of the water is greater than the partial pressure necessary to maintain the gas concentration in the solution, all the gas in the system will be dissolved and there will be no gas space. If the pressure is then reduced to less than the partial pressure corresponding to the concentration of gas in solution, bubbles of gas may start to form in the water. A common example of this phenomenon is the foaming (gas coming out of solution) which occurs when the cap is removed (sudden decrease in pressure) from a bottle of carbonated beverage.

220-6.4.2.2 Applicability of Henry's Law. Under some conditions, Henry's law is not an accurate description of aqueous solutions of gases. If a gas undergoes a chemical reaction with water, the validity of Henry's law cannot be predicted. The gases HCl (hydrogen chloride), NH_3 (ammonia), and CO_2 (carbon dioxide) all react with water. It has been found experimentally that Henry's law does not apply to solutions of HCl and NH_3 .The law does adequately describe the solubility of CO_2 in water up to partial pressures of a few atmospheres.

220-6.4.2.2.1 Another factor affecting the applicability of Henry's law is the concentration of gas in the solution. Generally, the law holds up to about 1000 cc/kg. Since, according to Henry's law, concentration is proportional to pressure, the concentration limit can be translated into a partial pressure limit of 68 to 100 atm (1000 to 1500 psia) for common gases such as O_2 , H_2 , and N_2 . Below these limits, Henry's law can be used with reasonable confidence.

220-6.4.2.3 The Henry's Law Constant. In order to apply Henry's law, the value of the constant, H(T), must be known for the particular gas and temperature involved. Such values are determined by experiment. The results are often shown in the form of graphs of H(T) versus T for a particular gas. Such graphs for several gases are given in Figure 220-6-1 and Figure 220-6-2. Notice in Figure 220-6-2, that the values of H(T) for O_2 , H_2 and N_2 , increase above about 200°F. This indicates the solubilities of these gases increase with increasing temperature above 200°F.

220-6.4.2.3.1 Within the limits given in paragraphs 220-6.4.2.2 and 220-6.4.2.2.1, the value of H(T) for a particular gas and a given temperature can be used at any pressure. If the temperature of the water changes, the value of H(T) changes. The examples and problems at the end of the section illustrate the use of Henry's law.

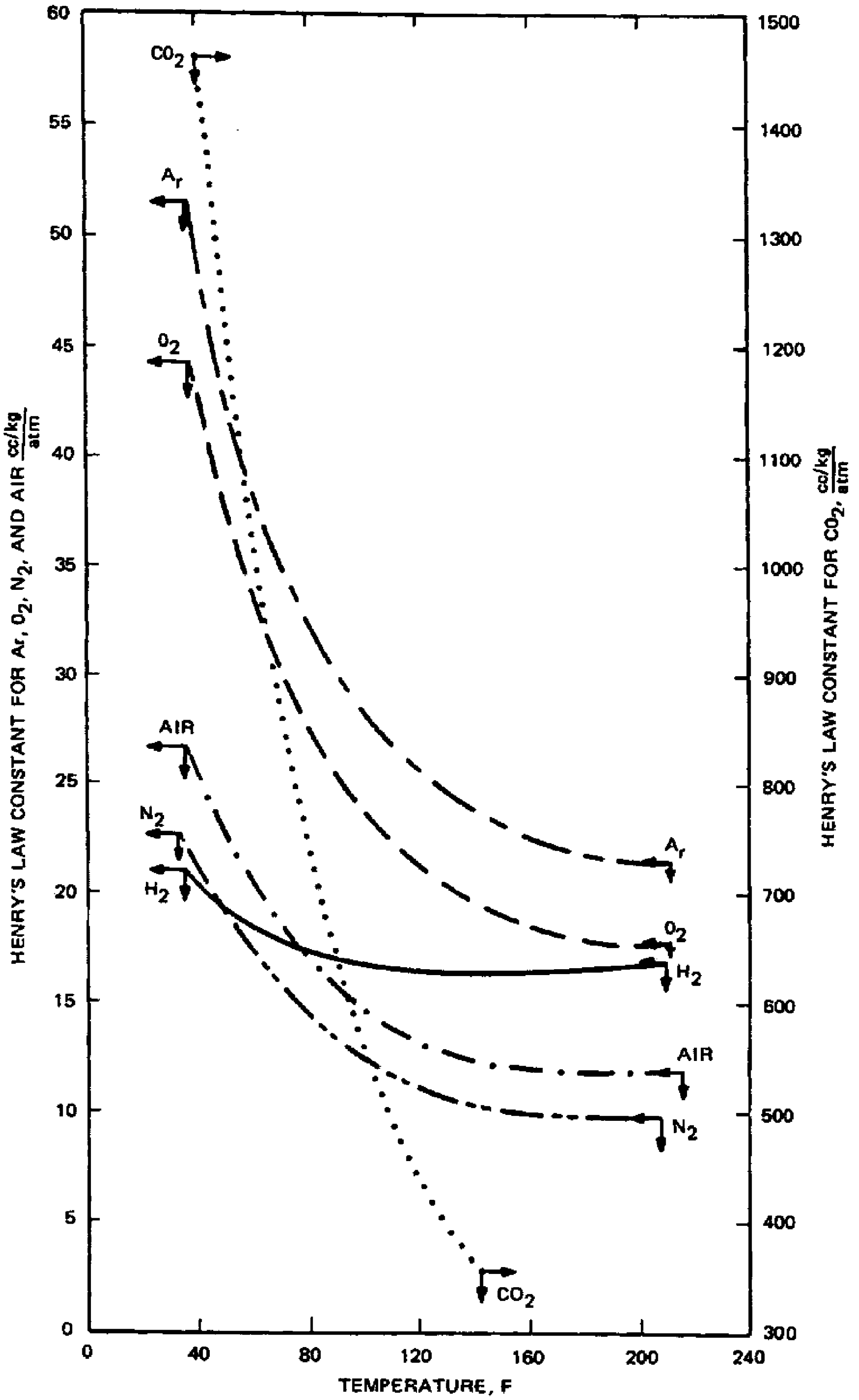


Figure 220-6-2 Henry’s Law Constant for Common Gases (Low Temperature)

220-6.4.2.4 The Vapor Pressure of Water. Although water boils at 100°C at 14.7 psia, it is a familiar fact that water evaporates at all temperatures. Evaporation is just a process in which molecules change from a liquid state to a gaseous state. The gas space above any sample of water will, thus, contain some water molecules which have evaporated. Even though the gas space may have been occupied by a pure gas initially, as the water evaporates the gas becomes a mixture of the original gas and water vapor. As with any gaseous mixture, a partial pressure is associated with each component.

220-6.4.2.4.1 The partial pressure of water vapor is called the vapor pressure of water. If one wishes to apply Henry's law and is given the total pressure above the water, the vapor pressure of water must be subtracted from the total pressure to obtain the pressure due to the gas (or gases) above the water. Examples in paragraph 220-6.6 further illustrate this point.

220-6.4.2.4.2 At temperatures near the freezing point of water, the vapor pressure is negligible for all but the most precise calculations. At 40°F, the vapor pressure of water is only 0.12 psia but at higher temperatures the vapor pressure increases. At 212°F (100°C) the vapor pressure of water is 14.7 psia. A more accurate definition of boiling point than the one given in Section 4 is: The boiling point of a liquid is that temperature at which the vapor pressure of the liquid is equal to ambient pressure (i.e., the pressure of the surrounding atmosphere). Values of the vapor pressure at other temperatures can be obtained from steam tables. A few representative values are given in Table 220-6-4.

Table 220-6-4 VAPOR PRESSURE OF WATER AT VARIOUS TEMPERATURES

Temperature		**Vapor Pressure**	
°C	**°F**	**atm**	**psia**
0	32	0.006	0.089
20	68	0.023	0.339
40	104	0.072	1.066
60	140	0.196	2.885
80	176	0.448	6.592
100	212	1.000	14.697
150	302	4.70	69.01
200	392	15.32	225.23

220-6.5 SUMMARY

220-6.5.1 The ideal gas law is a general description of the physical behavior of most gases under normal conditions of temperature and pressure. If the amount of gas and pressure are constant, the ideal gas law reduces to Charles' law which states that the volume of the gas is directly proportional to temperature. If the amount of gas and temperature are constant, Boyle's law indicates that the volume is inversely proportional to pressure. Avogadro's law, that volume is directly proportional to the amount of gas, applies if temperature and pressure are constant. In all these laws, temperature and pressure must be expressed in absolute units. Dalton's law of partial pressures extends the application of the ideal gas law to each component of a mixture of gases. According to this law, the total pressure of the mixture is the sum of the pressures of all the components. Henry's law describes the effect of pressure on the solubility of a gas in water by stating that the solubility is directly proportional to the pressure (or partial pressure) of the gas.

220-6.6 EXAMPLE PROBLEMS

Example 6-5: **Estimate the concentration of O_2, N_2 and argon dissolved in water exposed to air at 1 atmosphere pressure and 40°F and 120°F. Assume the water is saturated with dissolved gas.**

Solution 6-5. **The concentration of a gas dissolved in water at saturation can be calculated by applying Henry's law.**

$$C_i = H\ (T)\ p_i$$

Values for Henry's law constants can be obtained from Figure 220-6-3.

The partial pressures of the various gases in the gas phase above the water are also needed. To obtain these partial pressures, first obtain the partial pressure of air in the gas phase above the water; and then multiply the partial pressure of air by the fraction by volume of the gas in air (see Table 220-6-3). By Dalton's law, the partial pressure of air in the gas phase will equal 14.7 psia (1 atmosphere) minus the partial pressure of water vapor at each temperature.

The basic data are:

	Henry's Law Constant, $\frac{cc/kg}{atm}$ for:			Partial Pressure of water vapor,	Partial Pressure of air, $P_{atm} - p_{H2O}$	
T, F	O_2	N_2	Ar	psia	psia	atm
40	43.2	21.3	49.0	0.12	14.6	0.99
120	21.3	11.0	25.4	1.7	13.0	0.88

Composition of air (table 220-12)

Gas	Percent by Volume
N_2	78.1
O_2	21.0
Ar	0.93

Apply Henry's law.

$$C_i = H_i(T)p_i; p_i \text{ for each gas}$$

$$= p_{air} \times \frac{\text{Volume \%}}{100}$$

$$C_i = H_i(T)p_{air} \times \frac{\text{Volume \%}}{100}$$

At 40°F:

$$C_{N_2} = 21.3 \ \frac{cc/kg}{atm} \times 0.99 \text{ atm} \times 0.781 = 16.5 \text{ cc/kg}$$

$$C_{O_2} = 43.2 \ \frac{cc/kg}{atm} \times 0.99 \text{ atm} \times 0.21 = 9.0 \text{ cc/kg}$$

$$C_{Ar} = 49.0 \ \frac{cc/kg}{atm} \times 0.99 \text{ atm} \times 0.0093 = 0.45 \text{ cc/kg}$$

At 120°F:

$$C_{N_2} = 11.0 \ \frac{cc/kg}{atm} \times 0.88 \text{ atm} \times 0.781 = 7.55 \text{ cc/kg}$$

$$C_{O_2} = 21.3 \ \frac{cc/kg}{atm} \times 0.88 \text{ atm} \times 0.21 = 3.93 \text{ cc/kg}$$

$$C_{Ar} = 25.4 \ \frac{cc/kg}{atm} \times 0.88 \text{ atm} \times 0.0093 = 0.21 \text{ cc/kg}$$

Example 6-6: *Consider a completely enclosed container, partially filled with water at 150°C. A 5 liter volume of vapor, above the liquid, is composed of H_2O, O_2, H_2 and N_2. The concentrations of these gases in the water are:*

$$O_2 = 13.68 \text{ cc/kg}$$

$$N_2 = 29.83 \text{ cc/kg}$$

$$H_2 = 16.78 \text{ cc/kg}$$

Calculate the concentrations of the gases (volume percents) in the enclosed vapor space.

Solution 6-6: *This problem can be solved by the use of Henry's Law,*

$$C_i = H_i(T)p_i$$

which relates the concentration of a gas dissolved in a liquid to its partial pressure in the vapor phase.

Values for Henry's Law constants (figure 220-18) are:

$$O_2 \quad 22 \ \frac{\text{cc/kg}}{\text{atm}}$$

$$N_2 \quad 16 \ \frac{\text{cc/kg}}{\text{atm}}$$

$$H_2 \quad 27 \ \frac{\text{cc/kg}}{\text{atm}}$$

measured at 150°C (302°F).

Substituting these values and the known gas concentrations in the water into Henry's Law, the partial pressures for each gas in the vapor phase can be calculated.

$$p_i = C_i/H_i(T)$$

O_2

$$p_{O_2} = (13.68 \text{ cc/kg} + 22 \ \frac{\text{cc/kg}}{\text{atm}}) = 14.7 \ \frac{\text{psi}}{\text{atm}}$$

$$= 9.140 \text{ psi}$$

N_2

$$p_{N_2} = (29.83 \text{ cc/kg} \div 16 \ \frac{\text{cc/kg}}{\text{atm}}) \times 14.7 \ \frac{\text{psi}}{\text{atm}}$$

$$= 27.41 \text{ psi}$$

H_2 $$p_{H_2} = (16.78\ cc/kg \div 27\ \frac{cc/kg}{atm})\ x\ 14.7\ \frac{psi}{atm}$$

$$= 9.136\ psi$$

The partial pressure of the water in the vapor phase is simply the vapor pressure of water at these specific conditions. From table 220-13,

$$p_{H_2O} = 69.01\ psi \quad 150°C$$

Thus, the total pressure, P, is:

$$P = p_{H_2O} + p_{O_2} + p_{N_2} + p_{H_2}$$
$$= 114.7\ psi$$

The partial pressures can then be related to volume percentages by:

$$V\ percent = \frac{p_i}{P_T}\ x\ 100$$

$$V\ percent\ (O_2) = 9.140\ psi/114.7\ psi = 8.0\ percent$$

$$V\ percent\ (N_2) = 27.41\ psi/114.7\ psi = 23.9\ percent$$

$$V\ percent\ (H_2) = 9.136\ psi/114.7\ psi = 7.9\ percent$$

$$V\ percent\ (H_2O) = 69.01\ psi/114.7\ psi = 60.2\ percent$$

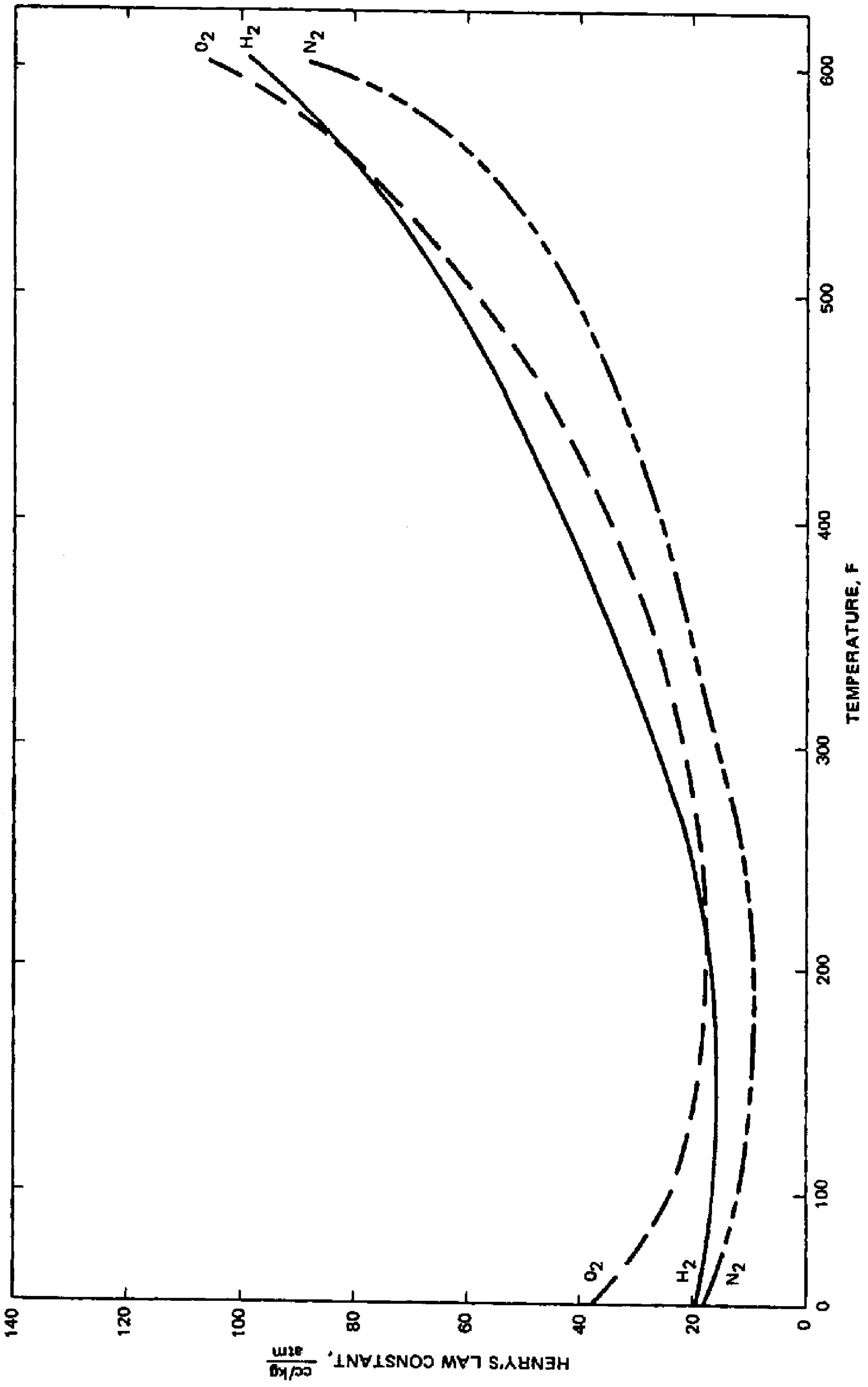


Figure 220-6-3 Henry’s Law Constant for Common Gases (Expanded Temperature Range)

SECTION 6 PROBLEMS

1. Calculate the density of N_2 , at 30°C and 20 psia.
2. A 1-gallon vessel contains hydrogen at a pressure of 630 psia and a temperature of 85°F. How many moles of H_2 are in the vessel? What would be the volume of this amount of H_2 at STP? (1 gallon = 3.78 liters)
3. The nitrogen contained in a cylinder exerts a pressure of 500 psia at 70°F. The pressure rating (maximum pressure) of the cylinder is 800 psia. At what temperature would the pressure of the gas equal the pressure rating of the cylinder?
4. Using information from Table 220-6-3 , calculate the density of air in grams/liter at STP. (Neglect the effects of CO_2 and Ne.)
5. **Dry ice** is solid CO_2 and, at atmospheric pressure, goes directly from the solid state to the gas state without passing through the liquid state. (A process called sublimation.) Calculate the volume of CO_2 gas at 350°F and 1 atmosphere pressure which will result from the sublimation of 500 grams of dry ice.
6. A quantity of water is exposed to a hydrogen atmosphere at 500 psia. Calculate the solubility (maximum concentration) of hydrogen in water at 200°F and 400°F. The vapor pressure of water is 11.5 psia at 200°F and 247.3 psia at 400°F.

SECTION 6 PROBLEM ANSWERS

1. 1.53 grams/liter
2. 6.53 moles H_2 146 liters (1.46 x 10^5 cc) at STP
3. 387°F
4. 1.29 grams/liter
5. 419 liters
6. 555 cc/kg at 200°F 739 cc/kg at 400°F

SECTION 7.

CHEMICAL EQUILIBRIUM

220-7.1 INTRODUCTION

220-7.1.1 One of the most important concepts in chemistry involves the completeness of chemical reactions. Numerous examples of reactions given in previous chapters perhaps imply that all reactions continue until at least one reactant is completely consumed. Many reactions, however, do not show such behavior because the products simultaneously react to form the reactants. Specific cases of these equilibrium reactions and their application in the chemistry control of marine boilers are considered in much of the remainder of this text. This section lays the foundation for the subsequent developments.

220-7.1.2 The fundamentals of chemical equilibrium are most easily illustrated using reactions in which gases are the reactants or products. Most of the examples used in this section are such reactions. In boiler water chemistry control, however, the most important reactions involve substances dissolved in the water. The major types of equilibrium processes which occur in boiler water are described in Section 8 and Section 9.

220-7.2 GLOSSARY OF TERMS

220-7.2.1 Terms used in this section are defined as follows:

a. **Equilibrium:** The state of a reversible chemical reaction in which the opposing reactions occur simultaneously at exactly equal rates; thus, there is no observable change in amount or concentration of any of the reactants or products.

b. **Equilibrium Constant:** A temperature-dependent numerical constant, K_{eq} , defined by:

$$K_{eq} = \frac{[C]^c\ [D]^d}{[A]^a\ [B]^b}$$

for the general reversible reaction:

$$aA + bB \rightleftarrows cC + dD$$

c. **Law of Mass Action:** The rate of a chemical reaction is directly proportional to the concentrations of the reactants raised to some power.

d. **LeChatelier's Principle:** If a system initially at equilibrium is subjected to a disturbance or stress that changes any of the factors which determine the equilibrium state, the system will react in such a way as to minimize the effect of the disturbance or relieve the stress.

e. **Reversible Reaction:** A chemical reaction which takes place in both forward and reverse directions at significant rates under the appropriate conditions.

220-7.3 REVERSIBILITY OF CHEMICAL REACTIONS

220-7.3.1 Under appropriate conditions of temperature and pressure, the gases N_2 and H_2 react to form the gas ammonia, NH_3 , by the reaction:

$N_2 + 3H_2 \rightarrow 2NH_3$ (7-1)

NOTE

As explained more fully in paragraphs 220-7.4 through 220-7.4.3, the conversion of N_2 and H_2 to NH_3 is not complete.

220-7.3.2 It can also be shown experimentally that if one begins with pure NH_3 at the same conditions of temperature and pressure as for the above reaction, the NH_3 partially decomposes into N_2 and H_2 by the reaction:

$2NH_3 \rightarrow N_2 + 3H_2$ (7-2)

Equations (7-1) and (7-2) are just the reverse of each other and can be combined into a single equation using a double arrow:

$$N_2 + 3H_2 \leftrightarrows 2NH_3 \qquad (7\text{–}3)$$

Reactions such as equation (7-3) in which two opposite reactions occur simultaneously are called reversible.

220-7.3.3 Theoretically, every chemical reaction is reversible. Very often, however, the reaction in one direction predominates to such an extent that for practical purposes, the reaction may be treated as irreversible or complete in one direction. This can be artificially forced to occur if one of the products is removed from the reacting system. For example, if calcium carbonate, $CaCO_3$, is heated in a closed container, the following reversible reaction occurs:

$$CaCO_3 \leftrightarrows CaO + CO_2 \qquad (7\text{–}4)$$

If the $CaCO_3$ is heated in an open vessel, the CO_2 gas can escape and only the forward reaction is significant:

$CaCO_3 \rightarrow CaO + CO_2 \uparrow$ (7-5)

(The arrow, ↑, indicates the CO_2 escapes as a gas.) In this case, the CO_2 is no longer available to react with CaO in the reverse reaction, so the forward reaction goes to completion.

220-7.4 THE EQUILIBRIUM STATE

220-7.4.1 Again consider the reaction,

$$N_2 + 3H_2 \leftrightarrows 2NH_3 \qquad (7\text{–}3)$$

and imagine the following experiments. First, 1 mole of N_2 and 3 moles of H_2 are mixed in a closed container at 500°C and 350 atmospheres (5150 psia). Periodically, say every 15 minutes, the composition of the gaseous mixture is determined. It will be found that the percentages of N_2 and H_2 decrease and the percentage of NH_3 increases in the first few samples. Eventually, however, the composition of the samples will not change no matter how great the time elapsed since the reaction began, provided the temperature does not change. Under the conditions stated above, the final unchanging composition of the reaction mixture will be approximately 0.7 moles N_2 , 2.1 moles H_2 , and 0.6 moles NH_3 .

220-7.4.2 Now suppose a similar experiment is conducted starting with 2 moles of pure NH_3 in a reaction vessel at 500 °C and 350 atmospheres. The first few periodic analyses will show a decreasing percentage of NH_3 and increasing percentages of H_2 and N_2 . Finally, a state will again be reached in which the composition of the reaction mixture does not change if temperature is constant. For the stated conditions, the constant-composition mixture is 0.7 moles N_2 , 2.1 moles N_2 , and 0.6 moles NH_3 . These are exactly the same as the previous results beginning with N_2 and H_2 .

220-7.4.3 The conclusion is that regardless of whether one starts with the substances on the left or on the right side of equation (7-3), the system reaches a state in which all substances are present in constant amounts, so long as the temperature is constant. In this state, all reaction appears to have stopped because the measurable amounts of reactants and products do not change. This appearance, however, is deceiving. A great body of experimental evidence proves that the steady state described above is characterized not by the complete absence of reaction, but by two opposite reactions occurring at exactly the same rates. **This state in which two opposite reactions take place simultaneously and at the same rate is called chemical equilibrium** or the **equilibrium state** . In the experiments described above, at equilibrium, the rate of formation of NH_3 by the forward reaction is exactly equal to the rate of decomposition of NH_3 in the reverse reaction.

220-7.5 THE LAW OF MASS ACTION

220-7.5.1 Experimental study of forward and reverse reaction rates for various concentrations of reactants leads to a useful relationship for reaction rates known as the **law of mass action** . This law states: **The rate of a chemical reaction is directly proportional to the concentrations of the reactants raised to some power** .

220-7.5.2 For the general reaction,

$$A + B \rightarrow C + D$$

the rate, R, is:

$$R = k\,[A]^m\,[B]^n$$

where:

a. k is a constant (called the rate constant) at any particular temperature

b. [ ] indicates concentration, usually in moles/liter

c. m and n are usually integers or half-integers.

220-7.5.3 If a reaction takes place exactly as written in the equation the exponents m and n are just the coefficients of the reactants in the balanced equation. For instance, consider the reaction in which molecules of A react with b molecules of B to form c molecules of C and d molecules of D.

$$aA + bB \leftrightarrows cC + dD$$

(In the reverse reaction, c molecules of C react with d molecules of D.) In this case, the rate of the forward reaction, R_f , is:

$$R_f = k_f\,[A]^a\,[B]^b$$

where k_f is the rate constant for the forward reaction. **For a given reaction at a given temperature, the rate constant does not change** . Similarly, the rate for the reverse reaction, R_r , is:

$$R_r = k_r\,[C]^c\,[D]^d$$

In reality, most chemical reactions do not take place exactly as indicated by the equation. That is, the reaction:

$$A_2 + 3B_2 \rightarrow 2AB_3$$

may not occur in a single step. Such a situation would require a highly improbable four-way collision between three molecules of B and one molecule of A. Instead, the net reaction may be the sum of several intermediate steps, such as:

$$\begin{array}{c}
\textbf{Step 1. } A_2 + B_2 \rightarrow 2AB \\
\underline{\textbf{Step 2. } 2AB + 2B_2 \rightarrow 2AB_3} \\
\textbf{Net Reaction: } A_2 + 3B_2 \rightarrow AB_3
\end{array}$$

220-7.5.4 If Step 1 is fast and Step 2 is slow then Step 2 would govern the rate of the overall reaction. Since A_2 does not participate directly in Step 2, it could be found that the rate of the net reaction is independent of the concentration of A_2 , but is proportional to the concentration of B_2 .

220-7.5.5 Because of the possibility that a reaction takes place in a series of steps, any one of which may be rate-controlling, the law of mass action cannot be applied to specific reaction rates unless the mechanism of the reaction is shown. The reaction mechanism and the exact reaction rate expression can only be determined by experiment. Despite this difficulty in applying the law of mass action, paragraphs 220-7.6 through 220-7.6.3 describe a very simple and perfectly general relationship among the concentrations of all the reactants and products in any reaction at equilibrium.

220-7.6 THE EQUILIBRIUM CONSTANT

220-7.6.1 GENERAL. Experimental evidence shows that for any reversible reaction of the general type:

$$aA + bB \leftrightarrows cC + dD$$

the equilibrium state is described by:

$$K_{eq} = \frac{[C]^c \; [D]^d}{[A]^a \; [B]^b} \qquad (7\text{-}7)$$

where K_{eq} is a constant for any particular temperature and is called the equilibrium constant. Equation (7-7) means that there exists a definite constant relationship among the concentrations of all the substances involved in a reversible reaction at equilibrium.

220-7.6.1.1 For those reactions which take place exactly as indicated by the overall equation, the equilibrium constant expression of equation (7-7) can be developed easily from the rate constant expressions. For instance, the rate of the forward step of the reaction in equation (7-6) is

$R_f = k_f \, [A]^{a} \, [B]^{b}$

and the rate of the reverse reaction is:

$R_r = k_f \, [C]^{c} \, [D]^{d}$

From the previous discussion, chemical equilibrium is defined as the state in which the rates of the forward and reverse steps of a reversible reaction are equal. Thus, at equilibrium:

$$R_f = R_r$$

$$k_f\,[A]^a\,[B]^b = k_r\,[C]^c\,[D]^d$$

$$k_f/k_r = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} \qquad (7\text{-}8)$$

Since k_f and k_r are constants at any given temperature, their ratio is also a constant, K_{eq} in Equation (7-7).

$$K_{eq} = \frac{k_f}{k_r} = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b} \qquad (7\text{-}9)$$

220-7.6.1.2 Even for those reactions which do not take place exactly as indicated by the net equation, equation (7-7) still applies although the reasons are not as clear as the above development. No matter how complex the actual mechanism for a reaction, the process can always be broken down into a series of simple reactions to which the law of mass action is directly applicable. Associated with each step is a particular rate constant and a rate expression. At equilibrium, the net forward rate is equal to the net reverse rate. The result of this treatment is always an equation of the same type as equation (7-7) in which the concentrations of each substance in the reaction is raised to a power equal to the coefficient of that substance in the balanced net equation.

220-7.6.1.3 Equation (7-7) is, thus, perfectly general. The only conditions on its applicability to any particular reaction are that the system must be at equilibrium and temperature must be constant. The equilibrium state is independent of the direction from which it is approached. Further, it is independent of the relative amounts or total amount of starting materials, provided of course, that some amount of each reactant in a particular direction is present. That is, some amount of both A and B or some amount of both C and D must be present. If only A and C were available, the forward and reverse reactions could not take place and equilibrium would not be established.

Example 7 - 1: Write the equilibrium constant expressions for the following reversible reactions:

1. $CO + NO_2 \leftrightarrows CO_2 + NO$

2. $H_2 + I_2 \leftrightarrows 2HI$

3. $2SO_2 + O_2 \leftrightarrows 2SO_3$

Solution 7-1:

1. $K_{eq} = \dfrac{[CO_2]\ [NO]}{[CO]\ [NO_2]}$

2. $K_{eq} = \dfrac{[HI]^2}{[H_2]\ [I_2]}$

3. $K_{eq} = \dfrac{[SO_3]^2}{[SO_2]^2\ [O_2]}$

220-7.6.2 EFFECTS OF PHYSICAL CONDITIONS ON EQUILIBRIUM. A system at equilibrium remains at equilibrium unless acted upon by some change in physical conditions. The two physical variables to be considered in this respect are concentration and temperature. The manner in which physical factors influence equilibrium is described, in general terms, by LeChatelier's principle: If a system at equilibrium is subjected to a disturbance or stress that changes any of the factors which determine the equilibrium state, the system will react in such a way as to minimize the effect of the disturbance (or relieve the stress). Thus, there will be a shift in the equilibrium either in the forward or reverse direction.

220-7.6.2.1 Concentration Effects. A change in the concentration of one of the reactants or products in an equilibrium system at constant temperature disturbs the equilibrium state (but not the equilibrium constant). LeChatelier's principle predicts that the system will react to reduce the effects of that disturbance. To illustrate, consider the equilibrium system

$$CO + H_2O \rightleftarrows H_2 + CO_2 \qquad (7\text{-}10)$$

for which the equilibrium constant expression is:

$$K_{eq} = \frac{[CO_2]\ [H_2]}{[CO]\ [H_2O]} \qquad (7\text{-}11)$$

220-7.6.2.1.1 An increase in the concentration of CO causes the forward reaction rate to increase. The equilibrium is now upset and the forward reaction rate is faster than the reverse reaction rate. Thus, the concentrations of CO and H_2 O will start to go down and the concentrations of CO_2 and H_2 will start to go up. As the concentrations of H_2 O and CO go down, the forward reaction rate slows down; as the concentrations of H_2 and CO_2

increase, the reverse reaction rate speeds up. The forward reaction rate will decrease and the reverse reaction rate will increase until the two are again equal at some new, higher level. The net effect on the concentrations of the reactants and the products can be determined by examining equation (7-11).

220-7.6.2.1.2 Since K_{eq} is constant for a given temperature, it is not affected by changes in concentration. An increase in the concentration of CO causes the denominator of equation (7-11) to increase. In order to maintain the constant value of K_{eq} , the system must react in such a way as to increase the numerator or decrease the denominator. Both effects are produced by a shift to the right of the reaction in equation (7-10). That is, some of the added CO reacts with H_2O to produce more CO_2 and H_2 . Conversely, if the original concentration of CO had been suddenly reduced, the equilibrium would shift to the left to consume CO_2 and H_2 and increase the concentrations of CO and H_2O.

220-7.6.2.1.3 In terms of LeChatelier's principle, an increase in the concentration of one of the reactants or products may be thought of as a stress on the equilibrium system. Inspection of the equation for the reaction shows that the stress can be relieved (i.e., the concentration reduced) by a shift in the appropriate direction. In such a case, the equilibrium concentrations change, but the equilibrium constant does not.

220-7.6.2.1.4 The foregoing discussion applies equally well to reactions of gases and reactions in solution. A gaseous reaction mixture, however, readily expands or contracts in response to pressure changes at constant temperature while a liquid does not. The concentration changes caused by changing volume must be considered for reactions which involve one or more gases.

220-7.6.2.1.5 A change in pressure affects the equilibrium state of a reversible reaction if and only if the following two conditions are met: (1) one or more of the reactants and products must be gaseous; (2) in the balanced equation, the total number of moles of gaseous reactants must differ from the total number of moles of gaseous products. The first condition is necessary because the volume of solids and liquids is essentially unaffected by pressure changes. Thus, at least one of the reactants or products must be a gas. Before illustrating the reason for the second condition, let us recall some features of gases which are discussed in Section 6. For a mixture of gases, Dalton's law of partial pressures indicates that the ideal gas law can be applied to each component of the mixture. Boyle's law is a special case of the ideal gas law and states that if the amount of gas and the temperature are constant, volume is inversely proportional to pressure.

$$V = \frac{k(n, T)}{P}$$

220-7.6.2.1.6 For equilibrium to be established, temperature must be constant. Thus, if a system is at equilibrium and if gases are involved, both Dalton's law and Boyle's law apply. Now consider the following two examples.

Example 7–2: $$CO + H_2O \leftrightarrows CO_2 + H_2 \qquad (7\text{–}10)$$

All the reactants and products in this reaction are gases, so condition 1 above is met. Condition 2, however, is not met because there are a total of 2 moles of gases on the left and the same number on the right. To see why this condition is necessary, suppose the total pressure on the equilibrium system is doubled. From equation (7-12) it is seen that the result would be a decrease in volume by a factor of 1/2. Since the same amount of each gas would be contained in 1/2 the original volume, the concentration of each gas would double.

If the original concentrations of CO, H_2 O, CO_2 , and H_2 were a, b, c, and d respectively, the equilibrium constant expression would be:

$$K_{eq} = \frac{(c)\ (d)}{(a)\ (b)} \qquad (7\text{-}13)$$

After the pressure doubled and the concentration also doubled, the new equilibrium constant expression would be:

$$\frac{(2c)\ (2d)}{(2a)\ (2b)} = \frac{(c)\ (d)}{(a)\ (b)} = K_{eq} \qquad (7\text{-}14)$$

Thus, regardless of the factor by which the pressure changes, all the concentrations are changed by the same factor which cancels out in the equilibrium constant expression. For that reason, a pressure change does not affect the equilibrium state of a reaction which meets condition 1 but not condition 2.

Example 7-3:

$$N_2 + 3H_2 \rightleftarrows 2NH_3 \qquad (7\text{-}3)$$

As in Example (7-2), all the reactants and products are gases, but in this case, there are a total of 4 moles of gases on the left and 2 moles on the right. This example, then, does meet condition 2 and should be affected by a pressure change.

If x, y and z are the equilibrium concentrations of N_2, H_2, *and* NH_3, *respectively, the equilibrium constant expression is:*

$$K_{eq} = \frac{(z)^2}{(x)(y)^3} \qquad (7\text{-}15)$$

If the pressure is then doubled, again the concentration of each substance also doubles, but now the new equilibrium expression would be:

$$K'_{eq} = \frac{(2z)^2}{(2x)(2y)^3} = \frac{4(z)^2}{16(x)(y)^3} = \frac{(z)^2}{4(x)(y)^3} = 1/4\ K_{eq} \qquad (7\text{-}16)$$

$$K'_{eq} \neq K_{eq}$$

This means either that the equilibrium constant must change or that the system is no longer at equilibrium. Repeated experiments have shown that the equilibrium constant does not change unless the temperature changes. In the example, temperature has not changed, so the conclusion is that the equilibrium has been disturbed.

220-7.6.2.1.7 LeChatelier's principle states that after the above pressure change, the system will respond in a manner which tends to reduce the effect of the change. The nature of this response can be seen by examining either equation (7-3) or equation (7-16). In equation (7-3) it is evident that the left side of the equation represents a greater total number of moles of gases than does the right side. The system can therefore reduce the pressure by shifting toward the right side of the equation, by using some of the N_2 and H_2 to form NH_3 . The same conclusion is reached by examining equation (7-15). There it is seen that after the pressure increase, the denominator has increased relative to the numerator. To offset this change the system must increase the concentration of NH_3 and reduce the concentration of H_2 and N_2 .

220-7.6.2.2 Temperature Effects. Of the factors which affect equilibrium, only temperature affects the equilibrium constant itself. The effect is due to the change in the kinetic energy distribution of the molecules or atoms which in turn produces changes in the forward and reverse reaction rates.

220-7.6.2.2.1 Most chemical reactions are either endothermic (absorb thermal energy or heat) or exothermic (release thermal energy). In a reversible reaction, heat is released when the reaction goes in one direction and absorbed when it goes in the other direction. At equilibrium, these heat releasing and heat absorbing reactions are balanced. If it is known for a particular reaction which direction is endothermic and which is exothermic, the qualitative effect of a change in temperature on the equilibrium state can be predicted.

220-7.6.2.2.2 Experiments have shown that heat is liberated when N_2 reacts with H_2 and heat is absorbed when NH_3 decomposes. This may be indicated as follows:

$$N_2 + 3H_2 \rightarrow 2NH_3 + \text{heat} \quad (7\text{-}17)$$

$$2NH_3 + \text{heat} \rightarrow N_2 + 3H_2 \quad (7\text{-}18)$$

220-7.6.2.2.3 Suppose the net reaction is initially at equilibrium and the temperature is increased. In effect, heat has been added to the system. According to LeChatelier's principle, the system will respond to this change in such a way as to minimize the change. The system can offset the added heat by shifting the equilibrium in the direction that absorbs heat, that is, in the direction indicated by equation (7-18). Thus, the new equilibrium state will be one in which the concentration $[NH_3]$ is smaller and the concentrations $[N_2]$ and $[H_2]$ are correspondingly larger. From equation (7-7) it is seen that this requires that K_{eq} be smaller at higher temperature. Experiments verify that K_{eq} does indeed change with temperature and in the direction predicted by LeChatelier's principle. For example, K_{eq} for the reactions in equations (7-17) and (7-18) changes from $\sim 6 \times 10^{-3}$ at 200°C to $\sim 4 \times 10^{-6}$ at 400°C with pressure held constant at 1 atmosphere.

220-7.6.2.2.4 Another effect of temperature changes on equilibrium concentrations is possible in the case of reactions involving gases, as seen from Charles' law:

$$V = k(n,P)T$$

Thus, if the absolute temperature is doubled at constant pressure, the volume would also double and the concentration would decrease by 1/2. Conditions 1 and 2 described in paragraph 220-7.6.2.1.5 for the effects of pressure changes also apply to this case. If these conditions are met, both the change in K_{eq} and the change in volume must be considered in calculating new equilibrium concentrations after a change in temperature at constant pressure. In most cases the change in K_{eq} has a much greater effect than the change in volume.

220-7.6.3 MEANING OF THE EQUILIBRIUM CONSTANT. The preceding discussion of equilibrium deals with reversible chemical reactions. Subsequent sections describe other equilibrium processes such as solubility and ionization for which an equilibrium constant expression can be written. Although the form of the expression differs slightly in some cases, the following conclusions apply to any equilibrium system:

a. A very large value of the equilibrium constant indicates that the forward reaction (toward the right) dominates.

b. A very small value of the equilibrium constant means that the reverse reaction (toward the left) dominates.

220-7.6.3.1 It is very important to note that a particular equilibrium constant depends on the way the equation is written. For example, the expression

$$K_{eq} = \frac{[C]^c\ [D]^d}{[A]^a\ [B]^b} \qquad (7\text{-}7)$$

applies to the reaction written as:

$$aA + bB \rightleftarrows cC + dD \qquad (7\text{-}6)$$

Since this is a reversible reaction, it may also be written

$$cC + dD \rightleftarrows aA + bB \qquad (7\text{-}19)$$

The equilibrium constant expression for Equation (7-19) is:

$$K'_{eq} = \frac{[A]^a\ [B]^b}{[C]^c\ [D]^d} = \frac{1}{K_{eq}} \qquad (7\text{-}20)$$

Thus, if K_{eq} , is small, then K'_{eq} is large. In terms of the particular compounds, however, the significance is the same in both cases. If K_{eq} in equation (7-7) is large, the formation of C and D predominates. A small value of K'_{eq} in equation (7-20) also indicates that formation of C and D predominates.

220-7.7 SUMMARY

220-7.7.1 Many chemical reactions are capable of proceeding in both forward and reverse directions simultaneously. When the rates of the forward and reverse reactions are exactly equal, the reacting system is at equilibrium if the temperature is constant. At equilibrium, there are no observable changes in the quantity or concentration of any of the reactants or products. Changes in temperature almost always affect the equilibrium state because the equilibrium constant changes. Changes in concentration of one or more of the reactants or products affect the equilibrium concentrations of all reactants and products but not the equilibrium constant. Besides the addition or removal of substances, changes in concentration may sometimes be produced by changes in pressure or temperature. LeChatelier’s principle can be used to predict how a system initially at equilibrium will respond to the above factors which may disturb the equilibrium state.

SECTION 8.

ACIDS AND BASES

220-8.1 INTRODUCTION

220-8.1.1 The study of the vast number of chemical compounds now known becomes manageable only by classifying or grouping compounds on the basis of their chemical properties. Knowledge of the general properties of an entire group can then be applied to individual members of the group. Among the most im portant categories of compounds are those called acids and bases. The general features of these groups and more detailed information on a few individual compounds are presented in this section.

220-8.2 GLOSSARY OF TERMS

220-8.2.1 Terms used in this section are defined as follows:

a. **Acid** : A compound which produces H_3O^+ ions directly when dissolved in water.

b. **Base** : A compound which produces OH^- ions directly when dissolved in water.

c. **Equivalent Weight** : For an acid, the amount of the acid capable of releasing 1 mole or 6.02×10^{23} H_3O^+ ions; for a base, the amount of the base capable of releasing 1 mole or 6.02×10^{23} OH^- ions.

d. **Hydronium Ion** : H_3O^+, the species formed in water by the interaction between H^+ ions (protons) and H_2O molecules.

e. **Ion Product Constant** : K_w, which relates $[H_3O^+]$ and $[OH^-]$ in water by the expression; $[H_3O^+][OH^-] = K_w$.

f. **Ionization Equilibrium** : The equilibrium established between the dissociation of a compound into ions and the recombination of these ions to form the original compound.

g. **Neutralization** : The reaction between an acid and a base. Neutralization is exact if the number of equivalents of acid and base are the same. If one reactant is in excess, neutralization is incomplete and the final solution is either acidic or basic.

h. **Neutral Solution** : Any aqueous solution or pure water in which $[H_3O^+] = [OH^-]$ or pH = pOH. At 25°C or 77°F, $[H_3O^+] = [OH^-] = 10^{-7}$ mole/liter and pH = pOH = 7.

i. **Normality** : Concentration units which express the number of equivalent weights dissolved in one liter of solution.

j. **pH** : A measure of the acidity (or basicity) of an aqueous solution and defined by $pH = -\log [H_3O^+]$ where $[H_3O^+]$ is in moles/liter of solution.

k. **pOH** : A measure of the acidity (or basicity) of an aqueous solution and defined by $pOH = -\log [OH^-]$ where $[OH^-]$ is in moles/liter of solution.

l. **Salt** : A type of ionic compound formed by the reaction between acids and bases and composed of the anion of the acid and the cation of the base.

m. **Strong Acids and Bases** : Those acids and bases which completely dissociate into ions when dissolved in water.

n. **Weak Acids and Bases** : Those acids and bases which only partially dissociate into ions in aqueous solution.

220-8.3 PROPERTIES OF ACIDS AND BASES

220-8.3.1 GENERAL In the following descriptions of acids and bases, an important point should be borne in mind. Unless specifically stated otherwise, the discussion pertains to aqueous solutions of the compounds. In many cases, the properties of the pure compound are quite different from those of an aqueous solution of the compound. For example, pure HCl is a covalent gas but in aqueous solutions HCl completely dissociates into ions. Although HCl is generally termed an acid, only aqueous solutions of the compound exhibit those properties which characterize acids as described in this text.

220-8.3.2 ACIDS. Among the characteristic properties of acids are:

1. Acids react with the active metals, such as Mg and Zn, to produce H_2 gas.
2. Acids conduct electricity, thus they are electrolytes.
3. Concentrated acids burn human skin (produce blisters).
4. Dilute acids taste sour. For example, citric acid gives citrus fruit its characteristic tart flavor.

NOTE

Besides burning the skin, many acids are also poisonous. Chemists often learn by painful experience to avoid trying to identify a chemical by taste or touch.

220-8.3.2.1 The following acids are used frequently throughout this text. The student is advised to memorize their names and formulas.

1. HCl, hydrochloric acid
2. HNO_3 , nitric acid
3. H_2SO_4 , sulfuric acid
4. $HC_2H_3O_2$, acetic acid
5. H_2CO_3 , carbonic acid
6. H_3PO_4 , phosphoric acid

220-8.3.3 Bases. The properties of bases include the following:

1. Solutions of bases conduct electricity, thus bases, like acids, are electrolytes.
2. Solutions of bases feel slippery. The reason for this property is that bases dissolve human skin and flesh. Concentrated base solutions produce open wounds as opposed to blisters caused by acids.
3. Dilute solutions of bases taste bitter. Examples are baking soda and milk of magnesia.

220-8.3.3.1 The bases used most frequently in this text are:

1. NaOH, sodium hydroxide.
2. NH_4OH, ammonium hydroxide.

220-8.3.4 THE IONIZATION OF WATER. The characteristic properties of acids and bases involve the behavior of these compounds in aqueous solutions. Before discussing this behavior and defining acids and bases, it is necessary to first describe an important aspect of water itself, namely, the partial ionization of water and the species produced by the ionization.

220-8.3.4.1 The Hydronium Ion. The equation for the reversible ionization of water is:

$$2H_2O \leftrightarrows H_3O^+ \ OH^- \qquad (8\text{–}1)$$

The ion H_3O^+ is called the hydronium ion. There is good experimental evidence that the H^+ ion does not exist independently in water. This conclusion is understandable if it is recognized that the H^+ ion is nothing but a bare proton. Due to the small size and, thus, the high charge density of the proton, it is reasonable to expect H^+ ions to be very reactive and strongly attracted to undissociated water molecules.

220-8.3.4.1.1 Although the evidence clearly shows that the proton does not exist alone, it is unclear exactly how many water molecules are associated with the proton. Since the exact formula for the species is of little importance in this text, the simplest designation, H_3O^+, is used throughout.

220-8.3.4.2 Ionization Equilibrium in Water. The ionization of water is a reversible, equilibrium process. The reaction occurs in both forward and reverse directions simultaneously. The discussion in Section 7 of chemical equilibrium and how it is affected by changes in temperature and concentration applies to the reaction of equation (8-1). Thus, the equilibrium constant expression for the ionization of water is:

$$K_{eq} = \frac{[H_3O^+][OH^-]}{[H_2O]_2} \quad \text{(at constant temperature)} \qquad (8\text{-}2)$$

As usual, the brackets indicate concentration in moles/liter. In pure water and in dilute solutions, however, the term $[H_2O]$ is essentially constant. The concentration of water **in water** is just the density of water which is 1 gm/ml at room temperature (25°C or 77°F). In moles/liter:

$$[H_2O] = 1000 \ \frac{\text{ml}}{\text{liter}} \times 1 \ \frac{\text{gm}}{\text{ml}} \times \frac{1 \text{ mole}}{18 \text{ gm}}$$

$$= 55.5 \text{ moles/liter}$$

Therefore, the term $[H_2O]^2$ in Equation (8-2) can be combined with the constant, K_{eq}, and the equation becomes:

$$K_w = K_{eq}[H_2O]^2 = [H_3O^+][OH^-] \qquad (8\text{-}3)$$

By common practice, the subscript w is used to indicate that the constant applies to water and also that it includes the constant $[H_2O]^2$. The constant, K_w is sometimes referred to as the ion-product constant of water.

220-8.3.4.2.1 The ionization of one water molecule produces one H_3O^+ ion and one OH^- ion. Thus, in pure water $[H_3O^+]$ and $[OH^-]$ are equal. At 25°C, $[H_3O^+] = [OH^-] = 10^{-7}$ mole/liter. By equation (8-3),

$$K_w = [H_3O^+][OH^-] = (10^{-7})(10^{-7}) = 10^{-14} \text{ (at 25°C)} \quad (8\text{-}4)$$

The relationship expressed in this equation is of great importance throughout this text and in the chemistry control of boiler water. Not only should the relationship be memorized but also its meaning should be clearly understood.

220-8.3.4.2.2 The meaning of equation (8-3), and the particular case of equation (8-4), is best understood in relation to LeChatelier's Principle: **If a system initially at equilibrium is perturbed by a change in the conditions which affect the equilibrium, the system will respond in a manner which minimizes the effect of the change.** Applying the discussion of LeChatelier's Principle given in Section 7 to the equilibrium represented by equation (8-1) and

$$K_w = [H_3O^+][OH^-] = 10^{-14} \text{ (at 25°C)} \quad (8\text{-}5)$$

it is seen that a change in concentration of either H_3O^+ or OH^- affects the concentration of the other. For instance, if $[H_3O^+]$ is increased by addition of some other substance, the system minimizes the effects of this change by a shift to the left in equation (8-1) to use up some of the added H_3O^+ and simultaneously reduce $[OH^-]$. When equilibrium is again established, equation (8-5) must apply if temperature has not changed. The net effect in this case is an increase in $[H_3O^+]$ and a decrease in $[OH^-]$. Similar reasoning shows that if $[OH^-]$ is increased by addition of another substance, there will be a net decrease in $[H_3O^+]$. Thus, if the concentration of either H_3O^+ or OH^- is changed, the concentration of the other must change by an amount such that the product of the two is always 10^{-14} at 25°C.

220-8.4 DEFINITION OF ACIDS AND BASES

220-8.4.1 Acids and bases owe their properties to their ability to produce H_3O^+ and OH^- ions, respectively, in aqueous solutions. These compounds thus disturb the water ionization equilibrium, but they do not change the value of K_w which is dependent only on temperature.

220-8.4.2 Acids are those compounds which produce H_3O^+ ions directly when dissolved in water. This behavior is typified by HCl:

$$HCl + H_2O \leftrightarrows H_3O^+ \ Cl^- \qquad (8\text{–}6)$$

220-8.4.3 Bases are those compounds which produce OH^- ions directly in aqueous solutions, as illustrated by NaOH:

$$NaOH \xrightarrow{H_2O} Na^+ + OH^- \quad (8\text{-}7)$$

Although water does not participate directly in the reaction of equation (8-7), it should be understood that the dissociation takes place in solution. This is indicated by H_2O above the arrow. Also, the process of dissolving and dissociating into ions illustrated by the above equations usually generates heat.

220-8.4.4 Compared to the equilibrium concentrations of [H_3O^+] and [OH^-] in pure water, acid solutions contain excess H_3O^+ ions ([H_3O^+] > 10^{-7} mole/liter at 25°C) and base solutions contain excess OH^- ions ([OH^-]) > 10^{-7} mole/liter at 25°C). The terms **alkaline** and **caustic** are also often used to mean basic. Pure water, or any solution in which [H_3O^+] = [OH^-], is neutral. Such solutions are neither acidic nor basic since neither [H_3O^+] nor [OH^-] is in excess.

220-8.5 CONCENTRATION UNITS OF ACIDS AND BASES-NORMALITY

220-8.5.1 The concentration of acids and bases may be expressed in terms of molarity, **moles per liter of solution** , but it is often more convenient to use another system of units called normality. Although the discussion of normality in this section is restricted to acids and bases, these units are also used for solutions of other types of compounds. Normality involves a quantity called equivalent weight. To illustrate the usefulness of these concentration units, consider the reaction:

$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O \quad (8\text{-}8)$$

From the equation, 2 moles of NaOH neutralize 1 mole of H_2SO_4, or 1 mole of NaOH neutralizes 1/2 mole of H_2SO_4. Thus, for the neutralization reaction of equation (8-8), 40 grams of NaOH (1 mole or 1 formula weight) are equivalent to 49 grams (1/2 mole or 1/2 formula weight) of H_2SO_4, regardless of the volume of solution in which these amounts are dissolved.

220-8.5.2 In general, the **equivalent weight** of any material is **the weight which would react with or be produced by the reaction of 1.0 gm of hydrogen or 8.0 gm of oxygen.** This definition can be simplified for acids and bases.

220-8.5.3 Since hydronium ions are the same (chemically) as hydrogen ions and since 1 mole of H^+ will form 1 gram of hydrogen, then the equivalent weight of an acid is the amount of the acid which will produce 1 mole (6.02×10^{23}) of hydronium ions. Also, since 1 mole of OH^- ions contains 8 grams of oxygen, the equivalent weight of a base is the amount of that base which will produce 1 mole (6.02×10^{23}) of hydroxyl ions.

220-8.5.4 For most of the acids and bases considered in this text, the equivalent weight can be determined from the formula for the compound. (Exceptions are noted as necessary.) From the formula, NaOH, it is seen that each mole of this compound produces 1 mole (6.02×10^{23}) OH^- ions. Thus, the equivalent weight of sodium hydroxide is the same as the formula weight or 40 grams. Each mole of H_2SO_4 can produce 2 moles (12.04×10^{23}) hydronium ions: therefore, the equivalent weight of sulfuric acid is half the formula weight or 98/2 = 49 grams.

Example 8-1: **Calculate the equivalent weight of:**

HCl

Solution 8-1: **Each mole of HCl produces 1 mole of H_3O^+, thus:**

$$\text{equivalent weight HCl} = \frac{\text{formula weight}}{1}$$

$$= 1.01 + 35.45 = 36.46 \text{ grams}$$

220-8.5.5 The concentration units of normality are analogous to molarity with the exception that normality is in terms of the number of equivalent weights per liter of solution rather than the number of moles per liter of solution. **A 1 normal solution (designated 1N) contains 1 equivalent weight per liter of solution.** (The letter N in normal concentration units is usually underlined to avoid confusing it with the symbol for nitrogen.) Similarly, a 0.5N solution contains 1/2 equivalent weight per liter of solution, and so on.

Example 8-2: Calculate the normality of a solution which contains 150 grams of NaOH in 2.50 liters of solution.

Example 8–2: Calculate the normality of a solution which contains 150 grams of NaOH in 2.50 liters of solution.

Solution 8-2: **As shown above, the equivalent weight of NaOH is 40 grams. Thus, the number of equivalent weights in 150 grams of NaOH is:**

$$\text{number of equivalent weights} = \frac{150 \text{ grams}}{40 \text{ grams}} = 3.75$$

From the definition of normality:

$$\text{normality} = \frac{\text{no. of equivalent weights}}{\text{liters of solution}}$$

$$= \frac{3.75}{2.50} = 1.5\underline{N}$$

220-8.5.6 The use of normal concentration units greatly simplifies many calculations involving acid-base reactions. This is due to the relationship: **one equivalent weight of an acid reacts completely with one equivalent weight of a base.** (Note that this statement is not always true if **mole** is substituted for **equivalent weight.**) The use of this relationship is illustrated in paragraph 220-8.6.

220-8.6 REACTION BETWEEN ACIDS AND BASES

220-8.6.1 GENERAL. In chemical reactions, acids and bases counteract each other. The essential feature of these reactions is the combination of H_3O^+ ions from the acid with OH^- ions from the base to form water. **Such a reaction which destroys (at least partially) the acidic or basic properties of the solution is called neutralization.** Suppose solutions of HCl and NaOH are mixed. Equations (8-6) and (8-7) show that this amounts to mixing H_3O^+ and Cl^- ions with Na^+ and OH^- ions:

$$H_3O^+ + Cl^- + Na^+ + OH^- \rightarrow 2H_2O + Na^+ + Cl^- \quad (8\text{-}9)$$

The H_3O^+ and OH^- ions combine to form water molecules until the final H_3O^+ and OH^- concentrations satisfy K_w , as discussed in paragraphs 220-8.3.4.2 through 220-8.3.4.2.2. Because so little of the water is ionized, it is properly shown in the molecular form in equation (8-9). The ions, Na^+ and Cl^- , remain uncombined in solution. Although not shown by equation (8-9), heat is usually generated by a neutralization reaction.

220-8.6.1.1 For convenience, **all** the reactants and products in a neutralization reaction are often written as if they were molecules. For example:

$$HCl + NaOH \rightarrow H_2O + NaCl. \quad (8\text{-}10)$$

This method relies on the reader’s general knowledge of chemistry to recognize that the reaction takes place in aqueous solution and that some of the compounds dissociate into ions in solution.

220-8.6.1.2 The products of any neutralization reaction are water and a compound composed of the cation (positive ion) of the base and the anion (negative ion) of the acid. This general type of compound is called a salt. Salts are ionic compounds and many are very soluble in water. Thus, after a neutralization reaction, the salt usually remains in solution as ions, such as Na^+ and Cl^- in equation (8-9). The solid compound can be obtained by evaporating the water from the solution.

220-8.6.1.3 In neutralization reactions there are two general situations depending on the relative amounts of acid and base: (1) exact neutralization, in which equal numbers of equivalent weights of acid and base are mixed; that is, the relative amounts of acid and base mixed are in the exact stoichiometric ratio required by the chemical reaction: (2) partial or incomplete neutralization, in which one of the reactants is limiting; that is, there is an excess of either acid or base.

220-8.6.2 EXACT NEUTRALIZATION. The case of **exact neutralization** is usually the simpler of the two cases and is described by a very simple equation:

$$V_a N_a = V_b N_b \text{ (for exact neutralization) } (8\text{-}11)$$

where:

subscripts a and b indicate acid and base, respectively

V is volume

N is the concentration in **normality**

The volume may be expressed in any units so long as both V_a and V_b are in the same units, but the concentration**must** be in units of normality.

220-8.6.2.1 Since normality is the number of equivalent weights per liter of solution, if V is in liters, then the product V x N gives the number of equivalent weights contained in V liters of solution. Equation (8-11) is a mathematical expression of the statement: **equal numbers of equivalent weights of an acid and a base react exactly.** If the volumes are expressed in units other than liters, equation (8-11) still applies because the factor required to convert to units of liters would appear on both sides of the equation and would cancel out.

220-8.6.2.2 The solution which remains after exact neutralization is neutral since it is neither acidic nor basic. From paragraph 220-8.4.4, this means that $[H_3O^+] = [OH^-]$ after exact neutralization.

Example 8-3: ***Calculate the volume of 0.5N KOH required to neutralize 3 liters of 1.5N HNO_3***

Solution 8-3:

$$V_a \times N_a = V_b \times N_b$$

$$V_b = \frac{V_a \times N_a}{N_b}$$

$$= \frac{3 \text{ liters} \times 1.5\underline{N}}{0.5\underline{N}}$$

$$= 9 \text{ liters of } 0.5\underline{N} \text{ KOH}$$

Example 8-4: ***Given that 300 ml of 0.75N H_2SO_4 exactly neutralize 800 ml of NaOH solution of unknown concentration, calculate the concentration of the NaOH solution.***

Solution 8-4:

$$V_a \times N_a = V_b \times N_b$$

$$N_b = \frac{V_a \times N_a}{V_b}$$

$$= \frac{300 \times 0.75\underline{N}}{800}$$

$$= 0.28\underline{N} \text{ NaOH}$$

220-8.6.3 INCOMPLETE NEUTRALIZATION. In this case, the amount of one of the reactants (either the acid or the base) is greater than the amount required to react exactly with the other reactant. Consequently, the solution remaining after the reaction will be either acidic or basic, depending on which reactant was in excess. For this situation, equation (8-11) cannot be used directly, but each side of the equation can be used separately.

V_a N_a = number of equivalents of acid (8-12)

V_b N_b = number of equivalents of base (8-13)

In this case, V must be in liters.

220-8.6.3.1 Often, one wishes to calculate whether the solution will be acidic or basic after a reaction and how much of the excess reactant remains. In determining the concentration of the excess reactant left in the final solution, one must always remember that the volume of the final solution is the sum of the volumes of the reactants. The following example illustrates one such calculation.

Example 8-5: *One liter of a 2.3N HNO_3 solution is added to 700 milliliters of 4N NaOH solution. Determine whether the final solution is acidic or basic, and calculate the concentration of the excess reactant in the final solution.*

Solution 8-5: *Apply Equations (8-12) and (8-13).*

$$\begin{aligned} \text{number of equivalent weights } HNO_3 &= V_a N_a \\ &= 1 \text{ liter} \times 2.3\underline{N} \\ &= 2.3 \end{aligned}$$

$$\begin{aligned} \text{number of equivalent weights of NaOH} &= V_b N_b \\ &= 0.7 \text{ liters} \times 4\underline{N} \\ &= 2.8 \end{aligned}$$

Thus, NaOH is in excess by 0.5 equivalent weights. The concentration of NaOH in the final solution (1 liter + 0.7 liter) is:

$$\begin{aligned} \text{Normality (NaOH)} &= \frac{0.5 \text{ equivalent weights}}{1.7 \text{ liters}} \\ &= 0.29\underline{N} \end{aligned}$$

Since the base is in excess, the final solution is basic.

220-8.6.4 ALTERNATE METHOD OF NEUTRALIZATION CALCULATIONS. Neutralization calculations can also be performed using the molar relationship expressed in the balanced chemical equation for the particular reaction involved. To illustrate this method, consider Example 8-4 again. The equation for this reaction is:

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$$

If, as in this case, concentrations are given in normality, first convert to molarity:

$$\underline{M}\ \frac{\text{moles}}{\text{liter}} = \underline{N}\ \frac{\text{equivalents}}{\text{liter}} \times \frac{\text{moles}}{\text{equivalent}}$$

For H_2SO_4, 1 mole = 2 equivalents, thus:

$$\underline{M} = 0.75\ \underline{N} \times \frac{1\ \text{mole}}{2\ \text{equivalents}}$$

$$= 0.375\ \text{mole/liter}$$

To calculate the number of moles of H_2SO_4 which react:

$$0.375\ \frac{\text{mole}}{\text{liter}} \times 0.300\ \text{liter} = 0.112\ \text{mole}\ H_2SO_4$$

From the equation, the amount of NaOH required is:

$$0.112\ \text{mole}\ H_2SO_4 \times \frac{2\ \text{moles NaOH}}{1\ \text{mole}\ H_2SO_4} = 0.224\ \text{mole NaOH}$$

This amount of NaOH is contained in 800 ml of solution; thus:

$$\underline{M}\ \text{NaOH} = \frac{0.224\ \text{mole}}{0.800\ \text{liter}} = 0.28\ \frac{\text{mole}}{\text{liter}}$$

Or, since 1 mole = 1 equivalent of NaOH:

$$0.28\underline{M} = 0.28\underline{N}$$

Solving incomplete neutralization problems by this method is analogous to Solution 8-5, substituting molarity and moles for normality and equivalent weights and using the balanced equation.

220-8.7 STRENGTH OF ACIDS AND BASES

220-8.7.1 GENERAL. It has been noted that the properties of acids are due to H_3O^+ ions and the properties of bases are due to OH^- ions in the respective solutions. It follows that the greater the concentration of H_3O^+ ions the more acidic the solution; that is, acidity increase as $[H_3O^+]$ increases. Similarly, basicity increases as $[OH^-]$ increases. The acidity of a solution varies directly with $[H_3O^+]$; however, $[H_3O^+]$ is determined by two factors; (1) the concentration of the compound which dissociates to produce H_3O^+ ions, and (2) the extent to which the compound dissociates.

220-8.7.1.1 Most of the specific acids discussed in this text dissociate completely at all concentrations. Such acids are called strong acids. Many acids, called weak acids, do not dissociate completely in aqueous solutions. Weak acids establish an equilibrium between the forward and reverse steps of the dissociation reaction. For the generalized weak acid, HX, the equation is:

The corresponding ionization constant expression is:

$$HX + H_2O \rightleftarrows H_3O^+ + X^- \qquad (8\text{–}14)$$

The corresponding ionization constant expression is:

$$K_i = \frac{[H_3O^+][X^-]}{[HX][H_2O]} \qquad (8\text{-}15)$$

Because the concentration of water in dilute solutions is constant, it is included in the left side of the equation and the ionization constant expression is:

$$K_i = K_{eq} = \frac{[H_3O^+][X^-]}{[HX]} \qquad (8\text{-}16)$$

220-8.7.1.2 Equations (8-14) and (8-15) may, in principle, be applied to all acids. For strong acids, however, the value of K_i is very large (much greater than 1) which means that the forward reaction predominates and essentially all the acid dissociates. For weak acids, K_i is small (much less than 1) and the reverse reaction predominates. Ionization reactions and values of the ionization constants for several acids and bases are given in Table 220-8-1. Notice that K_i for strong acids is simply indicated as large. Acids which undergo more than one ionization reaction are discussed in paragraphs 9.4.4 through 9.4.4.3.1.

220-8.7.1.3 The most familiar example of a weak acid is acetic acid, $HC_2H_3O_2$, which is the characteristic ingredient in vinegar and spoiled wine. For this acid,

$$HC_2H_3O_2 + H_2O \rightleftarrows H_3O^+ + C_2H_3O_2^- \qquad (8\text{-}17)$$

$$K_i = 1.8 \times 10^{-5} = \frac{[H_3O^+]\ [C_2H_3O_2^-]}{[HC_2H_3O_2]} \qquad (8\text{-}18)$$

220-8.7.1.4 To demonstrate the effect of the ionization constant on acidity, consider a 0.1N solution of the strong acid, HCl, and a 0.1N solution of the weak acid, $HC_2H_3O_2$, and determine the hydronium ion concentration. Both solutions contain 0.1 equivalent weight of compound per liter of solution. From the formulas for the compounds, it is seen that 1 mole of each compound is capable of producing 1 mole (6.02×10^{23}) of H_3O^+ ions. In each case, the formula weight is equal to the equivalent weight and the 0.1N solutions are also 0.1M .

220-8.7.2 HCl SOLUTION. Hydrochloric acid is a strong acid and the HCl in solution is completely dissociated.

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

From this equation, each mole of HCl dissolved in water produces 1 mole of H_3O^+ ions; thus, 0.1 mole of HCl produces 0.1 mole of H_3O^+ ions.

$$[H_3O^+] = 0.1\underline{M}$$

Table 220-8-1 IONIZATION CONSTANTS FOR ACIDS, BASES, AND WATER AT 25°C (77°F)

Acid or Base	Reversible Ionization Reaction	Ionization Constant, K_i
Acetic acid	$H_2O + HC_2H_3O_2 \rightleftarrows H_3O^+ + C_2H_3O_2^-$	1.8×10^{-5}
Ammonia	$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$	1.8×10^{-5}
Boric acid	$H_2O + H_3BO_3 \rightleftarrows H_3O^+ + H_2BO_3^-$	$K_1 = 5.8 \times 10$
Carbonic acid	$H_2O + H_2CO_3 \rightleftarrows H_3O^+ + HCO_3^-$ $H_2O + HCO_3^- \rightleftarrows H_3O^+ + CO_3^-$	$K_1 = 4.5 \times 10^{-7}$ $K_1 = 5.6 \times 10^{-11}$
Citric acid	$H_2O + H_3C_6H_5O_7 \rightleftarrows H_3O^+ + H_2C_6H_5O_7^-$	$K_1 = 8.7 \times 10^{-4}$
Hydrochloric acid	$H_2O + HCl \rightarrow H_3O^+ + Cl^-$	large
Hydrofluoric acid	$H_2O + HF \rightleftarrows H_3O^+ + F^-$	7.2×10^{-4}
Hydrogen sulfide	$H_2O + H_2S \rightleftarrows H_3O^+ + HS^-$ $H_2O + HS^- \rightleftarrows H_3O^+ + S^-$	$K_1 = 5.7 \times 10^{-8}$ $K_2 = 1.2 \times 10^{-15}$
Hydrazine	$H_2O + N_2H_4^- \rightleftarrows N_2H_5^+ + OH^-$	$K = 3 \times 10^{-6}$
Nitric acid	$H_2O + HNO_3 \rightarrow H_3O^+ + NO_3^-$	large
Phosphoric acid	$H_2O + H_3PO_4^- \rightleftarrows H_3O^+ + H_2PO_4^-$ $H_2O + H_2PO_4^- \rightleftarrows H_3O^+ + H_4PO_4^-$ $H_2O + HPO_4^- \rightleftarrows H_3O^+ + PO_4^-$	$K_1 = 7.5 \times 10^{-3}$ $K_2 = 6.2 \times 10^{-8}$ $K_3 = 4.8 \times 10^{-13}$
Sulfuric acid	$H_2O + H_2SO_4^- \rightarrow H_3O^+ + HSO_4^-$ $H_2O + HSO_4^- \rightleftarrows H_3O^+ + SO_4^-$	large $K_2 = 1.2 \times 10^{-2}$
Sulfurous acid	$H_2O + H_2SO_3^- \rightleftarrows H_3O^+ + HSO_3^-$ $H_2O + HSO_3^- \rightleftarrows H_3O^+ + SO_3^-$	$K_1 = 1.7 \times 10^{-2}$ $K_2 = 6 \times 10^{-8}$
Water	$2H_2O \rightleftarrows H_3O^+ + OH^-$	$K_w = 1 \times 10^{-14}$

220-8.7.3 $HC_2H_3O_2$ SOLUTION. Equations (8-17) and (8-18) must be used in determining $[H_3O^+]$ in a $0.1\underline{N}$ (or $0.1\underline{M}$) acetic acid solution. If none of the acetic acid dissociated there would be 0.1 mole $HC_2H_3O_2$ per liter of solution. Let the amount which actually does dissociate be X mole/liter. From equation (8-17), it is seen that if X mole/liter of $HC_2H_3O_2$ dissociates:

$$[H_3O^+] = [C_2H_3O_2^-] = X$$

$$[HC_2H_3O_2] = 0.1 - X$$

Then, by Equation (8-16):

$$1.8 \times 10^{-5} = \frac{(X)(X)}{0.1 - X}$$

which can be rearranged to give:

$$X^2 + (1.8 \times 10^{-5})X - 1.8 \times 10^{-6} = 0$$

The last equation is of the form $aX^2 + bX + c = 0$, where a, b, and c are constants. This type of equation can be solved using the quadratic formula:

$$X = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

In the above example,

$$a = 1$$

$$b = 1.8 \times 10^{-5}$$

$$c = -1.8 \times 10^{-6}$$

and the solution is:

$$X = 1.35 \times 10^{-3}$$

and

$$[H_3O^+] = 1.35 \times 10^{-3} \text{ mole/liter}$$

Thus, although enough acetic acid was initially dissolved to give 0.1 mole $HC_2H_3O_2$ per liter of solution, only 0.0013 mole/liter dissociates into H_3O^+ and $C_2H_3O_2^-$ ions.

220-8.7.3.1 Note in the preceding calculations, that the acid is considered to be the only source of H_3O^+ ions. The small amount of H_3O^+ ions produced by the ionization of water is ignored in determining $[H_3O^+]$. To show that this practice is valid, recall that for any acidic solution, $[H_3O^+]$ is greater than 10^{-7}. Suppose that sufficient acid is added to cause $[H_3O+]$ to be 10^{-6} $\underline{M}$. In any aqueous solution, K_w must be satisfied. Thus,

$$K_w = [H_3O^+][OH^-] = 10^{-14}$$

$$[OH^-] = \frac{K_w}{[H_3O^+]}$$

$$= \frac{10^{-14}}{10^{-6}}$$

$$= 10^{-8}$$

From equation (8-1), the amount of H_3O^+ produced by the ionization of water would also be 10^{-8} $\underline{M}$. This amount is insignificant compared to the amount contributed by the acid, 10^{-6} $\underline{M}$. In the preceding examples, the solutions are even more acidic, so it is valid to ignore water as a source of H_3O^+ ions.

220-8.7.3.2 The preceding description of strong and weak acids also applies to bases. Most of the bases encountered in this text are strong bases because the compounds dissociate completely in aqueous solutions; for example - NaOH. The most frequently used example of a weak base is NH_4OH. Purely by coincidence, K_i for NH_4OH is the same as K_i for acetic acid, i.e., 1.8×10^{-5}.

220-8.7.3.3 The conclusion to be drawn from the foregoing is that **at comparable concentrations** strong acids form much more acidic solutions than do weak acids and strong bases form much more basic solutions than do weak bases. It must be remembered, however, that acidity and basicity depend on both concentration and strength (extent of dissociation) of the acid or base. Thus, a very concentrated solution of the weak acid $HC_2H_3O_2$ is highly acidic and can produce burns on the skin. On the other hand, a very dilute solution of a strong acid, such as HCl, may be only slightly acidic.

220-8.8 THE pH SCALE

220-8.8.1 GENERAL. Many chemical processes are very sensitive to the acidity of the solution in which they take place. For example, in a solution which contains 0.1 $\underline{M}$ Zn^{++}, 0.1 $\underline{M}$ Fe^{++}, and 0.1 $\underline{M}$ S^-, essentially all the zinc can be precipitated as ZnS if the hydronium ion concentration is about 3.3×10^{-2} $\underline{M}$. At this value of $[H_3O^+]$, none of the Fe^{++} precipitates as FeS. If the $[H_3O+]$ is changed to ~3.3×10^{-3} $\underline{M}$, both ZnS and FeS precipitate, and separation is impossible. In addition, it is found that many types of corrosion occur most slowly over a relatively narrow range of hydronium ion concentration and more rapidly if $[H_3O^+]$ is above or below that range.

220-8.8.1.1 In order to treat these aspects of chemistry more precisely, a quantitative system of expressing acidity or basicity is needed. This need could be met by using the value of $[H_3O^+]$ as a measure of acidity, but in most of the cases of interest, $[H_3O^+]$ is in the range 10^{-1} to 10^{-14}. Since small numbers are inconvenient to work with, an alternate system for expressing the acidity of dilute solutions of acids and bases has been devised. This system is based on a quantity called **pH** which is**defined by:**

$$pH = -\log [H_3O^+] \quad (8\text{-}19)$$

where $[H_3O^+]$ is always in units of moles/liter (molarity). The negative of the logarithm is specified in equation (8-19) because the logarithm of any number less than 1.0 is negative; thus, multiplication by -1 causes the most frequently used values of pH to be positive. (The term pH was first defined by a Danish chemist and is derived from p for the Danish word potenz (power) and H for hydrogen.)

220-8.8.1.2 In effect, pH is just a mathematical device to simplify the scale of hydronium ion concentration. Because of the definition as the negative of the logarithm of the hydronium ion concentration, the pH scale is inverted. That is, low values of pH correspond to high values of $[H_3O^+]$ and vice versa.

Example 8-6: *Calculate the pH of solutions containing:*

1. $1 \times 10^{-2}\underline{M}\ H_3O^+$
2. $1 \times 10^{-10}\underline{M}\ H_3O^+$
3. $2.3 \times 10^{-14}\underline{M}\ H_3O^+$

Solution 8-6: $pH = -\log [H_3O^+]$

$$\begin{aligned} 1.\ pH &= -\log (1 \times 10^{-2}) \\ &= -\log 1 - \log 10^{-2} \\ &= 0-(-2)(1) = 2 \\ 2.\ pH &= -\log (1 \times 10^{-10}) \\ &= -\log 1 - \log 10^{-10} \\ &= 0 + 10 = 10 \\ 3.\ pH &= -\log (2.3 \times 10^{-4}) \\ &= -\log 2.3 - \log 10^{-4} \\ &= -0.36 + 4.0 = 3.64 \end{aligned}$$

220-8.8.1.3 Analogous to pH, the quantity **pOH** is defined as:

$$pOH = -\log [OH^-] \quad (8\text{-}20)$$

where $[OH^-]$ is always in moles/liter.

220-8.8.1.4 There is a very simple but exact relationship between pH and pOH which follows from equation (8-4) and the definitions of pH and pOH, equations (8-19) and (8-20).

$[H_3O^+][OH^-] = 10^{-14}$ (at 25°C) (8-4)

Taking the logarithm of both sides and multiplying by -1 gives:

$-\log([H_3O^+][OH^-]) = -\log(10^{-14})$

$-\log[H_3O^+] - \log[OH^-] = -(-14 \log 10)$

$= 14$

Substituting from equations (8-19) and (8-20) gives:

$pH + pOH = 14$ (at 25°C) (8-21)

Example 8-7: ***Calculate the pH of a solution which contains 1 x 10^{-3} mole/liter of NaOH at 25°C.***

Solution 8-7: ***Sodium hydroxide is a strong base and completely dissociates in aqueous solutions. Therefore, $[OH^-]$ = 1 x 10^{-3} mole/liter. The problem may now be solved in either of two ways.***

1. Use the relation for the ionization of water to calculate $[H_3O^+]$.

$$[H_3O^+][OH^-] = 10^{-14}$$

$$[H_3O^+] = \frac{10^{-14}}{[OH^-]}$$

$$= \frac{10^{-14}}{10^{-3}}$$

$$= 10^{-11}$$

$$\text{Then, } pH = -\log [H_3O^+]$$

$$= -\log (10^{-11})$$

$$= 11$$

2. First calculate pOH;

$$pOH = -\log [OH^-]$$

$$= -\log (10^{-3})$$

$$= 3$$

Then use Equation (8-21) to find pH.

$$pH + pOH = 14$$

$$pH = 14 - pOH$$

$$= 14 - 3$$

$$= 11$$

220-8.8.1.5 In paragraph 220-8.4.4 it is noted that pure water is neutral and $[H_3 O^+] = [OH^-]$. At room temperature (~25°C) for pure water:

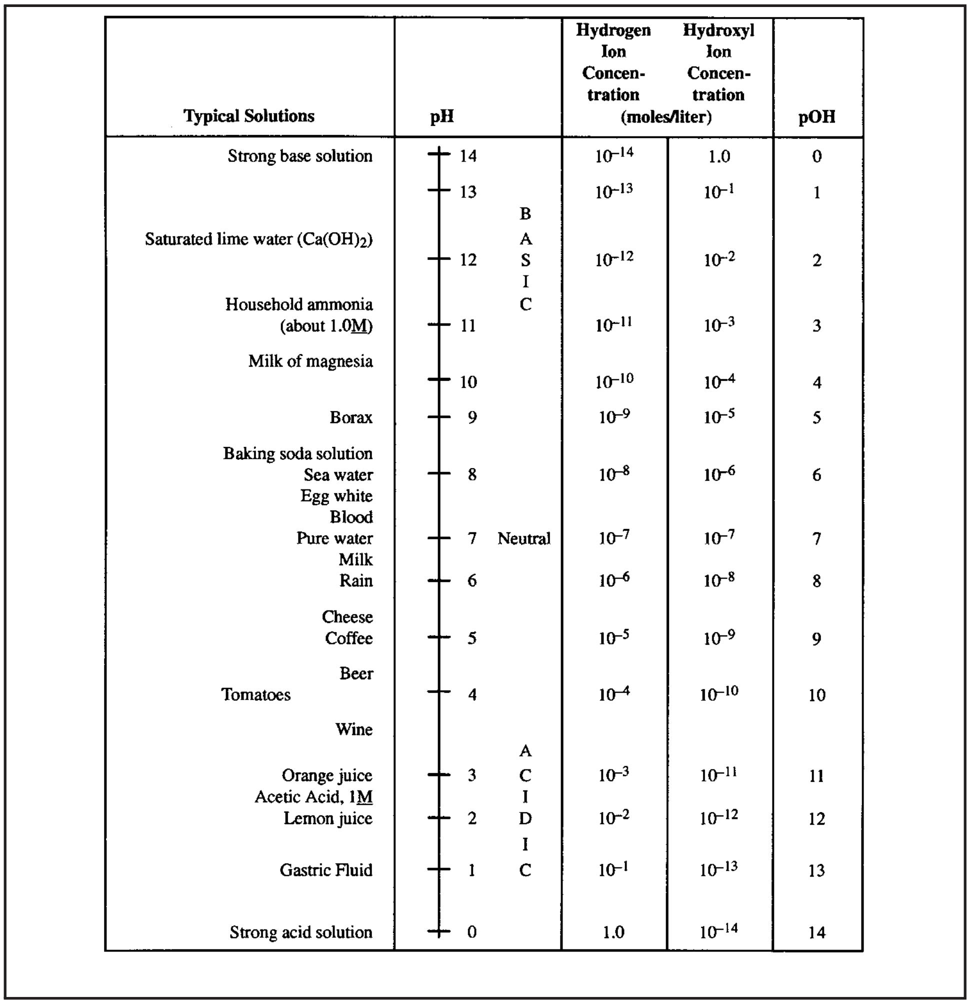
$$[H_3 O^+] = [OH^-] = 10^{-7} \text{ mole/liter}$$

Thus for pure water or any neutral solution at room temperature:

$$pH = pOH = 7$$

From the previous definitions of acids and bases, a solution which has pH < 7 at 25°C is acidic. A solution with pH > 7 at 25°C is basic. Table 220-8-2 illustrates the pH and pOH scales and gives a few examples of solutions with various values of pH. Calculations involving pH and pOH of weak acids and bases are described in Section 9.

Table 220-8-2 EXAMPLE SOLUTIONS ON THE pH AND pOH SCALES



Typical Solutions	pH		Hydrogen Ion Concentration (moles/liter)	Hydroxyl Ion Concentration	pOH
Strong base solution	14		10^{-14}	1.0	0
	13		10^{-13}	10^{-1}	1
Saturated lime water ($Ca(OH)_2$)	12	BASIC	10^{-12}	10^{-2}	2
Household ammonia (about 1.0M)	11		10^{-11}	10^{-3}	3
Milk of magnesia	10		10^{-10}	10^{-4}	4
Borax	9		10^{-9}	10^{-5}	5
Baking soda solution Sea water Egg white	8		10^{-8}	10^{-6}	6
Blood Pure water Milk	7	Neutral	10^{-7}	10^{-7}	7
Rain	6		10^{-6}	10^{-8}	8
Cheese Coffee	5		10^{-5}	10^{-9}	9
Beer Tomatoes	4		10^{-4}	10^{-10}	10
Wine Orange juice	3	ACIDIC	10^{-3}	10^{-11}	11
Acetic Acid, 1M Lemon juice	2		10^{-2}	10^{-12}	12
Gastric Fluid	1		10^{-1}	10^{-13}	13
Strong acid solution	0		1.0	10^{-14}	14

220-8.8.2 EFFECT OF TEMPERATURE ON PH AND THE IONIZATION OF WATER. As discussed in Section 7, a change in temperature always changes an equilibrium constant. Since the ionization of water is an equilibrium process, it is also affected by temperature. The ionization constant (or ion product constant) for water increases with increasing temperature up to ~500°F and then decreases.

220-8.8.2.1 Experimental values of K_w at various temperatures are listed in Table 220-8-3 and graphed in Figure 220-8-1. Notice in Table 220-8-3 that the pH of neutral water changes with temperature. At any temperature, however, for a neutral solution, $[H_3O^+] = [OH^-]$. It should also be noted that equation (8-21) is true only at or near 25°C (77°F).

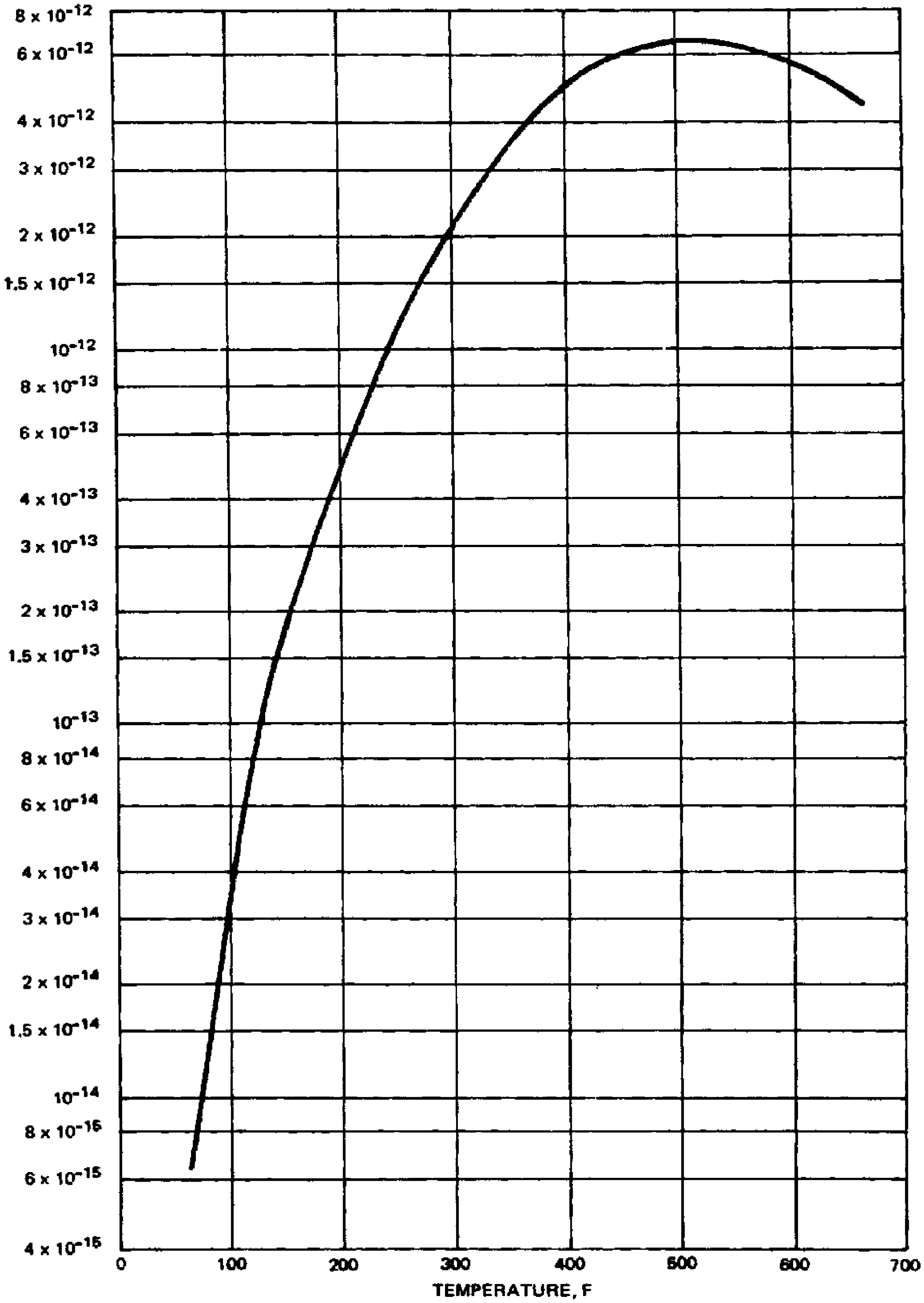


Figure 220-8-1 Ion Product Constant for Water

Table 220-8-3 ON PRODUCT CONSTANT AND NEUTRAL pH FOR WATER AT VARIOUS TEMPERATURES*

Temperature **°F °C**		**Ion Product Constant for Water**	**pH of Neutral Water**
64.4	18	0.64×10^{-14}	7.10
77	25	1.0×10^{-14}	7.00
140	60	8.9×10^{-14}	6.54
212	100	6.1×10^{-13}	6.10
302	150	2.2×10^{-12}	5.83
392	200	5.0×10^{-12}	5.65
482	250	6.6×10^{-12}	5.59
572	300	6.4×10^{-12}	5.60
662	350	4.7×10^{-12}	5.66

* J. W. Cobble, J. A. CHEM. Soc., 86.5394 (1964)

Example 8-8: ***For a 0.01$\underline{M}$ NaOH solution, estimate the pH at 77 and 200°F. (Assume that this dilute solution of NaOH is completely ionized at these temperatures and the density of the solution does not change.)***

Solution 8-8: ***The equation for the ionization of NaOH is***

$$NaOH \xrightarrow{H_2O} Na^+ + OH^-$$

Thus each mole of NaOH yields one mole of hydroxyl ions. As a result, $[OH^-] = 1.0 \times 10^{-2}$ for all conditions under consideration. To calculate pH the hydronium ion concentrations are needed. Hydronium ion concentrations can be calculated from the ion product constant for water.

$$K_w = [H_3O^+][OH^-], \text{ or } [H_3O^+] = \frac{K_w}{[OH^-]}$$

Obtain values of K_w from figure 220-19.

$$77°F \quad K_w = 1.0 \times 10^{-14}$$

$$200°F; \; K_w = 5.0 \times 10^{-13}$$

1. *at 77°F*

$$[H_3O^+] = K_w[OH^-] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-2}} = 1.0 \times 10^{-12}$$

$$pH = -\log [H_3O^+] = -\log [1.0 \times 10^{-12}] = 12.0$$

2. *at 200°F*

$$[H_3O^+] = K_w[OH^-] = \frac{5.0 \times 1.0^{-13}}{1.0 \times 10^{-2}} = 5.0 \times 10^{-11}$$

$$pH = -\log [H_3O^+] = -\log [5.0 \times 10^{-11}]$$

$$= -(\log 5.0 \times \log 10^{-11})$$

$$pH = -(0.70 - 11.0) = 10.3$$

220-8.8.2.2 Since [OH^-] is constant at 1.0×10^{-2} and K_w changes as temperature changes, then [H_3O^+], and thus pH, **must** change to conform to the new value of K_w. Also because [OH^-] is constant, pOH is constant.

220-8.8.2.3 Suppose the solution in Example 8-8 contained 1.0×10^{-2} $\underline{M}$ HCl instead of NaOH. Hydrochloric acid is a strong acid and is completely ionized.

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

In this case, [H_3O^+] and pH are constant and [OH^-] must change as K_w changes when the temperature is increased from 77°F to 200°F.

1. **77°F:**

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

$$[OH^-] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-2}} = 1.0 \times 10^{-12}$$

$$pH = -\log (1.0 \times 10^{-2}) = 2$$

$$pOH = -\log (1.0 \times 10^{-12}) = 12$$

2. **200°F:**

$$[OH^-] = \frac{5.0 \times 10^{-13}}{1.0 \times 10^{-2}} = 5.0 \times 10^{-11}$$

$$pH = -\log (1.0 \times 10^{-2}) = 2$$

$$pOH = -\log (5.0 \times 10^{-11}) = 10.3$$

220-8.8.2.4 In these examples the temperature change did not significantly change the density of the solution. (Density of water and dilute solutions is approximately 1 gm/ml over the range 32°F to 212°F.) Now suppose the temperature of the 1.0×10^{-2} $\underline{M}$ HCl solution were increased to 500°F. At this temperature the density of the solution would be about 0.8 gm/ml = 0.8 kg/liter. The total amount of dissolved HCl does not change, but the volume of solution and the concentration do change. To show this, consider one liter of the solution at 77°F then heat to 500°F.

1. 77°F; amount of HCl in 1 liter of solution is:

$$1.0 \times 10^{-2} \text{ mole/liter} \times 1 \text{ liter} = 1.0 \times 10^{-2} \text{ mole}$$

weight of 1 liter of solution is:

$$1.0 \text{ liter} \times 1.0 \text{ kg/liter} = 1.0 \text{ kilograms}$$

from part (1) of the previous calculation:

$$[OH^-] = 1.0 \times 10^{-12}$$

$$pH = 2$$

2. 500°F; Volume of 1 kg of solution is:

$$1 \text{ kg} \times \frac{1 \text{ liter}}{0.8 \text{ kg}} = 1.25 \text{ liters}$$

New concentration of HCl (and H_3O^+) is:

$$\frac{1.0 \times 10^{-2} \text{ mole}}{1.25 \text{ liters}} = 0.8 \times 10^{-2}\underline{M}$$

$$pH = -\log (8.0 \times 10^{-3})$$

$$= 2.18$$

The concentration of OH^- ions is again found from K_w:

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{6.7 \times 10^{-12}}{8.0 \times 10^{-3}} = 8.4 \times 10^{-10}\underline{M}$$

220-8.8.3 pH CHANGES IN MIXED SOLUTIONS. Very often in practical applications of chemistry, situations are encountered in which two solutions of different pH values are mixed. In calculations involving pH changes in these situations, care must be taken to always deal with the ion, H_3O^+ or OH^-, present in excess. That is:

1. When mixing two acidic solutions, always work with $[H_3O^+]$.
2. When mixing two basic solutions, always work with $[OH^-]$.
3. When mixing an acid and a base, first determine whether the final solution is acidic or basic, then use $[H_3O^+]$ if acidic or $[OH^-]$ if basic.

220-8.8.3.1 The reason for this precaution is due to the logarithmic nature of pH and pOH. For any given mixture problem the change in pH and each solution will be equal in magnitude (opposite in sign) to the change in pOH; however, the change in $[H_3O^+]$ will not be equal to the change in $[OH^-]$. This is illustrated in the following example.

Example 8-9 *How many moles of HNO_3 would be required to change the pH of 5 liters of a NaOH solution from 11 to 8? Assume volume does not change.*

Solution 8-9: *The problem statement indicates that the final solution will be basic, so the calculations should be performed in terms of $[OH^-]$.*

Initially;

$$\begin{aligned} pH &= 11 \\ pOH &= 14 - 11 = 3 \\ [OH^-] &= 1.0 \text{ x } 10^{-3}\underline{M} \\ \text{Total amount of } OH^- \text{ ions} &= 1.0 \text{ x } 10^{-3} \text{ mole/liter} \\ &\qquad \text{x } 5 \text{ liters} = 5 \text{ x } 10^{-3} \text{ mole} \end{aligned}$$

After addition of HNO_3;

$$\begin{aligned} pH &= 8 \\ pOH &= 14 - 8 = 6 \\ [OH^-] &= 1.0 \text{ x } 10^{-6}\underline{M} \\ \text{Total amount of } OH^- \text{ ions} &= 5 \text{ x } 10^{-6} \text{ mole} \end{aligned}$$

The change in OH^- is:

$$\begin{aligned} \Delta OH^- &= 5.0 \text{ x } 10^{-3} \text{ mole} - 5.0 \text{ x } 10^{-6} \text{ mole} \\ &= 5.0 \text{ x } 10^{-3} \text{ mole} - 0.005 \text{ x } 10^{-3} \text{ mole} \\ &= 4.995 \text{ x } 10^{-3} \text{ mole} \end{aligned}$$

Thus the amount of H_3O^+ ions required to react with 4.995 x 10^{-3} mole OH^- ions is 4.995 x 10^{-3} mole. Each mole of HNO_3 produces one mole of H_3O^+ ions so 4.995 x 10^{-3} mole HNO_3 is required.

220-8.8.3.2 Since in Example 8-9 $[OH^-]$ decreased, $[H_3O^+]$ must increase in order to satisfy K_w. The final $[OH^-]$ is 1 x 10^{-6} $\underline{M}$, thus:

$$\text{final } [H_3O^+] = \frac{K_w}{[OH^-]}$$

$$= \frac{1 \text{ x } 10^{-14}}{1 \text{ x } 10^{-6}}$$

$$= 1 \text{ x } 10^{-8}\underline{M}$$

NOTE

This value could also be obtained from the final pH of 8 given in the problem statement.

220-8.8.3.3 The change in the total amount of H_3O^+ ions is:

$$\Delta H_3O^+ = 5 \text{ liters x } 1 \text{ x } 10^{-8} \text{ mole/liter} - 5 \text{ liters x } 1 \text{ x } 10^{-11}$$

$$= 5 \text{ liters } (1.0 \text{ x } 10^{-8} - 0.001 \text{ x } 10^{-8})$$

$$= 4.995 \text{ x } 10^{-8} \text{ mole}$$

This value is extremely small compared to the change in OH^- of 4.995 10^{-3}. This is due to the fact that the overwhelming majority of H_3O^+ ions added to a basic solution combine with OH^- ions to form water. This will always be true unless sufficient acid is added to cause the final solution to be acidic as illustrated in the final example.

Example 8-10: 500 millileters of an HCl solution of pH = 2.5 are added to 250 milliliters of an NaOH solution with a pH of 11. Determine the pH of the final solution.

Solution 8-10: Since it is not apparent whether the final solution will be acidic or basic, first determine the total amounts of acid and base.

Acid:

$$pH = 2.5$$

$$[H_3O^+] = 10^{-2.5}$$

$$= 10^{0.5} \times 10^{-3}$$

$$= 3.16 \times 10^{-3}\underline{M}$$

$$\text{Total amount of } H_3O^+ = 3.16 \times 10^{-3} \text{ mole/liter} \times 0.5 \text{ liter.}$$

$$= 1.58 \times 10^{-3} \text{ mole.}$$

Base:

$$pH = 11$$

$$pOH = 3$$

$$[OH^-] = 1 \times 10^{-3}\underline{M}$$

$$\text{Total amount of } OH^- = 1 \times 10^{-3} \text{ mole/liter} \times 0.25\ .$$

$$= 2.5 \times 10^{-4} \text{ mole.}$$

Since 1 mole of acid reacts with 1 mole of base, the final solution will be acidic and will contain.

$$1.58 \times 10^{-3} - 0.25 \times 10^{-3} = 1.33 \times 10^{-3} \text{ mole of acid}$$

$$= 1.33 \times 10^{-3} \text{ mole } H_3O^+$$

The amount is contained in 750 milliliters, thus.

$$[H_3O^+] = \frac{1.33 \times 10^{-3} \text{ mole}}{0.75 \text{ liter}}$$

$$= 1.78 \times 10^{-3} \text{ mole/liter}$$

$$pH = -\log (1.78 \times 10^{-3})$$

$$= 2.75$$

220-8.9 SUMMARY

220-8.9.1 Water ionizes slightly into $H_3 O^+$ and OH^- ions. This ionization is described by:

$$[H_3 O^+][OH^-] = K_w$$

where K_w is a constant at a particular temperature (at 25°C or 77°F, $K_w\ 10^{-14}$).

220-8.9.2 Acids produce $H_3 O^+$ ions directly in aqueous solution and bases produce OH^- ions directly in aqueous solution; thus, these compounds disturb the ionization equilibrium of water. In pure water or neutral solutions, $[H_3 O^+] = [OH^-]$. In acidic solutions $[H_3 O^+] > [OH^-]$ and in basic solutions $[H_3 O^+] < [OH^-]$. In all aqueous solutions, however, $[H_3 O^+]$ and $[OH^-]$ are always such that $[H_3 O^+][OH^-] = K_w$ for the particular temperature.

220-8.9.3 Some acids, such as acetic acid, and some bases, such as ammonium hydroxide, ionize only partially in aqueous solution. These compounds are called weak acids and bases as opposed to strong acids and bases, such as HCl, HNO_3, NaOH, which are considered to be completely dissociated in aqueous solutions. The acidity of a particular solution depends on both the concentration and degree of ionization of the acid or base.

220-8.9.4 The concentrations of acid and base solutions are often expressed in units of normality (N) which is the number of equivalent weights per liter of solution. The use of normality simplifies calculations involving the reactions between acids and bases because of the relationship that one equivalent weight of an acid reacts exactly with one equivalent weight of a base. The products of acid-base reactions are always water and a salt composed of the anion of the acid and the cation of the base.

220-8.9.5 The acidity of aqueous solutions is expressed in terms of pH, which is related to the hydronium ion concentration by the definition:

$$pH = -\log [H_3 O^+] \quad ([H_3 O^+] \text{ in moles/liter})$$

A similar quantity, pOH, is related to the hydroxyl ion concentration by the definition:

$$pOH\ -\log [OH^-] \quad ([OH^-] \text{ in moles/liter})$$

Because $[H_3 O^+]$ and $[OH^-]$ are related to each other by the water ionization equilibrium, pH and pOH are also related.

$$pH + pOH = -\log K_w$$

At 25°C (77°F),

$$-\log K_w = 14$$

220-8.9.6 The value of K_w increases as temperature increases up to about 500°F. Thus, in this range, the pH of a neutral aqueous solution decreases with increasing temperature (at 25°C, neutral pH is 7). At all temperatures, however, in a neutral solution, $[H_3 O^+][OH^-] = \sqrt{K_w}$.

SECTION 8 PROBLEMS

1. Calculate the normality of a solution which contains 75 grams of H_2SO_4 in 750 milliliters of solution.
2. Twenty grams of NaOH are dissolved in enough water to give a final volume of 500 milliliters. Calculate the normality of NaOH.
3. Calculate the concentration of the following solutions in units of molarity and normality.
   a 15 grams of NaOH in 250 milliliters of solution
   b 25 grams of NH_4OH in 500 milliliters of solution
4. 25 milliliters of a 0.1N HCl solution are required to exactly neutralize 12.5 milliliters of NaOH. Calculate the concentration (normality) of the NaOH solution. How many grams of NaOH would be required to prepare 400 milliliters of this solution?
5. The pH of an HCl solution is 3. What is the hydronium ion concentration? What is the pOH?
6. A 0.1M solution of acetic acid has an hydronium ion concentration of 1.3 x 10^{-3} . What is the pH of the solution?
7. A 0.1M NH_4OH solution has an hydroxyl ion concentration of 1.3 x 10^{-3} . What is the pH of this solution?
8. The ionization constant for NH_4OH is 1.8 x 10^{-5} . For a 0.01M solution of ammonium hydroxide calculate:
   a The hydroxyl ion concentration
   b The pH
   c The percentage ionization
9. Calculate the hydroxyl ion concentration in solutions for which:
   a pH = 9.0
   b pH = 10.4
10. A solution of NaOH has a pH of 10.3. Calculate:
   a The hydroxyl ion concentration in molarity
   b The Na^+ concentration in parts per million

SECTION 8 PROBLEM ANSWERS

1. 2.04N
2. 1.0N
3.
   a 1.5N, 1.5M
   b 1.43N, 1.43M
4. 0.2N ; 3.2 grams
5. $[H_3O^+] = 1 \times 10^{-3}$ mole/liter pOH = 11
6. 2.89
7. 11.11
8.
   a $[OH^-] = 4.2\ 10^{-4}$ mole/liter
   b pH = 10.62
   c Percentage ionization = 4.2 percent

9.
- a $[OH^-] = 1 \times 10^{-5}$ mole/liter
- b $[OH^-] = 2.5 \times 10^{-4}$ mole/liter

10
- a $[OH^-] = 2.0 \times 10^{-4}\ \underline{M}$
- b $Na^+ = 4.6$ parts per million

SECTION 9.

AQUEOUS EQUILIBRIUM PROCESSES

220-9.1 INTRODUCTION

220-9.1.1 Section 7 describes the fundamental concepts of chemical equilibrium, primarily in terms of reactions involving gases. Of more practical interest in the study of boiler water chemistry are equilibrium processes which occur in aqueous solution. The ionization equilibrium of pure water and the effects of acids and bases on this equilibrium are described in the preceding section. This section extends the equilibrium discussion to other processes in aqueous solutions and elaborates on a few topics introduced previously. Chemical equilibrium is used extensively in steam propulsion plant fluid systems because by shifting the equilibrium concentrations the adverse effects of many disturbances are minimized.

220-9.1.2 As noted in Section 7, the equilibrium constant alone gives no information about the time required for equilibrium to be established. Such information is available only through experimentation. In aqueous solutions, however, it is generally found that equilibrium is achieved very rapidly, especially if the process involves reactions between ions. This great speed is mostly due to the attraction between ionic charges and the polarizing ability of water molecules. With the exception of dissolving a substance, it is to be assumed in all the processes discussed in this section that equilibrium is attained immediately upon bringing the appropriate substances together. This section discusses the equilibrium processes which occur when an ionizable material is added to water.

220-9.2 GLOSSARY OF TERMS

220-9.2.1 Terms used in this section are defined as follows:

a. **Buffer:** A solution containing appreciable quantities of both a weak electrolyte and a salt of the weak electrolyte. Within limits, buffers are capable of withstanding concentration or dilution processes or addition of small amounts of acid or base without a significant change in pH.

b. **Common Ion Effect:** The decrease in the ionization or solubility of a compound caused by the addition to the solution of an ionic compound containing one of the ions of the first compound.

c. **Hydrolysis:** The reaction between water and the anion of a weak acid or the cation of a weak base.

d. **Polyprotic Acid:** An acid having more than one ionizable hydrogen atom. → ←

e. **Saturated Solution:** A solution in which solid solute is in equilibrium with dissolved solute.

f. **Solubility Product Constant, K_{sp} :** The product of the concentrations of the ions of a solute in a saturated solution of that solute. The value of K_{sp} determines the solubility of the compound.

220-9.3 SOLUBILITY

220-9.3.1 GENERAL. In Section 5, a saturated solution is defined as a solution which contains as much of a particular solute as will dissolve at a particular temperature. A more accurate and descriptive definition can be formulated by considering a saturated solution as an equilibrium system.

220-9.3.2 SATURATION EQUILIBRIUM. When a solid ionic compound dissolves in water it dissociates into ions. Using silver chloride, AgCl, as an example:

$AgCl(s) \rightarrow Ag^+ + Cl^-$ (9-1)

The symbol (s) indicates the solid, undissolved compound. As the ionic concentrations build up in solution, the reverse reaction begins to occur:

$Ag^+ + Cl^- \rightarrow AgCl(s)$ (9-2)

If sufficient AgCl(s) is present, the rates of reactions in equations (9-1) and (9-2) eventually become equal and the concentrations of dissolved ions do not increase further. That is, the solution is saturated. At this point, solid AgCl is in equilibrium with the Ag^+ and Cl^- ions in solution. **A saturated solution can thus also be defined as a solution in equilibrium with an undissolved solute.**

220-9.3.2.1 Combining the reactions in equations (9-1) and (9-2) in a single reversible equation,

$$AgCl(s) \leftrightarrows Ag^+ \; Cl^- \qquad (9\text{–}3)$$

the equilibrium constant expression is:

$$K_{eq} = \frac{[Ag^+][Cl^-]}{[AgCl(s)]} \qquad (9\text{-}4)$$

The terms $[Ag^+]$ and Cl^- have their usual meaning (concentration in moles/liter), but the term [AgCl(s)] requires explanation. This term refers to the concentration of AgCl **in the solid compound** . This value is fixed by the density of solid AgCl and is constant. Similar to the term H_2O in the equilibrium constant expression for the ionization of water in Section 8, the constant value of [AgCl(s)] can be combined with K_{eq} in equation (9-4) to give a new constant.

$K_{sp} = K_{eq}\,[AgCl(s)] = [Ag^+\; Cl^-]$ (9-5)

The new constant, K_{sp} , is called **the solubility product constant.** As with all equilibrium constants, K_{sp} is constant at any particular temperature.

220-9.3.2.2 To generalize the above results, for any ionic compound, $A_x B_y$, the dissociation reaction is:

$$A_xB_y(s) \leftrightarrows xA^{+n} + yB^{-m} \qquad (9\text{–}6)$$

and the solubility product constant is:

$$K_{sp} = [A^{+n}]^x [B^{-m}]^y \qquad (9\text{–}7)$$

220-9.3.2.3 The solubility product constant is used primarily for slightly soluble compounds in calculations involving the solubility of the compound, the concentration of a particular ion in a solution (usually one containing two or more solutes), or the amount of a particular compound which will precipitate if two or more solutions are mixed. From the discussion in Section 5 , the solubility of most solid compounds increases with increasing temperature up to 200°C. Therefore the solubility product constants for such compounds increases with temperature. Table 220-9-1 lists the solubility product constants for some common substances.

Table 220-9-1 SOLUBILITY PRODUCT CONSTANTS FOR SLIGHTLY SOLUBLE SUBSTANCES (Values are at 25° C unless noted otherwise)

Substance	**Formula**	**Solubility Product Constant (K_{sp})**
Barium carbonate	$BaCO_3$	8.1×10^{-9}
Barium sulfate	$BaSO_4$	1.1×10^{-10}
Barium chromate	$BaCrO_4$	2.3×10^{-10}
Calcium carbonate	$CaCO_3$	8.7×10^{-9}
Calcium sulfate	$CaSO_4$	2.4×10^{-4}
Calcium phosphate	$Ca_3(PO_4)_2$	2×10^{-29}
Ferrous hydroxide	$Fe(OH)_2$	2×10^{-14}
Ferric hydroxide	$Fe(OH)_3$	1×10^{-37}
Lead sulfate	$PbSO_4$	*1.3×10^{-8}
Magnesium carbonate	$MgCO_3$	*4×10^{-5}
Magnesium hydroxide	$Mg(OH)_2$	1.46×10^{-12}
Magnesium sulfate	$MgSO_4$	**4.66×10^{-2}
Silver chloride	AgCl	1.56×10^{-10}
Silver phosphate	Ag_3PO_4	*1.3×10^{-20}
Silver sulfate	Ag_2SO_4	7.6×10^{-5}

Example 9-1: *Calculate the concentration of saturated $Fe(OH)_2$ at 25°C.*

Solution 9-1: *The governing equations are:*

$$Fe(OH)_2(s) \rightleftarrows Fe^{+2} + 2OH^-$$

and

$$K_{sp} = [Fe^{+2}][OH^-]^2 = 2 \times 10^{-14}$$

Let the unknown (X) be the moles of Fe^{+2} per liter. Then

$$[Fe^{+2}] = X$$

$$[OH^-] = 2X$$

and, using the solubility product expression:

$$2 \times 10^{-14} = (X)(2X)^2 = 4X^3$$

$$X^3 = 5 \times 10^{-15}$$

$$X = 1.71 \times 10^{-5}$$

$$[Fe^{+2}] = 1.71 \times 10^{-5}\underline{M}$$

$$[OH^-] = 3.42 \times 10^{-5}\underline{M}$$

Thus a $1.71 \times 10^{-5}\underline{M}$ $Fe(OH)_2$ solution is saturated at 25°C.

220-9.3.3 THE COMMON ION EFFECT AND PRECIPITATION FROM SOLUTION. Very often, a particular solution may contain two or more solutes and these solutes may have an ion in common. For instance, the Cl^- ion is common to both NaCl and KCl. The effects of the common ion appear primarily in two areas: (1) solubility and (2) ionization of weak electrolytes. Solubility effects are described in this paragraph and the effects on ionization are presented in paragraphs 220-9.6 through 220-9.6.3.7.

220-9.3.3.1 Ions in solution are independent of their source. In a solution of NaCl and KCl, Cl^- ions from NaCl are indistinguishable from those contributed by KCl. The concentration terms in equations (9-5) and (9-7) are all-inclusive. The total concentrations of the respective ions must be used in the solubility product for each compound. If the solubility product constant for one compound is exceeded by adding another compound with a common ion, the first compound will precipitate from solution. The amount that precipitates will be such that the product of the concentrations of the ions remaining in solution is just equal to the solubility product constant.

220-9.3.3.2 A more common situation which results in precipitation is the mixing of two solutions of different compounds which are capable of forming a slightly soluble compound. For example, NaCl is very soluble and $AgNO_3$ is moderately soluble. If solutions of these compounds are mixed, Ag^+ and Cl^- ions may be present in amounts which cause $[Ag^+][Cl^-]$ to exceed K_{sp} for AgCl. Thus, solid AgCl will precipitate until $[Ag^+][Cl^-]$ is just equal to K_{sp} .

Example 9-2: Calculate the maximum chloride ion concentration possible in a 0.3$\underline{M}$ $AgNO_3$ solution before precipitation occurs.

Solution 9-2: The equations which govern the equilibrium are:

$$AgCl(s) \leftrightarrows Ag^+ + Cl^-$$

$$K_{sp} = [Ag^+]\,[Cl^-]$$

The maximum $[Cl^-]$ possible is the concentration just at saturation:

$$[Cl^-] = \frac{K_{sp}}{[Ag^+]} \approx \frac{1.56 \text{ x } 10^{-10}}{(0.3)} = 5.2 \text{ x } 10^{-10}\underline{M}$$

Thus, as shown in this solution, one could add only 5.2 x 10^{-10} moles of Cl^- per liter (about 2 x 10^{-5} ppm) before the first precipitation would occur. In practice such minute quantities are not visible to the unaided eye and it is found that about 0.1 ppm Cl^- is required to give a detectable amount of precipitate.

220-9.3.3.3 Precipitation of salts from solution is common in boiling systems. For example, Ca^{+2} and Mg^{+2} ions which are usually present in untreated water form a hard scale which impedes heat transfer, may accelerate corrosion, and is difficult to remove. However, Ca^{+2} and Mg^{+2} ions can be precipitated by the addition of suitable chemicals to form a soft sludge which can be removed by boiler blowdown.

220-9.4 IONIZATION EQUILIBRIUM

220-9.4.1 GENERAL. The essential features of ionization equilibria are presented in Section 8 in the discussion of the ionization of H_2O and weak acids and bases. To summarize:

a. Any compound which partially dissociates into ions in aqueous solution (weak electrolytes) can be described by an equation of the general type:

$$X_aY_b \rightleftarrows aX^{+n} + bY^{-m} \qquad (9\text{–}8)$$

and the corresponding ionization constant expression:

$$K_i = \frac{[X^{+n}]^a[Y^{-m}]^b}{[X_aY_b]} \qquad (9\text{-}9)$$

b. In those cases in which water is involved directly in the reaction, the term [H_2 O] is constant and is included in the ionization constant.

220-9.4.1.1 Note carefully the difference between equations (9-8) and (9-6). Equation (9-6) describes the situation in which **a solid, undissolved** compound A_x B_y is in equilibrium with its ions in solution. In equation (9-8), **all** substances are in solution. The compound X_a Y_b is dissolved but some of it is undissociated. Although equations (9-6) and (9-8) appear very similar, the situations they describe are quite different.

220-9.4.1.2 Ionization equilibria involve weak electrolytes (weak acids and weak bases). As shown in the following paragraphs, such equilibria are established in solutions of salts of a weak acid or base as well as in solutions of the weak electrolyte itself.

220-9.4.2 AMMONIUM HYDROXIDE. It is well known that when the gas ammonia, NH_3 , dissolves in water, the solution is basic. There are two methods of describing such solutions and the equilibrium associated with them: Method 1 describes the equilibrium as

$$NH_3\text{ (solution)} + H_2O \rightleftarrows NH_4^+ + OH^- \qquad (9\text{–}10)$$

Part of the dissolved NH_3 reacts with the solvent to form ammonium (NH_4^+) and hydroxyl (OH^-) ions while part remains simply dissolved. Method 2 involves two steps:

$$NH_3 + H_2O \rightarrow NH_4OH \qquad (9\text{–}11)$$

$$NH_4OH \rightleftarrows NH_4^+ + OH- \qquad (9\text{–}12)$$

In this case, it is assumed that all the dissolved NH_3 forms ammonium hydroxide, NH_4 OH, which then partially dissociates into NH_4 $^+$ and OH^- ions.

220-9.4.2.1 It is easily seen that equation (9-10) is the sum of equations (9-11) and (9-12). Thus, the two methods are equivalent overall but the equilibrium constant expressions are written differently.

$$\text{By method 1 } K_i = \frac{[NH_4^+][OH^-]}{[NH_3]} \qquad (9\text{-}13)$$

$$\text{By method 2 } K_i = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \qquad (9\text{-}14)$$

As seen from equation (9-11), there is a one-to-one relationship between NH_3 and NH_4 OH. Regardless of whether the portion of ammonia which does not react to form NH_4 + and OH^- ions is assumed to exist as NH_3 or as NH_4 OH, the numerical values of the denominators in equations (9-13) and (9-14) are equal and, thus, the constants are equal, $K_i = 1.8 \times 10^{-5}$. (The constant is commonly referred to as the ionization constant of ammonia.) The mathematical treatment of the equilibrium in ammonia solutions is the same in either method.

220-9.4.2.2 In this text, method 1 is used to describe solutions of ammonia because it emphasizes that the basic solution results from dissolving NH_3 gas in water and also because of evidence that the species NH_4 OH does not exist except as a short-lived intermediate in the formation of NH_4^+ and OH^- ions. Thus, the following equations are used in this test:

$$NH_3 + H_2 \rightleftarrows NH_4^+ + OH^- \qquad (9\text{-}10)$$

$$K_i = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5} \text{ (at 25°C)} \qquad (9\text{-}13)$$

220-9.4.3 pH OF WEAK ELECTROLYTES. As explained in paragraphs 220-8.7 through 220-8.7.3.3, if the $[H_3O^+]$ contributed to a solution by an acid (strong or weak) is greater than $\sim 10^{-6}$ mole/liter, then the $[H_3O^+]$ due to the ionization of water is negligible. Similarly, if the $[OH^-]$ contributed by a base (strong or weak) is greater than 10^{-6} mole/liter, then the $[OH^-]$ contributed by the ionization of water is negligible. When dealing with weak electrolytes, even if the total amount added and the ionization constant are known, it is not always apparent that the conditions of the above assumptions are met. As in paragraphs 220-8.7 through 220-8.7.3.3, one can assume that the conditions are met, then calculate $[H_3O^+]$ and use the results to test the validity of the assumption. In that section, it is shown that for a $0.1\underline{N}$ acetic acid solution:

$[H_3O^+] = 1.35 \times 10^{-3}$ mole/liter

Thus,

$pH = -\log (1.35 \times 10^{-3})$

$= 3 - \log 1.35$

$= 2.87$

Since K_i for NH_3 solutions is the same as K_i for acetic acid, then for a $0.1\underline{N}$ NH_3 solution:

$[OH^-] = 1.35\ 10^{-3}$

$pOH = 2.87$

$pH = 14 - pOH$

= 11.13

220-9.4.3.1 If [H_3O^+] in an acid solution is less than 10^{-6} or if [OH^-] in basic solution is less than 10^{-6}, one must resort to an exact solution of ionization equilibria problems to take into account the ionization of water. The following discussion illustrates the exact solution and provides a firmer basis for several assumptions involving ionization equilibria. Consider the general weak base, BOH, (in this case, B should not be confused with the element boron).

$$BOH \rightleftarrows B^+ + OH^- \qquad (9\text{-}15)$$

$$K_b = \frac{[B^+][OH^-]}{[BOH]} \qquad (9\text{-}16)$$

Let $[BOH]_o$ be the known amount (moles) of BOH originally dissolved divided by the volume of the solution. Thus, $[BOH]_o$ would be the concentration of BOH in solution if none of the base dissociated. Of course, some does dissociate and the actual concentration of undissociated BOH is [BOH].

220-9.4.3.2 In any aqueous solution, the following equilibrium exists:

$$2H_2O \rightleftarrows H_3O^+ + OH^- \qquad (9\text{–}17)$$

$$K_w = [H_3O^+][OH^-] \qquad (9\text{–}18)$$

Hydroxyl ions are produced by both reactions in equations (9-15) and (9-17) so both equilibria must be considered in determining the pH of the solution.

220-9.4.3.3 Inspection of the above equations reveals there are four unknowns: [BOH], [B^+], [H_3O^+], and [OH^-]. (The known quantities are: $[BOH]_o$, K_b, and K_w.) By the familiar rules of algebra, the number of equations must be equal to the number of unknowns in order to solve for the unknowns. Two of the required equations are equations (9-16) and (9-18). Two others are easily formulated.

220-9.4.3.4 Since atoms are conserved in chemical reactions, the amount of BOH added to the water must be accounted for by the equation:

$[BOH]_o = [B^+] + [BOH]$ (9-19)

This is called the material balance equation and simply means that the amount of BOH added must be equal to the amount which dissociated plus the amount which did not dissociate.

220-9.4.3.5 The fourth equation results from the fundamental requirements that any solution must be electrically neutral. This means that the sum of all positive charges must equal the sum of all negative charges, or in this case:

$[B^+] + [H_3O^+] + [OH^-]$ (9-20)

This is the electrical neutrality equation.

220-9.4.3.6 Now there are four unknowns and four equations which can be solved simultaneously for the unknowns as follows. The easiest way of doing this is to find expressions for $[B^+]$ and [BOH] in terms of $[OH^-]$ and known quantities and substitute these expressions in equation (9-16). From equation (9-20),

$[B^+] = [OH^-] - [H_3O^+]$ (9-21)

The term $[H_3O]$ can be replaced by $K_w/[OH^-]$ from equation (9-18), thus:

$[B^+] = [OH^-] - K_w / [OH^-]$ (9-22)

From equation (9-19),

$[BOH] = [BOH]_o - [B^+]$

The term $[BOH]_o$ is known and $[B^+]$ can be replaced by equation (9-22).

$[BOH] = [BOH]_o - [OH^-] + K_w / [OH^-]$ (9-23)

Now substitute equations (9-22) and (9-23) in equation (9-16).

$$K_b = \frac{([OH^-] - K_w/[OH^-])[OH^-]}{[BOH]_o - [OH^-] + K_w/[OH^-]} \qquad (9\text{-}24)$$

220-9.4.3.7 Equation (9-24) can now be solved exactly for $[OH^-]$. However, this is a cubic equation ($[OH^-]^3$) and is difficult and tedious to solve without a computer. Whenever possible, simplifying assumptions should be used. The conditions under which these simplifications are valid can be shown using equation (9-24).

220-9.4.3.8 If a solution is basic, $[OH^-]$ must be greater than 10^{-7} $\underline{M}$ and is typically greater than 10^{-6} $\underline{M}$, even in solutions of weak bases. If $[OH^-] > 10^{-6}$, then

$$K_w / [OH^-] < \frac{10^{-14}}{10^{-6}} = 10^{-8}$$

Thus, in the numerator of equation (9-24), the term K_w / $[OH^-]$ is negligibly small with respect to $[OH^-]$ and the numerator becomes $[OH^-]^2$.

220-9.4.3.9 Also, in the denominator of equation (9-24), if $K_w/[OH^-]$ is much smaller than the other terms, it may be neglected and the equation becomes:

$$K_b = \frac{[OH^-]^2}{[BOH]_o - [OH^-]} \text{, if } [OH^-] >> K_w/[OH^-] \qquad (9\text{-}25)$$

If X is used in place of $[OH^-]$ equation (9-25) is the quadratic equation obtained in paragraphs 220-8.7 through 220-8.7.3.3. This is to be expected because the condition, $[OH^-] >> K_w/[OH^-]$, is equivalent to saying that the contribution of $[OH^-]$ from the ionization of water is negligible with respect to the amount produced by the base, which is the assumption used in paragraphs 220-8.7 →through 220-8.7.3.3. This equivalence can be seen by noting that $K_w / [OH^-] = [H_3O^+]$ and recalling that ionization of one water molecule produces 1 H_3O^+ ion and 1 OH^- ion. Thus, $[OH^-] >> K_w / [OH^-]$ means that total hydroxyl ion concentration is much greater than the concentration of hydroxyl ions produced by the ionization of water. In many cases, equation (9-25) can be simplified further. If $[OH^-] << [BOH]_o$, (by about a factor of 10) equation (9-25) becomes:

$$K_b = \frac{[OH^-]^2}{[BOH]_o}, \qquad \begin{array}{l} \text{if } [OH^-] >> K_w/[OH^-] \\ \text{and } [OH^-] << [BOH]_o \end{array} \qquad (9\text{-}26)$$

The second condition on this equation requires that a very small fraction of the total BOH present be ionized.

220-9.4.3.10 Equations (9-24) through (9-26) apply to solutions of weak bases. The corresponding equations for solutions of weak acids can be derived in the same manner or these equations may be obtained from the preceding equations by substituting $[H_3O^+]$ for $[OH^-]$, [HA]o for $[BOH]_o$, and K_a for K_b where K_a is the ionization constant for the weak acid, HA. The results are:

$$K_a = \frac{([H_3O^+] - K_w/[H_3O^+])[H_3O^+]}{[HA]_o - [H_3O^+] + K_w/[H_3O^+]} \qquad (9\text{-}27)$$

$$K_a = \frac{[H_3O^+]^2}{[HA]_o - [H_3O^+]} \quad , \text{ if } [H_3O^+] >> K_w/[H_3O^+] \qquad (9\text{-}28)$$

$$K_a = \frac{[H_3O^+]^2}{[HA]_o} \quad \begin{array}{l} \text{if } [H_3O^+] >> K_w/[H_3O^+] \\ \text{and } [H_3O^+] << [HA]_o \end{array} \qquad (9\text{-}29)$$

220-9.4.3.11 Although equations (9-26) and (9-29) are simplifications of the exact equation, they illustrate an important feature of weak electrolytes. Using equation (9-26) for example, suppose that the weak base concentration is $[BOH]_o = X$. Let y be the value of $[OH^-]$; thus:

$$y = [OH^-] = \sqrt{K_b X}$$

If $[BOH]_o$ is now doubled to 2X, Equation (9-26) shows that the new value of $[OH^-]$ is:

$$[OH^-] = \sqrt{K_b(2X)} = \sqrt{2}\,\sqrt{K_b X}$$

$$= \sqrt{2}\, y$$

Thus, although the weak base concentration was increased by a factor of 2, the hydroxyl ion concentration increased by only √2, or about 1.4. The conclusion is that $[OH^-]$ does not change linearly with $[BOH]_o$, and similarly for $[H_3O^+]$ and $[HA]_o$. In general, the greater the concentration of weak electrolyte, the smaller the fraction which ionizes. For very dilute solutions, a large fraction of the weak electrolyte is ionized, (i.e., $[H_3O^+] << [HA]$ o and $[OH^-] << [BOH]_o$ are not true), so equations (9-26) and (9-29) do not apply to such solutions.

220-9.4.3.12 In the example of a 0.1N acetic acid solution in paragraphs 220-8.7 through 220-8.7.3.3, the value of $[H_3O^+]$ calculated using what is now seen to be equation (9-28) is $[H_3O^+] = 1.35 \times 10^{-3}$. Clearly this value of $[H_3O^+]$ satisfies the condition for equation (9-28) to be valid. Also, since $[H_3O^+] << [HA]_o$, it is apparent that equation (9-29) could have been used. That equation gives:

$$
\begin{aligned}
[H_3O^+]^2 &= K_a[HA]_o \\
&= 1.8 \times 10^{-5}(0.1) \\
&= 1.8 \times 10^{-6} \\
[H_3O^+] &= 1.34 \times 10^{-3}\ \underline{M}
\end{aligned}
$$

The difference between 1.34 x 10^{-3} and 1.35 x 10^{-3} is insignificant.

220-9.4.3.13 The preceding discussion leads to the following conclusions on how to approach pH calculations (or calculations of $[H_3O^+]$ or $[OH^-]$) in weak electrolytes: First try the simplest method, equation (9-26) or (9-29). If the results indicate that the appropriate conditions are not met, try the next simplest method, equation (9-25) or (9-28). In all the examples used in the text, one of the simplified equations will suffice.

Example 9-3: *Calculate the pH of a solution prepared by dissolving enough NH_3 to give a concentration of 5.0×10^{-1} mole of NH_3 per of solution.*

Solution 9-3: *First use Equation (9-26):*

$$K_b = \frac{[OH^-]^2}{[NH_3]_o} = 1.8 \times 10^{-5}$$

$$[OH^-]^2 = (1.8 \times 10^{-5})(5.0 \times 10^{-1})$$

$$= 9.0 \times 10^{-6}$$

$$[OH^-] = 3.0 \times 10^{-3}\ \underline{M}$$

To test the validity of the answer, use the conditions for Equation (9-26). It is seen that,

$$[OH^-] << [NH_3]_o$$

$$(3.0 \times 10^{-3} << 5.0 \times 10^{-1})$$

and that

$$[OH^-] >> \frac{K_w}{[OH^-]}$$

$$(3.0 \text{ x } 10^{-3} >> \frac{10^{-14}}{3.0 \text{ x } 10^{-3}} = 3.3 \text{ x } 10^{-12})$$

Since both conditions are satisfied the calculated value of $[OH^-]$ is valid. Then determine pH as follows:

$$\begin{aligned} pOH &= -\log [OH^-] \\ &= -\log (3.0 \text{ x } 10^{-3}) \\ &= 3 - 0.48 \\ &= 2.52 \\ pH &= 14.0 - pOH \\ &= 11.48 \end{aligned}$$

220-9.4.3.14 Ionization equilibria in weak electrolytes must also be considered if one wishes to calculate total solute concentration for a given pH value.

Example 9-4: The pH of an NH_3 solution is 9.8. How much NH_3 is required to prepare such a solution?

Solution 9-4: Since the solution is basic, the value of $[OH^-]$ is needed.

$$
\begin{aligned}
pOH &= 14 - pH \\
&= 4.2 \\
[OH^-] &= \text{Antilog } (-4.2) \\
&= 10^{-4.2} \\
&= 10^{0.8} \times 10^{-5} \\
&= 6.3 \times 10^{-5} \underline{M}
\end{aligned}
$$

From this value of $[OH^-]$ it is seen that one of the conditions on Equation (9-26) is met:

$$[OH^-] >> \frac{K_w}{[OH^-]}$$

$$(6.3 \times 10^{-5} >> 1.59 \times 10^{-8})$$

Assume that Equation (9-26) is valid and calculate $[NH_3]_o$.

$$
\begin{aligned}
[NH_3]_o &= \frac{[OH^-]^2}{K_b} \\
&= \frac{(6.3 \text{ x } 10^{-5})^2}{1.8 \text{ x } 10^{-5}} \\
&= \frac{3.96 \text{ x } 1^{-9}}{1.8 \text{ x } 10^{-5}} \\
&= 2.2 \text{ x } 10^{-4} \underline{M}
\end{aligned}
$$

It is now seen that the second condition on Equation (9-26) is not satisfied since $[OH^-] = 6.3 \text{ x } 10^{-5}$ is not sufficiently less than $[NH_3]_o = 2.2 \text{ x } 10^{-4}$. In this case, Equation (9-25) must be used.

$$
\begin{aligned}
[NH_3]_o &= \frac{[OH^-]^2 + K_b[OH^-]}{K_b} \\
&= \frac{(6.3 \text{ x } 10^{-5})^2 + (1.8 \text{ x } 10^{-5})(6.3 \text{ x } 10^{-5})}{1.8 \text{ x } 10^{-5}} \\
&= \frac{3.96 \text{ x } 10^{-9} + 1.13 \text{ x } 10^{-9}}{1.8 \text{ x } 10^{-5}} \\
&= \frac{5.09 \text{ x } 10^{-9}}{1.8 \text{ x } 10^{-5}} \\
[NH_3]_o &= 2.83 \text{ x } 10^{-4}\underline{M}
\end{aligned}
$$

Thus, $2.83 \text{ x } 10^{-4}$ mole of NH_3 is required for each liter of solution to give a pH of 9.8.

220-9.4.4 POLYPROTIC ACIDS. Table 220-8-1 lists the ionization reactions and the ionization constants of several acids and bases. Some of the acids in that table contain more than one ionizable hydrogen atom and undergo successive ionization reactions in aqueous solution. Such acids are called polyprotic acids. **Polyprotic comes** from **poly** meaning several and **protic** referring to protons or H^+ . The following examples illustrate the most important aspects of the behavior of polyprotic acids.

220-9.4.4.1 Sulfuric Acid. Although most polyprotic acids are weak electrolytes, the most notable exception is sulfuric acid, H_2 SO_4 SO_4 . This acid is formed by dissolving SO_3 gas in water:

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Sulfuric acid ionizes as follows:

$$1.\quad H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$$

$$K_1 = \frac{[H_3O^+][HSO_4^-]}{[H_2SO_4]} = \text{very large}$$

$$2.\quad HSO_4^- + H_2O \leftrightarrows H_3O^+ + SO_4^{=}$$

$$K_2 = \frac{[H_3O^+][SO_4^{=}]}{[HSO_4^-]} = 1.2 \times 10^{-2}$$

By common practice, the ionization constant for the first of successive ionization reactions is designated K_1 , the second K_2 , and so on, as necessary. Sulfuric acid is classified as a strong acid because the first ionization constant is very large. For practical purposes, the first ionization reaction is complete and the concentration of undissociated H_2 SO_4 is essentially zero.

220-9.4.4.1.1 The second ionization reaction, however, is not complete and this equilibrium must be considered when calculating the concentration of SO_4^{-} ions in sulfuric acid solutions.

Example 9-5: *Calculate the sulfate ion concentration in a 0.2 $\underline{M}$ H_2SO_4 solution.*

Solution 9-5: *The first ionization reaction is complete.*

$$H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-$$

Sulfate ions are produced by the second, incomplete ionization.

$$HSO_4^- + H_2O \rightleftarrows H_3O^+ + SO_4^=$$

The value of $[SO_4^=]$ must be calculated from the expression:

$$K_2 = \frac{[H_3O^+][SO_4^=]}{[HSO_4^-]} = 1.2 \times 10^{-2}$$

Since the first ionization reaction is complete, $[H_3O^+]$ is at least 0.2 $\underline{M}$ and $[HSO_4^-]_o = 0.2\underline{M}$. Since $[H_3O^+]$ is at least $0.2\underline{M}$ the contribution of $[H_3O^+]$ from the ionization of water can be neglected.

If the amount of HSO_4^- which undergoes the second ionization is X moles/liter then:

$$[H_3O^+] = 0.2 + X$$

$$[HSO_4^-] = 0.2 - X$$

$$[SO_4 =] = X$$

$$1.2 \times 10^{-2} = \frac{(0.2 + X)X}{(0.2 - X)}$$

Since K_2 is small, let us assume that $X << 0.2\underline{M}$ (i.e., very little HSO_4^- ionizes further). In this case:

$$1.2 \times 10^{-2} = \frac{0.2\ X}{0.2} = X$$

The result indicates the assumption is valid (0.012 is sufficiently smaller than 0.2). The student can further this by solving quadratic equation (9-30) for X. The result is 1.1 10^{-2} .

220-9.4.4.2 Carbonic Acid. Carbonic acid, H_2CO_3 is a typical weak, polyprotic acid. It is formed by dissolving CO_2 gas in water by the reaction:

$$H_2O + CO_2 \rightarrow H_2CO_3$$

Carbonic acid ionizes as follows:

$$1)\quad H_2CO_3 + H_2O \rightleftarrows H_3O^+ + HCO_3^-$$

$$K_1 = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} = 4.5 \times 10^{-7}$$

$$2)\quad HCO_3^- + H_2O \rightleftarrows H_3O^+ + CO_3^=$$

$$K_2 = \frac{[H_3O^+][CO_3^=]}{[HCO_3]} = 5.6 \times 10^{-11}$$

220-9.4.4.2.1 This acid, as well as H_2SO_4 , illustrates a very useful generalization concerning polyprotic acids: The ionization constant for the first ionization step is always several orders of magnitude greater than the ionization constant for succeeding steps. In addition, the H_3O^+ ions produced in the first step suppress further ionization, as seen from the second ionization constant expression and LeChatelier’s principle.

220-9.4.4.2.2 For these reasons, when calculating [H_3O^+] in solutions of polyprotic acids, it is usually necessary to consider only the first ionization reaction. The amount of H_3O^+ ions produced by the second reaction is negligible with respect to the amount produced by the first. This was verified by Example 9-5.

Example 9-5.

Example 9-6: *Find* $[H_3O^+]$ *in a* $0.3\underline{M}$ H_2CO_3 *solution.*

Solution 9-6: *Assuming that the second ionization reaction is negligible with respect to the first, the equilibrium of importance is:*

$$H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$$

$$K_1 = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} = 4.5 \times 10^{-7}$$

This equilibrium is equivalent to the weak-electrolyte equilibrium described in paragraphs 220-8.14 through 220-8.16, so the simplest approximation, Equation (9-29), can be used in a first attempt at calculating $[H_3O^+]$.

$$K_a = \frac{[H_3O^+]^2}{[HA]_o} \qquad (9\text{-}29)$$

$$4.5 \times 10^{-7} = \frac{[H_3O^+]^2}{0.3}$$

$$[H_3O^+]^2 = (0.3)(4.5 \times 10^{-7})$$

$$= 1.35 \times 10^{-7}$$

$$[H_3O^+] = 3.67 \times 10^{-4}\ \underline{M}$$

220-9.4.4.2.3 Testing the result against the conditions in equation (9-29) it is seen that:

$$[H_3O^+] >> \frac{K_w}{[H_3O^+]}$$

$$(3.67 \text{ x } 10^{-4} >> 2.62 \text{ x } 10^{-9})$$

and,

$$[H_3O^+] << [H_2CO_3]_o$$

$$(3.67 \text{ x } 10^{-4} << 0.3)$$

Thus, the use of equation (9-29) is valid.

220-9.4.4.2.4 The assumption that the second ionization reaction is negligible can be verified as follows: The amount of $H_3 O^+$ and HCO_3^- produced by the first ionization is 3.67 x 10^{-4} M . If the amount of HCO_3^- which then ionizes is X moles/liter, then:

$$[H_3O^+] = 3.67 \text{ x } 10^{-4} + X$$

(The $[H_3O^+]$ due to the dissociation of water is negligible.)

$$[CO_3^{=}] = X$$

$$[HCO_3^-] = 3.67 \text{ x } 10^{-4} - X$$

$$K_2 = 5.6 \text{ x } 10^{-11} = \frac{(3.67 \text{ x } 10^{-4} + X)X}{(3.67 \text{ x } 10^{-4} - X)}$$

If the assumption is correct, X is negligible with respect to 3.67 x 10^{-4} so the above equation becomes:

X = 5.6 x 10^{-11} M

This is the amount of HCO_3^- which ionizes and is certainly insignificant compared to 3.67 x 10^{-4} which is the amount of HCO_3^- available.

220-9.4.4.3 Phosphoric Acid. Phosphoric acid, $H_3 PO_4$, is an example of an acid with three ionizable hydrogen atoms. The ionization reactions and ionization constants are:

$$1)\ H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$$

$$K_1 = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = 7.5 \times 10^{-3}$$

$$2)\ H_2PO_4 + H_2O \rightleftharpoons H_3O^+ + HPO_4^=$$

$$K_2 = \frac{[H_3O^+][HPO_4^=]}{[H_2PO_4^-]} = 6.2 \times 10^{-8}$$

$$3)\ HPO_4^= + H_2O \rightleftharpoons H_3O^+ + PO_4^\equiv$$

$$K_3 = \frac{[H_3O^+][PO_4^\equiv]}{[HPO_4^=]} = 4.8 \times 10^{-13}$$

220-9.4.4.3.1 In a solution of $H_3 PO_4$, all the above equilibria are established and all are interdependent because $[H_3 O^+]$ appears in all three expressions, $[H_2 PO_4^-]$ appears in the first two, and $[HPO_4^=]$ appears in the last two. The previous generalization concerning the relative magnitude of successive ionization constants holds in this case because $K_1 >> K_2 >> K_3$. This greatly simplifies most calculations dealing with $H_3 PO_4$ solutions.

Solution 9-7: As in Example 9-6, assume that the only ionization of significance is the first:

$$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$$

Further assume that Equation (9-29) applies, calculate $[H_3O^+]$, and test the validity of the assumption.

$$K_a = \frac{[H_3O^+]^2}{[HA]_o} \qquad (9\text{-}29)$$

$$7.5 \times 10^{-3} = \frac{[H_3O^+]^2}{0.4}$$

$$[H_3O^+]^2 = 3.0 \times 10^{-3}$$

$$[H_3O^+] = 5.48 \times 10^{-2}\ \underline{M}$$

Testing the conditions on Equation 9-29,

$$[H_3O^+] >> \frac{K_w}{[H_3O^+]}$$

$$(5.48 \times 10^{-2} >> 1.82 \times 10^{-11})$$

so the first condition is satisfied. However, satisfaction of the condition,

$$[H_3O^+] << [H_3PO_4]_o$$

is marginal, since $[H_3O^+] = 5.48 \times 10^{-2}$ and $[H_3PO_4]_o = 4 \times 10^{-1}$. If only an approximate answer is needed, the above calculations suffice. A more accurate value of $[H_3O^+]$ can be obtained by solving the quadratic of Equation (9-28):

$$K_a = \frac{[H_3O^+]^2}{[H_3PO_4]_o - [H_3O^+]} = 7.5 \times 10^{-3}$$

This equation gives:

$$[H_3O^+] = 5.12 \times 10^{-2}\ \underline{M}$$

220-9.5 HYDROLYSIS OF SALTS

220-9.5.1 GENERAL. Salts are classified according to the type of acid and base from which they are formed. Thus, there are salts of:

1. A strong base and a strong acid, (NaCl)
2. A weak base and a strong acid, (NH_4 Cl)
3. A strong base and a weak acid, (NaC_2 H_3 O_2)
4. A weak base and a weak acid, (NH_4 C_2 H_3 O_2)

220-9.5.1.1 All salts are ionic compounds and dissociate completely into ions in solution. It is found that when some types of salts are dissolved in water, one or both ions react with the water to establish an equilibrium similar to that established by weak electrolytes. The salts which show this behavior are those which contain an ion from a weak acid or a weak base. **The reaction between water and an ion of a salt is called hydrolysis.**

220-9.5.2 HYDROLYSIS OF SALTS OF A WEAK BASE AND A STRONG ACID. Ammonium chloride, NH_4 Cl, is formed from the weak base, NH_4 and the strong acid, HCl. When dissolved in water, NH_4 Cl dissociates by the reaction

$$NH_4Cl \rightarrow NH_4^+ + Cl^-$$

Ammonium ions then react with water (hydrolyze) as follows:

$$NH_4^+ + H_2O \leftrightarrows NH_3 = H_3O^+ \qquad (9\text{–}31)$$

Since H_3 O^+ ions are produced in the reaction of equation (9-31), the solution is acidic.

220-9.5.2.1 An alternate way of viewing the hydrolysis of NH_4 Cl may give more insight into the process. The reaction of equation (9-31) may be treated as the net result of the following two familiar reactions:

$$2H_2O \leftrightarrows H_3O^+ + OH^- \tag{9–32}$$

and

$$NH_4^+ + OH^- \leftrightarrows NH_3 \;\; H_2O \tag{9–33}$$

Net Reaction

$$NH_4^+ + H_2O \leftrightarrows NH_3 + H_3O \tag{9–31}$$

220-9.5.2.2 Equation (9-33) is just equation (9-10) written in reverse order, which is valid for any reversible reaction. In this case, the ammonia ionization equilibrium is established starting with the ions instead of the compounds NH_3 and H_2O. The formation of some of these compounds removes OH^- ions from solution. This disturbs the equilibrium of equation (9-32) and forces the reaction to the right side of the equation in order to maintain the relationship $[H_3O^+][OH^-] = K_w$. Thus $[H_3O^+]$ is greater than the neutral equilibrium value and the solution is acidic.

220-9.5.2.3 Chloride ions do not undergo hydrolysis as NH_4^+ ions do. Such a reaction would produce HCl, but this is a strong acid and is completely dissociated in solution. The equilibrium constant expression for the reaction of equation (9-31) is:

$$K_{eq} = \frac{[NH_3][H_3O^+]}{[NH_4^+][H_2O]}$$

As before, the constant value of $[H_2O]$ may be included in the equilibrium constant. Using K_h to indicate hydrolysis:

$$K_h = \frac{[NH_3][H_3O^+]}{[NH_4^+]} \tag{9-34}$$

220-9.5.2.4 There is no need to determine values of K_h experimentally because they can be easily derived as follows:

First, multiply the right side of Equation (9-34) by $\frac{[OH^-]}{[OH^-]}$

$$K_h = \frac{[NH_3][H_3O^+][OH^-]}{[NH_4^+][OH^-]} \qquad (9\text{-}35)$$

Since $[H_3O^+]\ [OH^-] = K_w$, Equation (9-35) becomes:

$$K_h = \frac{[NH_3]K_w}{[NH_4^+][OH^-]} \qquad (9\text{-}36)$$

The remaining concentration terms are the reciprocal of the ionization constant for NH_3.

$$\frac{[NH_3]}{[NH_4^+][OH^-]} = \frac{1}{K_i}$$

With the substitution,

$$K_h = \frac{K_w}{K_i} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.5 \times 10^{-10} \qquad (9\text{-}37)$$

The hydrolysis of a weak-base ion, B^+, can be generalized as:

$$B^+ + 2H_2O \rightleftharpoons BOH + H_3O^+ \qquad (9\text{-}38)$$

$$K_h = \frac{[BOH][H_3O^+]}{[B^+]} = \frac{K_w}{K_b} \qquad (9\text{-}39)$$

220-9.5.2.5 Since the reaction of equation (9-38) is incomplete and produces acidic solutions, it may be considered analogous to the ionization of a weak acid. Thus, the reaction of equation (9-38) can be described by equations analogous to equations (9-27) through (9-29). Of most importance are:

$$K_h = \frac{[H_3O^+]^2}{[B^+]_o - [H_3O^+]}; \quad \text{if } [H_3O^+] >> \frac{K_w}{[H_3O^+]} \qquad (9\text{-}40)$$

$$K_h = \frac{[H_3O^+]^2}{[B^+]_o}; \quad \text{if } [H_3O^+] >> \frac{K_w}{[H_3O^+]} \text{ and } [H_3O^+] << [B^+]_o \qquad (9\text{-}41)$$

220-9.5.2.6 The conditions for the validity of equation (9-41) state that the H_3O^+ due to the hydrolysis is greater than that formed by the ionization of water, and that most of the weak electrolyte does not undergo hydrolysis. As in the previous treatment of problems involving weak-electrolyte ionization, in hydrolysis problems first assume that the simplest approximation, equation (9-41), is valid then test the results against the conditions on the equation.

Example 9-8: *Calculate $[H_3O^+]$ and $[NH_3]$ in a 0.2 $\underline{M}$ NH_4Cl solution.*

Solution 9-8: *From the hydrolysis reaction,*

$$NH_4^+ + H_2O \rightleftarrows NH_3 + H_3O^+$$

it is seen that $[NH_3] = [H_3O^+]$, neglecting any H_3O^+ ions contributed by the ionization of water. Now apply Equation (9-41).

$$K_b = 5.5 \times 10^{-10} = \frac{[H_3O^+]^2}{[NH_4^+]_o}$$

$$[H_3O^+]^2 = (0.2)\,(5.5 \times 10^{-10})$$

$$= 1.1 \times 10^{-10}$$

$$[H_3O^+] = [NH_3] = 1.05 \times 10^{-5}\ \underline{M}$$

With this value of $[H_3O^+]$, the student can verify that the conditions on Equation (9-41) are satisfied.

220-9.5.3 HYDROLYSIS OF SALTS OF A STRONG BASE AND A WEAK ACID. Sodium acetate, $NaC_2H_3O_2$ is the salt of the strong base NaOH and the weak acid $HC_2H_3O_2$. The acetate ions formed by dissolving $NaC_2H_3O_2$ in water hydrolyze as follows:

$$C_2H_3O_2^- + H_2O \rightleftarrows HC_2H_3O_2 + OH^- \qquad (9\text{–}42)$$

The general equation for the hydrolysis of weak–acid ions, A^-, is:

$$A^- + H_2O \rightleftarrows HA + OH^- \qquad (9\text{–}43)$$

Hydrolysis of such salts produces OH^- ions and the solutions are basic. In this case, as in the preceding section it can be shown that

$$K_h = \frac{K_w}{K_i}$$

where K_i is the ionization constant of the weak electrolyte formed by hydrolysis (HA in equation 9-43).

220-9.5.3.1 Equation (9-43) may be treated as the ionization of a weak base to obtain equations corresponding to equations (9-25) and (9-26).

$$K_h = \frac{[OH^-]^2}{[A^-]_o - [OH^-]}; \text{ if } [OH^-] >> \frac{K_w}{[OH^-]} \qquad (9\text{-}44)$$

$$K_h = \frac{[OH^-]^2}{[A^-]_o}; \quad \begin{array}{l} \text{if } [OH^-] >> \dfrac{K_w}{[OH^-]} \\ \text{and} [OH^-] << [A^-]_o \end{array} \qquad (9\text{-}45)$$

The use of these equations should by now be familiar.

220-9.5.4 OTHER TYPES OF SALTS. Besides the types of salts described in the preceding paragraphs, there are also salts of a strong acid and a strong base, and those of a weak acid and a weak base. Strong acid-strong base salts do not hydrolyze. As noted previously, hydrolysis of a strong-acid ion or a strong-base ion would form the respective strong acid or base. Since such compounds dissociate completely in solution, there is no reason to expect the undissociated compounds to be formed by a hydrolysis reaction. Thus, solutions of salts of a strong acid and a strong base are neutral.

220-9.5.4.1 Salts of a weak acid and a weak base are somewhat more complicated. These salts contain two hydrolyzable ions: one which produces a weak acid and one which produces a weak base. The acidity or basicity of the final solution depends on the relative strength of the acid and base. Equations describing these solutions can be derived, but since they find no practical application in this subject, the derivations are not presented in this text.

220-9.5.5 HYDROLYSIS OF PHOSPHATE. A rather complicated hydrolysis equilibrium extensively used involves phosphate salts. Phosphoric acid, H_3PO_4, is triprotic and under appropriate conditions the following salts can be prepared.

NaH_2PO_4 (monosodium phosphate)

Na_2HPO_4 (disodium phosphate)

Na_3 PO_4 (trisodium phosphate) Like all ionic compounds, these salts completely dissociate in solution. For example:

$$Na_3PO_4 \xrightarrow{H_2O} 3Na^+ + PO_4^{\equiv}$$

Since $PO_4^{\equiv}$ is the ion of a weak acid, it hydrolyzes by the reaction:

$$PO_4^{\equiv} + H_2O \rightleftarrows HPO_4^{=} + OH^- \qquad (9\text{-}46)$$

$$K_h = \frac{K_w}{K_3} = 2.08 \times 10^{-2}$$

The weak acid formed in the reaction of Equation (9-46) is itself the anion of the weak acid $H_2PO_4^-$ and can hydrolyze.

$$HPO_4^{=} + H_2O \rightleftarrows H_2PO_4^- + OH^- \qquad (9\text{-}47)$$

$$K_h = \frac{K_w}{K_2} = 1.61. \times 10^{-7}$$

Still another hydrolysis reaction is possible since $H_2PO_4^-$ is the anion of H_3PO_4.

$$H_2PO_4^- + H_2O \rightleftarrows H_3PO_4 + OH^- \qquad (9\text{-}48)$$

$$K_h = \frac{K_w}{K_1} = 1.33 \times 10^{-12}$$

Although three successive hydrolysis reactions are possible, the last two can be neglected in all but the most precise calculations and very dilute solutions. The reason for this is apparent from the respective hydrolysis constants. The value of K_h in equation (9-47) is about five orders of magnitude (100,000 times) smaller than K_h for the first hydrolysis, and K_h for the third hydrolysis is another factor of 105 smaller. Just as only the first ionization of polyprotic acids contributes significantly to $[H_3 O^+]$ so only the first of successive hydrolysis reactions is normally of importance. (Recall that the larger the equilibrium constant, the farther to the right or the more complete the reaction.)

220-9.5.5.1 Also as before, hydrolysis of an acid anion to produce OH^- ions may be treated as the ionization of a weak base so equations (9-44) and (9-45) apply.

Example 9-9: *Calculate the pH of a 0.3 M Na_3PO_4 solution.*

Solution 9-9: *The pertinent equations are:*

$$PO_4^{\equiv} + H_2O \rightleftarrows HPO_4^{=} + OH^-$$

$$K_b = \frac{K_w}{K_3} \text{ x } 2.08 \text{ x } 10^{-2}$$

Assuming that Equation (9-45) holds:

$$K_b = \frac{[OH^-]^2}{[PO_4^{\equiv}]_o}$$

$$2.08 \text{ x } 10^{-2} = \frac{[OH^-]^2}{0.3}$$

$$[OH^-]^2 = 6.24 \text{ x } 10^{-3}$$

$$[OH^-] = 7.90 \text{ x } 10^{-2}$$

This value of $[OH^-]$ satisfies the first condition (9-45):

$$[OH^-] >> \frac{K_w}{[OH^-]}$$

$$(7.9 \text{ x } 10^{-2} >> 1.27 \text{ x } 10^{-13})$$

However, the second condition;

$$[OH^-] << [PO_4^{\equiv}]_o$$

is questionable since $7.9 \text{ x } 10^{-2}$ is not much less than $3.0 \text{ x } 10^{-1}$.

Thus, a more accurate value of $[OH^-]$ can be obtained by solving the quadratic of Equation (9-44):

$$2.08 \text{ x } 10^{-2} = \frac{[OH^-]^2}{[PO_4^{\equiv}]_o - [OH^-]}$$

$$[OH^-] = 6.9 \text{ x } 10^{-2} \underline{M}$$

To find pH:

$$pOH = -\log (6.9 \text{ x } 10^{-2})$$

$$= 2.0 - 0.84$$

$$= 1.16$$

$$pH = 14.0 - 1.16$$

$$= 12.84$$

220-9.6 BUFFERS AND THE COMMON ION EFFECT ON IONIZATION

220-9.6.1 GENERAL. Previous paragraphs describe the ionization equilibria which occur in solutions of pure weak electrolytes and in solutions of pure salts of weak electrolytes. The following paragraphs consider the situation in which a solution contains both a weak electrolyte and a salt of the same weak electrolyte. Such solutions have some unique properties which lead to important practical applications. The equations which describe these solutions are first developed for NH_3 -NH_4 Cl solutions and then are applied to Na_3 PO_4 $^-$ Na_2 HPO_4 solutions. The development given in the following paragraphs is based primarily on logical arguments which result from preceding paragraphs.

220-9.6.2 AMMONIA-AMMONIUM CHLORIDE. Suppose that 0.5 mole of NH_3 and 0.5 mole of NH_4 Cl are added to enough water to make one liter of solution and one wishes to calculate OH^- . It is known that NH_3 produces $NH_4{}^+$ and OH^- ions and that the $NH_4{}^+$ ions from NH_4 Cl hydrolyze to form NH_3 and H_3O^+ ions according to the following equations:

$$NH_3 + H_2O \rightleftharpoons NH_4{}^+ + OH^- \qquad (9\text{-}10)$$

$$K_b = \frac{[NH_4{}^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5} \qquad (9\text{-}13)$$

$$NH_4^+ \; H_2O \rightleftharpoons NH_3 + H_3O^+ \qquad (9\text{-}31)$$

$$K_h = \frac{[NH_3][H_3O^+]}{[NH_4{}^+]} = \frac{K_w}{K_b} = 5.5 \times 10^{-10} \qquad (9\text{-}37)$$

220-9.6.2.1 From the values of K_b and K_h it is seen that the reaction of equation (9-10) is of greater significance than that of equation (9-31). equation (9-13) can be rearranged to give:

$$[OH^-] = \frac{[NH_3]}{[NH_4{}^+]} K_b \qquad (9\text{-}49)$$

Thus, $[NH_3]$ and $[NH_4{}^+]$ must be known in order to calculate $[OH^-]$.

220-9.6.2.2 In Example 9-3, it is shown that in a pure 0.5 M NH_3 solution, a very small amount (0.003 mole/liter) reacts, so essentially all the NH_3 remains unreacted. According to LeChatelier's principle the presence of additional $NH_4{}^+$ ions (from NH_4 Cl) will further suppress the reaction of ammonia with water. The final consideration is whether the hydrolysis of $NH_4{}^+$ by equation (9-31) produces a significant amount of NH_3 compared to the amount originally added.

220-9.6.2.3 Example 9-8 shows that in a 0.2 M NH_4 Cl solution, the amount of NH_3 formed by hydrolysis was only 1 x 10^{-5} M . The results would not be greatly different for a 0.5 M NH_4 Cl solution. In addition, the presence of NH_3 added as the pure compound would suppress the hydrolysis reaction. Thus it can be concluded that the amount of NH_3 formed by hydrolysis is insignificant compared to the amount originally added. Based on these arguments, the value of [NH_3] in equation (9-49) is, to a good approximation, just the amount added, 0.5 M . A similar line of reasoning shows that the amount of $NH_4{}^+$ ions lost by hydrolysis and the amount produced by reaction of NH_3 with H_2 O is insignificant compared to the amount added as NH_4 Cl. Thus, a good approximation to the value of [$NH_4{}^+$] in equation (9-49) is the amount of $NH_4{}^+$ formed by the dissociation of NH_4 Cl, 0.5 M . Then:

Comparing this value with the results of Example 9-3 for a 0.5 M solution of pure NH_3 shows that the presence of the common ion, $NH_4{}^+$, greatly suppresses the ionization of NH_3 .

220-9.6.2.4 With very little effort, the student can verify that the arguments used above are valid only if the concentration of base is much greater than its ionization constant **and** if there is an **appreciable** amount of the salt present. **Appreciable** in this case may be taken to mean:

$$[OH^-] = \frac{[NH_3]}{[NH_4{}^+]} K_b$$

$$= \frac{0.5}{0.5} (1.8 \text{ x } 10^{-5}) \qquad (9\text{-}49)$$

$$= 1.8 \text{ x } 10^{-5} \underline{M}$$

$$0.1 < \frac{[NH_3]}{[NH_3{}^+]} < 10, \text{ or in general, } 0.1 < \frac{[\text{base}]}{[\text{salt}]} < 10.$$

220-9.6.2.5 **A solution which** meets these requirements, that is,**contains appreciable amounts of both an electrolyte and a salt of the same electrolyte, is called a buffer solution.** The properties of such solutions can be seen by examining the general form of equation (9-49) for the base, BOH, and its ion, B^+ :

$$[OH^-] = \frac{[BOH]}{[B^+]} K_b \qquad (9\text{-}50)$$

The corresponding equation for a weak acid, HA, and its ion, A^-, is:

$$[H_3O^+] = \frac{[HA]}{[A^+]} K_a \qquad (9\text{-}51)$$

220-9.6.2.6 Equation (9-50) shows that [OH^-] in a buffer solution depends only on the ratio, [BOH]/[B^+], since K_b is constant. This means that if such a solution is diluted by adding pure water, the pH will not change because both [BOH] and [B^+] would change by the same factor and their ratio would not change. Similarly, if the solution is concentrated by evaporating some of the water, both concentration terms are affected equally. Again, the ratio, and thus pH, does not change.

220-9.6.2.7 Obviously, there are limits on the ability of buffer solutions to maintain constant pH despite dilution or concentration. If dilution is carried too far the conditions on equation (9-49) would be violated and the equation cannot be expected to remain valid. If too much water is evaporated, the solution may become so concentrated that the solubility of one or more dissolved substances is exceeded. The substance(s) would then precipitate and the ratio $[BOH]/[B^+]$ would not remain constant.

220-9.6.2.8 Another remarkable feature of buffer solutions is their ability to maintain an approximately constant pH even if a small amount of a strong acid or a strong base is added. To illustrate this property, suppose 1 ml of 1 $\underline{M}$ HCl is added to 1 liter of the solution containing 0.5 $\underline{M}$ NH_3 O and 0.5 $\underline{M}$ NH_4 Cl. The amount of H_3O^+ added is:

0.001 liter x 1 mole/liter = 1 x 10^{-3} mole.

The volume of the mixture is essentially 1 liter so the concentration of H_3O^+ added is 1 x 10^{-3} $\underline{M}$. Inspection of equations (9-10) and (9-31) and application of LeChatelier's principle indicates that the most immediate effect of the added H_3O^+ will be a disturbance of the equilibrium of the reaction in equation (9-31). That reaction will be forced to the left by the increased $[H_3O^+]$:

$$NH_4^+ + H_2O \leftrightarrows NH_3 + H_3O^+ \qquad (9\text{–}31)$$

That the reaction in this direction is virtually complete is shown by the very large value of the equilibrium constant for the reaction in equation (9-31) to proceed to the left.

Thus, it is safe to assume that all the added H_3O^+ (1 x 10^{-3} $\underline{M}$) is consumed by reacting with 1 x 10^{-3} $\underline{M}$ of NH_3 and producing 1 x 10^{-3} $\underline{M}$ of NH_4^+. Equation (9-49) then becomes:

$$\frac{[NH^{4}_{+}]}{[NH_3][H_3O^+]} = \frac{1}{K_b} = \frac{1}{5.5 \times 10^{-10}} = 1.8 \times 10^{9} \qquad (9\text{-}52)$$

$$\begin{aligned}
[OH^-] &= \frac{[NH_3]}{[NH_4{}^+]} K_b \\
&= \frac{0.5 - 0.001}{0.5 + 0.001}\,(1.8 \times 10^{-5}) \qquad (9\text{-}49) \\
&= \frac{0.499}{0.501}\,(1.8 \times 10^{-5}) \\
&\simeq 1.8 \times 10^{-5}\ \underline{M}
\end{aligned}$$

The value of $[OH^-]$ is essentially unchanged by the addition of 1×10^{-3} $\underline{M}$ of strong acid. If the same amount of HCl had been added to one liter of pure water;

$$[H_3O^+] = 1 \times 10^{-3}$$

$$\begin{aligned}
[OH^-] &= \frac{1 \times 10^{-14}}{[H_3O^+]} \\
&= 1 \times 10^{-11}\ \underline{M}
\end{aligned}$$

220-9.6.2.9 If a strong base is added to the above buffer solution, producing extra OH^- ions, the equilibrium of the reaction in equation (9-10) will be disturbed. By LeChatelier's principle this reaction then shifts to the left ($K = 1/K_b = 5.5 \times 10^4$) and consumes virtually all the added OH^- , and pH again does not change significantly.

220-9.6.2.10 In effect, then, a buffer solution of a weak base and its salt stores a reserve supply of acid as the cation of the salt and a reserve of base as the unassociated weak electrolyte (NH_3 in example above). As might be expected, however, there is a limit to the amount of strong acid or strong base that a buffer solution can tolerate without changing pH. Reference to equation (9-49) shows that if the acid or base addition significantly changes the ratio, $[NH_3\ ]/[NH_4\ ^+\ ]$, then pH will change. This means that the amount of acid or base added must be small compared to the amount of weak electrolyte and salt in the solution.

220-9.6.2.11 A buffer formed by dissolving a weak acid and its salt is also resistant to pH changes caused by dilution, evaporation, or additions of small amounts of acid or base. The arguments to show this correspond to the preceding discussion of a weak base-salt buffer with appropriate changes for the applicable reactions.

220-9.6.3 TRISODIUM PHOSPHATE-DISODIUM PHOSPHATE. As noted before, hydrolysis of $PO^=$ ions is widely used in chemistry control of boiling systems. Actually the process involves both $Na_3\ PO_4$ and $Na_2\ HPO_4$. The equilibria in a solution containing these compounds are governed by the following equations.

220-9.6.3.1 Note that equation (9-54) is the third step in the ionization of $H_3\ PO_4{}^{nm}$; thus, $HPO_4{}^=$ is a weak acid and $Na_3\ PO_4$ is its salt. Equation (9-46) is the hydrolysis of the acid anion, $PO_4{}^=$. It is obvious, however, from the values of K_h and K_3 , that the effect of equation (9-54) on pH is totally insignificant compared to the effect of equation (9-46). In this case, as opposed to an NH_3 -NH_4 Cl solution it is the hydrolysis reaction which dominates rather than the weak electrolyte ionization.

220-9.6.3.2 Based on the argument that hydrolysis of $PO_4^{\underline{=}}$ is an incomplete reaction and produces OH^- ions (a basic solution), paragraphs 220-9.5.5 and 220-9.5.5.1 use the mathematical device of treating

$$PO_4^{\equiv} + H_2O \rightleftarrows HPO_4^{=} + OH^- \qquad (9\text{-}46)$$

$$K_h = \frac{[HPO_4^{=}][OH^-]}{[PO_4^{\equiv}]} = \frac{K_w}{K_3} = 2.08 \times 10^{-2} \qquad (9\text{-}53)$$

$$HPO_4^{=} + H_2O \rightleftarrows PO_4^{\equiv} + H_3O^+ \qquad (9\text{-}54)$$

$$K_3 = \frac{[PO_4^{\equiv}][H_3O^+]}{[HPO_4^{=}]} = 4.8 \times 10^{-13} \qquad (9\text{-}55)$$

Equation (9-46) as a weak-base ionization. That approach is also fruitful in the case of Na_3PO_4 -Na_2HPO_4 solutions. If equation (9-46) is treated as a weak base ionization and equation (9-54) as the hydrolysis of a salt of the weak base, then this solution is analogous to an NH_3 -NH_4 Cl solution. Thus, equation (9-49) should apply if the conditions on that equation are satisfied. That is:

$$[OH^-] = \frac{[PO_4^{\equiv}]}{[HPO_4^{=}]} K_h; \begin{cases} \text{if } [PO_4^{\equiv}] >> K_h \\ \text{and } 0.1 < \dfrac{[PO_4^{\equiv}]}{[HPO_4^{=}]} < 10 \end{cases} \qquad (9\text{-}56)$$

In many applications of Na_3PO_4 -Na_2HPO_4 equilibria, the amounts of Na_3PO_4 and Na_2HPO_4 added are such that $[PO_4^{=}]$ and $[HPO_4^{=}]$ are usually in the range 10^{-3} to 10^{-4} $\underline{M}$. Since $K_h = 2.08 \times 10^{-2}$, the first condition on equation (9-56) is not met and this equation cannot be expected to accurately describe such solutions.

220-9.6.3.3 Before developing better equations for these solutions, let us consider the question of whether these solutions are really buffers. Unfortunately, the answer is not clear-cut because it is largely a matter of degree. The processes responsible for the characteristic properties of buffers do occur in dilute Na_3PO_4 -Na_2HPO_4 solutions but to a lesser extent than in more concentrated solutions. If OH^- ions are added, they react with the weak acid $HPO_4^{=}$ by shifting the equilibrium of equation (9-46) to the left; if H_3O^+ ions are added, they react with the weak-acid anion $PO_4^{\underline{=}}$ by shifting the equilibrium of equation (9-54) to the left. The calculations in paragraphs

220-9.6.2 through 220-9.6.2.11 show that 0.5 M NH_3 -0.5M NH_4Cl solution can tolerate addition of 10^{-3} M acid base with no significant change in pH. At the concentrations normally used an Na_3PO_4 -Na_2HPO_4 solution can withstand the addition of ~10^{-4} M acid or base without a significant change in pH. It should be noted, however, that if this Na_3PO_4 -Na_2HPO_4 solution undergoes evaporation, the concentrations of all dissolved substances increase and the solution approaches true buffer behavior. Thus, even for an initially dilute solution, pH will not change drastically upon evaporation.

220-9.6.3.4 Now consider the method of calculating pH in dilute Na_3PO_4 -Na_2HPO_4 solutions. As noted previously, the hydrolysis reaction in equation (9-46), predominates in such solutions. Suppose that sufficient Na_3PO_4 and Na_2HPO_4 are dissolved to give a solution which would contain 2 x 10^{-3} M Na_3PO_4 and 1 x 10^{-3} M Na_2HPO_4 if no reactions occurred. Both compounds dissociate completely into ions:

$$Na_3PO_4 \rightarrow 3Na^+ + PO_4^{\equiv}$$

$$Na_2HPO_4 \rightarrow 2Na^+ + HPO_4^{=}$$

The $PO_4^{\equiv}$ hydrolyzes to:

$$PO_4^{\equiv} + H_2O \rightleftharpoons HPO_4^{=} + OH^- \qquad (9\text{-}46)$$

$$K_h = \frac{[HPO_4^{=}][OH^-]}{[PO_4^{\equiv}]} = 2.08 \times 10^{-2} \qquad (9\text{-}53)$$

However, $HPO_4^{=}$ ions were initially added to the solution as Na_2HPO_4 . Since the equilibrium constant, K_3 , from equation (9-55) is negligibly small, it can be assumed that essentially none of the $HPO_4^{=}$ added ionizes by the reaction in equation (9-54). Thus, if X moles/liter of $PO_4^{\equiv}$ hydrolyze to form X moles/liter of both $HPO_4^{=}$ and OH^- , equation (9-53) becomes

$$2.08 \text{ x } 10^{-2} = \frac{(X + 1 \text{ x } 10^{-3})(X)}{(2 \text{ x } 10^{-3} - X)} \qquad (9\text{-}57)$$

Rearrangement gives the quadratic:

$$X^2 + 2.18 \text{ x } 10^{-2} X - 4.16 \text{ x } 10^{-5} = 0$$

which can be solved to give:

$$X = 1.75 \text{ x } 10^{-3} \underline{M} = [OH^-]$$

Then,

$$\begin{aligned} pOH &= -\log(1.75 \text{ x } 10^{-3}) \\ &= 3 - 0.24 \\ &= 2.76 \\ pH &= 14.00 - 2.76 \\ &= 11.24 \end{aligned}$$

220-9.6.3.5 Using $[OH^-]$ for X and $[PO_4^{\overline{=}}]_o$ and $[HPO_4^{\overline{=}}]$ for the initial concentrations. Equation (9-57) becomes the general equation for calculating $[OH^-]$ in Na_3PO_4-Na_2HPO_4 solution:

$$K_h = 2.08 \text{ x } 10^{-2} = \frac{([HPO_4^{=}]_o + [OH^-])[OH^-]}{[PO_4^{\equiv}]_o - [OH^-]} \qquad (9\text{-}58)$$

For solutions in which $[OH^-] << [HPO_4^{=}]_o$ and $[OH^-] << [PO_4^{\equiv}]_o$, the student can verify that Equation (9-58) reduces to Equation (9-56).

220-9.6.3.6 Calculations for pH in dilute Na_3PO_4-Na_2HPO_4 solutions can often be simplified even further with only a small loss of accuracy. In the calculation above, it is shown that:

$X = 1.75 \text{ x } 10^{-3} \underline{M} = [OH^-]$

Since one OH^- ion is produced for each $PO_4^{\overline{=}}$ ion which hydrolyzes, the amount of $PO_4^{\overline{=}}$ which reacted is also $1.75 \text{ x } 10^{-3} \underline{M}$. The initial concentration was $2 \text{ x } 10^{-3} \underline{M}$; thus, the fraction which reacted is

$$\frac{1.75 \text{ x } 10^{-3}}{2.0 \text{ x } 10^{-3}} = 0.88 \text{ or } 88 \text{ percent}$$

220-9.6.3.7 As a rough approximation, it can be assumed that in dilute (10^{-3} - 10^{-4} $\underline{M}$) solutions of Na_3PO_4 -Na_2HPO_4 , all the $PO_4^{=}$ hydrolyzes to produce OH^- on a one-to-one basis. Applying that assumption to the above case, 2 x 10^{-3} $\underline{M}$ $PO_4^{=}$ would produce 2 x 10^{-3} $\underline{M}$ OH^- and:

$$
\begin{aligned}
pOH &= \log (2 \times 10^{-3}) \\
&= 3.0 - 0.30 \\
&= 2.70 \\
pH &= 14.0 - 2.70 \\
&= 11.30
\end{aligned}
$$

This value is a fairly good approximate to the more accurate value 11.24 calculated above. If the Na_3PO_4 -Na_2HPO_4 concentrations were lower, the percentage hydrolysis would be greater and the approximation would be even better. The approximation may be used with no more than a 10 percent error up to concentrations of about 10^{-3} $\underline{M}$.

Example 9-10: Calculate the pH of a solution which is 1×10^{-4} $\underline{M}$ in Na_2HPO_4 and 3.0×10^{-4} $\underline{M}$ in Na_3PO_4.

Solution 9-10: Using Equation (9-58):

$$2.08 \times 10^{-2} = \frac{([HPO_4^{=}]_o + [OH])[OH^-]}{[PO_4^{\equiv}]_o - [OH^-]}$$

$$2.08 \times 10^{-2} = \frac{(1.0 \times 10^{-4} + [OH^-])[OH^-]}{3.0 \times 10^{-4} - [OH^-]}$$

$$[OH^-]^2 + 2.09 \times 10^{-2} [OH^-] - 6.24 \times 10^{-6} = 0$$

Solution of this quadratic gives:

$$[OH^-] = 3.0 \times 10^{-4}$$

$$pOH = -\log (3.0 \times 10^{-4})$$

$$= 4.0 - 0.48$$

$$= 3.52$$

$$pH = 14.0 - 3.52$$

$$= 10.48$$

The assumption of 100 percent hydrolysis of PO_4 gives:

$$[OH^-] = [PO_4^{\equiv}]_o = 3.0 \times 10^{-4}$$

which is the same value as that obtained in the previous calculations. Within the accuracy of those calculations, Na_3PO_4 is 100 percent hydrolyzed at this concentration.

220-9.7 NON-BUFFERED WATER CHEMISTRY CONTROL

220-9.7.1 Data for this paragraph will be provided in a future change to this volume.

220-9.8 SUMMARY

220-9.8.1 This section describes several special cases of chemical equilibrium in aqueous solutions, including solubility of ionic compounds, the ionization of weak electrolytes, and the hydrolysis of salts of weak electrolytes. In buffer solutions, both ionization and hydrolysis equilibria occur simultaneously and exert considerable influence on each other. In all these processes, equilibrium expressions can be written and each process is governed by an equilibrium constant. Although exact expressions can be written, in some cases the expressions are very complex and difficult to solve. The general approach to solving problems involving complex equilibria is to use the simplest approximate method and then use the results to test the validity of the assumptions. This process often requires a good understanding of the chemical processes involved and the physical meaning of the assumptions.

SECTION 9 PROBLEMS

1. Calculate the saturation concentration of $Fe(OH)_2$ (K_{sp} = 2 x 10^{-14}) and the pH of a saturated solution of $FE(OH)_2$.
2. The solubility of silver bromide (AgBr) is 1.86 x 10^{-6} mole/liter at 20°C. Calculate K_{sp} for AgBr at 20°C.
3. 50.0 ml of 2.5 10^{-2} $\underline{M}$ $AgNO_3$ solution are added to 50 ml of 5.00 x 10^{-2} $\underline{M}$ NaCl solution. Calculate the concentration of Ag^+ in the final solution.
4. What is the chloride ion concentration in a saturated solution of lead chloride (PbCl2)? K_{sp} ($PbCl_2$) = 1.6 x 10^{-5} .
5. Calculate [$H_3 O^+$] and pH in a 0.2$\underline{M}$ acetic acid ($HC_2 H_3 O_2$) solution.
6. Calculate the percent dissociation of a 0.1$\underline{M}$ HCN solution, given:

$$HCN + H_2O \leftrightarrows H_3O^+ + CN^-$$

$$K_i = 7.2 \times 10^{-10}$$

7. What is the OH^- concentration and pH of a 0.15$\underline{M}$ NH_3 solution?
8. Determine [OH^-] and pH of a solution which contains 0.20$\underline{M}$ NH_3 and O.1 $\underline{M}$ NH_4 Cl.
9. How many grams of NH_3 must be dissolved to prepare one liter of solution with a pH of 10.8?
10. Estimate the pH of a solution which contains 5.0 x 10 -4 mole/liter $Na_3 PO_4$ and 2.0 x 10^{-4} mole/liter $Na_2 HPO_4$.

SECTION 9 PROBLEM ANSWERS

1. 1.71 x 10^{-5} $\underline{M}$ $Fe(OH)_2$ pH = 9.53

2. K_{sp} (AgBr) = 3.46 x 10^{-12}
3. [Ag^{+}] = 1.25 x 10^{-8} mole/liter
4. [Cl^{-}] = 3.2 x 10^{-2} mole/liter
5. [H_3 O^{+}] = 1.89 x 10^{-3} mole/liter pH = 2.72
6. 0.0085 percent
7. [OH^{-}] = 1.64 x 10^{-3} mole/liter pH = 11.22
8. [OH^{-}] = 3.6 x 10^{-5} mole/liter pH = 9.56
9. 0.38 grams
10. pH $\simeq$ 10.7

SECTION 10.

CONCENTRATION AND DILUTION PROCESSES

220-10.1 INTRODUCTION

220-10.1.1 One of the important practical aspects of dealing with solutions is the effect of various physical processes on the concentration of solute and the pH of the solution. Processes which decrease the solute concentration are called dilution processes. Those which increase the solute concentration are called concentration processes. Dilution processes include addition of solvent to a solution and addition of a solution of lower concentration. The most common means of concentrating a solution is evaporation of the solvent by heating. Another way is addition of a highly concentrated solution to a more dilute solution. The obvious method of adding additional pure solute is not considered in this section because it is treated in previous sections.

220-10.2 GLOSSARY OF TERMS

220-10.2.1 Terms used in this section are defined as follows:

a. **Batch Process:** Any process which is carried out in one or more discrete steps.

b. **Concentration Process:** Any operation which increases the concentration of solute in a solution.

c. **Continuous Process:** Any process which is carried out constantly over some period of time.

d. **Dilution Process:** Any operation which decreases the concentration of solute in a solution.

e. **Material Balance:** A statement of the Law of Conservation of Mass to the effect that after any process, the amount of material left in the system is equal to the amount originally in the system plus the amount added minus the amount removed from the system. **If no chemical reactions (including partial ionization) occur during the process,** material balance applies to each chemical species in the system as well as to total material in the system. For weak electrolytes, the total (ionized plus nonionized) concentration of weak electrolyte must be used in material balance equations, because the extent of ionization varies with concentration.

220-10.3 TYPES

220-10.3.1 Concentration and dilution processes fall into two general categories based on the method by which they are performed. Processes which are carried out in one or more discrete steps are called batch processes. Examples of batch processes are:

a. The addition of pure water (or another solution) to the initial solution in a single step process.

b. Draining a portion of the initial solution from a vessel and refilling with pure water (or another solution) in a two-step process.

c. Boiler blowdown to reduce the concentration of various chemicals.

220-10.3.2 The second type of process includes those which occur continually over some period of time and are called **continuous processes.** For example, a feed and bleed operation is the process of continuously draining solution from a tank and at the same time continuously adding (feeding) pure water into the tank. This is a dilution process and if the feed rate is equal to the bleed rate, the total volume of solution stays constant while the concentration continuously decreases. An example of a continuous concentration process is continuously feeding solution into a boiling system. In this case, if the feed rate is equal to the evaporation rate, the total volume of solution remains constant while the concentration continuously increases.

220-10.4 GENERAL PRINCIPLES

220-10.4.1 The general approach to solving calculations involving either continuous or batch processes is application of the principle of material balance, although the final equations may differ. **Material balance** is just a mathematical statement of the law of conservation of mass and may be stated in words as follows:**For any concentration or dilution process, the material remaining must be equal to the material initially present plus any material added less any material removed.**

220-10.4.2 If no chemical reactions occur during the process, material balance applies to each chemical species as well as the total mass of the solution. If a substance is completely ionized in solution, material balance can be applied to each ion. Partial ionization is considered a chemical reaction and requires special treatment as described in paragraphs 220-10.5.3 through 220-10.5.3.2.1.

220-10.4.3 The application of material balance to each type of concentration and dilution process is described in the following sections. Throughout these descriptions, the following set of symbols and subscripts is used:

Symbols	Meaning
v	volume of solution or solvent
C	concentration
R	rate of addition or removal of solute
a	indicates solution or solvent added to a system (V_a , C_a)
f	indicates final conditions (V_f , C_f)
r	indicates solution or solvent removed from the system, by draining, bleeding, or evaporation, (V_r , C_r)
o	indicates original conditions (V_o , C_o)
t	indicates conditions in the system at some particular time, t (V_t , C_t)

220-10.4.4 In all the following discussions, complete and instantaneous mixing is assumed. That is, whenever one solution is added to another, the two are assumed to mix immediately and completely to give a new solution of uniform concentration. Unless stated otherwise, it is also to be assumed that no chemical reactions occur in a concentration or dilution process.

220-10.5 BATCH PROCESSES

220-10.5.1 GENERAL. Application of the principle of material balance to general batch processes gives two straightforward algebraic equations. One equation is in terms of the solute and one is in terms of the total solution.

a. **Solute Material Balance** - mass of solute in the final solution = mass of solute in original solution + mass of solute added - mass of solute removed. If the concentration of solute is expressed as amount per liter (or kilogram) of solution, then the amount of solute in any particular volume of solution is:

$$\text{amount of solute} = \text{Concentration} \times \text{Volume} \qquad (10\text{–}1)$$

For example,

$$\text{moles of solute} = \frac{\text{moles of solute}}{\text{liter of solution}} \times \text{liters of solution}$$

This relationship is also true for concentrations expressed as parts-per-million because of the approximation (Section 5), 1 part-per-million = (1 milligram)/liter. Thus, milligram solvent = (milligram)/liter x liters of solution. The same holds true for equivalents-per-million. Using equation (10-1) and the appropriate subscripts from paragraph 220-10.4.3, the material balance equation for a solute becomes:

$C_f\ V_f = C_o\ V_o + C_a\ V_a - C_r\ V_r$ (10-2) Any units may be used for C and V in this equation so long as the same units are used throughout the equation. If no chemical reactions take place during the concentration or dilution process, equation (10-2) applies to each solute in a multi-component solution. In some cases, however, some caution must be observed in choosing the particular species in terms of which the equation is stated. In particular, this applies to solutions of weak electrolytes. For example, in an NH_3 solution, some fraction of the NH_3 originally dissolved forms NH_4^+ ions and this fraction changes if the concentration changes. For that reason, equation (10-2) must be stated in terms of total NH_3 (the amount present as NH_3 plus the amount present as NH_4^+). This feature is discussed further in paragraphs 220-10.5.3 through 220-10.5.3.2.1.

b. **Solution Material Balance** - mass of final solution = mass of original solution + mass of solution added - mass of solution removed. The mass of any solution is given by the product of the density, d, of the solution and volume; thus, the above equation becomes:

$d_f\ V_f = d_o\ V_o + d_a\ V_a - d_r\ V_r$ (10-3)

As noted in previous sections, the density of dilute aqueous solutions is approximately the same as the density of water, 1 gram per milliliter. In this case, all the density terms in Equation (10-3) are approximately equal and the equation reduces to:

$V_f = V_o + V_a - V_r$ (10-4)

Equations (10-2) and (10-4) apply to any batch concentration or dilution process. As illustrated in the following examples, these equations may be simplified further in certain cases.

220-10.5.2 SPECIFIC BATCH PROCESSES. The examples in this section illustrate some special cases of batch processes.

220-10.5.2.1 Single-Step Processes

Example 10-1: ***Eleven liters of pure water are added to 6 liters of a solution which contains 100 parts-per-million NaCl. What is the concentration of NaCl in the final solution?***

Solution 10-1: ***Since no solution was removed, $V_r = 0$, and Equation (10-4) becomes:***

$$V_f = V_o + V_a$$

$$= 6 \text{ liters} + 11 \text{ liters}$$

$$= 17 \text{ liters}$$

No solute was added or removed; thus $C_aV_a = C_rV_r = 0$, and Equation (10-2) becomes:

$$C_fV_f = C_oV_o$$

$$C_f = \frac{C_oV_o}{V_f} = \frac{100 \text{ ppm} \times 6 \text{ liters}}{17 \text{ liters}}$$

$$= 35 \text{ parts-per-million}$$

Example 10-2: One and a half liters of a solution containing 900 parts-per-million NaCl are added to 6 liters of a solution containing 100 parts-per-million NaCl. What is the NaCl concentration in the final solution?

Solution 10-2: Again no solution was removed ($C_rV_r = 0$) but some was added. Using Equations (10-4) and (10-2):

$$V_f = V_o + V_a$$

$$= 6 \text{ liters} + 1.5 \text{ liters}$$

$$= 7.5 \text{ liters}$$

$$C_fV_f = C_oV_o + C_aV_a$$

$$C_f = \frac{C_oV_o + C_aV_a}{V_f}$$

$$= \frac{(100 \text{ ppm} \times 6 \text{ liters}) + (900 \text{ ppm} \times 1.5 \text{ liters})}{7.5 \text{ liters}}$$

$$= 260 \text{ parts-per-million}$$

220-10.5.2.2 Batch Evaporation

Example 10-3: ***A tank contains 400 gallons of a 3.0 parts-per-million chloride solution. What is the chloride concentration if the solution is evaporated until only 25 gallons remain?***

Solution 10-3: ***No solute or solvent is added to the solution ($V_a = 0$ and $C_aV_a = 0$). No solute is removed ($C_rV_r = 0$), but most of the solvent is removed to give a final volume, V_f, of 25 gallons.***

Using Equation (10-2):

$$C_fV_f = C_oV_o$$

$$C_f = \frac{C_oV_o}{V_f}$$

$$= \frac{400 \text{ gallons} \times 3 \text{ ppm}}{25 \text{ gallons}}$$

$$= 48 \text{ parts-per-million}$$

220-10.5.2.3 Multi-Step Processes. Because of the concentrating effect of evaporation, chemicals accumulate in the boiler. To reduce the concentration of these chemicals, a common operation, called blowdown, is performed. This operation usually consists of adding water for initial dilution, draining part of the solution to a volume less than the original volume, then adding more water to give a final volume about the same as the original volume. Sometimes it is necessary to repeat this sequence more than once to produce the desired dilution. Each step of the fill-drain-fill sequence can be treated as a batch process as illustrated in the following example. (Actually, in the second step, solution is blown out of the boiler by the steam pressure if the temperature is above 200°F. The distinction between draining and blowing is important operationally, but the effects on concentration are the same in both cases.)

Example 10-4: *A boiler contains 600 gallons of a 5 parts-per-million NaCl solution. To this solution are added 200 gallons of pure water, 400 gallons are drained from the system, and then 200 gallons of pure water are added. What is the final concentration of NaCl in the boiler? What is the final concentration if the above sequence is carried out twice?*

Solution 10-4: *Consider each step independently. Let* V_{a1} *and* V_{a2} *be the volumes of the two additions and let* C'_f *and* V'_f *be the concentration and volume in the system after the first addition.*

Step 1: Add 200 gallons of water. From Equation (10-4):

$$V_f' = V_o + V_{a1} - V_r$$

In this step, $V_r = 0$*. Thus:*

$$V'_f = V_o + V_{a1}$$

From Equation (10-2):

$$C'_f V'_f = C_o V_o + C_{a1} V_{a1} - C_r V_r$$

Since pure water is added and no solution is removed in this step;

$$C_{a1} V_{a1} = 0$$

and $C_r V_r = 0$. *Thus:*

$$C'_f V'_f = C_o V_o$$

$$C'_f = \frac{C_o V_o}{V'_f} = \frac{C_o V_o}{V_o + V_{a1}} \qquad (10a)$$

$$= \frac{(5\ \text{ppm})\ (600\ \text{gallons})}{600\ \text{gallons} + 200\ \text{gallons}}$$

$$= \frac{3000\ (\text{ppm})\ (\text{gallons})}{800\ \text{gallons}}$$

$$= 3.75\ \text{parts-per-million}$$

Step 2: Drain 400 gallons of solution. This step removes solute from the system but it does not change the concentration of solute in the solution left in the system, which can be shown as follows.

Letting V''_f *and* C''_f *be the volume and concentration left in the boiler after draining, Equation (10-4) gives:*

$$V''_f = V_o + V_{a1} - V_r$$

Equation (10-2) becomes:

$$C''_f V''_f = C_o V_o + C_{a1} V_{a1} - C_r V_r$$

Using the above expression for V''_f:

$$C''_f (V_o + V_{a1} - V_r) = C_o V_o + C_{a1} V_{a1} - C_r V_r$$

However, $C_{a1} V_{a1} = 0$ *and* $C_o V_o = C'_f (V_o + V_{a1})$ *from Equation (10-a). Thus:*

$$C''_f (V_o + V_{a1} - V_r) = C'_f (V_o + V_{a1}) - C_r V_r$$

The concentration of the solution drained is just the concentration after Step 1; $C_r = C'_f$

$$C_f''(V_o + V_{a_1} - V_r) = C_f'(V_o + V_{a_1}) - C_f'V_r$$

$$= C_f'(V_o + V_{a_1} - V_r)$$

$$C_f'' = C_f'$$

Step 3: *Add 200 gallons of water.*

Equation (10-4) gives:

$$V_f = V_o + V_{a_1} + V_{a_2} - V_r$$

From Equation (10-2):

$$C_f V_f = C_o V_o + C_{a_1} V_{a_1} + C_{a_2} V_{a_2} - C_r V_r$$

Substituting for V_f

$$C_f = \frac{C_o V_o + C_{a_1} V_{a_1} + C_{a_2} V_{a_2} - C_r V_r}{V_o + V_{a_1} + V_{a_2} - V_r}$$

As before $C_{a_1} V_{a_1} = 0$ *and* $C_{a_2} V_{a_2} = 0$ *because pure water is added.*

$$C_f = \frac{C_o V_o - C_r V_r}{V_o + V_{a_1} + V_{a_2} - V_r}$$

Using the same relationships as in Step 2,

$$C_o V_o - C_r V_r = C_f'(V_o + V_{a_1} - V_r)$$

Thus:

$$C_f = \frac{C_f'(V_o + V_{a_1} - V_r)}{V_o + V_{a_1} + V_{a_2} - V_r} \qquad (10\text{-}b)$$

This equation can be used to calculate C_f

$$C_f = \frac{3.75 \text{ ppm } (600 \text{ gallons} + 200 \text{ gallons} - 400 \text{ gallons})}{600 \text{ gallons} + 200 \text{ gallons} + 200 \text{ gallons} - 400 \text{ gallons}}$$

$$= \frac{3.75 \text{ ppm } (400 \text{ gallons})}{600 \text{ gallons}}$$

$$= 2.5 \text{ parts-per-million}$$

To obtain a simplified general solution, substitute Equation (10-a) for C_f *in Equation (10-b):*

$$C_f = \frac{C_o V_o (V_o + V_{a_1} - V_r)}{(V_o + V_{a_1})(V_o + V_{a_1} - V_r + V_{a_2})} \qquad (10\text{-}c)$$

In this problem, $V_r = V_{s_1} + V_{s_2}$. *Substituting this for* V_r *in Equation (10-c);*

$$C_f = \frac{C_o V_o (V_o + V_{s_1} - V_{s_1} - V_{s_2})}{(V_o + V_{s_1})(V_o + V_{s_1} - V_{s_1} - V_{s_2} + V_{s_2})}$$

$$= C_o \frac{(V_o - V_{s_2})}{(V_o + V_{s_1})} \qquad (10\text{-}d)$$

The final concentration can now be calculated directly from the information given in the problem without going through each step.

$$C_f = 5 \text{ ppm } \frac{(600 \text{ gallons} - 200 \text{ gallons})}{(600 \text{ gallons} + 200 \text{ gallons})}$$

$$= 5 \text{ ppm } \frac{400 \text{ gallons}}{800 \text{ gallons}}$$

$$= 2.5 \text{ parts-per-million}$$

If the fill-drain-fill sequence is performed a second time, Equation (10-d) can be used again, letting C_o *be the concentration after the first sequence, 2.5 parts-per-million.*

$$C_f = 2.5 \frac{(600 \text{ gallons} - 200 \text{ gallons})}{(600 \text{ gallons} + 200 \text{ gallons})}$$

$$= 1.25 \text{ parts-per-million}$$

An even more general equation can be derived as follows.

From Equation (10-d), after the first sequence:

$$C_f = C_o \frac{(V_o - V_{s_2})}{(V_o + V_{s_1})} \qquad (10\text{-}d)$$

The concentration after the second sequence, C_{f2} *is:*

$$C_{f2} = C_f \frac{(V_o - V_{s_2})}{(V_o + V_{s_1})} \qquad (10\text{-}e)$$

since V_o, V_{s_1}, *and* V_{s_2} *are the same in each sequence. Substituting (10-d) for* C_f *in (10-e);*

$$C_{f2} = C_o \left(\frac{V_o - V_{s_2}}{V_o + V_{s_1}}\right) \left(\frac{V_o - V_{s_2}}{V_o + V_{s_1}}\right)$$

$$= C_o \left(\frac{V_o - V_{s_2}}{V_o + V_{s_1}}\right)^2$$

It follows that if a fill-drain-fill operation is repeated n times and if $V_r = V_{s_1} + V_{s_2}$ in each operation, then:

$$C_{fn} = C_o\left(\frac{V_o - V_{s_2}}{V_o + V_{s_1}}\right)^n$$

In the above problem, for n = 2:

$$C_{f2} = C_o\left(\frac{V_o - V_{s2}}{V_o + V_1}\right)^2$$

$$= 5\ ppm\left(\frac{400\ gal}{800\ gal}\right)^2$$

$$= 5\ ppm\ (0.5)^2$$

$$= 1.25\ \text{parts-per-million}$$

220-10.5.3 pH CHANGES IN BATCH PROCESSES. Since pH is a measure of the concentration of $H_3 O^+$ or OH^- ions, the basic problem in calculating pH changes in any concentration or dilution process is determining the change in $[H_3 O^+]$ or $[OH^-]$. The first step is always to convert any given pH or pOH to $[H_3 O^+]$ or $[OH^-]$. After this, the method depends on whether the particular acid or base is strong or weak.

220-10.5.3.1 Strong Acids and Bases. If the solution contains a strong acid or base, then $[H_3 O^+]$ or $[OH^-]$ can be used directly for the concentration terms in equation (10-2). This can be done because strong acids and bases are treated as being completely ionized in aqueous solutions.

220-10.5.3.2 Weak Acids and Bases. If the solution contains a weak acid or base, then the appropriate ionization equilibrium must be accounted for in the calculation. This is necessary because the percentage ionization of a weak electrolyte varies with concentration. The method of accounting for this variation is generally:

1. Use the value of $[H_3 O^+]$ or $[OH^-]$ calculated from pH or pOH in the ionization constant expression to determine the total weak electrolyte concentration. This total value is the amount ionized plus the amount not ionized.
2. Use the total concentration in the material balance equations and calculate the new total concentration after the concentration or dilution process.
3. Use the new total concentration and the equilibrium constant expression in calculating the new value of $[H_3 O^+]$ or $[OH^-]$ and then calculate the new pH or pOH.

220-10.5.3.2.1 In all cases, if the initial and final values of pH are less than 6 or greater than 8, the concentrations of [H_3 O^+] and [OH^-] in pure water can be neglected in the calculations. The student can verify that this is valid from the discussion in paragraphs 220-8.7 through 220-8.7.3.3. A few examples illustrate the application of these procedures.

Example 10-5: An HC1 solution has a pH of 4. Three liters of pure wataer are added to 1 liter of the HC1 solution. Calculate the pH of the final solution.

Solution 10-5: First, calculate [H_3 O^+] from the given pH.

$$pH = 4$$

$$[H_3O^+] = \text{antilog } (-4)$$

$$= 10^{-4} \text{ mole/liter}$$

From Equation (10-2):

$$V_f = V_o + V_a - V_r$$

In this case, $V_r = 0.$

$$V_f = V_o + V_a$$

$$= 1 \text{ liter} + 3 \text{ liters}$$

$$= 4 \text{ liters}$$

HCl is a strong acid, so Equation (10-2) can be used:

$$C_fV_f = C_oV_o + C_aV_a - C_rV_r$$

$$C_a = 0,\ C_aV_a = 0$$

$$V_r = 0,\ C_rV_r = 0$$

$$C_f = \frac{C_oV_o}{V_f}$$

$$= \frac{(1 \times 10^{-4} \text{ mole/liter})\ (1 \text{ liter})}{4 \text{ liters}}$$

New $[H_3O^+] = C_f = 2.5 \times 10^{-5}$ *mole/liter.*

Finally, calculate the new pH.

$$pH = -\log\ (2.5 \times 10^{-5})$$

$$= 5 - 0.40$$

$$= 4.6$$

Example 10-6: *Four liters of pure water are added to four liters of an NaOH solution of pH 11. What is the new pH?*

Solution 10-6: *The solution is basic, so the calculations should be carried out in terms of* $[OH^-]$.

$$pOH = 14 - pH$$

$$= 14 - 11$$

$$= 3$$

$$[OH^-] = \text{antilog}\ (-3)$$

$$= 10^{-3}\ \text{mole/liter}$$

Since NaOH is a strong base, Equation (10-2) can be used directly.

$$C_f V_f = C_o V_o + C_a V_a - C_r V_r$$

$$C_a = 0,\ C_a V_a = 0$$

$$V_r = 0,\ C_r V_r = 0$$

$$V_f = V_o + V_a$$

$$= 4\ \text{liters} + 4\ \text{liters}$$

$$= 8\ \text{liters}$$

$$C_f = \frac{C_o V_o}{V_f}$$

$$= \frac{(1 \times 10^{-3}\ \text{mole/liter})\ (4\ \text{liters})}{8\ \text{liters}}$$

New $[OH^-] = C_f = 5 \times 10^{-4}$ mole/liter.

Finally, calculate the new pOH and pH.

$$pOH = -\log\ (5 \times 10^{-4})$$

$$= 4 - 0.7$$

$$= 3.3$$

$$pH = 14 - pOH$$

$$= 10.7$$

Example 10-7: Four liters of pure water are added to 4 liters of an NH_3 solution of pH = 10. Calculate the new pH.

Solution 10-7: Again the solution is basic so $[OH^-]$ is used in the calculations.

$$pH = 10$$

$$pOH = 14 - pH$$

$$= 4$$

$$[OH^-] = \text{antilog}\,(-4)$$

$$= 10^{-4}$$

Ammonia is a weak base, so the total NH_3 concentration, $[NH_3]_t$, must be used in the material balance equation. The value of $[NH_3]_t$ is determined from the following equations.

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^- \qquad (10\text{-}5)$$

$$K_i = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5} \qquad (10\text{-}6)$$

(Values of K_i for various substances are listed in table 220-14.)

$$[NH_3]_t = [NH_3] + [NH_4^+]$$

From Equation (10-5); $[NH_4^+] = [OH^-] = 1 \times 10^{-4}$ mole/liter. Using the values in Equation (10-6) gives:

$$1.8 \times 10^{-5} = \frac{(1 \times 10^{-4})(1 \times 10^{-4})}{[NH_3]}$$

$$[NH_3] = \frac{1 \times 10^{-8}}{1.8 \times 10^{-5}}$$

$$= 5.56 \times 10^{-4} \text{ mole/liter}$$

Thus,

$$[NH_3]_t = 5.56 \times 10^{-4} + 1 \times 10^{-4}$$

$$= 6.56 \times 10^{-4} \text{ mole/liter}$$

Now using the material balance equation ($C_aV_a = 0$, $C_rV_r = 0$):

$$C_fV_f = C_oV_o$$

where:

$$V_f = V_o + V_a = 4 \text{ liters} + 4 \text{ liters} = 8 \text{ liters}$$

$$C_f = \frac{C_oV_o}{V_f}$$

$$= \frac{(6.56 \times 10^{-4} \text{ mole/liter})(4 \text{ liters})}{8 \text{ liters}}$$

New $[NH_3]_t = C_f = 3.28 \times 10^{-4}$ mole/liter.

The new value of [OH⁻] must now be calculated using Equation (10-6). From section 9, Equation (9-25) is applicable. The reader can verify that this solution does not meet the conditions of simpler Equation (9-26).

$$1.8 \times 10^{-5} = \frac{[OH^-]^2}{(3.28 \times 10^{-4}) - [OH^-]}$$

This reduces to the quadratic:

$$[OH^-]^2 + 1.8 \times 10^{-5}\,[OH^-] - 5.90 \times 10^{-9} = 0$$

This equation can be solved to give:

$$[OH^-] = 6.8 \times 10^{-5} \text{ mole/liter}$$

$$pOH = -\log(6.8 \times 10^{-5})$$

$$= 5.0 - 0.83$$

$$= 4.17$$

$$pH = 14 - pOH$$

$$= 9.83$$

220-10.6 CONTINUOUS PROCESSES

220-10.6.1 GENERAL. Material balance equations for continuous processes are slightly more complicated than those for batch processes because some of the terms in the equation change continuously as the process is carried out. For this reason, material balance for a continuous process results in a differential equation.

220-10.6.1.1 Consider a system containing a solution. To this system another solution is continuously added and some of the resulting solution is continuously removed. The symbols and subscripts listed in paragraph 220-10.4.3 are used.

220-10.6.1.2 In all the practical examples of continuous processes used in this text, the volume rate of addition to the system is equal to the volume rate of removal. Both rates are denoted by R. Since solution is removed at the same rate another solution is added, the volume of solution in the system at any given time is constant and is equal to the original volume, V_o . However, unless C_a = Co, the concentration of solute in the system changes with time. This change in concentration per unit time is indicated by dC_t/dt and the change in the total amount of solute in the system is $V_o\, dC_t/dt$. This change is just the difference between the rates of addition and removal of solute, $RC_a - RC_r$. Thus:

$$V_o\, dC_t/dt = RC_a - RC_r \quad 10\text{-}7)$$

This is the solute material balance equation for a continuous process.

220-10.6.2 SPECIAL CASES OF CONTINUOUS PROCESSES. There are two special cases of continuous processes of major interest in this text. The useful forms of equation (10-7) for these cases are developed in the following paragraphs.

220-10.6.2.1 Feed to a Boiling System. In this case, a solution is added to the system while only solvent is removed by evaporation. If the solution is added at the same rate as solution is removed by evaporation, the volume of solution in the system remains constant but the concentration of solute increases. That is, in equation (10-7), $C_r = 0$ and:

$$V_o dC_t/dt = RC_a \qquad (10\text{-}8)$$

Integration of this equation gives:

$$\int_{C_o}^{C_t} dC_t = \int_0^t \frac{RC_a}{V_o} dt$$

$$C_t = C_o + \frac{RC_a}{V_o} t \qquad (10\text{-}9)$$

Equation (10-9) can now be used in calculating the effects of this process on concentration.

Example 10-8: *A boiler contains 1000 gallons of a solution with an initial chloride ion concentration of 0.3 parts-per-million. Feedwater is added at a rate equal to the steam generation rate of 10,000 gallons/hour. If the feedwater contains 0.002 ppm chloride, what is the chloride concentration in the boiler after 8 hours.*

Solution 10-8: *This problem is solved by direct substitution of the appropriate values into Equation (10-9).*

$$C_t = C_o + \frac{RC_a}{V_o} t$$

$$C_t = 0.3 \text{ ppm} + \frac{(10{,}000 \text{ gallons/hr})(0.002 \text{ ppm})}{1000 \text{ gallons}} (8 \text{ hours})$$

$$= 0.3 \text{ ppm} + 0.16 \text{ ppm}$$

$$= 0.46 \text{ parts-per-million}$$

220-10.6.2.2 Feed and Bleed Operations. In this process, solute is removed from the system, so equation (10-7) applies.

$V_o\ dC_t/dt = RC_a - RC_r$

Since C_r is just the concentration of the solution in the system, $C_r = C_t$ and the equation is

$V_o\ dC_t/dt = RC_a - RC_t = R(C_a - C_t)$ (10-10)

This equation must be integrated to obtain a usable form.

$$1/R \int_{C_o}^{C_t} \frac{dC_t}{(C_a - C_t)} = 1/V_o \int_0^t dt$$

$$-1/R \ \ln \ \frac{(C_a - C_t)}{(C_a - C_o)} = t/V_o$$

$$C_t = C_o e^{-Rt/V_o} + C_a(1 - e^{-Rt/V_o}) \tag{10-11}$$

Example 10-9: *A tank contains 5000 gallons of a 200 parts-per-million NaCl solution. Feed and bleed are constant at 1.0 gallon/minute and the feed solution contains 28,000 parts-per-million NaCl (sea water). What is the NaCl concentration after 1.0 hour?*

Solution 10-9: *Substitute into Equation (10-11).*

$$C_t = C_o e^{-Rt/V_o} + C_a(1 - e^{-Rt/V_o})$$

$$= 200 \text{ ppm } e^{-\frac{(1 \text{ gallon/minute})(60 \text{ minutes})}{(5000 \text{ gallon})}}$$

$$+ 28{,}000\left(1 - e^{-\frac{(1 \text{ gallon/minute})(60 \text{ minutes})}{(5000 \text{ gallon})}}\right)$$

$$= 200 \text{ ppm } e^{-0.012} + 28{,}000 \text{ ppm } (1 - e^{-0.012})$$

$$= 200 \text{ ppm } (0.99) + 28{,}000 \text{ ppm } (1 - 0.99)$$

$$= 198 + 280$$

$$C_t = 478 \text{ parts-per-million}$$

Example 10-10: *If the feed solution in Example 10-9 contains 5 ppm NaCl, what is the NaCl concentration in the tank after 1 hour?*

Solution 10-10: *Again use Equation (10-11).*

$$C_t = C_o e^{-Rt/V_o} + C_a(1 - e^{-Rt/V_o})$$

$$= 200 \text{ ppm } e^{-\frac{(1 \text{ gallon/minute})(60 \text{ minutes})}{5000 \text{ gallon}}}$$

$$+ 5 \text{ ppm}\left(1 - e^{-\frac{(1 \text{ gallon/minute})(60 \text{ minutes})}{5000 \text{ gallon}}}\right)$$

$$= 200 \text{ ppm } (0.99) + 5 \text{ ppm } (1 - 0.99)$$

$$= 198\ ppm + 0.05\ ppm$$

$$C_t = 198.05\ parts\text{-}per\text{-}million$$

220-10.6.2.2.1 A special case of feed and bleed operations applies if the concentration of solute in the feed water is zero, $C_a = 0$. equation (10-11) then becomes.

$$C_t = C_o e^{-Rt/V_o} \tag{10-12}$$

Mathematically, a feed-and-bleed half-life, $t_{fb_{1/2}}$, can be defined as:

$$t_{fb_{1/2}} = \frac{0.693}{R/V_o} = \frac{0.693V_o}{R}$$

Therefore, Equation (10-12) may be written as:

$$C_t = C_o e^{-0.693t/t_{fb_{1/2}}} \tag{10-13}$$

Example 10-11: *Suppose the feed water in Example 10-9 contains no NaCl. Calculate the NaCl concentration in the tank after 1 hour.*

Solution 10-11: *From Equation (10-12):*

$$\begin{aligned} C_t &= C_o e^{-Rt/V_o} \\ &= 200 \text{ ppm } e^{-\frac{(1 \text{ gallon/minute})(60 \text{ minutes})}{5000 \text{ gallons}}} \\ &= 200 \text{ ppm } (0.99) \\ C_t &= 198 \text{ parts-per-million} \end{aligned}$$

Example 10-12: *A tank holds 2000 gallons of a solution containing 10 parts-per-million* Cl^-. *Using pure water as feed and a feed-and-bleed rate of 100 gallons/hour, how long will it take to reduce the chloride concentration to 5 parts-per-million?*

Solution 10-12: *From Equation 10-12,*

$$C_t = C_o e^{-Rt/V_o}$$

$$\frac{C_t}{C_o} = e^{-Rt/V_o}$$

$$\frac{5 \text{ ppm}}{10 \text{ ppm}} = 1/2 = e^{-Rt/V_o}$$

Taking the natural logarithm of both sides of this equation,

$$\ln(1/2) = -\ln(2) = -Rt/V_o$$

$$0.693 = Rt/V_o$$

$$t = \frac{0.693\ V_o}{R}$$

$$= \frac{(0.693)(2000\ \text{gallon})}{100\ \text{gallon/hour}}$$

$$= 13.86\ \text{hour}$$

The same result is obtained by noting that reduction by a factor of 1/2 corresponds to one half-life and that

$$t_{fb_{1/2}} = \frac{0.693\ V_o}{R}$$

220-10.6.3 pH CHANGES IN CONTINUOUS PROCESSES. The method of treating pH changes in continuous processes is much the same as that for batch processes. That is, if a strong acid or base is involved, then [H_3O^+] or [OH^-] can be used directly in the material balance equations. If a weak electrolyte is involved, then the appropriate ionization equilibrium must be considered, as outlined in paragraphs 220-10.5.3 through 220-10.5.3.2.1 for batch processes.

$$= 1 \times 10^{-5} \text{ mole/liter}$$

Since pure water is used as feed water, Equation (10-12) applies.

$$C_t = C_o e^{-Rt/V_o} \quad \text{or} \quad C_t/C_o = e^{-Rt/V_o}$$

Taking the natural logarithm of both sides;

$$\ln C_t/C_o = -Rt/V_o$$

$$t = (V_o/R)(-\ln C_t/C_o)$$

$$= (V_o/R)\ln C_o/C_t$$

$$= (2.303)\frac{8000 \text{ gallons}}{12 \text{ gallons/minute}} \log \frac{10^{-4}}{10^{-5}}$$

$$= (2.303)\frac{8000 \text{ gallons}}{12 \text{ gallons/minute}} \log 10$$

$$= 1535 \text{ min}$$

$$t = 25 \text{ hours } 35 \text{ minutes.}$$

Example 10-14: For the system described in Example 10-13 how long will it take to reduce the pH to 9.7?

Solution 10-14: As calculated before, for pH = 10,

$$C_o = [OH^-] = 1 \times 10^{-4} \text{ mole/liter.}$$

For a new pH of 9.7:

$$pOH = 14.0 - 9.7$$

$$= 4.3$$

$$C_t = [OH^-] = \text{antilog } (-4.3)$$

$$= 10^{0.7} \times 10^{-5}$$

$$= 5.0 \times 10^{-5} \text{ mole/liter}$$

These values of C_o and C_t can now be used in Equation (10-12) to calculate t as before. However, note that, in this case:

$$C_t = 1/2 \; C_o$$

Thus, the time required to reduce the $[OH^-]$ by 1/2 is just the feed-and-bleed half-life which can be calculated using Equation (10-13)

$$t_{fb_{1/2}} = \frac{0.693 \; V_o}{R}$$

$$= \frac{0.693 \; (8 \times 10^3 \text{ gallons})}{12 \text{ gallons/minutes}}$$

$$= 462 \text{ minutes}$$

$$= 7 \text{ hours } 42 \text{ minutes}$$

Example 10-15: A tank contains 500 gallons of a 0.025 M NH_3 solution (pH = 10.8). What is the pH of the solution after 1 hour of feed and bleed at 10 gallons/minute if the feed water contains 10^{-4} mole/liter of NH_3?

Solution 10-15: Ammonia is a weak base, so the total NH_3, concentration must be used. The original total NH_3 concentration is given (0.025 M). Since the feedwater also contains NH_3, Equation (10-11) must be used.

$$[NH_3]_t = C_t = C_o e^{-Rt/V_o} + C_a(1 - e^{-Rt/V_o})$$

$$= (0.025 \; \underline{M}) e^{-\frac{(10 \text{ gallons/minute})(60 \text{ minutes})}{500 \text{ gallons}}}$$

$$+\ 10^{-4}\ \underline{M}\ 1 - e^{-\frac{(10\ \text{gallon/minute})(60\ \text{minutes})}{500\ \text{gallon}}}$$

$$= 0.025\ \underline{M}\ e^{-1.2} + 10^{-4}\ \underline{M}\ (1 - e^{-1.2})$$

$$= 0.025\ \underline{M}\ (0.30) + 10^{-4}\ \underline{M}(1 - 0.30)$$

$$= 0.0075\ \underline{M} + 0.7 \times 10^{-4}\ \underline{M}$$

$$= 7.5 \times 10^{-3}\ \underline{M} + 0.07 \times 10^{-3}\ \underline{M}$$

$$C_t = 7.57 \times 10^{-3}\ \underline{M}$$

Using Equation (9-26),

$$K_i = \frac{[OH^-]^2}{[NH_3]_t} = 1.8 \times 10^{-5}$$

$$[OH^-]^2 = (1.8 \times 10^{-5})(7.57 \times 10^{-3})$$

$$= 13.6 \times 10^{-8}$$

$$[OH^-] = 3.69 \times 10^{-4}\ \text{mole/liter}$$

220-10.6.3.1 The student should verify that the conditions on the validity of equation (9-26) are satisfied by these values of $[OH^-]$ and $[NH_3]$. Finally,

$$pOH = -\log\ (3.69 \times 10^{-4})$$

$$= 4 - 0.57$$

$$= 3.43$$

$$pH = 14.0 - 3.43$$

$$= 10.57$$

220-10.7 SUMMARY

220-10.7.1 The basic approach to concentration and dilution calculations is application of material balance equations for the total solution and a particular solute **if no chemical reactions (including partial ionization) occur during the process.** For batch processes, material balance results in simple algebraic equations. For continuous processes, the continuous variation of some of the concentration terms gives rise to differential equations. The pH changes caused by either batch or continuous processes can be calculated by using $[H_3O^+]$ or $[OH^-]$, as appropriate, in the material balance equations for strong acids or bases. For weak acids and bases, the total (ionized and non-ionized) concentration of the weak electrolyte must be used in the material balance equation because the degree of ionization changes as the concentration of weak electrolyte changes. Such cases always require use of the ionization constant expression to calculate the final values of $[H_3O^+]$ or $[OH^-]$ and, thus, pH or pOH.

SECTION 10 PROBLEMS

1. How much pure water must be added to 3 liters of a 0.06 $\underline{M}$ NaOH solution to reduce the concentration to 0.011 $\underline{M}$?
2. A solution contains 100 parts-per-million NaCl. Eleven liters of a 15 parts-per-million NaCl solution are added to 6 liters of this solution. What are the final concentrations of NaCl and Cl^- ions?
3. A boiler contains 500 gallons of a 100 parts-per-million sodium sulfite (Na_2SO_3) solution. If 150 gallons of pure deoxygenated water are added, then 300 gallons of solution are drained, and another 150 gallons of water are added, what is the final concentration of Na_2SO_3. What is the final concentration if this operation is performed four times?
4. Four liters of an NaOH solution of pH 11 are added to 4 liters of an NaOH solution of pH 12. What is the hydroxyl ion concentration and pH of the final solution?
5. One thousand gallons of pure water are added to 600 gallons of a solution of pH 10.0. What is the hydroxyl ion concentration and pH of the final solution if:
   a the solute in the basic solution is NaOH?
   b the solute in the basic solution is NH_3 ?
6. The feed rate (and steaming rate) of a boiler is 110 gallons/minute. The boiler contains 500 gallons of a solution in which the Cl^- ion concentration is 0.1 parts-per-million. If the feedwater contains 0.01 parts-per-million Cl^- how soon will the Cl^- ion concentration in the boiler reach 0.5 parts-per-million?

SECTION 10 PROBLEM ANSWERS

1. 13.4 liters
2. 45 parts-per-million NaCl 27 parts-per-million Cl^-
3. 54 parts-per-million 8.5 parts-per-million
4. $[OH^-] = 5.5\ 10^{-3}$ mole/liter pH 11.7
5. a) $[OH^-] = 3.75 \times 10^{-5}$ mole/liter, pH = 9.57
6. b) $[OH^-] = 6.45 \times 10^{-5}$ mole/liter, pH = 9.8
6. 181.8 minutes (~3 hours)

SECTION 11.

OXIDATION-REDUCTION AND ELECTROCHEMISTRY

220-11.1 INTRODUCTION

220-11.1.1 As often stated previously, electrons are directly involved in chemical bonding and chemical reactions. Since electrons are also involved in electricity, it might be expected that there are electrical aspects of chemistry, and vice versa. There definitely are such aspects and they fall into two general categories: Those chemical reactions which are capable of producing an electrical current; and those reactions which can be forced to occur by an electrical current. Major attention in this section is focused on the first category and on a type of reaction, called oxidation-reduction, which occurs in both categories.

220-11.1.2 Among the many practical features of oxidation-reduction reactions is their role in the corrosion of metals. The fundamentals of oxidation-reduction and electrochemistry are presented in this section and are then applied to the subject of corrosion in the following section.

220-11.2 GLOSSARY OF TERMS

220-11.2.1 Terms used in this section are defined as follows:

a. **Cell:** Any combination of an oxidation half-reaction and a reduction half-reaction which produces a spontaneous net reaction or a reaction which results from an applied electrical potential. The term usually includes the entire physical arrangement such as the reactants, electrodes, salt bridge, and external circuitry in, for example, a galvanic cell. It may also refer to those reactions in which the reactants are not physically separated, for example, by a salt bridge.

b. **Concentration Cell:** A cell in which the reactants are solutions of the same substance at different concentrations.

c. **Electrochemistry:** The study of the electrical effects on or produced by chemical reactions.

d. **Electrode:** The electrically conducting site at which cell half-reactions occur. The electrode may be one of the reactants or it may be inert such as platinum in the hydrogen gas electrode.

e. **Electrolysis:** The process in which an externally applied electrical potential causes an oxidation-reduction reaction to occur.

f. **Electrolytic Cell:** A cell in which electrolysis is performed.

g. **Galvanic Cell:** A cell in which a spontaneous oxidation-reduction reaction occurs between two different substances.

h. **Half-Reaction:** A reaction which involves either the oxidation or reduction portion of an overall oxidation-reduction reaction.

i. **Oxidation:** Any process in which a substance gives up electrons and, as a result, undergoes an increase in oxidation number.

j. **Oxidation Potential:** A measure in volts of the tendency of a substance to give up electrons (be oxidized) referenced to the hydrogen oxidation half-reaction.

k. **Oxidation-Reduction Reaction:** A chemical reaction in which one reactant is oxidized and another is reduced.

l. **Oxidizing Agent:** The substance which causes the oxidation of another substance and is itself reduced.

m. **Reducing Agent:** The substance which causes the reduction of another substance and is itself oxidized.

n. **Reduction:** Any process in which a substance gains electrons and, as a result, undergoes a decrease in oxidation number.

o. **Standard Oxidation Potential (E°):** The oxidation potential developed when all reactants are at standard conditions (25°C, 1 atmosphere pressure for gases, and a concentration of 1 $\underline{M}$ for dissolved reactants).

220-11.3 OXIDATION-REDUCTION

220-11.3.1 GENERAL. The original (now obsolete) meaning of oxidation was the reaction of a substance with oxygen. For example:

$2Zn + O_2 \rightarrow 2ZnO$ (11-1)

It became apparent, however, that with respect to zinc the chemical significance of reaction (11-1) is that metallic zinc loses two electrons and that the same process occurs in reactions such as:

$Zn + Cu^{+2} \rightarrow Zn^{+2} + Cu$ (11-2)

$Zn + Cl_2 \rightarrow ZnCl_2$ (11-3)

$Zn + 2H_3O^{+} \rightarrow Zn^{+2} + H_2 + 2H_2O$ (11-4)

Oxidation thus came to mean any process in which a substance such as an atom, ion, or molecule loses electrons. In all the reactions above, Zn metal loses two electrons in being oxidized to Zn^{+2} .

220-11.3.1.1 Any time one substance loses electrons another substance must gain those electrons. Such **a process in which a substance gains electrons is called reduction** . In the above equations, O_2 , Cu^{+2} , Cl_2 , and H_3O^{+} , respectively, are reduced.

220-11.3.1.2 Two other terms are used frequently in discussions of oxidation-reduction reactions. These are oxidizing agent and reducing agent. An **oxidizing agent is the substance which causes the oxidation of another substance and is itself reduced** . In reaction (11-1) oxygen is the oxidizing agent and is reduced. A **reducing agent is the substance which brings about the reduction of another and is itself oxidized** . Again referring to reaction (11-1), zinc metal is the reducing agent and is oxidized.

220-11.3.1.3 The concept of oxidation number or oxidation state was introduced in Section 3 in connection with the bonding capacity of elements in compounds. If a substance gains or loses electrons in an oxidation-reduction reaction, its oxidation number must change. As in Section 3, it is emphasized that oxidation numbers are assigned as if electrons were completely transferred between atoms. In the case of ions this is correct, but in covalent ions or molecules it is not strictly correct. The assignment of oxidation numbers is governed by the rules given in Section 3 and repeated here for reference. With these rules the oxidation numbers of all atoms in a compound or polyatomic ion can usually be determined.

a. The oxidation number of an element in ionic form is the same as the charge on the ion. Thus,
   1 Group IA elements almost always have a +1 oxidation number
   2 Group IIA elements almost always have a +2 oxidation number
   3 Group VIIA elements almost always have a -1 oxidation number
b. The oxidation number of all pure elements is zero. This includes elements which exist as diatomic molecules such as H_2 , O_2 , Cl_2 .
c. The oxidation number of hydrogen is +1 in all its compounds except metal hydrides, such as NaH and CaH_2 , in which it is - 1.
d. The oxidation number of oxygen is -2 in all its compounds except peroxides such as H_2O_2 , in which it is - 1.

e. The sum of oxidation numbers of all the elements in a neutral compound is zero.

f. The sum of oxidation numbers of all the elements in a polyatomic ion is equal to the charge on the ion.

220-11.3.1.4 **Oxidation-reduction reactions are those reactions in which electrons are transferred from one substance to another or, in other words, those reactions in which the oxidation number of one substance increases and that of another substance decreases** . The oxidation number of the substance which is reduced decreases. As shown in paragraphs 220-11.3.2 through 220-11.3.2.4, it is possible to write partial or half-reaction equations for the individual oxidation or reduction process, but it is emphasized that oxidation and reduction are just different sides of the same coin. One never occurs without the other.

220-11.3.1.5 Numerous examples of oxidation-reduction have been used in previous sections without being called such. For instance,

$2Na + Cl_2 \rightarrow 2NaCl$

is an oxidation-reduction reaction in which sodium metal is oxidized to the +1 oxidation state and Cl is reduced to the -1 oxidation state.

220-11.3.1.6 Examples of previously encountered reactions which are not oxidation-reduction reactions include:

$$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$$

$$HCl + NaOH \rightarrow NaCl + H_2O$$

$$CO_2 + H_2O \leftrightarrows H_2CO_3$$

$$AgNO_3 + NaCl \rightarrow AgCl\downarrow + NaNO_3$$

These reactions are **not** oxidation-reduction reactions because there is no change in the oxidation number of any of the reactants.

Example 11-1: For the following reaction, determine: the oxidation number of each atom; which substance is oxidized and which is reduced, the oxidizing agent; and the reducing agent.

$2SO_2 + O_2 \rightarrow 2SO_3$

Solution 11-1: It is usually convenient to write the oxidation number of an atom directly above its symbol. By rule 2, the oxidation number of pure chemical oxygen is zero. In compounds the oxidation number of oxygen is almost always -2. Thus in SO_2 the oxidation number of each oxygen atom is -2 and there are two atoms so the oxidation number of sulfur in SO_2 must be +4 because by rule 5, the sum of the oxidation numbers in a neutral molecule must be zero. The three oxygen atoms in SO_3 requires that the oxidation number of sulfur in this compound be +6. Thus:

$$\overset{+4-2}{2SO_2} + \overset{0}{O_2} \rightarrow \overset{+6-2}{2SO_3}$$

Inspection of the oxidation numbers shows that sulfur increases from +4 to +6; therefore it is oxidized (loses electrons) and is the reducing agent. Oxygen in the elemental form shows a decrease in oxidation number from 0 to -2, so it is reduced (gains electrons) and is the oxidizing agent.

220-11.3.2 THE HALF-REACTION CONCEPT. One very interesting feature of oxidation-reduction reactions is that they can take place even if the reactants are physically separate as long as an electrical connection is maintained. One such arrangement is shown in Figure 220-11-1. This particular type of arrangement is called a galvanic cell which is discussed in paragraphs 220-11.4.3 and 220-11.4.3.1.

220-11.3.2.1 One beaker contains a $ZnSO_4$ solution and a zinc bar and the other contains a $CuSO_4$ solution and a copper bar. The two beakers are connected by a device called a **salt bridge** which consists of a tube filled with an electrolyte, in this case NH_4 NO_3 , and plugged at each end with glass wool or a semipermeable membrane to prevent free flow of the solution in the bridge. The electrical circuit is completed through an ammeter between the two metal bars. As soon as the circuit is complete, the deflection of the ammeter needle shows that an electrical current is produced and indicates that the flow of electrons is from the zinc bar to the copper bar. As the process continues, the chemical reaction which produces the electrical current also causes visible effects on the reactants. The zinc bar begins to dissolve and additional copper is deposited on the copper bar.

220-11.3.2.2 Combining the foregoing observations, the processes which occur at each metal bar can be described. Since electrons move from the zinc bar and zinc dissolves, then:

$Zn \rightarrow Zn^{+2} + 2e^-$ (at the zinc bar) (11-5)

(e^- indicates an electron)

Electrons flow to the copper bar where metallic copper is deposited. Thus:

$Cu^{+2} + 2e^- \rightarrow Cu$ (at the copper bar) (11-6)

It is easily seen that reaction (11-5) is an oxidation reaction and reaction (11-6) is a reduction reaction. These two reactions are called half-reactions because each describes only half of the net reaction and one cannot occur without the other. The sum of the two half-reactions gives the overall oxidation-reduction reaction for the cell:

$$Zn \rightarrow Zn^{+2} + 2e^- \qquad (11\text{-}5)$$

$$Cu^{+2} + 2e^- \rightarrow Cu \qquad (11\text{-}6)$$

$$\overline{Zn + Cu^{+2} + 2e^- \rightarrow Zn^{+2} + Cu + 2e^-} \qquad (11\text{-}7)$$

220-11.3.2.3 The purpose of the salt bridge shown in Figure 220-11-1 is not clear from the foregoing discussion, but the bridge is essential to the operation of the cell. In effect, the bridge completes the electrical circuit by allowing ions to migrate from one beaker to the other. The consequences of not having the bridge in place can be seen from equations (11-5) and (11-6). At the zinc bar, Zn^{+2} ions go into solution as electrons leave the bar. If nothing else happened, this beaker would accumulate a net positive charge. At the copper bar, Cu^{+2} ions leave the solution and deposit on the bar. This process tends to produce a net negative charge. With the bridge, however, negative ions can migrate from the beaker on the right to the one on the left and positive ions can migrate from left to right. Thus, the bridge prevents the accumulation of net charges which would immediately stop the reaction.

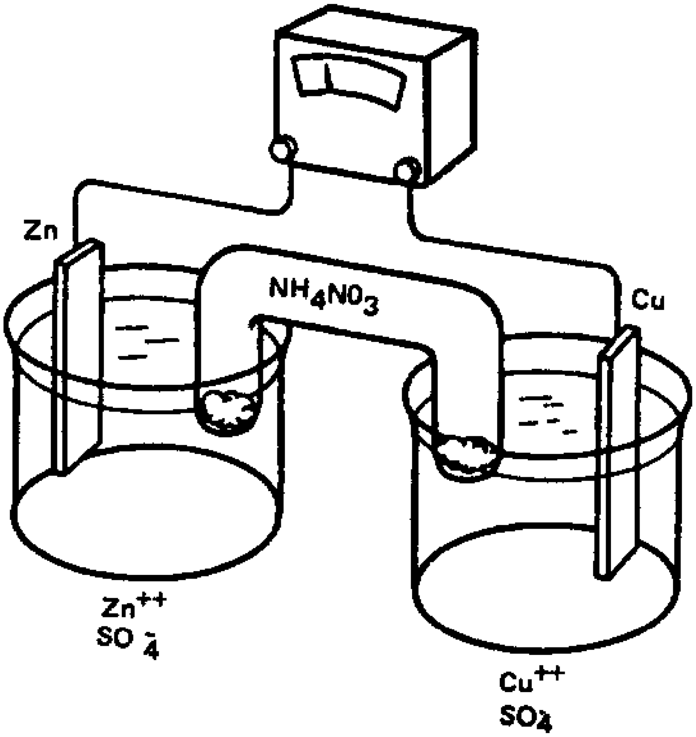


Figure 220-11-1 Simple Galvanic Cell

220-11.3.2.4 The half-reaction concept is used extensively in the following discussion of electrochemistry and the chemical reactivity of substances. Another important application of half-reactions is in balancing equations for oxidation-reduction reactions, some of which can be very complex. Since the examples used in this text can be balanced by inspection, the half-reaction method of balancing equations is not treated in this text.

220-11.3.3 OXIDATION POTENTIALS. Substances have a natural tendency to either gain or lose electrons. Most metals tend to lose electrons (be oxidized) but this tendency varies greatly from one metal to another. **This tendency of a substance to lose electrons is called its oxidation potential** . Figure 220-11-1, for example, shows that the reaction which occurs spontaneously is:

$$Zn + Cu^{+2} \rightarrow Zn^{+2} + Cu$$

This means that the oxidation potential of zinc is greater than that of copper.

220-11.3.3.1 If the zinc bar in Figure 220-11-1 is replaced with a silver bar, it would be observed that current would flow in the opposite direction and the following spontaneous reaction takes place:

$2Ag^{+} + Cu \rightarrow 2Ag\ Cu^{+2}$ (11-8)

In this case, copper is oxidized and silver is reduced; thus, it is concluded that the oxidation potential of copper is greater than that of silver.

220-11.3.3.2 Oxidation potentials are expressed in units of volts. When two half-reactions are combined in a galvanic cell such as that shown in Figure 220-11-1 , a cell potential is developed. The cell potential is the difference between the oxidation potentials of the two half-reactions. Cell potentials are easily measured by substituting a voltmeter for the ammeter in Figure 220-11-1.

220-11.3.3.3 Cell potentials, thus, are a comparison of the oxidation potentials of two half-reactions. It would be much more advantageous to have definite values of the oxidation potential for each half-reaction. One advantage of such data is that it would enable one to predict whether or not a particular reaction occurs spontaneously.

220-11.3.3.4 Unfortunately, there is no absolute scale for oxidation potentials, so an arbitrary scale must be defined because only relative differences can be measured. For this purpose, the oxidation potential of hydrogen is **defined** to be 0.00 volts at all temperatures. All other oxidation potentials are then referenced to the potential for this half-reaction.

$H_2 + 2H_2O \rightarrow 2H_3O^{+} + 2e$ (11-9)

220-11.3.3.5 An experimental arrangement using a hydrogen gas electrode is shown in Figure 220-11-2. The platinum metal simply serves as a site at which the reaction takes place as hydrogen gas is passed over the metal.

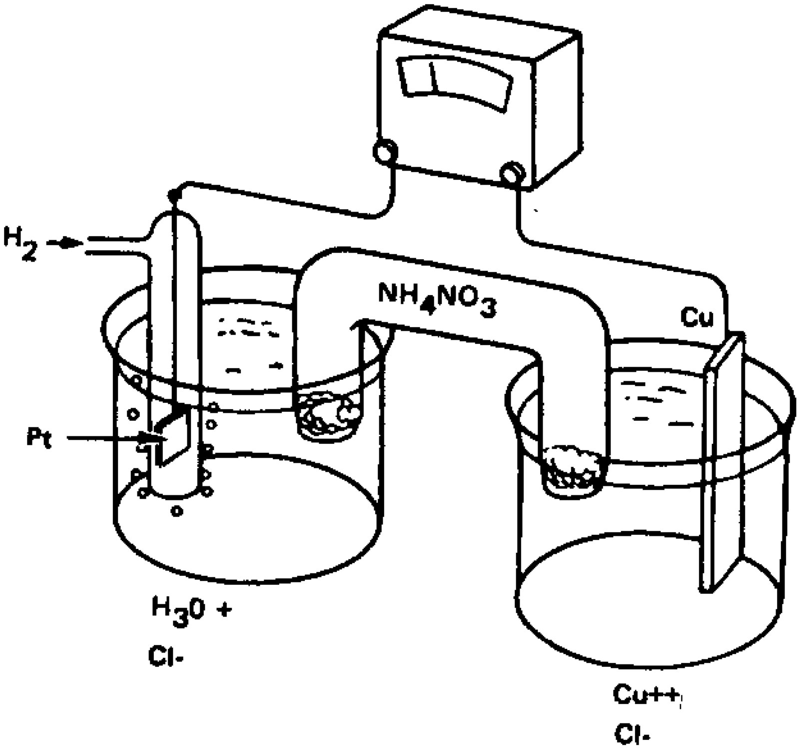


Figure 220-11-2 Galvanic Cell Using Hydrogen Gas Electrode on the Left

220-11.3.3.6 It has been found that the potential developed by a cell is influenced by the conditions of the reactants, including temperature and concentration. It is therefore necessary to define standard conditions for measuring oxidation potentials similar to the necessity of defining standard conditions for measuring gas volumes. For oxidation potentials, standard conditions are defined as 25°C, 1 atmosphere pressure for gaseous reactant, and a concentration of 1 $\underline{M}$ for reactants in solution. The potential developed under these conditions is called the **standard oxidation potential** and is denoted by E. Thus, for the hydrogen gas half-reaction:

$$H_2 \text{ (1 atm)} + 2H_2 O \rightarrow 2H_3{}^{+} \text{ (1 } \underline{M} \text{)} + 2e^{-} \quad E^{o} = 0.00V \quad (11\text{-}10)$$

220-11.3.3.7 The oxidation potential of many half-reactions can be measured against the hydrogen gas half-reaction using arrangements similar to that in Figure 220-11-2. Others can then be measured against a half-reaction of known oxidation potential and referenced to the hydrogen standard using the relationship:

(Potential at standard conditions of the A/B cell) = (standard oxidation potential for half-reaction A) - (standard oxidation potential for half-reaction B)

220-11.3.3.8 Through this process, the standard oxidation potentials of a very large number of half-reactions have been determined. A few are listed in Table 220-11-1. Oxidation potentials greater than that of hydrogen have positive values and those less than hydrogen have negative values. For consistency, all half-reactions in the table are written as oxidation reactions. When two half-reactions are combined to form a galvanic cell at standard conditions, the one of lower oxidation potential will occur as a reduction reaction which is just the reverse of the oxidation reaction. Thus, whenever an oxidation half-reaction is reversed it becomes a reduction half-reaction and the standard reduction potential is obtained by reversing the sign of the standard oxidation potential. For example, the reduction half-reaction and standard reduction potential for Fe^{+3} , Fe^{+2} are:

$$Fe^{+3} + e^{-} \rightarrow Fe^{+2} \qquad E^{\circ} = +0.77V$$

220-11.3.3.9 Use of the data in Table 220-11-1 in determining whether a particular reaction will take place spontaneously can be illustrated as follows. The general process is to first determine which substance is oxidized and which is reduced, unless the reaction is given in a particular direction as in Example 11-2. Next, a cell potential is calculated from the two half-reaction potentials. **If the sign of the cell potential is positive, the reaction takes place spontaneously as written. A negative cell potential indicates the reaction does not occur spontaneously as written** . In the latter case, the spontaneous reaction is in the opposite direction. Consider the Zn, Zn^{+2} and Cu, Cu^{+2} cell described previously. Table 220-11-1 shows that Zn has a higher standard oxidation potential than does Cu.

$$Zn \rightarrow Zn^{+2} + 2e^{-} \qquad E^{\circ} = +0.76V \qquad (11\text{-}12)$$

$$Cu \rightarrow Cu^{+2} + 2e^{-} \qquad E^{\circ} = -0.34V \qquad (11\text{-}13)$$

Thus, Zn has a greater tendency to release electrons than does Cu and will force Cu^{+2} ions to accept the electrons. Reversing equation (11-13) and adding to equation (11-12), which is the same as subtracting equation (11-13) from (11-12):

$$\begin{array}{ll} Zn \rightarrow Zn^{+2} + 2e^{-} & E^{\circ} = +\ 0.76V \\ Cu^{+2} + 2e^{-} \rightarrow Cu & E^{\circ} = +\ 0.34V \\ \hline Zn + Cu^{+2} \rightarrow Zn^{+2} + Cu & \Delta E^{\circ} = +\ 1.10V \end{array}$$

The information in 220-11-1 therefore indicates that at standard conditions, the reaction takes place exactly as described in paragraphs 220-11.3.2 through 220-11.3.2.4.

220-11.3.3.10 Now consider the following two half-reactions

$Ni \rightarrow Ni^{+2} + 2e^{-}$ $E^{\circ} = 0.25V$ (11-14)

$Ag \rightarrow Ag^{+} + e^{-}$ $E^{\circ} = -0.80V$ (11-15)

Since Ni has the higher oxidation potential it should be capable of reducing Ag^{+} to Ag, so the Ag, Ag^{+} half-reaction and the sign of its E° are reversed.

$Ag^+ + e^- \rightarrow Ag \quad E° = 0.80V$

Before the equations can be combined the Ag, Ag^+ equation must be multiplied by a factor of 2 to allow a total cancellation of electrons in the net equation.

Table 220-11-1 STANDARD OXIDATION POTENTIALS AT 25°C

Half Reaction	**Standard Potential (E°) in Volts**
$K \rightleftarrows K^{+} + e^{-}$	2.93
$Na \rightleftarrows Na^{+} + e^{-}$	2.71
$Mg \rightleftarrows Mg^{++} + 2e^{-}$	2.37
$U \rightleftarrows U^{+++} + 3e^{-}$	1.80
$Al \rightleftarrows Al^{+++} + 3e^{-}$	1.66
$Zr \rightleftarrows Zr^{+4} + 4e^{-}$	1.53
$Mn \rightleftarrows Mn^{++} + 2e^{-}$	1.18
$H_2 + 2OH^{-} \rightleftarrows 2H_2O + 2e^{-}$	0.83
$Zn \rightleftarrows Zn^{++} + 2e^{-}$	0.76
$Cr \rightleftarrows Cr^{+++} + 3e^{-}$	0.71
$Fe \rightleftarrows Fe^{++} + 2e^{-}$	0.44
$Cd \rightleftarrows Cd^{++} + 2e^{-}$	0.40
$Pb + SO_4^{--} \rightleftarrows PbSO_4 + 2e^{-}$	0.36
$Co \rightleftarrows Co^{++} + 2e^{-}$	0.28
$Ni \rightleftarrows Ni^{++} + 2e^{-}$	0.25
$Pb \rightleftarrows Pb^{++} + 2e^{-}$	0.13
$Fe \rightleftarrows Fe^{+++} + 3e^{-}$	0.04
$2H_2O + H_2 \rightleftarrows 2H_3O^{+} + 2e^{-}$	0.00
$Cu \rightleftarrows Cu^{++} + 2e^{-}$	–0.34
$2I \rightleftarrows I_2 + 2e^{-}$	–0.53
$4OH^{-} + MnO_2 \rightleftarrows MnO_4^{-} + 2H_2O + 3e^{-}$	–0.57
$2H_2O + H_2O_2 \rightleftarrows O_2 + 2H_3O^{+} + 2e^{-}$	–0.68
$Fe^{++} \rightleftarrows Fe^{+++} + e^{-}$	–0.77
$Ag \rightleftarrows Ag^{+} + e^{-}$	–0.80
$Hg \rightleftarrows Hg^{++} + 2e^{-}$	–0.85
$2Br^{-} \rightleftarrows Br_2 + 2e^{-}$	–1.07
$I_2 + 18H_2O \rightleftarrows 2IO_3^{-} + 12H_3O^{+} + 10e^{-}$	–1.20
$6H_2O \rightleftarrows O_2 + 4H_3O^{+} + 4e^{-}$	–1.23
$2Cl^{-} \rightleftarrows Cl_2 + 2e$	–1.36
$6H_2O + Pb^{++} \rightleftarrows PbO_2 + 4H_3O^{+} + 2e^{-}$	–1.46
$Au \rightleftarrows Au^{+++} + 3e^{-}$	–1.50
$6H_2O + MnO_2 \rightleftarrows MnO_4^{-} + 4H_3O^{+} + 3e^{-}$	–1.67
$6H_2O + PbSO_4 \rightleftarrows PbO_2 + SO_4^{-} + 4H_3O^{+} + 2e^{-}$	–1.69
$2F^{-} \rightleftarrows F_2 + 2e^{-}$	–2.87

$$\begin{array}{lll} \mathrm{Ni} \rightarrow \mathrm{Ni}^{+2} + 2e^- & E^\circ = 0.25\mathrm{V} & \\ 2\mathrm{Ag}^+ + 2e^- \rightarrow 2\mathrm{Ag} & E^\circ = 0.80\mathrm{V} & \\ \hline \mathrm{Ni} + 2\mathrm{Ag}^+ \rightarrow \mathrm{Ni}^{+2} + 2\mathrm{Ag} & \Delta E^\circ = +1.05\mathrm{V} & (11\text{-}16) \end{array}$$

Notice that when the Ag, Ag^+ half-reaction was multiplied by 2, the value of E° was *not*. The value of E° does not change because it is based on standard conditions. The factor of two does not change the concentration of the species involved, but only balances the equation. That is, for every nickel atom oxidized, two Ag^+ ions are reduced.

Example 11-2: *Determine whether the following reaction occurs spontaneously (at standard conditions).*

$$Ni + Co^{+2} \rightarrow Ni^{+2} + Co$$

Solution 11-2: *The half-reactions involved are:*

$$Ni \rightarrow Ni^{+2} + 2e^- \qquad E^\circ = 0.25V \qquad (11\text{-}17)$$

$$Co^{+2} + 2e^- \rightarrow Co \qquad E^\circ = -0.28V \qquad (11\text{-}18)$$

The sign of E° for Equation (11-18) has been reversed because the reaction is written as a reduction reaction. Adding the values of E° gives $\Delta E^\circ = -0.03$. Thus, the reaction does not take place spontaneously as written. The spontaneous reaction at standard conditions would be:

$$Co + Ni^{+2} \rightarrow Co^{+2} + Ni \qquad \Delta E^\circ = +0.03V$$

220-11.3.4 THE NERNST EQUATION. In all the examples discussed in the preceding paragraphs, all reactants are at standard conditions. That is, the concentration of all ionic substances is 1.0 M and temperature is 25°C. In example 11-2 it is shown that if the concentration of both Ni^{+2} and Co^{+2} is 1.0 M then the spontaneous reaction is:

$$\mathrm{Co} + \mathrm{Ni}^{+2}\ (1\ \underline{\mathrm{M}}) \rightarrow \mathrm{Co}^{+2}\ (1\ \underline{\mathrm{M}}) + \mathrm{Ni} \qquad \Delta E^\circ = 0.03\mathrm{V} \qquad (11\text{-}19)$$

However, experiments show that if the concentration of Ni^{+2} is 0.01 M and that of Co^{+2} is 1 M then the spontaneous reaction is the reverse of Equation (11-19).

$$\mathrm{Co}^{+2}\ (1\ \underline{\mathrm{M}}) + \mathrm{Ni} \rightarrow \mathrm{Co} + \mathrm{Ni}^{+2}\ (0.01\ \underline{\mathrm{M}}) \qquad (11\text{-}20)$$

220-11.3.4.1 The reaction of equation (11-19) is reversed because the ionic concentration of Ni has changed and is no longer at standard conditions. This variation in concentration has an important effect on the cell potential. Thus, in order to predict the direction of reactions between substances at non-standard concentrations, the variation of cell potential with concentration must be described. The equation which describes the variation is called the Nernst equation. This equation states that for any general reaction,

$$aA + bB \rightarrow cC + dD,$$

the cell potential for any conditions of reactant concentration and temperature is given by:

$$\Delta E = \Delta E^\circ - 2.303 \frac{RT}{nF} \log \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad (11\text{-}21)$$

where:

ΔE = the cell potential at the given conditions

ΔE° = the standard cell potential

n = the number of electrons transferred in the reaction as written

R = the ideal gas constant (8.314 joules/deg mole)

T = absolute temperature

F = the Faraday constant (96,500 coulombs or joules/volt equivalent)

In most of the cases considered in the text, temperature is 25°C (77°F). For this value of temperature, the term 2.303 RT/F is 0.059 and the Nernst equation becomes:

$$\Delta E = \Delta E^\circ - \frac{0.059}{n} \log \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad (11\text{-}22)$$

220-11.3.4.2 Let us now apply this equation to the cell Co, Co^{+2} (1 molar)/Ni, Ni^{+2} (0.01 molar). It has been shown that **at standard conditions** $\Delta E^o = 0.03V$ and the spontaneous reaction is:

$$Co + Ni^{+2}\ (1\ \underline{M}) \rightarrow Co^{+2}\ (1\ \underline{M}) + Ni \qquad \Delta E^\circ = 0.03V \qquad (11\text{-}19)$$

Applying the Nernst equation,

$$\Delta E = 0.03V - \frac{0.059}{2} \log \frac{[Ni][Co^{+2}]}{[Co][Ni^{+2}]}$$

The values of $[Co^{+2}]$ and $[Ni^{+2}]$ are known to be 1.0 $\underline{M}$ and 0.01 $\underline{M}$ respectively. The terms [Ni] and [Co] refer to the pure metals and are taken to be unity. The chemical concentration terms in the Nernst equation approximate a quantity known as *chemical activity*. Chemical activity is beyond the scope of this test; however, this approximation is sufficient for most applications. By convention, the chemical activity of a solid is unity.

$$\begin{aligned} \Delta E &= 0.03V - 0.0295 \log \frac{1}{0.01} \\ &= 0.03V - 0.0295 \log 10^2 \\ &= 0.03V - (0.0295)(2) \\ &= 0.03V - 0.059 \\ &= -0.029V \end{aligned}$$

The negative value of ΔE indicates that the reaction does *not* take place spontaneously in the direction indicated by Equation (11-19) but rather in the opposite direction as in Equation (11-20).

220-11.3.4.3 To illustrate the effect of temperature on the cell potential, suppose that in the above case the temperature is increased to 100°C. The term (2.303) (RT)/nF in the Nernst equation must be recalculated.

$$\begin{aligned} E &= 0.03V - \frac{(2.303)(8.315)(373)}{(2)(96{,}500)} \log \frac{1}{0.01} \\ &= 0.03V - 0.0369 \log 10^2 \\ &= -0.044 \end{aligned}$$

Thus, an increase in temperature causes the cell potential to decrease.

220-11.3.4.4 Another very important application of the Nernst equation is described in paragraphs 220-11.4.6 through 220-11.4.6.6.

220-11.4 ELECTROCHEMICAL CELLS

220-11.4.1 GENERAL. Up to this point, the discussion of electrochemistry has involved only galvanic cells. Other types of cells and some special cases of galvanic cells are presented in the following paragraphs.

220-11.4.2 TERMINOLOGY. In electrochemical cells, chemical reactions occur at the electrodes. In some cases, such as in Figure 220-11-3 the electrodes themselves participate in the reaction. In other cases, such as the hydrogen gas electrode, the metal (platinum) does not participate directly in the reaction but provides a conducting site for the reactions. This latter type is called an inert electrode. The electrode at which an oxidation half-reaction occurs is called the **anode** . The electrode at which reduction takes place is the **cathode** . An easy way of remembering these relationships is: **AN** ode **-** **OX** idation and **RED** uction **-** **CAT** hode. Thus, in Figure 220-11-1, for example the Zn electrode is the anode and the Cu electrode is the cathode.

220-11.4.3 GALVANIC CELLS. A galvanic cell consists of any two dissimilar substances in electrical contact and capable of producing an electrical current. Figure 220-11-1 is one example of such a cell. Two other examples are shown in Figure 220-11-3. In the first cell shown in Figure 220-11-3, copper is oxidized and Ag^+ ions are reduced. The cell will continue to operate until one of the reactants (the copper strip or Ag^+ ions in solution) is consumed. The voltage developed by the cell will continually decrease during operation, because of the change in concentration, consistent with the Nernst equation.

220-11.4.3.1 The other example in Figure 220-11-3 is similar but in this case, Cu^{+2} ions are reduced and Fe metal is oxidized. The principles of the galvanic cell are directly applicable to a type of corrosion called galvanic corrosion and the use of sacrificial anodes to prevent galvanic corrosion (see paragraphs 12.7.1 through 12.7.1.3). Galvanic cells which provide useful amounts of electricity are often called batteries. An example of such cells is described in the following section.

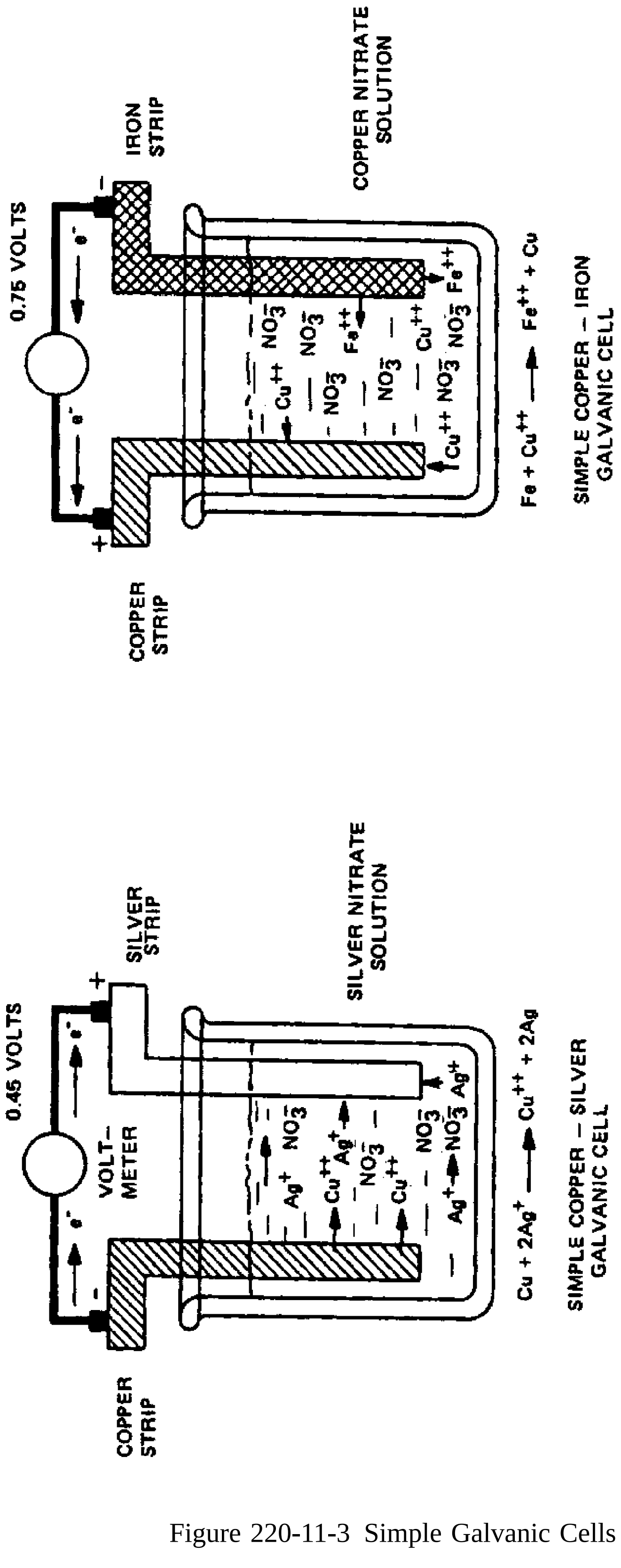


Figure 220-11-3 Simple Galvanic Cells

220-11.4.4 THE LEAD STORAGE BATTERY. A storage battery is a device for storing electrical energy in the form of chemical energy. When the electrical energy is used, a chemical reaction occurs inside the battery. By reversing the flow of energy, electrical energy can be supplied to the battery and the chemical reaction proceeds in the opposite direction. Thus, energy is stored.

220-11.4.4.1 The most common type of storage battery is the lead storage battery, examples of which are automobile batteries and batteries used in ships. A battery is made of a series of cells, each of which consists of an electrode plate of spongy elemental lead (Pb) and another of lead oxide (PbO_2). An electrolyte solution of dilute sulfuric acid surrounds both plates in each cell. This arrangement is illustrated in Figure 220-11-4.

220-11.4.4.2 On discharge, the oxidation half-reaction which occurs at the lead anode (negative plate) is:

$$Pb + SO_4^{=} \rightarrow PbSO_4 \downarrow + 2e^- \qquad E° = 0.36V \qquad (11\text{-}23)$$

The following reduction half-reaction takes place at the PbO_2 cathode (positive plate):

$$PbO_2 + 4H_3O^+ + SO_4^{=} + 2e^- \rightarrow PbSO_4 \downarrow + 6H_2O \qquad E° = 1.69V \qquad (11\text{-}24)$$

The overall discharge reaction is:

$$Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O \qquad \Delta E° = 2.05V \qquad (11\text{-}25)$$

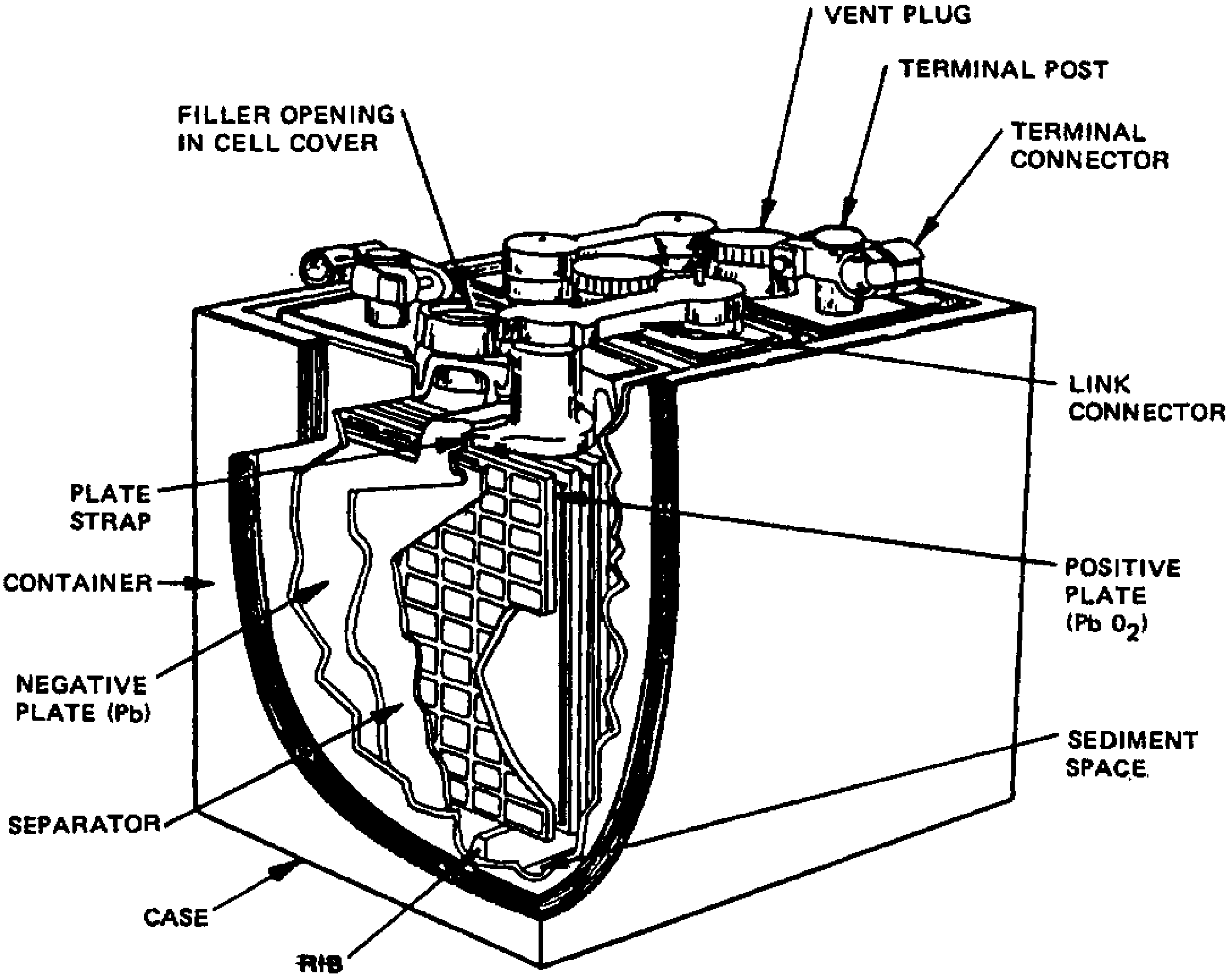


Figure 220-11-4 Construction of Lead Storage Battery

220-11.4.4.3 Each cell of a lead storage battery develops a maximum voltage of about 2.05 volts. By connecting several cells in series, the battery can deliver electrical current at voltages substantially greater than 2.05 volts (0.36 volts 1.69 volts), 6 and 12 volt automobile batteries are common examples.

220-11.4.4.4 Note that both reactions in equations (11-23) and (11-24) produce $PbSO_4$ which is relatively insoluble in the dilute sulfuric acid electrolyte. Both the spongy lead plate and the lead oxide plate build up a coat of insoluble $PbSO_4$ as the battery discharges. Also, reaction (11-25) shows that the overall reaction consumes $H_2\ SO_4$ and produces $H_2\ O$. Thus, the concentration of the electrolyte continually decreases as discharge continues. Because of this, the density (or specific gravity) of the electrolyte solution also decreases. Since this decrease in density is directly proportional to the extent of the discharge reaction, a convenient method of determining the state of discharge of the battery is measuring the density of the electrolyte.

220-11.4.4.5 The discharge reaction continues until so much of the active materials (Pb, PbO_2 , $H_2\ SO_4$) are consumed that the battery cannot produce sufficient current to be of practical value. At this point the battery is said to be discharged (or dead).

220-11.4.4.6 A lead storage battery is recharged by supplying direct current at a voltage slightly higher than the voltage developed by the fully charged battery. Under this condition the reaction in equation (11-25) is forced to proceed in the opposite direction, that is:

$$2PbSO_4 + 2H_2O \rightarrow Pb + PbO_2 + 2H_2SO_4 \quad (11\text{-}26)$$

Thus, all the active materials are regenerated and the battery is again capable of producing useful electrical energy.

220-11.4.4.7 The discharging and charging processes described above represent the ideal situation. In reality, other processes occur and some of these require special attention for the safe operation (both discharging and charging) of batteries.

220-11.4.4.8 The conversion of chemical to electrical energy, and vice versa, is not 100 percent efficient. Some of the energy is lost as heat which raises the temperature of the electrolyte and plates both when charging and discharging a battery. If not controlled, the increased temperature can cause permanent damage to a battery. Even when confirmed within the limits, the increased temperature enhances the evaporation of water from the cell. (Each cell is vented to prevent over-pressurization.) Thus, water must be periodically added to the battery.

220-11.4.4.9 On charging, the applied voltage is sufficient to electrolyze water and produce gaseous O_2 and H_2. This evolution of gases is slow when charging is begun, but increases until, near the completion of charging, most of the applied electrical energy is consumed in this manner. Besides being another cause of water loss, this process produces an extremely explosive mixture of gases unless adequately ventilated. Hydrogen is also produced by a process called chemical self-discharge which occurs when a battery is discharging or standing. Chemical self-discharge is primarily due to a slow reaction which occurs at the lead anode (negative plate.

$$Pb + H_2SO_4 \rightarrow PbSO_4 \downarrow + H_2 \uparrow$$

Chemical self-discharge is minimized by proper operation and maintenance of the battery (such as maintaining the purity of the electrolyte).

220-11.4.5 ELECTROLYTIC CELLS. The electrolytic cell is a second kind of electrochemical cell. In an electrolytic cell, **electrical energy is supplied from an outside source to force an oxidation-reduction reaction to occur that would not occur spontaneously** . In contrast, the oxidation-reduction processes in galvanic cells occur spontaneously and they serve to produce electrical energy. The process which takes place in an electrolytic cell is called electrolysis.

220-11.4.5.1 Consider, for example, a cell containing molten NaCl. If a sufficiently high electrical potential is applied to electrodes within such a cell, the chloride ion can be forced to give up its extra electron thereby forming elemental chlorine; similarly, the sodium ion can be forced to accept an electron thereby forming elemental sodium. Thus the applied electrical potential forces the following reactions to occur:

$$2Na^+ + 2e^- \rightarrow 2Na \quad (11\text{-}28)$$

$$2Cl^- \rightarrow Cl_2\ 2e^-$$

Electrolytic cells containing molten NaCl are used commercially for the manufacture of elemental sodium and chlorine.

220-11.4.5.2 One method used to produce hydrogen gas is the electrolysis of water in an electrolytic cell. The reaction which takes place when an electrical potential is applied to a cell containing water is as follows:

$$2H_2\ O \rightarrow 2H_2 + O_2 \quad (11\text{-}29)$$

220-11.4.5.3 Standard oxidation potentials, Table 220-11-1, can be used to determine the particular oxidation-reduction reactions that occur when an electrical potential is applied to an electrolytic cell containing a salt solution. Competing reduction reactions are the gain of electrons by either a metal ion or by water molecules (to form hydrogen). Competing oxidation reactions in an electrolytic cell are the loss of electrons by either the negative ions in solution or by water molecules (to form oxygen). This use of the electrochemical series is illustrated in the following example.

Example 11-3: Determine the reactions which would take place in an electrolytic cell containing aqueous solutions of (a) NaCl, and (b) $CuCl_2$ at standard conditions.

Solution 11-3. Potentials for the possible oxidation and reduction reactions can be found by referring to Table 220-11-1.

1. NaCl solution Note that this is an aqueous solution of NaCl as opposed to the case of molten NaCl discussed above. Thus, the possibility of oxidizing or reducing water must be considered. Possible reduction reactions are:

Reaction	**Potential (reduction)**
$Na^+ + e^- \rightarrow Na$	–2.71
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	–0.83

Since water accepts electrons more readily than sodium ions do, the second reaction will occur in the electrolytic cell.

Possible oxidation reactions are:

Reaction	**Potential (oxidation)**
$6H_2O \rightarrow O_2 + 4H_3O^+ + 4e^-$	–1.23
$2Cl^- \rightarrow Cl_2 + 2e^-$	–1.36

Since water gives up electrons more readily than chloride ions do, the water reaction will occur in the electrolytic cell.

In adding the two favored reactions to obtain the net reaction for the electrolytic cell, the reduction reaction must be multiplied by 2 since it only involves 2 electrons while the oxidation reaction involves 4 electrons.

$4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$ $E° = -0.83$

$6H_2O \rightarrow O_2 + 4H_3O^+ + 4e^-$ $E° = -1.23$

$10H_2O + 4e^- \rightarrow 2H_2$

$+O_2 + 4H_3O^+ + 4OH^- + 4e^-$ $\Delta E° = -2.06$

Noting that $4H_3O^+ + 4OH^- \rightarrow 8H_2O$, the net reaction is:

$$2H_2O \rightarrow 2H_2 + O_2$$

Since a voltage is applied to the cell to force the reaction to occur, it is, by definition, an electrolytic cell rather than a galvanic cell.

Note that the sign of $\Delta E°$ above indicates that the reverse reaction should occur spontaneously. However, although the reverse reaction is possible, the rate of reaction is so extremely small (due to the large activation energy) that the reaction can be considered as not occurring spontaneously.

2. $CuCl_2$ solution

Possible reduction reactions are:

Reactions	**Potential (reduction)**
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	-0.83
$Cu^{++} + 2e^- \rightarrow Cu$	$+0.34$

Thus, Cu^{+2} ions accept electrons more easily than do water molecules.

Possible oxidation reactions are:

Reactions	**Potential (oxidation)**
$6H_2O \rightarrow O_2 + 4H_3O^+ + 4e^-$	-1.23
$2Cl^- \rightarrow Cl_2 + 2e^-$	-1.36

Thus, water molecules give up electrons more easily than do chloride ions, and oxidation of water is the favored reaction.

Adding the two half reactions to obtain net reaction

$$2Cu^{++} + 4e^- \rightarrow 2Cu \qquad E° = +0.34$$

$$6H_2O \rightarrow O_2 + 4H_3O^+ + 4e^- \qquad E° = -1.23$$

$$2Cu^{++} + 6H_2O + 4e^- \rightarrow 2Cu + O_2 + 4H_3O^+ + 4e^- \qquad \Delta E° = -0.89$$

or

$$2Cu^{++} + 6H_2 \rightarrow 2Cu + O_2 + 4H_3O^+$$

Again, this is an electrolytic cell since voltage is applied. The reverse of the above reaction is a spontaneous reaction and may occur when elemental copper is placed in an acidic solution containing oxygen; however, the favored reaction in this case is the reduction of **hydronium ions rather than oxygen because of the lower reduction potential.**

220-11.4.6 CONCENTRATION CELLS. The observation in paragraphs 220-11.3.4 through 220-11.3.4.4 that concentration effects may cause a galvanic cell to develop a potential opposite to that derived from the standard oxidation potentials suggests the possibility that a potential might be generated by concentration differences alone, even though the standard cell potential might be zero. This possibility has been verified experimentally and one example is shown in Figure 220-11-5.

220-11.4.6.1 Both beakers contain Ag^+ solutions: one at a concentration of 1 $\underline{M}$ and the other at 0.01 $\underline{M}$. Both electrodes are silver bars. The experiment indicates that electrons travel from dilute solution to the concentrated solution; thus, silver plates out on the bar in the concentrated solution while the bar in the dilute solution begins to dissolve. The appropriate half-reactions are:

$$Ag \rightarrow Ag^+ \ (0.01\underline{M}) + e^- \ \text{(dilute solution)}$$

$$Ag^+ \ (1\underline{M}) + e^- \rightarrow Ag \ \text{(concentrated solution)}$$

and the net cell reaction is:

$$Ag^+ \ (1\underline{M}) \rightarrow Ag^+ \ (0.01\underline{M})$$

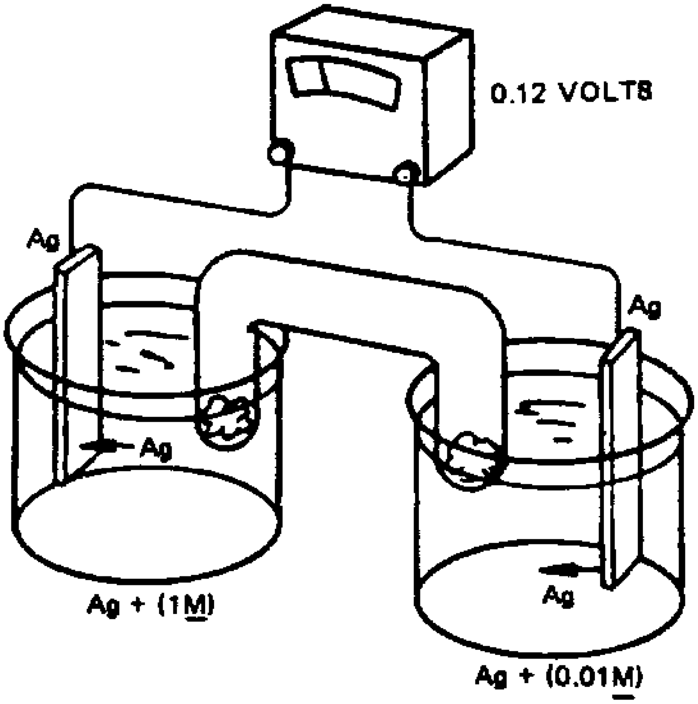


Figure 220-11-5 Concentration Cell

Since reduction reaction is just the reverse of the oxidation reaction, the standard cell potential, ΔE°, is zero. The Nernst equation can be used to calculate the cell potential at the non-standard conditions.

$$\begin{aligned}\Delta E &= \Delta E^\circ - \frac{0.059}{1}\log\frac{(0.01)}{(1)}\\ &= 0 - 0.059\log(10^{-2})\\ &= -0.059\,(-2)\end{aligned}$$

$$\Delta E = 0.118V$$

220-11.4.6.2 Concentration cells, especially those involving dissolved oxygen concentration also play an important role in corrosion (see 220-12.6.4 and see 220-12.6.4.1).

220-11.4.6.3 Another practical application of concentration cells is the measurement of the pH of a solution. Consider a cell composed of one hydrogen electrode immersed in a 1 molar acid solution ($[H_3O^+]_A = 1$) and another hydrogen electrode in a solution in which the hydrogen-ion concentration is unknown, $[H_3O^+]_B = X$. In both electrodes, hydrogen gas is at a pressure of 1 atmosphere and the temperature is 25°C; thus, both electrodes are at standard conditions with the possible exception of the unknown hydrogen-ion concentration. Suppose it is observed that the cell reaction is:

$$\begin{array}{ll} H_2 + 2H_2O \rightarrow 2H_3O^+ \ (X\underline{M}) + 2e^- & \text{(oxidation) } E^\circ = 0 \\ 2H_3O^+ \ (1\underline{M}) + 2e^- \rightarrow H_2 + 2H_2O & \text{(reduction) } E^\circ = 0 \\ \hline 2H_3O^+ \ (1\underline{M}) \rightarrow 2H_3O^+ \ (X\underline{M}) & \Delta E^\circ = 0 \end{array}$$

The Nernst equation for this cell is:

$$\Delta E = \Delta E^\circ - \frac{0.059}{2} \log \frac{[H_3O^+]^2_B}{[H_3O^+]^2_A}$$

$$= 0 - \frac{0.059}{2} \log \frac{[H_3O^+]^2_B}{1}$$

$$= 0 - \frac{(2)0.059}{2} \log [H_3O^+]_B$$

$$\frac{\Delta E}{0.059} = -\log [H_3O^+]_B$$

From the definition of pH, the last equation becomes:

$$\text{pH (of solution B)} = \frac{\Delta E}{0.059}$$

By appropriate calibration of the potentiometer used to measure the cell potential, the pH can be read directly.

220-11.4.6.4 In practice, hydrogen electrodes are seldom used in routine measurements because of the inconvenience and difficulty of controlling the gas pressure. In pH measurements, for example, a cell similar to the one shown in Figure 220-11-6 may be used. In this case, the standard hydrogen electrode has been replaced by a **reference electrode** .

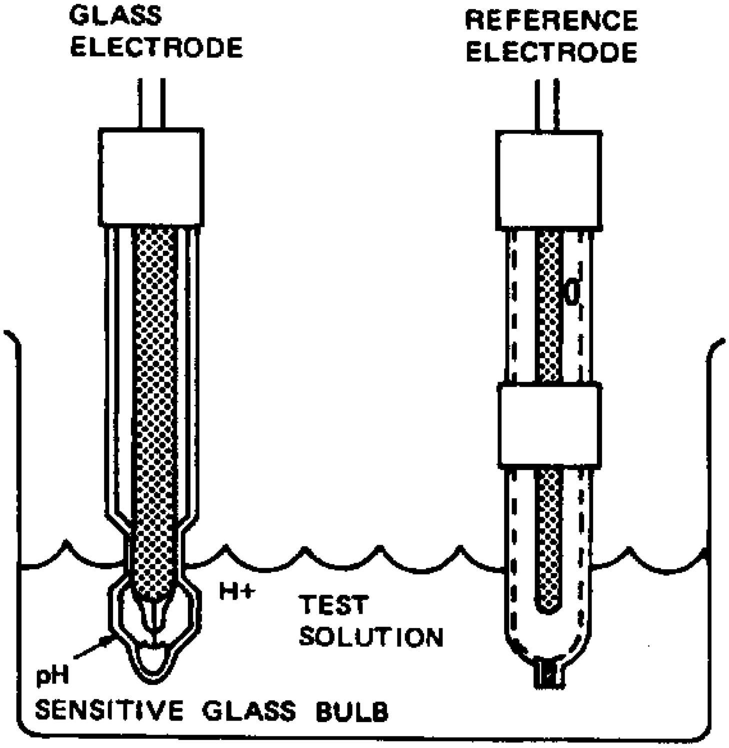


Figure 220-11-6 Electrodes for Measuring pH

220-11.4.6.5 There are several different types of reference electrodes, but all are constructed in such a way that they develop a constant half cell potential when used with some other electrode in a galvanic cell. The constant half-cell potential of the reference electrode is measured experimentally, for example against the standard hydrogen electrode, then the reference electrode can be used to measure unknown half-cell potentials of other electrodes. Reference electrodes are, thus, indirect or secondary standards and are much more convenient to use than hydrogen electrodes.

220-11.4.6.6 For measuring pH, as shown in Figure 220-11-6, a reference electrode is used with a **glass electrode** . The sensitive portion of a glass electrode is a thin membrane of a special glass. It is found experimentally that the potential of the glass electrode varies with the hydronium-ion concentration in exactly the same way as does the potential of a hydrogen electrode. Thus, the potential developed between the glass electrode and the reference electrode is a direct measure of the pH of the test solution. The two electrodes are used in conjunction with a device called a pH meter which measures the cell potential and indicates pH directly.

220-11.5 SUMMARY

220-11.5.1 In an oxidation half-reaction, a substance gives up electrons and its oxidation number increases. In a reduction half-reaction, a substance gains electrons and its oxidation number decreases. The substance which is oxidized is called the reducing agent and the one which is reduced is called the oxidizing agent. Standard oxidation potential (E^{o}) is a measure of the tendency of a substance to give up electrons (be oxidized) at standard conditions (25°C, 1 $\underline{M}$ concentration or 1 atmosphere pressure for gases). Reversing the oxidation half-reaction and the sign of E° gives the reduction half-reaction and the standard reduction potential. The standard cell potential, developed by a galvanic cell is obtained by adding the standard potentials of the oxidation and reduction half-reactions. If the cell potential, ΔE, is positive, the reaction occurs spontaneously. If ΔE is negative, the reverse reaction is the spontaneous process.

220-11.5.2 For reactants at non-standard conditions, the Nernst equation can be used to calculate the cell potential. This equation also explains why a potential develops between two solutions of the same substance at different concentrations. Some types of galvanic cells, such as the lead storage battery, are used extensively for obtaining useful amounts of electrical energy from oxidation-reduction reactions.

SECTION 11 PROBLEMS

1. Determine the oxidation number of each atom in each of the following compounds: Fe_2O_3, LiOH, Na_3PO_4, NH_4OH, KIO_3, KI.

2. In the following reactions, determine which substance is oxidized and which is reduced.
   a $Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$
   b $2Cr_2O_3 + 3O_2 + 4H_2O \rightarrow 4H_2CrO_4$
   c $5KI + KIO_3 + 6HCl \rightarrow 3I_2 + 3H_2O + 6KCl$

3. A strip of lead is placed in a beaker containing a 1 $\underline{M}$ $CuSO_4$ solution. A strip of copper is placed in a beaker containing a 1 $\underline{M}$ $PbSO_4$ solution. In which beaker does a spontaneous reaction occur?

4. Using Table 220-11-1, which metals will react with acids to produce H_2 gas? (Assume standard conditions)

5. What is the standard cell potential for a cell made up of a Cd electrode in a $CdCl_2$ solution and an Ni electrode in an $NiCl_2$ solution?

6. A galvanic cell is made up of a copper strip in a $CuSO_4$ solution and a zinc strip in a $ZnSO_4$ solution. Determine:
   a the standard cell potential;
   b the cell potential if the $ZnSO_4$ concentration is 10^{-3} $\underline{M}$ and the $CuSO_4$ concentration is 0.1 $\underline{M}$;
   c what happens to the cell potential as the cell continues to operate.

SECTION 11 PROBLEM ANSWERS

1.

Fe_2O_3,	LiOH,	Na_3PO_4,	NH_4OH,	KIO_3,	KI
Fe - +3	Li - +1	Na - +1	N - −3	K - +1	K - +1
O - −2	O - −2	P - +5	H - +1	I - +5	I - −1
	H - +1	O - −2	O - −2	O - −2	
			H - +1		

2. (a) Fe is oxidized, H^+ is reduced
   (b) Cr^{+3} is oxidized, O_2 is reduced
   (c) I^- is oxidized, IO_3^- (or I^{+5}) is reduced

3. Spontaneous reaction occurs with the lead strip in the $CuSO_4$ solution.

4. All metals with positive values of E°: K, Na, Mg, U, Al, Zr, Mn, Cr, Fe, Cd, Pb, Co, Ni.

5. $\Delta E° = 0.15$ volt

6. (a) $\Delta E° = 1.10$ volts
   (b) $\Delta E = 1.16$ volts
   (c) ΔE continuously decreases as the cell operates due to depletion of ionic copper and buildup of ionic zinc.

SECTION 12.

CORROSION

220-12.1 INTRODUCTION

220-12.1.1 **Corrosion is the destructive attack of a metal by chemical or electrochemical reaction with its environment** . According to this definition, the term corrosion is used exclusively in conjunction with metals. Plastics for example, may crack or erode but the destructive interaction between such materials and their environment is not called corrosion. Also, this definition excludes such destructive processes as erosion and wear, although in some specific cases the attack on a metal must be described by a combination of terms, such as corrosion-erosion, corrosion-wear or fretting-corrosion.

220-12.1.2 In any discussion of corrosion, it is extremely difficult to make general statements covering all types of corrosion and all metals. It is often found that metal A is resistant to corrosion in environment X while metal B corrodes rapidly: in environment Y, metal B resists corrosion but metal A is readily attacked. An example is the behavior of iron and aluminum. In acetic acid with a pH between 5 and 6, iron corrodes rapidly while aluminum corrodes very slowly. In an NaOH solution with a pH of 8 to 9, iron corrodes slowly, but the corrosion of aluminum is rapid.

220-12.1.3 Generally, every metal corrodes under certain conditions. Because of the difficulty of developing general principles of corrosion for all metals and also for reasons of practical interest, this chapter focuses primarily on the corrosion of iron alloys in aqueous environments.

220-12.2 GLOSSARY OF TERMS

220-12.2.1 Terms used in this section are defined as follows:

a. **Cathodic Protection:** The protection of the more active of two galvanically coupled metals by the addition of a third, even more active metal which is preferentially attacked.

b. **Caustic:** Alkaline or basic

c. **Chemisorption:** The formation of a thin, monomolecular layer of a compound on the surface of a metal between metal atoms and other atoms or ions in the metal's environment.

d. **Corrosion:** The destructive attack of a metal by chemical or electrochemical reaction with its environment.

e. **Depolarization:** The process of removing the polarizing layer on an electrode of an electrochemical cell.

f. **Fretting-Corrosion:** Damage which occurs at the interface of two contacting metal surfaces subject to slight relative slip. Fretting-corrosion is characterized by discoloration of the metal and, often, formation of pits at which fatigue cracks begin.

g. **Galvanic Corrosion:** The electrochemical reaction between two dissimilar metals in electrical contact and exposed to water or an aqueous solution.

h. **General Corrosion:** The uniform attack of a metal surface by corrosion. That is, the corrosion rate is uniform over the surface of the metal.

i. **Micro-Cells:** Microscopic electrochemical cells established between cathodic and anodic regions on a metal surface due to impurities in the metal or variations in temperature or environment.

j. **Passivity:** The property of a metal being more resistant to corrosion than would be expected from its oxidation potential due to the formation of a thin protective oxide layer on the surface of the metal.

k. **Pitting Corrosion:** A type of corrosion in which the corrosion rate in a localized area is significantly greater than the general corrosion rate usually due to concentration differences in the metal's environment.

l. **Polarization:** Any process which lowers the potential of an electrochemical cell. The most important example in this text is the formation of a layer of atomic hydrogen on the surface of a metal.

m. **Sacrificial Anode:** The third metal used in cathodic protection, such as zinc used to protect an iron-bronze coupling.

n. **Stainless Steels:** Iron alloys containing at least 12 percent chromium.

o. **Stress Corrosion Cracking:** A type of corrosion which results in cracks in a metal when the metal is in a stressed condition and exposed to a specific environment, such as stressed stainless steel exposed to a solution containing chloride and oxygen.

220-12.3 TYPES OF CORROSION

220-12.3.1 GENERAL. The most familiar type of corrosion is uniform or **general** corrosion. In this type of attack, the entire surface of the metal corrodes at a fairly uniform rate. The rusting of untreated iron and the tarnishing of silverware are examples of general corrosion.

220-12.3.2 PITTING CORROSION. **Pitting** corrosion is a type of **localized** corrosive attack on a metal. As the name implies, the visible effects are pits in the metal surface. The number and depth of pits usually depend on the relative rates of general and localized attack. If the rate of localized attack is only moderately greater than the general corrosion rate, the result is usually a large number of shallow pits. If the localized corrosion rate is much greater that the general rate, the effect is more likely to be fewer but much deeper pits. In the latter case, the localized corrosion rate may be so great that the pits entirely penetrate thin metallic sheets or tubes before most of the metal has experienced significant attack. Pitting is discussed in more detail in paragraphs 220-12.7.2 through 220-12.7.2.4.

220-12.3.3 STRESS CORROSION. **Stress corrosion cracking** usually occurs in a well-defined environment and under conditions of tensile stress. The tensile stress may be an applied stress or residual stresses from either cold working of the metal or construction of a component. The environment in which stress corrosion cracking occurs varies with the type of the metal but is very specific for a particular metal. For example, stressed stainless steel will crack in high temperature water if chloride ions and dissolved oxygen are present, but it does not crack if chloride or oxygen is not present. Thus, the stress corrosion cracking can be avoided by excluding chloride or oxygen from the environment of stainless steels.

220-12.4 UNITS OF CORROSION RATE

220-12.4.1 The rate at which a metal corrodes may be expressed in several different units. For some metals it is convenient to use units of inches of penetration per year (ipy). For materials such as stainless steel, which are very corrosion resistant, units of ipy result in very small numbers. In this case it is usually more convenient to use units of milligrams of metal corroded per square decimeter of metal surface per month, abbreviated mg/dm^2 /mo(1 decimeter = 10 cm, 1 dm^2 = 100 cm^2). In these units, the usual corrosion rates of corrosion resistant materials are greater than 1.0. For example, a typical corrosion rate for stainless steels in high temperature water is about 1 mg/dm^2 /mo as opposed to about 10-5 in units of ipy.

220-12.5 CORROSION THEORY

220-12.5.1 OVERVIEW . Almost all types of corrosion involve oxidation-reduction reactions. Electrochemical cells and oxidation potentials discussed in Section 11 find direct applicability in understanding most corrosion processes. Several examples of electrochemical cells are given in Section 11, and include cells made up of electrodes of two different substances, **galvanic cells** , and cells containing electrodes of the same substance under different conditions of concentration, **concentration cells** . When the electrodes are connected, current flows between the electrodes and oxidation-reduction reactions occur at the electrodes.

220-12.5.1.1 It is now believed that the surface of any metal is a composite of a very large number of micro-electrodes. These electrodes set up many micro-cells connected through the bulk of the metal. This situation is illustrated schematically in Figure 220-12-1. In order for corrosion to occur, the micro-cells must also be connected through some conducting path external to the metal (analogous to the salt bridge described in Section 11). Usually the external connection is provided by water or aqueous solutions. Thus, as long as the metal remains dry, the cell currents cannot flow and corrosion does not occur. In the presence of water or aqueous solutions, the cells produce a current and the chemical reactions responsible for corrosion are able to proceed.

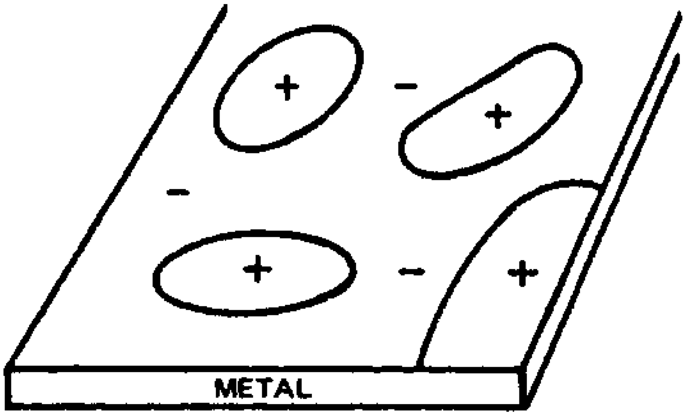


Figure 220-12-1 Enlarged Section of Metal Surface Showing Schematic Arrangement of Micro-cells

220-12.5.1.2 The actual corrosion of a metal, that is, the chemical transformation which is recognized as destructive to the metal, is the oxidation step of the overall oxidation-reduction process. The metal atoms release electrons (are oxidized) and become positive ions. Typical oxidation half-reactions and their standard oxidation potentials are:

$Zn \rightarrow Zn^{+2} + 2e^{-}$ E° = 0.76 volts (12-1)

$Al \rightarrow Al^{+3} + 3e^{-}$ E° = 1.66 volts (12-2)

$Fe \rightarrow Fe^{+2} + 2e^{-}$ E° = 0.44 volts (12-3)

The cations may then go into solution or they may combine with any available anions or water to form ionic compounds. The exact fate of the cations is important to subsequent processes, but the primary effect is that atoms leave the metallic state and, thus, the metal deteriorates.

220-12.5.1.3 As often stated in Section 11, an oxidation process cannot take place without a simultaneous reduction process. The nature of the reduction step in corrosion sometimes varies with the metal and the environment to which it is exposed. For most metals in an aqueous environment, however, the important reduction half-reaction is the reduction of hydronium ions:

$H_3O^{+} + e^{-} \rightarrow H + H_2O$ (12-4)

220-12.5.1.4 The standard oxidation potentials listed in Table 220-11-1 clearly show that at standard conditions, metallic iron, for example, is capable of reducing H_3O^{+} ions. In practical applications, the environment to which a particular metal is exposed seldom corresponds to the conditions required for standard oxidation potentials to apply. As shown in Section 11 using the Nernst equation, the prevailing conditions can cause changes in the magnitude and even the sign of cell potentials. Small concentration variations within a solution in contact with the metal may also affect the rate and nature of corrosion reactions. Therefore, it is often impossible to **predict** the exact nature of corrosion reactions. It is generally found, however, that for most metals exposed to an aqueous environment, the half-reactions involved in corrosion are the reduction reaction of equation (12-4) **and** an oxidation half-reaction of the type shown in equations (12-1) through (12-3).

220-12.5.2 LOCALIZED VERSUS GENERAL CORROSION. The micro-cells previously described may originate from a variety of factors. It was originally believed that these cells resulted solely from impurities in the metal because it was observed that the purer the metal, the greater the corrosion resistance. It is now known, however, that impurities are not the only cause of micro-cells. Other factors include variations in temperature, surface condition, heat treatment, and the environment.

220-12.5.2.1 In general corrosion, there are established on the metal surface a nearly infinite number of micro-cells. Oxidation occurs at anodic areas and reduction at cathodic areas. The micro-cells are uniformly distributed over the metallic surface and as the reaction proceeds, the cells may migrate or disappear and reform. That is, any particular micro-region may be alternately anodic and cathodic. The result is a uniform attack on the metal surface.

220-12.5.2.2 Under some conditions, relatively large regions become anodic or cathodic. Such regions have less tendency to migrate and may remain operative for long periods of time. In this case, there will be severe attack of the metal at the anodic (oxidation) region. The result may be a visible pit in the metal surface. Some of the conditions under which this localized attack occurs are described in paragraphs 220-12.7.2 through 220-12.7.2.4 in relation to the corrosion of iron and steel.

220-12.5.3 PASSIVITY. Since corrosion is an oxidation process, it is reasonable to expect that the tendency of a metal to corrode is indicated by its position in the table of oxidation potentials (Table 220-11-1). A metal with a large positive standard oxidation potential would be expected to be more susceptible to corrosion than one with a large negative oxidation potential. In many cases this is consistent with the observed behavior of metals. Experience shows that iron (E^o = +0.44 V) corrodes fairly rapidly and that gold (E^o = -1.50 V) is very resistant to corrosion.

220-12.5.3.1 Based on these considerations alone, however, chromium ($E°$= +0.71 V) would be expected to corrode very easily. In practice it is observed that chromium is very resistant to corrosion. Metals which do not corrode as easily as expected from their oxidation potentials are said to be **passive metals** .

220-12.5.3.2 **Passivity** is generally believed to be due to the buildup of a stable, tenacious layer of metal oxide on the surface of the metal. This oxide layer is formed by corrosion on an initially fresh metal surface and it is necessary, of course, that the corrosion products be insoluble in the particular environment to which the metal is exposed. Once the layer or film is formed, it acts as a barrier separating the metal surface from the environment. In order for further corrosion to occur the reactants ust diffuse through the oxide film. Such diffusion is either very slow or apparently impossible in some cases; thus, corrosion either decreases markedly or stops.

220-12.5.3.3 Metals such as chromium, and the stainless steels form thin, tenacious oxide films when exposed to the atmosphere or to pure water at room temperature. In some cases, the film is extremely thin and may be invisible to the unaided eye, but it is still very effective in giving these metals a marked passivity.

220-12.5.4 POLARIZATION. If there is a net conversion of reactants to products in a system, the system is chemically unstable and the reaction will continue until a stable state is attained. This stable state is the equilibrium condition discussed in Section 7.

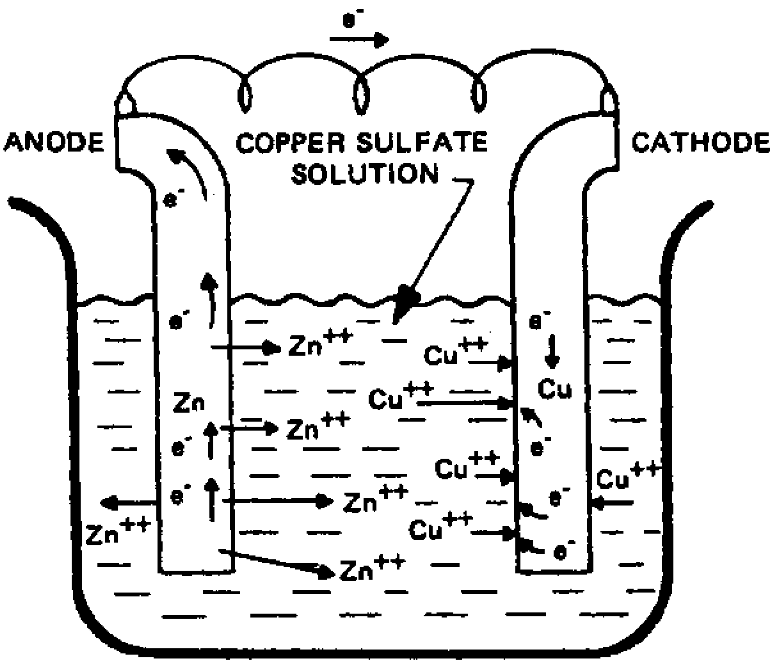
220-12.5.4.1 An active electrochemical cell (oxidation-reduction reaction) is an unstable chemical system. The potential associated with a galvanic cell, for example, steadily decreases as current flows and the oxidation-reduction reaction proceeds. Eventually, the potential falls to zero, the cell no longer supplies electrical energy, and no further net reaction takes place. At this point, the system is at equilibrium. In electrochemical cells, the decrease in cell potential caused by the actual operation of the cell (current flow) is called **polarization** .

220-12.5.4.2 This change in cell potential can be determined quantitatively using the Nernst equation. Consider the zinc-copper galvanic cell shown in Figure 220-12-2. As the reaction takes place, Zn^{+2} ions produced by the oxidation of zinc metal pass into solution and copper metal plates out as Cu^{+2} ions are reduced; thus, the concentration of Zn^{+2} in solution increases and the concentration of Cu^{+2} decreases, according to the overall reaction:

$$Zn + Cu^{+2} \rightarrow Zn^{+2} + Cu \qquad (12\text{-}5)$$

The Nernst equation for the cell is:

$$E = E^{\circ} - \frac{0.059}{2} \log \frac{[Zn^{+2}]}{[Cu^{+2}]} \qquad (12\text{-}6)$$



ZINC ATOMS RELEASE ELECTRONS, BECOME Zn^{+2} IONS AND GO INTO SOLUTION AT THE ANODE. POSITIVE COPPER IONS ACCEPT THE ELECTRONS THEREBY BECOMING COPPER METAL WHICH PLATES OUT ON THE CATHODE.

Figure 220-12-2 Galvanic Cell

220-12.5.4.3 As $[Zn^{+2}]$ increases and $[Cu^{+2}]$ decreases, the second term in equation (12-6) increases and therefore, the value of E decreases. This decrease in cell potential which results from changes in concentrations is one form of polarization called concentration polarization.

220-12.5.4.4 Now consider a galvanic cell with zinc and hydrogen electrodes such as that shown in Figure 220-12-3. The half-reactions in the cell are:

$Zn \rightarrow Zn^{+2} + 2e^{-}$ (12-1)

$H_3O + e^{-} \rightarrow H + H_2O$ (12-4)

Again, as this cell operates, the cell potential drops. The decrease is partially due to the increase in Zn^{+2} concentration and the decrease in H_3O^{+} concentration, but another type of polarization also occurs in this cell. This second type is associated with the reduction half-reaction.

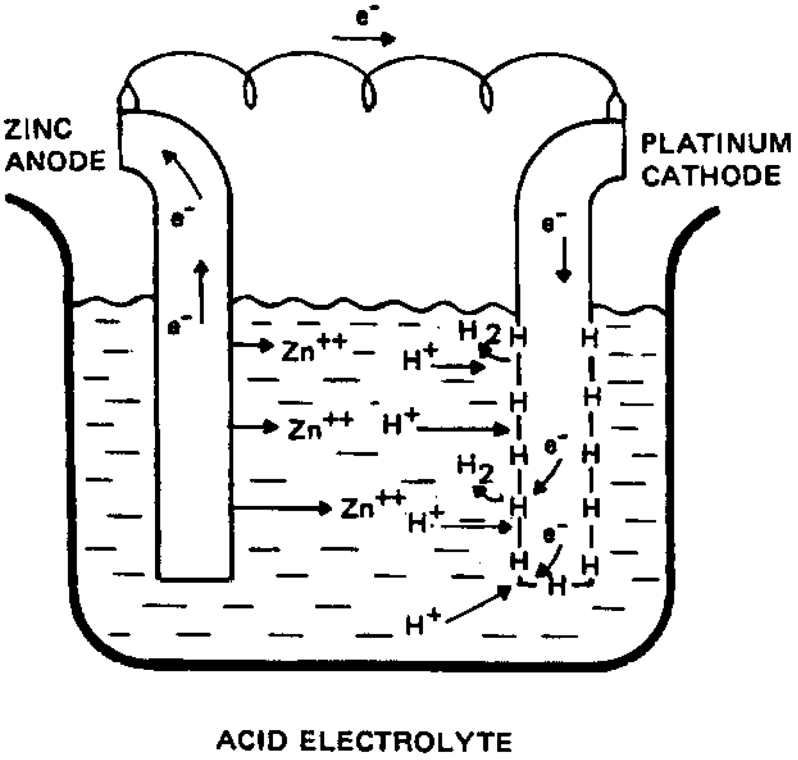


Figure 220-12-3 Galvanic Cell (Adsorbed Hydrogen Atoms on Cathode)

220-12.5.4.5 The hydrogen atoms formed by the reaction of equation (12-4) adsorb on the surface of the metal and remain there until removed by one of two processes: combination of two hydrogen atoms to form molecular hydrogen which is then released as a gas; or reaction with dissolved oxygen to form water. The second process is discussed in paragraphs 220-12.6.4 and 220-12.6.4.1. In the absence of oxygen (deaerated solutions), the first process applies:

$2H \rightarrow H_2$ (12-7)

Combining this with equation (12-4), the net reduction half-reaction is obtained:

$2(H_3O^{+} + e^{-} \rightarrow H + H_2O)$ (12-4)

$2H \rightarrow H_2$ (12-7)

$2H_3O^{+} + 2e^{-} \rightarrow H_2 + 2H_2O \quad E° = 0$ (12-8)

220-12.5.4.6 Until the adsorbed hydrogen atoms are removed from the metal surface, they effectively block the sites at which the reaction of equation (12-4) can occur. At low temperatures, the reaction of equation (12-7) is slow relative to the reaction of equation (12-4) because, although the reaction is energetically favored, the combination of two hydrogen atoms requires a large activation energy. (Activation energy is discussed in Section 7.) Thus, equation (12-7) shows the rate-controlling step of the net reduction half-reaction. Since the oxidation half-reaction can occur no faster than the reduction half-reaction, the rate of the overall oxidation-reduction reaction is controlled by the reaction of equation (12-7).

220-12.5.4.7 The layer of adsorbed atomic hydrogen is said to polarize the cell. This type of polarization is called activation polarization and is sometimes referred to as hydrogen polarization or cathodic polarization since the polarizing reaction occurs at the cathode.

220-12.5.4.8 Both concentration and activation polarization decrease the rate of the net oxidation-reduction reaction. In corrosion processes, activation polarization usually has the greater effect.

220-12.5.5 TIME-DEPENDENT BEHAVIOR OF CORROSION. When a fresh metal is first exposed to a corrosive environment, chemical reaction between the metal surface and the environment will begin at some rate, R. As time passes, the value of this corrosion reaction rate may decrease, increase, or remain relatively constant. The way in which the corrosion rate changes with time for a particular system is governed by a number of factors. The two most important of these factors are the nature of the oxide film formed on the metal surface and the time-dependent characteristics of the environment to which the metal is exposed.

220-12.5.5.1 In determining the time-dependent corrosion behavior of a metal or alloy in a particular environment, one can expose a specimen of the metal to the environment and then measure the weight of the specimen as a function of time. Experiments of this type show that the weight of the metal specimen and the corrosion rate of the metal can vary in a number of ways. Let us consider two specific examples which illustrate different types of time-dependent corrosion behavior:

a. **Iron in Acid** - When iron is exposed to an acidic solution containing dissolved oxygen, the weight change of a metal specimen per unit time is observed to remain quite uniform (weight is lost). A plot of the **total** weight change of the specimen as a function of time is linear, as shown in Figure 220-12-4(a). In this case it appears that the rate of corrosion of the iron is relatively constant. The constant corrosion rate is attributed to the **non-protective** nature of the oxide film which forms when iron is exposed to an acid solution containing dissolved oxygen.

b. **Stainless Steel in High Temperature Water** - When a specimen of corrosion-resistant stainless steel is exposed to high temperature water, the weight change per unit time of the specimen is observed to decrease with increasing exposure time as shown in Figure 220-12-4 (b). A plot of the **total** weight change as a function of time is shown in Figure 220-12-4 (c). The decreasing corrosion rate is attributed to a thickening protective oxide film which forms on the metal surface.

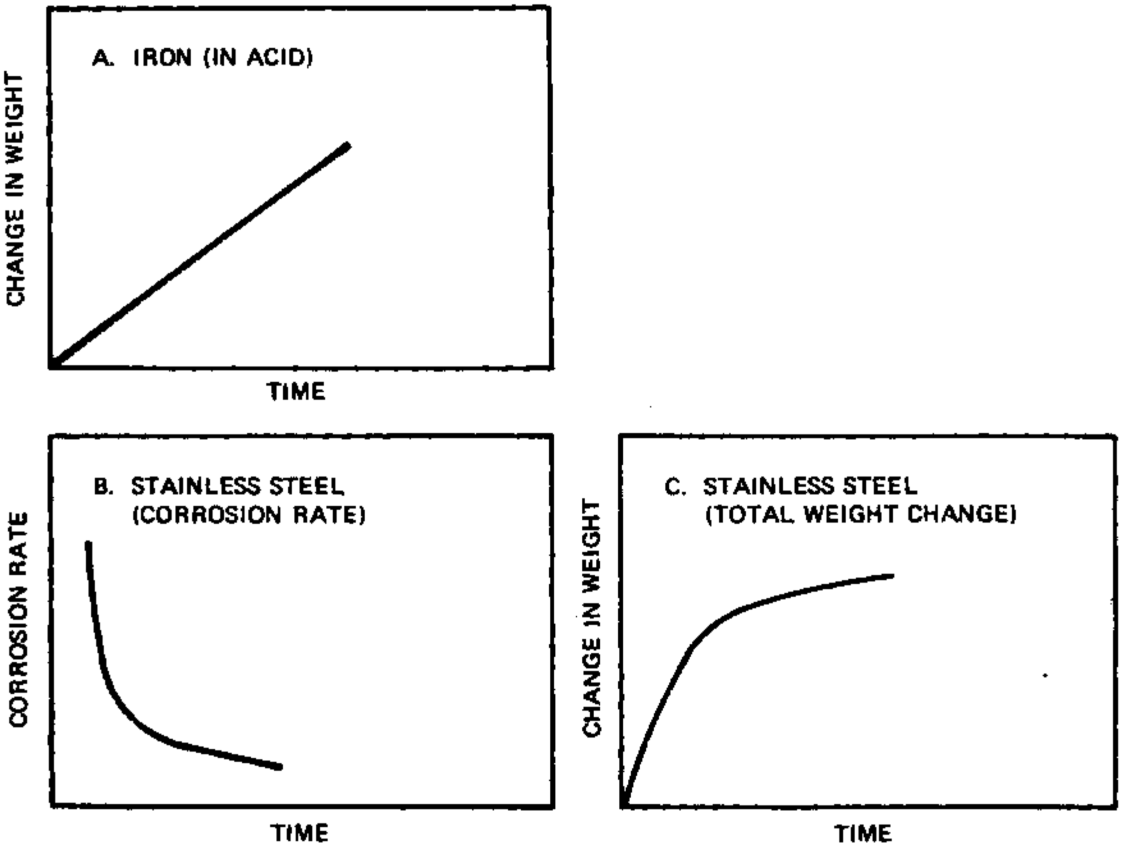


Figure 220-12-4 Weight Change of Metal Specimens as a Function of Time

220-12.5.5.2 These examples illustrate two general types of corrosion behavior which are of interest in this text. These two types of behavior are:

1. A linear weight change with time.
2. A decreasing rate of weight change with time.

220-12.5.5.3 If the weight change per unit time of a metal follows a linear relationship, the rate of corrosion of the metal is relatively constant. For the corrosion rate to remain relatively constant, the environment must have ready access to the metal surface through cracks or pores in the oxide film.

220-12.5.5.4 It was noted earlier that iron exposed to an acidic solution containing dissolved oxygen exhibits this type of corrosion behavior. In such an environment (pH less than 4), iron corrosion products are soluble; thus, no protective layer forms and corrosion can proceed at a nearly constant rate.

220-12.5.5.5 A decrease with time of the weight change per unit time of a metal specimen indicates that the corrosion rate of the metal is decreasing with time. That is, reaction between the metal and the environment becomes increasingly slower with time. Metals which form protective oxide films exhibit this type of corrosion behavior.

220-12.5.5.6 Diffusion of ions or the migration of electrons through the oxide film most probably control the rate of the corrosion reaction in this case (paragraphs 220-12.5.2 through 220-12.5.2.2). As the oxide film thickens, diffusion and migration are more difficult. As noted earlier, corrosion resistant stainless steels exposed to alkaline, high temperature water exhibit this type of corrosion behavior. After a period of exposure to the environment, corrosion rates decrease to very low values (less than 1 mg/dm^2 /month).

220-12.6 GENERAL CORROSION

220-12.6.1 GENERAL. The following paragraphs describe the general corrosion process of iron and carbon steel (not stainless steels) in an aqueous environment. Of particular interest is the formation of the oxide film and the effects of system variables on the corrosion process. Unless noted otherwise, the discussion applies to deaerated water at room temperature and approximately neutral pH. The effects of temperature, oxygen, and pH are discussed separately later in this section.

220-12.6.2 FILM FORMATION. The oxidation and reduction half-reactions in the corrosion of iron are:

$Fe \rightarrow Fe^{+2} + 2e^{-}$ (oxidation) (12-3)

$H_3O^{+} + e^{-} \rightarrow H + H_2O$ (reduction) (12-4)

The overall reaction is the sum of these half-reactions:

$Fe + 2H_3O^{+} \rightarrow Fe^{+2} + 2H + 2H_2O$ (12-9)

The Fe^{+2} ions readily combine with OH^{-} ions at the metal surface, first forming $Fe(OH)_2$ which decomposes to FeO:

$Fe^{+2} + 2OH^{-} \rightarrow Fe(OH)_2 \rightarrow FeO + H_2O$ (12-10)

Ferrous oxide (FeO) then forms a layer on the surface of the metal. Below about 1000°F, however, FeO is unstable and undergoes further oxidation.

$2FeO + H_2O \rightarrow Fe_2O_3 + 2H$ (12-11)

(Atomic hydrogen then reacts to form molecular hydrogen as described in paragraphs 220-12.5.4 through 220-12.5.4.8.) Thus, a layer of ferric oxide (Fe_2O_3) builds up on the FeO layer. Between these two layers is another layer which has the apparent composition Fe_3O_4 . The oxidation number of iron in FeO is +2 and in Fe_2O_3 it is +3. The formula Fe_3O_4 indicates that the oxidation number of iron is +2 2/3. Atoms do not gain or lose fractions of electrons and, thus, do not actually exhibit fractional oxidation states. It is believed that Fe_3O_4 is a distinct crystalline state composed of O^{-2} , Fe^{+2} and Fe^{+3} in proportions such that the **apparent** composition is Fe_3O_4 . These three layers are shown schematically in Figure 220-12-5.

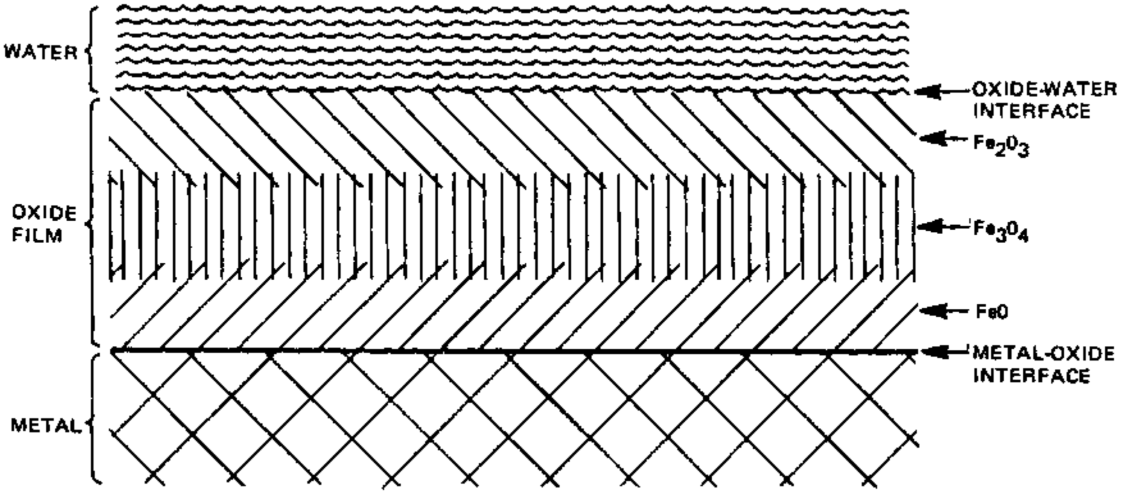


Figure 220-12-5 Simplified Schematic Diagram of Oxide Corrosion Film on the Surface of a Metal

220-12.6.2.1 Once the oxide film begins to form, the metal surface is no longer in direct contact with the aqueous environment. For further corrosion to occur, the reactants must diffuse through the oxide barrier. It is believed that the actual oxidation step, equation (12-3), occurs at the metal-oxide interface. The Fe^{+2} ions and electrons then diffuse through the oxide layer toward the oxide-water interface. Eventually, Fe^{+2} ions encounter OH^- ions and form FeO. The electrons participate in the reduction reaction with hydronium ions. These latter reactions are believed to take place predominantly at the oxide-water interface, but some reaction may occur within the oxide layer by the diffusion of H^+ , OH^- , and H_2O into the layer.

220-12.6.2.2 Regardless of the exact diffusion mechanism, the oxide layer represents a barrier to continued corrosion and tends to slow the corrosion rate. Obviously, the exact effect of this layer on the corrosion rate depends on the uniformity and tenacity of the film. If the film is loosely attached, develops defects, or is removed, the metal surface is again exposed to the environment and corrosion occurs more readily. The time dependence of such a corrosion rate is of the type shown in Figure 220-12-4(a). Note, however, that Figure 220-12-4(a) is for corrosion in an acid solution, not water.

220-12.6.2.3 It is found that iron and steel are resistant to rapid corrosion in water despite the tendency of iron to oxidize as indicated by its oxidation potential. The reasons for this resistance are the passivating effect of the oxide film and cathodic polarization due to atomic hydrogen which adsorbs on the oxide surface. The following paragraphs describe the effects of various factors on the passivity and polarization of iron.

220-12.6.3 EFFECT OF TEMPERATURE. Like most other chemical reactions, corrosion rates increase as temperature increases. Beginning at room temperature, the corrosion rate of iron in neutral water approximately doubles for every 50°F increase in temperature. This linear increase with temperature does not continue indefinitely due, in part, to a change in the oxide film.

220-12.6.3.1 As described in paragraphs 220-12.6.2 through 220-12.6.2.3, the outer layer of the oxide film is Fe_2O_3 . There are two crystalline forms of this compound, denoted by αFe_2O_3 and γFe_2O_3 . The first, αFe_2O_3 , is the stable form at low temperatures and is the familiar red rust which forms on iron. This form of Fe_2O_3 adheres rather loosely to the metal and is easily removed. The other form, γFe_2O_3 , is dark brown or black in color and is much more adherent to the metal, thus providing better protection against further corrosion. The latter form is stable at high temperatures (greater than about 400°F) and its formation is promoted by alkaline solutions (pH > 7) and the absence of oxygen.

220-12.6.4 EFFECT OF DISSOLVED OXYGEN. The presence of oxygen in water to which iron is exposed increases the corrosion rate. The reason for this increase is the rapid reaction between oxygen and the polarizing layer of atomic hydrogen adsorbed on the oxide layer. The reaction

$$O_2 + 4H \rightarrow 2H_2O \quad (12\text{-}12)$$

rapidly removes the polarizing layer. The overall reaction can be obtained by combining equations (12-4) and (12-12) to obtain:

$$O_2 + 4H_3O^+ + 4e^- \leftrightarrows 6H_2O \qquad E^\circ = 1.23V$$

220-12.6.4.1 A cell composed of the oxidation half-reaction of equation (12-3) and the reduction half-reaction of equation (12-13) will have a larger standard cell potential, ΔE°, than one composed of the oxidation half-reaction of equation (12-3) and the reduction half-reaction of equation (12-8) because the value of E° for the half-reaction of equation (12-8) is zero. Thus, the reaction of equation (12-7) no longer occurs and, therefore is not the rate-controlling step. Instead, the controlling step is believed to be diffusion of O_2 to the metal surface where it can react directly with iron or with FeO:

$$2Fe + O_2 \rightarrow 2FeO$$

$$4FeO + O_2 \rightarrow 2Fe_2O_3$$

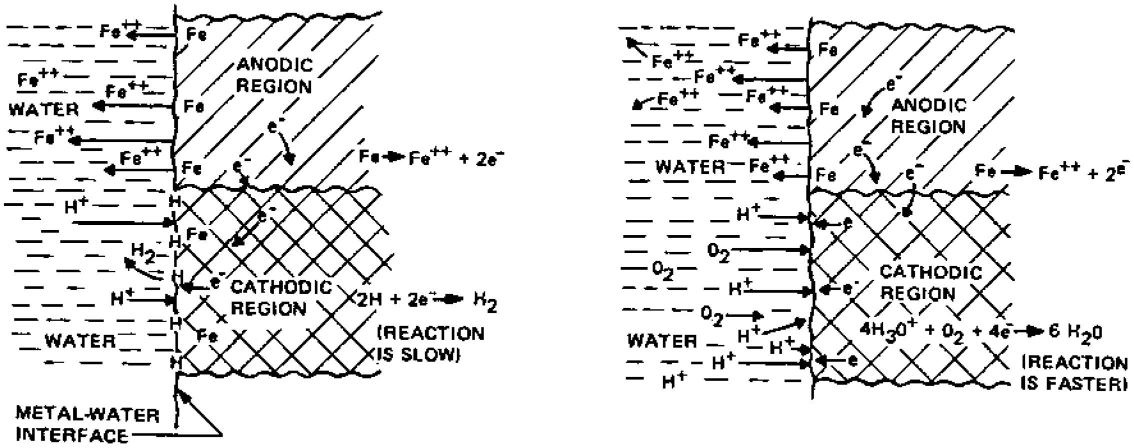
Oxygen thus has two effects: it removes the polarizing layer of atomic hydrogen and it can react directly with the metal or metal oxide. Thus, the corrosion rate increases. Substances, such as O_2 in this case, which remove the adsorbed atomic hydrogen are called depolarizers. The depolarizing effect of O_2 is illustrated in Figure 220-12-6.

220-12.6.5 EFFECT OF pH. The effect of the pH of water to which iron or steel is exposed is influenced by temperature. First, consider the exposure of iron to **aerated water at room temperature** (aerated water will contain dissolved oxygen). The corrosion rate for iron **as a function of pH** is illustrated in Figure 220-12-7. In the range of pH 4 to pH 10, the corrosion rate of iron is relatively independent of the pH of the solution. In this pH range, the corrosion rate is governed largely by the rate at which oxygen reacts with adsorbed atomic hydrogen, thereby depolarizing the surface and allowing the reduction reaction to continue.

220-12.6.5.1 For pH values below 4.0, ferrous oxide (FeO) is soluble. Thus the oxide dissolves as it is formed rather than depositing on the metal surface to form a film. In the absence of the protective oxide film, the metal surface is in direct contact with the acid solution and the corrosion reaction proceeds at a greater rate than it does at higher pH values. It is also observed that hydrogen is evolved in acid solutions below a pH of 4, indicating that the corrosion rate no longer depends entirely on depolarization by oxygen but on a combination of the two factors (hydrogen evolution and depolarization).

220-12.6.5.2 For pH values above about pH 10, the corrosion rate is observed to fall as pH is increased. This is believed to be due to an increase in the rate of the reaction of oxygen with $Fe(OH)_2$ (hydrated FeO) in the oxide layer to form the more protective $Fe_2 O_3$. (This effect is not observed in deaerated water at high temperatures.) Although not shown on this graph, in very caustic solutions, for example 16M NaOH, the corrosion rate again increases due to the formation of a soluble complex ion, FeO_2^- .

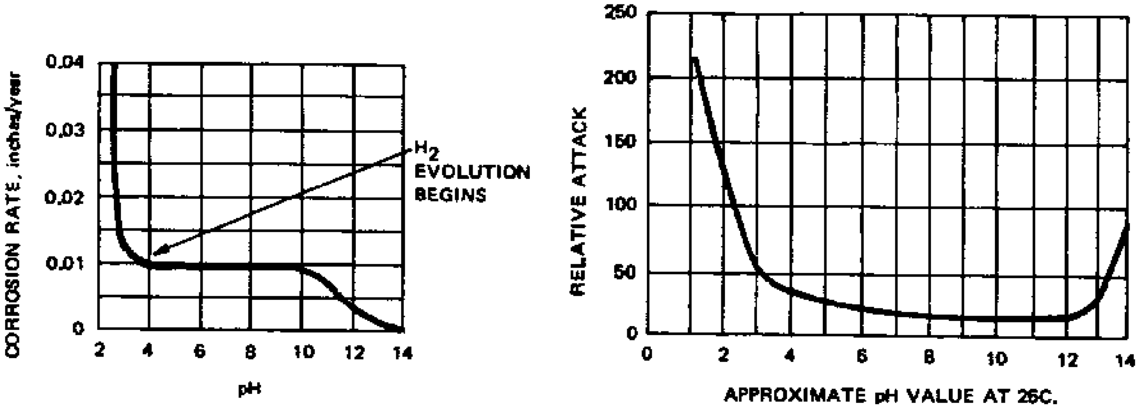
220-12.6.5.3 A plot of the relative corrosion rate for iron **at various pH values** in 590°F, **oxygen-free water** is also presented as part of Figure 220-12-7. Although there is considerable uncertainty in the data from which this curve was derived, the curve does illustrate that the corrosion rate of iron in high temperature water is lower in the general pH range of 7 to 12 than it is at either lower or higher pH values (at very high pH values, greater than pH 13.0, the oxide film becomes increasingly more soluble due to increased formation of soluble FeO_2^- at high temperatures and so corrosion rates increase). As a result of the data plotted in Figure 220-12-7 and other similar measurements, it is general practice to maintain high temperature water in the alkaline condition (but below very high pH values) in order to minimize the corrosion of iron and the steels exposed to the high temperature water.



CORROSION OF IRON IN ABSENCE OF DISSOLVED OXYGEN. CATHODIC OR REDUCTION REACTION IS SLOW THEREBY REDUCING THE CORROSION RATE.

CORROSION OF IRON WITH DISSOLVED OXYGEN PRESENT IN WATER. RATE OF CATHODIC OR REDUCTION REACTION HAS INCREASED AS A RESULT OF OXYGEN DEPOLARIZATION. NET RESULT IS AN INCREASE IN CORROSION RATE.

Figure 220-12-6 Schematic Representation of Cathodic Depolarization by Oxygen



EFFECT OF pH ON THE CORROSION OF IRON EXPOSED TO AERATED WATER AT ROOM TEMPERATURE

RELATIVE RATE OF ATTACK ON IRON BY 590F WATER OF VARYING pH.

Figure 220-12-7 Effect of pH on the Corrosion Rate of Iron in Water

220-12.6.5.4 In naval steam plants, it is desired to minimize the corrosion of iron and steels exposed to high temperature boiler water. Thus, boiler water is normally maintained in an alkaline condition.

220-12.6.6 EFFECT OF THE RATE OF SOLUTION FLOW. Much of the corrosion testing of iron and steels is performed in systems where the flow velocity of the solution is either very low (a few feet per second) or else the solution is static. In an actual system, flow velocities of the solution environment may range up to 20 feet per second. In a few localized regions of a system, velocities may be even greater. Test data are available concerning the effects of flow velocities upon the corrosion rates of steels and of nickel-based alloys. Flow rates in these tests ranged up to 60 feet per second. The data indicate that the total corrosion during the early stages of exposure, **while the protective oxide film is forming on the metal surface** , is somewhat greater for flow velocities above 30 feet per second than is the total corrosion in static water. However, the rate of corrosion **after the protective oxide film has formed** , that is, after a few thousand hours of exposure, is low for all velocities. **After a few thousand hours the rate of corrosion does not depend upon velocity** .

220-12.6.7 TIME DEPENDENT BEHAVIOR OF THE CORROSION OF IRON AND STEEL. When iron or steels are exposed to high temperature water, the rate of corrosion of the metal is observed to decrease with exposure time **during the early period of exposure** . After a few thousand hours, the corrosion rate becomes relatively constant at a low value. For stainless steels, the rate of corrosion in this second phase is usually less than 1 mg/dm^2 /month. During the early period of exposure while the corrosion rate is decreasing, the oxide film on the surface of the metal grows in thickness. However, the rate at which the film grows also decreases with time. The thickness of the oxide film soon reaches a relatively constant value and thereafter film thickness does not change appreciably with further exposure. As might be expected, a relatively constant corrosion rate and oxide film thickness are attained at about the same time.

220-12.6.7.1 The observation that both the corrosion rate and the thickness of the oxide film reach relatively constant values does not mean that the corrosion process has stopped. The metal continues to lose weight although usually at a slow rate. At this stage in the corrosion process, it appears that iron oxide is being lost both from and through the corrosion film. Since the thickness of the corrosion film remains relatively constant, the rate at which oxide is being lost from the existing film must be about the same as the rate at which new oxide is being formed by the corrosion process. For example, loss of oxide to the water from the corrosion film can result from erosion from the surface of the film, and from a change in the nature of the film as Fe_2O_3 is formed in the outer layers of the film via oxidation of FeO or Fe_3O_4 . In any event, new Fe^{4++} ions are continually being formed (at a slow rate) at the metal surface. By their subsequent reactions, these ions can replace any oxide lost from the film. The overall result of the processes is net corrosion of iron or steel at a low rate and the formation of an oxide film whose thickness remains relatively constant. Rates of reaction (or corrosion) in the later stage of corrosion will be substantially less than were the rates during the earlier stages of corrosion when an oxide film was forming on the metal surface.

220-12.7 LOCALIZED CORROSION

220-12.7.1 GALVANIC CORROSION. Of all the different types of corrosion, galvanic corrosion corresponds most closely to the electrochemical cells described in Section 11. Galvanic corrosion occurs when two different metals are in contact and exposed to an electrolytic solution, as illustrated in Figure 220-12-8

220-12.7.1.1 Figure 220-12-8 shows the junction of iron and copper pipes containing a solution of a copper salt. The electrochemical effects in this situation are the same as those for the galvanic cell shown in Figure 220-11-3. The oxidation potential of iron is sufficiently greater than that of copper so that iron is capable of reducing Cu^{+2} ions to copper metal. In galvanic corrosion, ions of the more active metal go into solution. Electrons from the more active metal flow through the metal junction to the less active metal and participate in a reduction reaction. In Figure 220-12-8 , Cu^{+2} ions are reduced to metal. In this case, iron corrodes near the junction and additional copper builds up on the copper pipe near the junction.

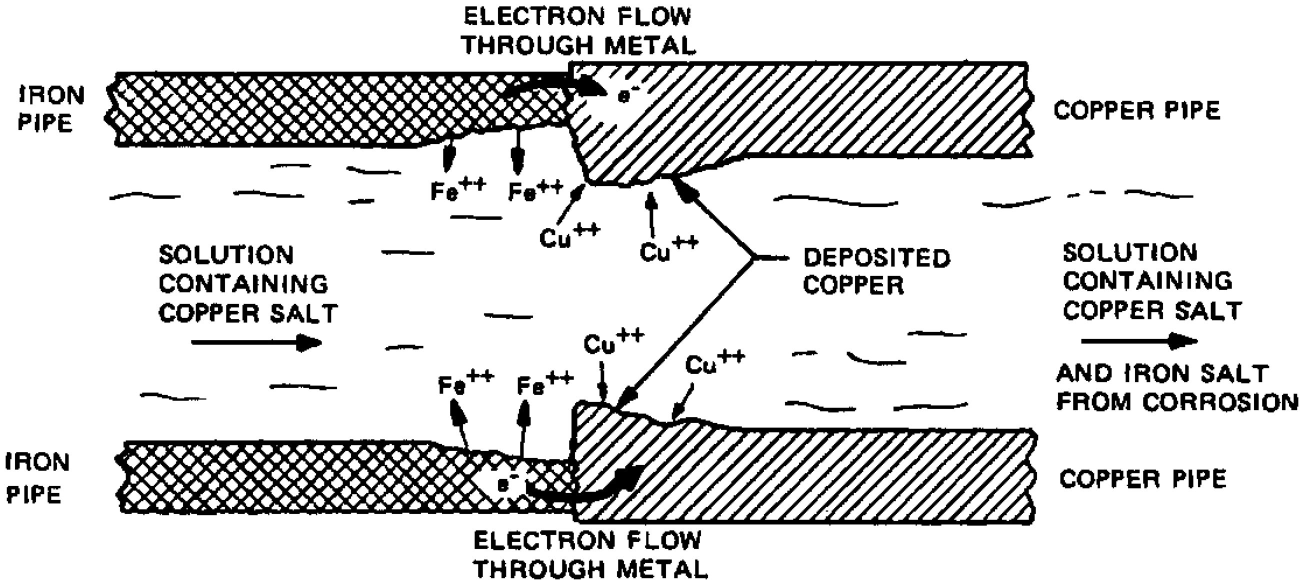


Figure 220-12-8 Galvanic Corrosion at Iron-Copper Pipe Junction

220-12.7.1.2 The solution to which the metal junction is exposed need not contain a salt of one of the metals in order for galvanic corrosion to occur. If the iron-copper junction in Figure 220-12-8 were exposed to water without Cu^{+2} ions, the reduction reaction would be:

$H_3O^+ + e^- \rightarrow H + H_2O$ (12-4)

Again, iron would corrode near the junction, but in this case, hydrogen would be formed on the surface of the copper.

220-12.7.1.3 Galvanic corrosion is an important consideration in the maintenance of ships' hulls. The hull is largely steel; however, other metals which have lower oxidation potentials than steel are often attached to the outer hull. One example is the ship's propeller which is often bronze (an alloy of copper and tin). The junction of two metals of different oxidation potentials can lead to enhanced corrosion when exposed to seawater. A method called **cathodic protection** is often used to retard or eliminate galvanic corrosion. In this method, a third metal is added to the metal to be protected. This metal has an oxidation potential even greater than that of the metal which is to be protected. The most active metal then tends to corrode in place of the protected metal. The metal that corrodes to protect another metal is called a **sacrificial anode** . For example, sacrificial anodes of zinc are often added to hulls of ships and are installed inside seawater heat exchangers since zinc has a greater oxidation potential than does iron. A strip of zinc attached to a ship's hull near an iron-bronze junction, for example, will corrode in place of the iron in seawater.

220-12.7.2 PITTING AND CREVICE CORROSION. Another possible effect of oxygen is accelerated localized attack or pitting. This is especially likely in areas of limited circulation such as crevices.

220-12.7.2.1 To illustrate pitting attack, consider a special type of galvanic cell called a differential aeration cell such as the one illustrated in Figure 220-12-9. In this type of cell, two iron electrodes are exposed to a dilute solution of an electrolyte (NaCl, for example). Air (or oxygen) is bubbled about one electrode and nitrogen is bubbled about the other. A current flows through the wire connecting the two electrodes. The difference in potential is a result of the difference in oxygen concentration at the two electrode surfaces, similar to the Ag+ concentration cell described in paragraphs 220-11.4.6 through 220-11.4.6.6. At the electrode exposed to nitrogen, electrons given up as the iron is oxidized readily flow through the external circuit to the electrode exposed to oxygen. At this depolarized electrode they can participate in a reduction reaction. As a result, oxidation occurs at the electrode exposed to nitrogen and reduction occurs at the aerated electrode. Oxidation at one electrode and reduction at the other creates a potential and a flow of current through the connecting wire. **Note that loss of metal occurs at the electrode deficient in oxygen** .

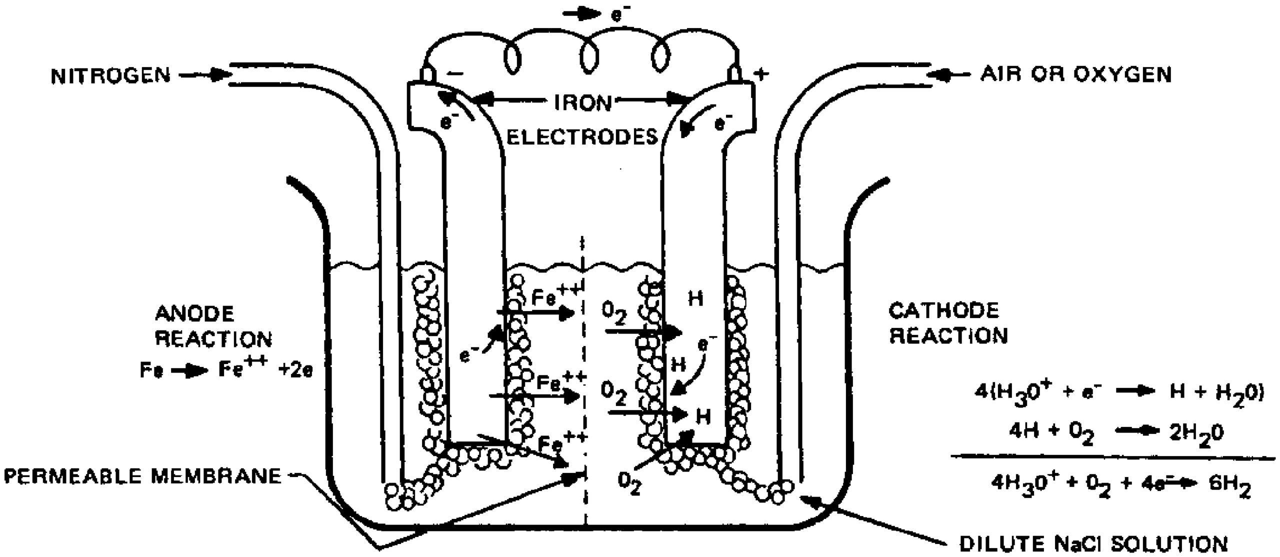


Figure 220-12-9 Differential Aeration Cell

220-12.7.2.2 In iron exposed to water, similar action can occur if adjacent areas of the metal surface become exposed to solutions with different oxygen concentrations. For example, the solution in a crevice exchanges slowly with the bulk of the solution outside the crevice. Oxygen in the solution inside the crevice will be depleted initially by the corrosion reaction:

$$2Fe + O_2 \rightarrow 2FeO$$

This reaction alone does not produce a protective film on the metal. Because of restricted flow into the crevice, replenishment of oxygen will be very slow; thus, the solution inside the crevice will have a low oxygen concentration relative to that outside the crevice (Figure 220-12-10). The two adjacent areas then establish a concentration cell with electrons flowing from the region of low oxygen concentrations to the region of high concentration. Thus metal goes into solution (oxidation) inside the crevice and reduction occurs outside the crevice. Metal ions diffuse out of the crevice, more metal dissolves, and the process continues with the result that a pit forms inside the crevice.

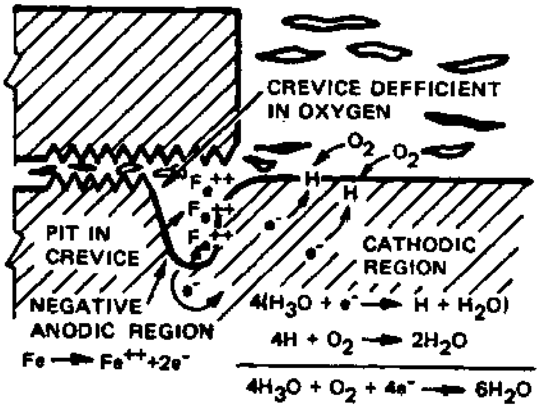


Figure 220-12-10 Schematic Representation of Crevice Pitting

220-12.7.2.3 The presence of oxygen can also promote pitting at areas on the metal surface that are initially anodic with respect to an adjacent area. For example, suppose that adjacent areas on a metal surface exhibit slightly different oxidation potentials. Oxidation, or loss of metal, proceeds at the region of higher potential. Corrosion in the region of higher potential leads to formation (at least initially) of a porous oxide film. The thickness of the film formed on the adjacent cathodic region will be much less. Oxygen in the bulk of solution can reach the cathodic surface (with the thin film) more readily than it can the nearby anodic surface region (with the thicker oxide film). Depolarization of the cathodic region (thin film) by oxygen tends to maintain this region cathodic, while a deficiency of oxygen under the thicker porous corrosion film assists in maintaining an anodic condition in this region. The overall result is corrosion or wasting away of the metal in the anodic region under the thicker film. Thus a pit in the metal surface is formed under the mound of surface oxide, Figure 220-12-11. Pitting of this type is common in both low temperature and high temperature iron-water systems if precautions are not taken to remove the oxygen from the water within the system.

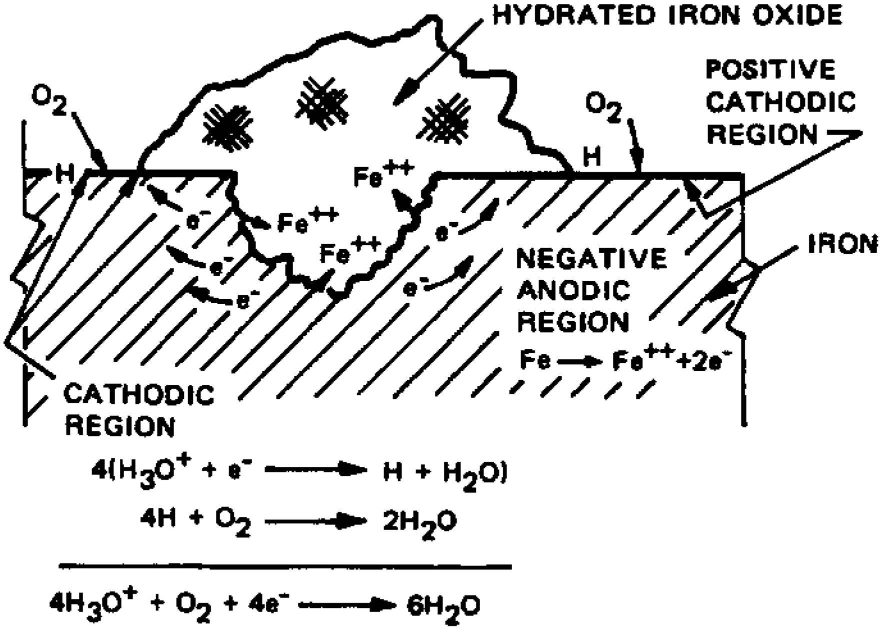


Figure 220-12-11 Pit in Metal Surface Promoted by Depolarization of Adjacent Surface Regions by Oxygen

220-12.7.2.4 It is also found that certain ions, notably chloride ions, cause pitting of iron and steel. The exact mechanism by which this occurs is not clear, but in some way, chloride ions cause defects in the passivating oxide layer on the metal surface. The defects are highly localized and are surrounded by large passive areas which tend to be cathodic. Thus, a small anodic (oxidation) site is surrounded by a large cathodic (reduction) area. The current density will then be very large at the anodic site and attack on the metal will be rapid. In some test cases, deep pits have been observed within a few hours.

220-12.7.3 STRESS CORROSION CRACKING. Experience has shown that many alloys crack when exposed to a particular, specific environment if the alloy is in a stressed condition. This phenomenon is called **stress corrosion cracking** . Stress cracking appears to be relatively independent of general uniform corrosion processes. Thus, the extent of general uniform attack can be essentially nil and stress cracking can still occur. Most pure metals are immune to this type of attack.

220-12.7.3.1 Stress corrosion cracking is of great concern, for it can readily crack metal of appreciable thickness. A specific example of concern in naval steam plants is that of the tubes of the boilers. Many of the stainless steels are susceptible to stress corrosion cracking. Stainless steels containing 18 percent chromium and 8 percent nickel (the types often employed in 1200 psi boiler superheaters) are susceptible to cracking in environments containing chloride ions and in concentrated caustic environments, that is, in environments where the hydroxyl ion concentration is high.

220-12.7.3.2 According to the most widely accepted theory, stress corrosion cracking is due to a process called **chemisorption** . Unlike relatively weak physical adsorption, such as hydrogen gas on platinum metal, chemisorption may be thought of as the formation of a compound between the metal atoms on the surface and a monomolecular layer of the chemisorbed substance, such as Cl^- , OH^- , Br^- and some other ions. The formation of this chemisorbed layer greatly reduces the attraction between neighboring metal atoms. A defect initially present then grows as the metal atoms separate under stress, more chemisorption occurs, and the process continues. In some severe cases, the time required for this cracking to occur is only a matter of minutes.

220-12.7.3.3 Chloride-Induced Stress Corrosion (Stainless Steels). Observations show that two environmental conditions and one mechanical condition are necessary before 18-8 stainless steels exhibit chloride stress corrosion cracking. These necessary conditions are:

a. The presence of **chloride ion** in the environment,

b. The presence of **dissolved oxygen** in the environment,

c. The presence of **tensile stress** in the metal.

220-12.7.3.3.1 In naval steam plants, environments containing dissolved oxygen and chloride ion can readily be created in boilers and in auxiliary water systems. Chloride ions can enter these systems via leaks in condensers or at other locations where the waters associated with the steam plant are cooled by unpurified cooling water. Dissolved oxygen can readily enter these systems with feed and makeup water. Thus chloride stress corrosion cracking is of concern and controls must be used to prevent its occurrence.

220-12.7.3.3.2 Tests show that the 18-8 stainless steels are susceptible to chloride stress attack when both the chloride ion concentration and dissolved oxygen concentration are above certain values. The region of susceptibility is illustrated in Figure 220-12-12. Note that when dissolved oxygen is present at about 1 ppm, chloride stress corrosion cracking can be initiated at chloride ion concentrations near only 1 ppm. However, when the concentration of dissolved oxygen is very low, susceptibility to chloride stress corrosion cracking is reduced. Methods used to reduce the concentration of dissolved oxygen to very low levels in the boiler water environment are discussed in paragraphs 220-12.9 through 220-12.9.2.

220-12.7.3.3.3 High temperature tends to decrease the time required for chloride-induced cracking to occur, but there appears to be no **practical** temperature limit below which cracking will not occur, given sufficient time and severe conditions. The curve in Figure 220-12-12 is valid for temperatures in the range 470° to 500°F.

220-12.7.3.4 Caustic-Induced Stress Corrosion Cracking. Mild steels (steels with a low carbon and a low alloy content) and stainless steels will crack if they are exposed to concentrated caustic environments with the metal under a tensile stress. In stress cracking induced by a caustic environment, the presence of dissolved oxygen is not necessary for the cracking to occur.

220-12.7.3.4.1 Caustic stress corrosion cracking was first encountered in the operation of riveted steam boilers. These boilers were found to fail on occasion along riveted seams. Failure was attributed to caustic-induced cracking at the highly stressed regions near and under the rivets. Boiler water could easily flow into the crevices which existed under the rivets. Radiative heating would cause the water in the crevices to boil. As steam was formed, it would escape from the crevice. More boiler water would then flow into the crevice, boil, and pass from the crevice as steam. The net result of this continuing process was concentration of caustic under the rivet. The combination of high stress and high caustic concentrations eventually lead to destructive cracking of the boiler vessel.

220-12.7.3.4.2 In the design of boilers for naval steam propulsion plants, care is taken to eliminate cracks and other regions where caustic might concentrate. However, it is more difficult to eliminate the problem of solute concentration in regions of the boiler where the rate of steam generation (boiling) is high. Caustic may concentrate in such regions as the water evaporates rapidly, but sufficient concentration of caustic by such a mechanism to induce stress cracking is considered unlikely.

220-12.7.3.4.3 So far as the conditions necessary to induce caustic stress cracking are concerned, available data indicate that caustic concentrations greater than 10,000 ppm and probably up to 50,000 ppm are required (40,000 ppm NaOH is equivalent to 40 grams per liter or 1 mole per liter. Hence, the pH of such a solution is on the order of 14). Caustic concentrations of this magnitude are not considered likely in naval boilers. To reduce the likelihood of caustic-induced stress cracking in boilers, an alkaline environment can be produced and controlled by use of a solution having some properties of a buffer. (See paragraphs 220-9.6 through 220-9.6.3.7 for basic theory of buffer solutions.)

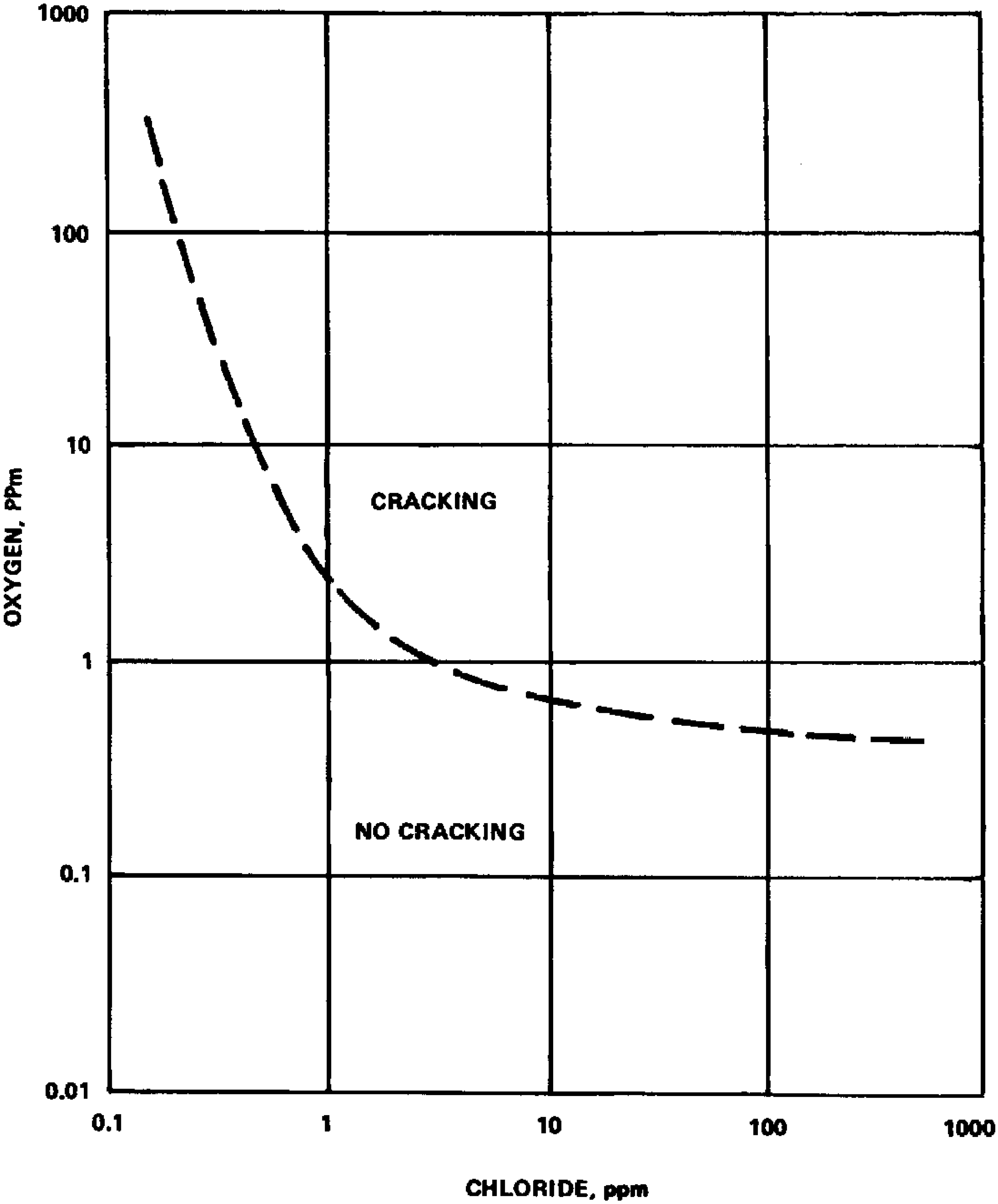


Figure 220-12-12 Regions of Chloride and Oxygen Content where Austenitic Stainless Steels (18-8) Undergo Stress Corrosion Cracking (Temperature Range, 470-500°F)

220-12.8 COMPARISON OF CORROSION OF IRON AND STEEL VERSUS CORROSION-RESISTANT MATERIALS

220-12.8.1 GENERAL. One effective means of increasing the resistance of iron to corrosion by a water environment is that of alloying iron with other metals. Desirable alloys are those which are more resistant to corrosion (more passive) than is iron itself. Paragraphs 220-12.8.2 through 220-12.8.3.3 describe two such alloys, **stainless steels** and **nickel-based alloys** .

220-12.8.2 STAINLESS STEELS. One metal which exhibits a high degree of resistance to corrosion in both water and atmospheric environments is chromium. Surfaces of metallic chromium exposed to water or the atmosphere remain bright and tarnish free for substantially longer periods than do surfaces of iron and mild steel exposed to the same environments, although Table 220-11-1 shows that chromium exhibits a larger oxidation potential than does iron. Thus, as discussed in paragraphs 220-12.5.3 through 220-12.5.3.3 chromium is a passive metal.

220-12.8.2.1 The addition of chromium to iron can increase the passivity of the alloy mixture. The effect of chromium content upon the corrosion rate of iron-chromium alloys is shown in Figure 220-12-13. Chromium increases the passivity of the alloy if the chromium content is greater than about 12 percent. **Iron alloys containing a minimum of 12 percent chromium are known as the stainless steels** . The stainless steels are appreciably more resistant to corrosion in high and low temperature water environments, and in atmospheric environments, than are iron and mild steels. The corrosion resistance (passivity) of stainless steel is a result of the passive oxide film which develops on a stainless steel surface. There are two theories for explaining the way in which the passive film functions in reducing corrosion. One theory suggests that the tight, protective oxide film typical of stainless steels forms only when the alloy contains more than 12 percent chromium. This very protective oxide film is probably a combination of chromic and iron oxides ($Cr_3 O_4$ and $Fe_3 O_4$). The exact composition of the film has not been established. However, it is apparent that for alloys containing less than 12 percent chromium, the oxide film which forms on the steel does not contain sufficient $Cr_3 O_4$ to give the film the desired corrosion resistance.

220-12.8.2.2 The second theory suggests that the presence of chromium in the alloy promotes chemisorption of oxygen and other substances upon the metal surface. These adsorbed species effectively cover the surface, thereby passivating it and reducing the corrosion rate. As before, at least 12 percent chromium is required before the adsorbed layer or film is effective in reducing the corrosion rate of the metal.

220-12.8.2.3 Regardless of which theory proves correct, it is established that stainless steels exposed to water exhibit very low corrosion rates both at low temperatures and at the high temperatures encountered in steam plants. The corrosion rate of stainless steel in high temperature water, after a protective oxide film has formed on the metal surface, is less than 1 mg/dm^2 per month. The period required for formation of this protective film normally does not exceed a few thousand hours of exposure.

220-12.8.2.4 Stainless steels of various compositions have been prepared for a wide variety of general and specific applications. For the principal types of stainless steel used in steam plant applications, nickel and chromium are the major alloying elements added to the iron-base material. These steels usually contain about 18 percent chromium and 8 percent nickel (leaving an iron content of about 74 percent). As a result of their composition, these types of stainless steels are often called the 18-8 stainless steels. Other alloying and impurity elements usually found in the 18-8 stainless steels are cobalt, manganese, carbon, titanium, niobium, and molybdenum.

220-12.8.3 NICKEL-BASED ALLOYS. Certain of the nickel-based alloys also exhibit excellent corrosion resistance when exposed to high temperature water. One widely-used nickel-based alloy contains about 16 percent chromium, 7 percent iron, and trace impurity elements like cobalt. The remainder of the alloy is nickel (about 76 percent). This alloy is sometimes called Inconel (a trade name), although it is usually designated as NiCrFe alloy 600.

220-12.8.3.1 Like the stainless steels, NiCrFe alloy 600 exhibits outstanding corrosion resistance in high temperature water. After formation of a protective oxide film, the corrosion rate of this material in water is less than 1 mg/dm^2 per month. It takes a few thousand hours to form the protective film in high temperature water. The mechanisms by which NiCrFe alloy 600 corrodes in high temperature water are very similar to the mechanisms by which iron and steels corrode (with nickel substituted for iron). The presence of chromium in NiCrFe alloy 600 certainly **assists** in the formation of the passive oxide film which is responsible for the low rate of corrosion of this alloy.

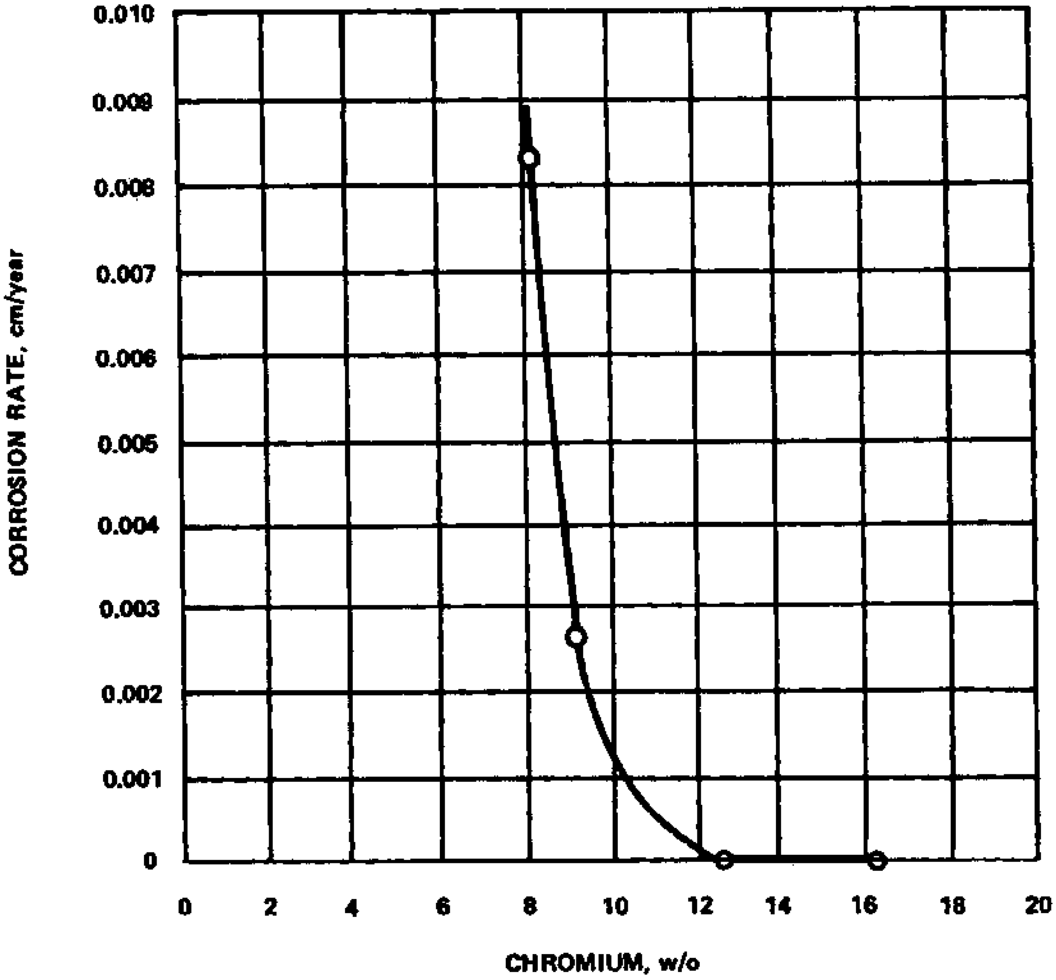


Figure 220-12-13 Effect of Chromium Content on the Corrosion Rate of Chromium-Iron Alloys

220-12.8.3.2 The principal advantage of NiCrFe alloy 600 in comparison to stainless steel is that NiCrFe alloy 600 is much less susceptible to chloride stress corrosion cracking than are the stainless steels (stress corrosion cracking is discussed in paragraphs 220-12.7.3 through 220-12.7.3.4.3). The principal disadvantage of NiCrFe alloy 600 in comparison with stainless steel is its higher cost.

220-12.8.3.3 Other alloys containing nickel find use in systems auxiliary to steam plants. For example, copper-nickel alloys (alloys of copper containing 10 to 30 percent nickel) exhibit excellent resistance to attack by aerated seawater (stainless steels and NiCrFe alloy 600 pit in an aerated seawater environment). Copper-nickel alloys also exhibit excellent corrosion resistance in stagnant or slowly moving seawater. Addition of 1 to 2 percent iron creates an alloy with resistance to corrosion in fast moving seawater. Monel (70 percent nickel and 30 percent copper) exhibits lower corrosion rates and better resistance to pitting in aerated seawater than do the alloys cited above so long as the seawater is moving. In stagnant seawater, Monel tends to pit. These alloys of copper and nickel are used extensively in seawater condensers and other auxiliary seawater cooling systems.

220-12.9 METHODS OF CORROSION CONTROL IN STEAM GENERATING SYSTEM

220-12.9.1 In those industrial water systems where corrosion represents a potential problem, it is common practice to adjust and control the chemical environment of the water in such a way as to minimize corrosion. This kind of approach is also followed in the water systems associated with a steam plant. In the paragraphs which follow, the principles employed in the control of the environment of the major water system associated with a naval steam plant and the steam generating system will be discussed. The type of water control employed to minimize corrosion in the boiler is based directly upon control methods developed and used in industrial boiler systems.

220-12.9.2 Data for this paragraph will be provided in a future change to this volume.

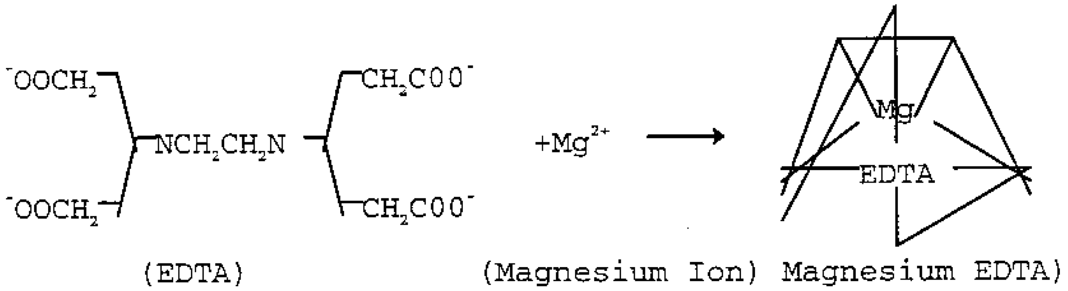
220-12.10 CHELANT BOILER FEEDWATER TREATMENT FOSSIL-FUELED STEAM PLANTS

220-12.10.1 GENERAL. A chelant boiler feedwater treatment was developed in the 1980’s for conventional fossil-fueled propulsion steam generators and implemented in the United States Navy during the 1990’s. The previous phosphate based treatment required frequent waterside cleanings because the phosphate chemistry produced sludge deposits that had to be removed to avoid tube boiler failures due to overheat. In addition, boilers experienced pitting on watersides as a result of oxygen corrosion particularly during lay-up periods. Chelant treatment avoids sludge deposits by formation of metal chelates that are kept in solution by tying up the metal contaminants so that they are unable to precipitate as scale on boiler heat transfer surfaces. For example, the trisodium salt of ethylenediaminetetracetic acid (EDTA) will react with an incoming scale former such as magnesium to form a soluable metal complex of chelate:

Na_3 EDTA + Magnesium (Mg) → MgEDTA (12-13)

(soluble) (soluble) (soluble)

As shown in the equation below the magnesium is completely surrounded (sequestered) and is unavailable to react further with other materials that might be present:



220-12.10.1.1 Hydrolysis. At high temperatures, the EDTA undergoes a reaction with water (hydrolysis) to form iminodiacetic (IDA), hydroxyethyliminodiacetic acid (HEIDA), and ethylene glycol as well as other minor products:

$EDTA + H_2\ O \rightarrow HEIDA + IDA$

$HEIDA + H_2\ O \rightarrow IDA + \text{ethylene glycol}$ (12-15)

Fortunately, IDA and HEIDA are chelating agents also, and scale forming metal contaminants will still be kept soluble. While steaming, soluble chelated metal accumulations are limited or controlled by continuous blowdown. To avoid corrosion, chelant treatment shall only be metered into feedwater at controlled rates while steaming as described in Volume Two and shall never be batch injected.

220-12.10.1.2 Oxygen Scavengers. In dilute solution, dissolved oxygen reacts with EDTA at elevated temperatures to render it completely ineffective. Therefore hot solutions of the chelant must be protected from exposure to oxygen. The chelant may be protected by use of oxygen scavengers such as sodium sulfite or hydrazine. Sodium sulfite reacts with oxygen at room temperature as shown below:

$2NaSO_2\ SO_3 + O_2 \rightarrow 4NA^+ + 2SO_{4-}$ (12-16)

Sodium Sulfite + Oxygen Sodium Sulfate

Sodium sulfite is being employed in waste heat boiler chelant treatment currently in development. Use of sodium sulfite is limited to low pressure boiler applications because of the generation of additional dissolved solids (sodium sulfate) and its tendency at high temperatures to decompose with formation of corrosive acidic products in the steam. At higher boiler temperatures, hydrazine is used as the oxygen scavenging component of chelant treatment:

$O_2 + N_2\ H_4 \rightarrow N_2 + 2H_2\ O$ (12-17)

Oxygen Hydrazine Nitrogen Water

Note that unlike sodium sulfite, additional solids are not generated when using hydrazine. The speed with which the reaction proceeds depends on the temperature, pH, hydrazine concentration and other factors. The higher any one of these is, the faster the reaction. When a catalyst is added to the hydrazine, reaction with oxygen can proceed even at room temperature. An organic catalyst is specified for the hydrazine in Chelant Treatment and boiler lay-up. Morpholine is added to the hydrazine to increase pH of the lay-up solution and thereby increase the speed of reaction with oxygen. High dissolved oxygen in feedwater must be avoided not only to prevent oxygen attack through pitting, but also to avoid loss of effectiveness of the dilute Chelant Treatment Solution. Because hydrazine is toxic, it must be handled carefully to avoid personnel exposure.

220-12.10.1.3 Metal Passivation. Hydrazine reduces metal oxides to more passive forms which act as a barrier against corrosion. For example, hydrazine will reduce rust (hematite) to magnetic iron oxide:

$6Fe_2O_3 + N_2H_4 \rightarrow 4Fe_3O_4 + 2H_2O + N_2$ (12-18)

Hematite Hydrazine Magnetite Water Nitrogen

It is interesting to note that EDTA promotes formation of protective magnetite films on boiler waterside surfaces even without hydrazine.

220-12.10.1.4 Volatility. Hydrazine will volatilize with the steam and undergo thermal decomposition at temperatures in the area of 600°F which are encountered in the superheater.

$3N_2H_4 \rightarrow 4NH_3 + N_2$ (12-19)

Hydrazine Ammonia Nitrogen

220-12.10.1.5 Supporting Chemistry. Disodium or trisodium phosphate is employed as part of the chelant treatment to serve as back-up in the event feedwater contamination is excessive. The phosphates will react with scale formers in the bulk boiler water rather than as scale on the tube metal surface. Excessive phosphate levels are to be avoided because phosphate competes with the chelants. For lay-up, morpholine is added to the catalyzed hydrazine to provide sufficient alkalinity. Continuous Chelant Treatment with continuous blowdown and conductivity monitoring allows significant decreases in workload:

a. Decreased batch sampling
b. Simplified control testing
c. Reduced bottom blowdown
d. Reduced waterside inspection and cleaning
e. Easier and more effective lay-up

220-12.10.2 POLYMER TREATMENT. Polymers are natural or synthetic compounds which can be composed of millions of repeatedly linked units, each a relatively light and simple molecule. Polymers are currently being considered as a means for enhancing boiler water treatment. The polymer acts as a dispersant by absorbing onto sludge particles and covering them with negative charges. The negatively charged sludge particles repel each other. This renders the particles nonadherent to each other and to boiler waterside surfaces. The dispersed sludge can then be readily removed by blowdown. Polymers can also act as scale control agents in that they inhibit scale crystal formation and growth which are important factors in sea water distiller treatment.

REAR SECTION

NOTE

TECHNICAL MANUAL DEFICIENCY/EVALUATION EVALUATION REPORT (TMDER) Forms can be found at the bottom of the CD list of books. Click on the TMDER form to display the form.