Practical Medical Chemistry

MODULE 1

THEME 1

CHEMICAL ELEMENTS. PERIODIC TABLE

Atoms, molecules and ions

Chemistry is the study of matter, its composition, structure and properties, and the chemical changes it undergoes.

Matter is anything that occupies space and has mass.

A substance is a form of matter that has a definite (constant) composition and distinct properties. Examples are water, ammonia, sugar, gold, oxygen, and etc.

Substances can be either elements or compounds. *An element* is a substance that cannot be separated into simpler substances by chemical means.

The symbols of some elements are derived from their Latin names – for example, Au from aurum (gold), Fe from ferrum (iron), and Na from natrium (sodium) – whereas most of them come from their English names.

On the basis of atomic theory, we can define *an atom* as the basic unit of an element that can enter into chemical combination.

Atoms actually possess *internal structure*; that is, they are made up of electrons, protons, and neutrons. The protons and neutrons of an atom are packed in an extremely small nucleus. Electrons are as «clouds» around the nucleus. The properties of these subatomic particles are summarized in Table 1.1 .

The *atomic number* is the number of protons in the nucleus of each atom of an element. As atom is a neutral particle the number of protons is equal to the number of electrons, so the atomic number also shows the number of electrons in the atom.

The chemical identity of an atom can be determined solely from its atomic number. For example, the atomic number of oxygen is 8. This means that each oxygen atom has 8 protons and 8 electrons so each atom in the universe that contains 8 protons is oxygen.

The *mass number* of an atom is the total number of neutrons and protons present in the nucleus of an atom of an element. The *number of neutrons* in an atom is equal to the difference between the mass number and the atomic number. If we have oxygen atom for which mass number is 16, this means the atom has 8 neutrons.

Table 1.1. Masses and charges of the basic subatomic particles

Particle	Charge	Charge (Coulombs)	Mass (atomic units)	Mass (grams)
Electron ($\bar{e}$)	–1	-1.6022×10^{-19}	5.4×10^{-4}	9.1095×10^{-28}
Proton (*p*)	+1	$+1.6022\times10^{-19}$	1	1.6725×10^{-24}
Neutron (*n*)	0	0	1	1.6750×10^{-24}

Most elements have two or more isotopes. Isotopes are atoms that have the same atomic number but different mass numbers. For example, there are three isotopes of hydrogen, called hydrogen (or protium), deuterium, and tritium. Hydrogen nucleus has one proton and no neutrons, deuterium has one proton and one neutron, and tritium has one proton and two neutrons.

A *molecule* is an aggregate of at least two atoms in a definite arrangement held together by chemical forces (also called chemical bonds). A molecule may contain atoms of the same element or atoms of two or more elements joined in a fixed ratio.

An *ion* is an atom or a group of atoms that has a net positive or negative charge. The number of positively charged protons in the nucleus of an atom remains the same during ordinary chemical changes (called chemical reactions), but negatively charged electrons may be lost or gained. The loss of one or more electrons from a neutral atom results in a *cation*, an ion with a net positive charge. The acceptance of electron(s) by an atom results in an *anion*, a particle with a net negative charge.

Periodic law and periodic table

Recognition of periodic regularities in physical and chemical behavior and the need to organize the large volume of available information about the structure and properties of elemental substances led to the development of the periodic law by Russian chemist D. I. Mendeleev.

The modern formulation of *periodic law* states that the physical and chemical properties of elements are periodic functions of their atomic numbers. It is important to remember that the periodic table of elements was organized by Mendeleev according to increasing atomic weights, but not by nuclear charge.

Visual expression of the periodic law is the periodic table – a chart in which elements having similar chemical and physical properties are grouped together. The periodic table is a handy tool that correlates the properties of the elements in a systematic way and helps us to make predictions about chemical behavior.

The modern periodic table is presented below. In the periodic table the elements are arranged by atomic number (shown above the element symbol) in horizontal rows called *periods* and in vertical columns known as *groups* or *families*, according to similarities in their chemical properties. All elements can be divided into three categories – *metals*, *nonmetals*, and *metalloids*. Elements are often referred to collectively by their periodic table group number (Group 1, Group 2, and so on). However, for convenience, some element groups have been given special names. The Group 1 of the elements (Li, Na, K, Rb, Cs, and Fr) are called *alkali metals*, and the Group 2 elements (Be, Mg, Ca, Sr, Ba, and Ra) are called *alkaline earth metals*. Elements in Group 17 (F, Cl, Br, I, and At) are known as *halogens*, and elements in Group 18 (He, Ne, Ar, Kr, Xe, and Rn) are called *noble gases* (or *rare gases*).

IUPAC Periodic Table of the Elements

Key:

atomic number
Symbol
name
conventional atomic weight
standard atomic weight

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** hydrogen 1.008 [1.0078, 1.0082]																	2 **He** helium 4.0026
3 **Li** lithium 6.94 [6.938, 6.997]	4 **Be** beryllium 9.0122											5 **B** boron 10.81 [10.806, 10.821]	6 **C** carbon 12.011 [12.009, 12.012]	7 **N** nitrogen 14.007 [14.006, 14.008]	8 **O** oxygen 15.999 [15.999, 16.000]	9 **F** fluorine 18.998	10 **Ne** neon 20.180
11 **Na** sodium 22.990	12 **Mg** magnesium 24.305 [24.304, 24.307]											13 **Al** aluminium 26.982	14 **Si** silicon 28.085 [28.084, 28.086]	15 **P** phosphorus 30.974	16 **S** sulfur 32.06 [32.059, 32.076]	17 **Cl** chlorine 35.45 [35.446, 35.457]	18 **Ar** argon 39.948
19 **K** potassium 39.098	20 **Ca** calcium 40.078(4)	21 **Sc** scandium 44.956	22 **Ti** titanium 47.867	23 **V** vanadium 50.942	24 **Cr** chromium 51.996	25 **Mn** manganese 54.938	26 **Fe** iron 55.845(2)	27 **Co** cobalt 58.933	28 **Ni** nickel 58.693	29 **Cu** copper 63.546(3)	30 **Zn** zinc 65.38(2)	31 **Ga** gallium 69.723	32 **Ge** germanium 72.630(8)	33 **As** arsenic 74.922	34 **Se** selenium 78.971(8)	35 **Br** bromine 79.904 [79.901, 79.907]	36 **Kr** krypton 83.798(2)
37 **Rb** rubidium 85.468	38 **Sr** strontium 87.62	39 **Y** yttrium 88.906	40 **Zr** zirconium 91.224(2)	41 **Nb** niobium 92.906	42 **Mo** molybdenum 95.95	43 **Tc** technetium	44 **Ru** ruthenium 101.07(2)	45 **Rh** rhodium 102.91	46 **Pd** palladium 106.42	47 **Ag** silver 107.87	48 **Cd** cadmium 112.41	49 **In** indium 114.82	50 **Sn** tin 118.71	51 **Sb** antimony 121.76	52 **Te** tellurium 127.60(3)	53 **I** iodine 126.90	54 **Xe** xenon 131.29
55 **Cs** caesium 132.91	56 **Ba** barium 137.33	57-71 lanthanoids	72 **Hf** hafnium 178.49(2)	73 **Ta** tantalum 180.95	74 **W** tungsten 183.84	75 **Re** rhenium 186.21	76 **Os** osmium 190.23(3)	77 **Ir** iridium 192.22	78 **Pt** platinum 195.08	79 **Au** gold 196.97	80 **Hg** mercury 200.59	81 **Tl** thallium 204.38 [204.38, 204.39]	82 **Pb** lead 207.2	83 **Bi** bismuth 208.98	84 **Po** polonium	85 **At** astatine	86 **Rn** radon
87 **Fr** francium	88 **Ra** radium	89-103 actinoids	104 **Rf** rutherfordium	105 **Db** dubnium	106 **Sg** seaborgium	107 **Bh** bohrium	108 **Hs** hassium	109 **Mt** meitnerium	110 **Ds** darmstadtium	111 **Rg** roentgenium	112 **Cn** copernicium	113 **Nh** nihonium	114 **Fl** flerovium	115 **Mc** moscovium	116 **Lv** livermorium	117 **Ts** tennessine	118 **Og** oganesson

57 **La** lanthanum 138.91	58 **Ce** cerium 140.12	59 **Pr** praseodymium 140.91	60 **Nd** neodymium 144.24	61 **Pm** promethium	62 **Sm** samarium 150.36(2)	63 **Eu** europium 151.96	64 **Gd** gadolinium 157.25(3)	65 **Tb** terbium 158.93	66 **Dy** dysprosium 162.50	67 **Ho** holmium 164.93	68 **Er** erbium 167.26	69 **Tm** thulium 168.93	70 **Yb** ytterbium 173.05	71 **Lu** lutetium 174.97
89 **Ac** actinium	90 **Th** thorium 232.04	91 **Pa** protactinium 231.04	92 **U** uranium 238.03	93 **Np** neptunium	94 **Pu** plutonium	95 **Am** americium	96 **Cm** curium	97 **Bk** berkelium	98 **Cf** californium	99 **Es** einsteinium	100 **Fm** fermium	101 **Md** mendelevium	102 **No** nobelium	103 **Lr** lawrencium

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For notes and updates to this table, see www.iupac.org. This version is dated 28 November 2016.

Valence electrons and chemical properties of the elements

The chemical reactivity of the elements is largely determined by their *valence electrons*, which are the outermost electrons. For the representative elements, the valence electrons are those in the highest occupied shell. All nonvalence electrons in an atom are referred to as core electrons. Looking at the electron configurations of the representative elements, a clear pattern emerges: all the elements in a given group of the periodic table have the same number and type of valence electrons. The similarity of the valence electron configurations is what makes the elements in the same group resemble one another in chemical behavior. Thus, for instance, all the alkali metals have the valence electron configuration of ns^1 and they all tend to lose one electron to form the unipositive cations. Similarly, the alkaline earth metals (the Group 2 of the elements) all have the valence electron configuration of ns^2, and they all tend to lose two electrons to form the dipositive cations. As a group, the noble gases behave very similarly. Helium and neon are chemically inert, and there are few examples of compounds formed by the other noble gases. This lack of chemical reactivity is due to the completely filled *ns* and *np* subshells, a condition that often correlates with great stability. Although the valence electron configuration of the transition metals is not always the same within a group and there is no regular pattern in the change of the electron configuration from one metal to the next in the same period, all transition metals share many characteristics that set them apart from other elements. The reason is that these metals all have an incompletely filled *d* subshell. Likewise, the lanthanide (and the actinide) elements resemble one another because they have incompletely filled *f* subshells.

Three important atomic properties

A biological role of an element is a consequence of its *electronic structure*. We now need to understand how electronic structure affects atomic and ionic radii, and the thermodynamic ability of an atom to release or acquire electrons to form ions or chemical bonds.

Three important atomic properties are the atomic and ionic radii, the ionization energy, the electron affinity.

These properties are of great significance in chemistry and biology, for they are controls on the number and types of chemical bonds the atom can form.

The atomic and ionic radii. The atomic radius of an element is half the distance between the centers of neighboring atoms in a solid (such as Cu) or, for nonmetals, in a homonuclear molecule (such as H_2 or S_8). If there is one single attribute of an element that determines its chemical properties (either directly, or indirectly through the variation of other properties), then it is atomic radius.

In general, atomic radii decrease from left to right across a period and increase down each group.

The ionic radius of an element is its share of the distance between neighboring ions in an ionic solid. That is, the distance between the centers of a neighboring cation and anion is the sum of the two ionic radii.

Table 1.2. lists the radii of some ions that play important roles in biochemical processes.

Table 1.2. Atomic radii and main biochemical function

Ion	r/pm[*]	Main biochemical function
Mg^{2+}	72	Binds to ATP, constituent of chlorophyll, control of protein folding and muscle contraction
Ca^{2+}	100	Component of bone and teeth, control of protein folding, hormonal action, blood clotting, and cell division
Na^+	102	Control of osmotic pressure, charge balance, and membrane potentials
K^+	138	
Cl^-	167	

The ionization energy. The minimum energy necessary to remove an electron from a many-electron atom is its *first ionization energy*, I_1. *The second ionization* energy, I_2, is the minimum energy needed to remove a second electron (from the singly charged cation).

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[*] 1 picometer (pm) = $1 \cdot 10^{-12}$ m

The ionization energy of an element plays a central role in determining the ability of its atoms to participate in bond formation. After atomic radius, it is the most important property for determining an element's chemical characteristics.

The electron affinity. *The electron affinity*, E_{ea}, is the difference in energy between a neutral atom in the gaseous state and its anion. It is the energy released in the process:

$$X(g) + \bar{e}(g) \rightarrow X^{-}(g), \quad E_{ea} = E(X) - E(X^{-}).$$

The electron affinity is positive if the anion has a lower energy than the neutral atom.

Further analysis of ionization energies and electron affinities can begin to tell us *why carbon is an essential building block of complex biological structures*.

Among the elements in Period 2, carbon has *intermediate values of the ionization energy and electron affinity*, so it can share electrons (that is, form covalent bonds) with many other elements, such as H, N, O, S, and, more importantly, other C atoms.

As a consequence, such networks as long carbon–carbon chains (as in lipids) and chains of peptide links can form readily. Because the ionization energy and electron affinity of C are neither too high nor too low, the bonds in these covalent networks are neither too strong nor too weak.

As a result, biological molecules are sufficiently stable to form viable organisms but are still susceptible to dissociation (essential to catabolism) and rearrangement (essential to anabolism).

Bioelements

Chemical elements can be classified according to an importance for human and animal organisms as *organogenic* and *biogenic*.

Organogenic elements compose 97.5 mass% from total mass of human organism, i.e. O (62.4 %), C (21.0 %), H (9.7 %), N (3.1 %), P (0.95 %), S (0.16 %).

Biogenic elements can be classified as following.

I. Chemical elements essential to life forms can be broken down into four major categories:

1) bulk elements (H, C, N, O, P, S);

2) macrominerals (Na, K, Mg, Ca, Cl);

3) trace elements (Fe, Zn, Cu);

4) ultratrace elements, comprised of nonmetals (F, I, Se, Si, As, B) and metals (Mn, Mo, Co, Cr, V, Ni, Cd, Sn, Pb, Li).

II. Biological essentiality of these elements has been defined by certain criteria:

1) a physiological deficiency appears when the element is removed from the diet;

2) the deficiency is relieved by the addition of that element to the diet;

3) a specific biological function is associated with the element.

Bioelements can be divided for physiological processes as following:

1) elements for physiological processes in bioliquids (C, H, O, N, P, Cl, K, Na, Ca, Mg);

2) elements for metabolism (Fe, Zn, Cu, Mo, Co, I). Of special interest are the trace elements, such as iron (Fe), copper (Cu), zinc (Zn), iodine (I), and cobalt (Co), which together make up about 0.1 % of the body's mass. These elements are necessary for biological functions such as growth, transport of oxygen for metabolism, and defense against disease. There is a delicate balance in the amounts of these elements in our bodies. Too much or too little over an extended period of time can lead to serious illness, retardation, or even death;

3) elements decreasing generation and growth of microorganisms (As, Sb, Ag);

4) elements for regulation of redox reactions (Mn, Cu, Cr).

THEME 2
PROPERTIES AND QUALITATIVE REACTIONS OF SOME IMPORTANT IONS

Qualitative analysis consists of methods for establishing the qualitative chemical composition of a substance – that is, the identification of atoms, ions, and molecules that present in the substance being analyzed. The most important characteristics of all methods of qualitative analysis are *specificity* and *sensitivity*. *Specificity* characterizes the ability to detect the presence of an unknown element in the presence of other elements – for example, iron in the presence of nickel, manganese, chromium, vanadium or silicon. *Sensitivity* is defined as the smallest quantity of an element that can be detected by a given method.

Reaction of the cations. For the purpose of systematic qualitative analysis, cations are classified into five groups on the basis of their behaviour against some reagents. The group reagents used for the classification of most common cations are hydrochloric acid, hydrogen sulphide, ammonium sulphide, and ammonium carbonate. Classification is based on whether a cation reacts with these reagents by the formation of precipitates or not. It can therefore be said that classification of the most common cations is based on the differences of solubilities of their chlorides, sulphides, and carbonates.

The five groups of cations and the characteristics of these groups are as followsю

Group I. Cations of this group form precipitates with dilute hydrochloric acid. Ions of this group are lead, mercury (I), and silver.

Group II. The cations of this group do not react with hydrochloric acid, but form precipitates with hydrogen sulphide in dilute mineral acid medium. Ions of this group are mercury (II), copper, bismuth, cadmium, arsenic (III), arsenic (V), antimony (III), antimony (V), tin (II), and tin (III) and tin (IV). The first four form the sub-group IIa and the last six the sub-group IIb. While sulphides of cations in Group IIa are insoluble in ammonium polysulphide, those of cations in Group IIb are soluble.

Group III. Cations of this group do not react either with dilute hydrochloric acid, or with hydrogen sulphide in dilute mineral acid medium. However, they form precipitates with ammonium sulphide in neutral or ammoniac medium. Cations of this group are cobalt (II), nickel (II), iron (II), iron (III), chromium (III), aluminium, zinc, and manganese (II).

Group IV. Cations of this group do not react with the reagents of Groups I, II, and III. They form precipitates with ammonium carbonate in the presence of ammonium chloride in neutral or slightly acidic medium. Cations of this group are: calcium, strontium, and barium.

Group V. Common cations, which do not react with reagents of the previous groups, form the last group of cations, which include magnesium, sodium, potassium, ammonium, lithium, and hydrogen ions.

Reaction of the anions. The methods available for the detection of anions are not as systematic as those which have been described for the cations. Essentially the processes employed may be divided into (A) those involving the identification by volatile products obtained on treatment with acids, and (B) those dependent upon reactions in solution. Class (A) is subdivided into (i) gases evolved with dilute hydrochloric acid or dilute sulphuric acid, and (ii) gases or vapours evolved with concentrated sulphuric acid. Class (B) is subdivided into (i) precipitation reactions, and (ii) oxidation and reduction in solution.

Class (A). (i) Gases evolved with dilute hydrochloric acid or dilute sulphuric acid: carbonate, hydrogen carbonate, sulphite, thiosulphate, sulphide, nitrite, hypochlorite, cyanide, and cyanate. (ii) Gases or acid vapours evolved with concentrated sulphuric acid. These include those of (i) with the addition of the following: fluoride, chloride, bromide, iodide, nitrate, chlorate, perchlorate, permanganate, bromate, borate, hexacyanoferrate (II), hexacyanoferrate (III), thiocyanate, formate, acetate, oxalate, tartrate, and citrate.

Class (B). (i) Precipitation reactions. Sulphate, peroxodisulphate, phosphate, hypophosphite, arsenate, arsenite, chromate, dichromate, silicate, hexafluorosilicate, salicylate, benzoate, and succinate. (ii) Oxidation and reduction in solution. Manganate, permanganate, chromate, and dichromate.

Problems

Examples

Problem 1. Give the number of protons, neutrons, and electrons in each of the following species: (a) $^{20}_{11}\text{Na}$, (b) $^{22}_{11}\text{Na}$, (c) ^{17}O, and (d) carbon-14.

Solution. Recall that the superscript denotes the mass number (*A*) and the subscript denotes the atomic number (*Z*). Mass number is always greater than atomic number. (The only exception is $^{1}_{1}\text{H}$, where the mass number is equal to the atomic number.) In a case where no subscript is shown, as in parts (c) and (d), the atomic number can be deduced from the element symbol or name. To determine the number of electrons, remember that because atoms are electrically neutral, the number of electrons is equal to the number of protons.

(a) The atomic number is 11, so there are 11 protons. The mass number is 20, so the number of neutrons is 20 – 11 = 9. The number of electrons is the same as the number of protons; that is, 11.

(b) The atomic number is the same as that in (a), or 11. The mass number is 22, so the number of neutrons is 22 – 11 = 11. The number of electrons is 11. Note that the species in (a) and (b) are chemically similar isotopes of sodium.

(c) The atomic number of O (oxygen) is 8, so there are 8 protons. The mass number is 17, so there are 17 – 8 = 9 neutrons. There are 8 electrons.

(d) Carbon–14 can also be represented as ^{14}C. The atomic number of carbon is 6, so there are 14 – 6 = 8 neutrons. The number of electrons is 6.

Problem 2. Assign oxidation numbers to all the elements in the following compounds: (a) Li_2O, (b) HNO_3.

Solution. In general, we follow the rules for assigning oxidation numbers. Remember that all alkali metals have an oxidation number of +1, and in most cases hydrogen has an oxidation number of +1 and oxygen has an oxidation number of –2 in their compounds.

(a) Lithium has an oxidation number of +1 (Li^{+}), and oxygen's oxidation number is –2 (O^{2-}).

(b) This is the formula for nitric acid, which yields a H^{+} ion and a NO_3^{-} ion in solution. We see that H has an oxidation number of +1. Thus the other group (the nitrate ion) must have a net oxidation number of –1. Oxygen has an oxidation number of –2, and if we use x to represent the oxidation number of nitrogen, then the nitrate ion can be written as:

$$[N^{(x)}O_3^{(2-)}]^-$$

so that

$$x + 3\times(-2) = -1$$

or

$$x = +5.$$

Problem 3. Heavy water or deuterium oxide is a form of water that contains the hydrogen isotope deuterium. The atomic nucleus of deuterium consists of one proton and one neutron. What is the molecular mass of the heavy water?

Solution. To calculate the molecular mass it is required to add together the atomic masses of the constituent atoms. The mass of the deuterium atom is 2 atomic mass units (a.m.u.) because it built of two subatomic particles with mass of 1 a.m.u.

Molecular mass of heavy water equals: (1 × atomic mass of oxygen) + (2 × atomic mass of the heavy hydrogen) = 16 + 2×2 = 20 a.m.u.

Problems for self-solving

1. For each of the following atoms $^{4}_{2}He$ and $^{24}_{12}Mg$ determine the number of electrons, the number of protons and neutrons in the nucleus.

2. Use the periodic table and indicate the group (alkali metals, alkaline earth metals, halogens, noble gases) for the elements Kr, Cl, Ca, Rb.

3. The electronic configuration of a neutral atom is $1s^22s^22p^63s^23p^2$. Name the element. Write the number of valence s- and p-electrons of the atom. Is this element metal or nonmetal?

4. Show the electronic configuration of an atom(s) that represents chemical properties similar to magnesium with configuration $1s^22s^22p^63s^2$. Name this element(s).

(a) $1s^22s^22p^3$; (b) $1s^22s^2$; (c) $1s^22s^22p^63s^1$; (d) $1s^22s^22p^63s^23p^64s^2$;

(e) $1s^22s^22p^63s^23p^63d^24s^2$.

5. Determine and indicate the oxidation numbers for the nitrogen atoms in the following molecules and ions: N_2O (nitrous oxide), NH_3 (ammonia), NO_3^- (nitrate ion), NO_2^- (nitrite ion).

6. Write down the electronic configurations of the following particles: (a) chlorine atom; (b) chloride ion Cl^-; (c) chlorine atom in the state with oxidation number +1; (d) helium atom; (e) neon atom; Cu^{2+} ion.

7. Determine and indicate the oxidation numbers for the sulfur atoms in the following molecules and ions: H_2S (hydrogen sulfide), SO_4^{2-} (sulfate ion), SO_3^{2-} (sulfite ion).

8. Determine and indicate the oxidation numbers for the chlorine atom in the following family of its oxoanions: ClO_4^- (perchlorate), ClO_3^- (chlorate), ClO_2^- (chlorite), ClO^- (hypochlorite).

9. Calculate the molecular mass of the following organic compounds: (a) methane, CH_4; (b) ethanol, C_2H_5OH, (c) glycine, NH_2CH_2COOH; (d) sucrose, $C_{12}H_{22}O_{11}$.

10. For each of the following series determine which element represents nonmetal, metal, and metalloid. (a) Ca, Co, Si; (b) Fe, Mg, B; (c) Br, Ba, Pt; (d) Ag, Na, Se; (e) Li, Cr, As.

Problems

Examples

Problem 1. Write the ground-state electron configurations for sulfur atom.

Solution. How many electrons are in the S ($Z = 16$) atom? We start with $n = 1$ and proceed to fill orbitals. For each value of l, we assign the possible values of m_l. We can place electrons in the orbitals according to the Pauli exclusion principle and Hund's rule and then write the electron configuration. The task is simplified if we use the noble-gas core preceding S for the inner electrons.

Sulfur has 16 electrons. The noble gas core in this case is [Ne]. (Ne is the noble gas in the period preceding sulfur.) [Ne] represents $1s^22s^22p^6$. This leaves us 6 electrons to fill the 3*s* subshell and partially fill the 3*p* subshell. Thus, the electron configuration of S is $1s^22s^22p^63s^23p^4$ or $[Ne]3s^23p^4$.

Problem 2. Write the formula of magnesium nitride, containing the Mg^{2+} and N^{3-} ions.

Solution. Our guide for writing formulas for ionic compounds is electrical neutrality; that is, the total charge on the cation(s) must be equal to the total charge on the anion(s). Because the charges on the Mg^{2+} and N^{3-} ions are not equal, we know the formula cannot be MgN. Instead, we write the formula as Mg_xN_y, where x and y are subscripts to be determined. To satisfy electrical neutrality, the following relationship must hold

$$(+2)x + (-3)y = 0.$$

Solving, we obtain $x/y = 3/2$. Setting $x = 3$ and $y = 2$, we write Mg_3N_2.

Problem 3. The atomic masses of the two stable isotopes of copper equal 63 a.m.u. and 65 a.m.u. The molar fractions of these isotopes in the nature are 69.17 % and 30.83 %, respectively. Calculate the average atomic mass of copper.

Solution. The contribution of each isotope to the average atomic mass bases on its relative abundance. The multiplying the mass of each isotope by its fractional abundance gives its constituent to the average atomic mass. The average atomic mass of the natural mixture of copper isotopes equals the sum of these contributions:

$$\text{Average mass} = 0.6917 \times 63 + 0.3083 \times 65 = 63.62 \text{ a.m.u.}$$

Problems for self-solving

1. How many electrons are present in each of the following atoms? Assuming that each is a neutral atom, identify the element.

(a) $1s^2 2s^2 2p^6 3s^2$

(b) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$

2. Write electronic configuration of Zn.

3. What are typical chemical properties of transition metals?

4. Write electronic configuration of Mn^{2+} ion.

5. Identify the element from the following partial configuration of neutral atom: $4s^2 3d^2$.

6. Write the formula of potassium bromide, zinc iodide, aluminum oxide, manganese oxide (containing the Mn^{3+} ion), magnesium phosphate, iron sulfide (containing the Fe^{2+} ion), cobalt sulfate (containing the Co^{3+}).

7. Name the following compounds: (a) Na_2CrO_4, (b) K_2HPO_4, (c) HBr (gas), (d) HBr (in water), (e) Li_2CO_3, (f) $K_2Cr_2O_7$, (g) NH_4NO_2, (h) PF_3, (i) PF_5, (j) P_4O_6, (k) CdI_2, (l) $SrSO_4$, (m) $Al(OH)_3$, (n) Na_2CO_3.

8. Write chemical names of the oxoanions formed by: (a) chlorine: ClO_4^-, ClO_3^-, ClO_2^-, ClO^-; (b) sulfur: SO_3^{2-}, SO_4^{2-}.

9. Chlorine is the most abundant halogen in Earth's crust. There are two principal stable chlorine isotopes: ^{35}Cl and ^{37}Cl, their molar fractions in the natural mixture are 75.78 % and 24.22 %, respectively. Calculate the average atomic mass of the natural chlorine. *Answer: average mass = 35.48 a.m.u.*

10. The most abundant of the naturally occurring isotopes of antimony are Sb-121 and Sb-123, and the average atomic mass of antimony is 121.760 a.m.u. Exact atomic masses of these isotopes are 120.904 and 122.904. Calculate the isotopic composition of the natural antimony. *Answer:* ^{121}*Sb fraction is 57.2 %, and* ^{123}*Sb is 42.8 %.*

THEME 3

CHEMICAL BONDING

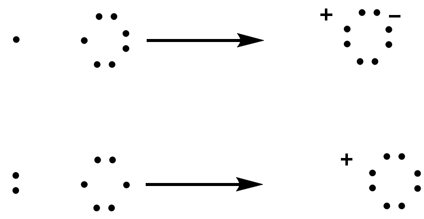
Chemical bond

Atoms of most elements can interact with one another to form compounds. The forces that hold these atoms together in compounds are called *chemical bonds*. When atoms interact to form a chemical bond, only their outer electronic shells are in contact. For this reason, when we study chemical bonding, we are concerned with the valence electrons of the atoms.

In general, the bonding of the atoms lowers the potential energy of the reacting particles. As the electron configuration and the strength of the nucleus-electron attraction determine the properties of an atom, the type and strength of chemical bonds determine the properties of a forming substance.

Ionic bond

An *ionic bond* is the electrostatic force that holds ions together in an ionic compound. Consider, for example, the reaction between lithium and fluorine to form lithium fluoride. The electronic configuration of lithium is $1s^22s^1$, and that of fluorine is $1s^22s^22p^5$. When lithium and fluorine atoms come in contact with each other, the outer $2s^1$ valence electron of lithium is transferred to the fluorine atom. After this process the ions with stable electronic configurations are formed. The lithium cation (Li^+) has electronic configuration like helium atom, $1s^2$; the fluorine anion (F^-) – like neon, $1s^22s^22p^6$. The ionic bond in LiF is formed by the electrostatic attraction between the positively charged lithium ion and the negatively charged fluoride ion. The compound itself is electrically neutral.



Ionic bonding occurs between elements when the energy required to remove the outer shell electrons (the ionization energy) of one of reacting elements is relatively low. Elements with such low ionization energies are metals. Therefore, compounds containing a metal tend to be ionic. Non-metals generally contain more than three electrons in the outer shells of their atoms and have high tendency to accept electrons from another atoms. Consequently substances formed by typical metals and nonmetals are ionic.

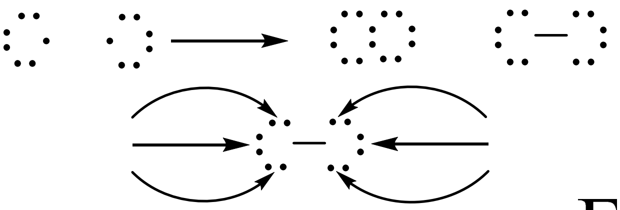
In the formation of an ionic compound such as LiF or CaO, it is not only the electron transfer leads to formation of a stable substance. Much more energy lowering value corresponds to the process of interaction of the gaseous ions giving a crystalline solid. The *lattice energy* is defined as *the energy needed to separate the ions in one mole of a solid substance to give a gaseous ions*. For example, this value for NaF equals 910 kJ/mol, for NaCl: 788 kJ/mol, for CsI: 613 kJ/mol. The lattice energy indicates the strength of ionic interactions, which influences melting point, hardness, solubility, and other properties of ionic crystalls.

Covalent bond

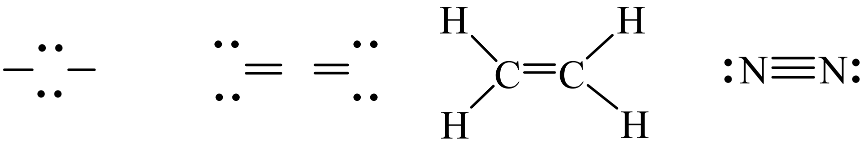
When two or more non-metals combine their atoms have to share electrons forming common electronic pair and achieving the stable electronic configuration of a noble gas. This type of bonding is called *covalent bonding*. So, in this type of chemical bond two electrons are shared by two atoms. Covalent compounds are substances that contain only covalent bonds. For the simplicity, the shared pair of electrons is often represented in the molecule by a single line. Thus, the covalent bond in the hydrogen molecule can be written as H–H, in hydrogen chloride molecule as H–Cl.

In a covalent bond, each electron in a shared pair is attracted to the nuclei of both atoms. This attraction holds the two atoms in the molecule together and is responsible for the formation of covalent bonds in other molecules. Covalent bonding between many-electron atoms involves only the valence electrons.

Consider, for example, the fluorine molecule, F_2. The electron configuration of F atom is $1s^22s^22p^5$. The $1s$ electrons are low in energy and stay near the nucleus most of the time. For this reason they do not participate in bond formation. Thus, each F atom has seven valence electrons (the $2s$ and $2p$ electrons), but there is only one unpaired electron on F, so the formation of the F_2 molecule can be represented as coupling and sharing of these electrons. Note, that only two valence electrons participate in the formation of F_2. The other, nonbonding electrons, are called *lone pairs* – pairs of valence electrons that are not involved in covalent bond formation. Thus, each F atom in F_2 molecule has three lone pairs of electrons.



If two atoms are held together by one electron pair, the bond is called a *single* bond. Sometimes, more than one pair of electrons is shared. Consider, for example, oxygen gas molecule, O_2. Here, each oxygen shares two pairs of electrons to achieve the electron configuration of neon. The structural formula of oxygen molecule is written as O = O. If two atoms share two pairs of electrons, the covalent bond is called a *double* bond. Double bonds exist in molecules of carbon dioxide and ethylene. In a molecular structure, where three pairs of electrons are shared, the bond is called a *triple* bond, for example in nitrogen molecule, N_2.



The formation of these molecules illustrates the *octet rule*: *an atom of s- and p-elements (other than hydrogen) tends to form bonds until it is surrounded by eight valence electrons*. In other words, a covalent bond forms when there are not enough electrons for each individual atom to have a complete octet. By sharing electrons in a covalent bond, the individual atoms can complete their octets. The requirement for hydrogen is that it attain the electronic configuration of helium, or a total of two electrons.

Multiple bonds are shorter than single covalent bonds. *Bond length* is defined as the distance between the nuclei of two covalently bonded atoms in a molecule. For a given pair of atoms, such as carbon and nitrogen, triple bonds are shorter than double bonds, which, in turn, are shorter than single bonds. The shorter multiple bonds are also more stable than single bonds.

For the predicting whether compounds are ionic or covalent we use general rule:

metal + non-metal → ionic bonding,

non-metal + non-metal → covalent bonding.

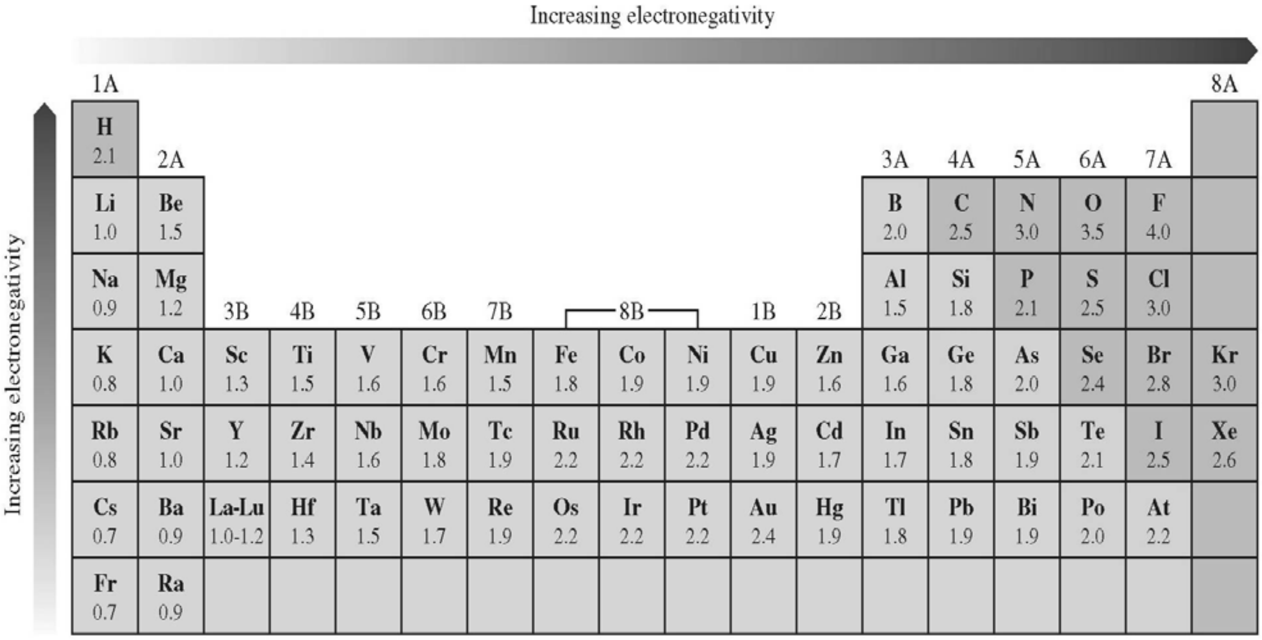
Oxidation number (oxidation state) refers to the number of charges an atom would have, if electrons were transferred completely to the more electronegative of the bonded atoms in a molecule.

Electronegativity of the elements and the type of the bond

A covalent bond is formed due to sharing of an electron pair by two atoms. In a molecule like H_2, in which the atoms are identical, the electrons to be equally attracted by two hydrogen nucleus. However, if we have the covalently bonded HF molecule, the H and F atoms do not share the bonding electrons equally, because H and F atoms are characterized by different ability to attract electrons. The bond in HF is called a *polar covalent bond*, because the electrons are shifted in the vicinity of the fluorine atom. This «unequal sharing» of the bonding electron pair results in a relatively greater electron density near the fluorine atom and a correspondingly lower electron density near hydrogen. The HF bond and other polar bonds can be thought of as being intermediate between a nonpolar covalent bond, in which the sharing of electrons is exactly equal, and an ionic bond, in which the transfer of the electrons is nearly complete.

A property of atoms that helps us distinguish a nonpolar covalent bond from a polar covalent bond is *electronegativity*, the ability of an atom to attract toward itself the electrons in a chemical bond. Elements with high electronegativity have a greater tendency to attract electrons than do elements with low electronegativity. Thus, an atom such as fluorine, which has a high electron affinity (tends to pick up electrons easily) and a high ionization energy (does not lose electrons easily), has a high electronegativity. On the other hand, sodium has a low electron affinity, a low ionization energy, and a low electronegativity.

Electronegativity is a relative value, showing that an element's electronegativity can be measured only in relation to the electronegativity of other elements. L. Pauling proposed a method for calculating relative electronegativities of most elements. These values are shown below. A careful examination of this table reveals trends and relationships among electronegativity values of different elements. In general, electronegativity increases from left to right across a period in the periodic table, as the metallic character of the elements decreases. Within each group, electronegativity decreases with increasing atomic number, and increasing metallic character. Note, that the transition metals do not follow these trends. The most electronegative elements – the halogens, oxygen, nitrogen, and sulfur – are placed in the upper right-hand corner of the periodic table, and the least electronegative elements (the alkali and alkaline earth metals) are located near the lower left-hand corner.



1A	2A	3B	4B	5B	6B	7B	8B			1B	2B	3A	4A	5A	6A	7A	8A
H 2.1																	
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr 3.0
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe 2.6
Cs 0.7	Ba 0.9	La-Lu 1.0-1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.2	
Fr 0.7	Ra 0.9																

Atoms of elements with widely different electronegativities tend to form ionic bonds (such as KCl and CaO, etc.) with each other, because the atom of the less electronegative element gives up its electron(s) to the atom of the more electronegative element. An ionic bond generally joins an atom of a metallic element and an atom of a nonmetallic element. Atoms of elements with comparable electronegativities tend to form polar covalent bonds with each other, because the shift in electron density is relatively small. Most covalent bonds involve atoms of nonmetallic elements. Only atoms of the same elements, which have the same electronegativity, can be joined by a pure covalent bond (*non-polar*).

There is no sharp distinction between a polar covalent bond and an ionic bond, but the following general rule is helpful in distinguishing between them: an ionic bond forms when the electronegativity difference between the two bonding atoms is 1.7 or more.

Coordination compounds

Coordination compounds (also called *complexes*) are substances that contain at least one *complex ion or particle*, a species consisting of *a central metal cation* (usually a transition metal) that is bonded to molecules and/or anions called *ligands.* This name originates from the Latin word «ligare» – «to bind». The complex ions in crystal lattice are typically associated with other ions, called *counter ions*, and are capable for independent existence in solutions.

As an example of coordination compound we may discuss compound with formula $[Co(NH_3)_6]Cl_3$. Here the complex ion is $[Co(NH_3)_6]^{3+}$, it is always enclosed in square brackets; the central ion is Co^{3+}, the six NH_3 molecules bonded to the central ion are ligands, and the three Cl^- ions are counter ions. Another example of the complex compound is $K_3[Fe(CN)_6]$. Here the complex ion $[Fe(CN)_6]^{3-}$ is formed by central ion Fe^{3+} and six CN^- ions as a ligands, the K^+ ions are counter ions.

Each ligand in a complex particle donates a pair of electrons and central ion accepts these pairs forming the *coordinate bond*. Thus, every ligand has at least one atom with lone pair of valence electrons and each central ion has free electronic orbital(s). The number of coordination bonds, which the ligand may form with the central metal ion in a complex particle, depends on the number of donor atoms. This property of the ligand is called *denticity*. Ligands having only one donor atom are called *monodentate ligands* (from the Latin, meaning «one-toothed»). These ligands are capable to occupy only one site in a coordination sphere. Ligands having two donor atoms are *bidentate ligands* («two-toothed»), and those having three or more donor atoms are *polydentate ligands* («many-toothed»). In both bidentate and polydentate species, the donor atoms can bond to the metal ion, thus occupying two or more sites around the central ion. The examples of monodentate ligands are: NH_3, H_2O, Cl^-, Br^-, OH^-, CN^-; bidentate ligands are: ethylenediamine, bipyridine, oxalate ion; polydentate ligands are: diethylenetriamine, ethylenediaminetetraacetate ion.

Any complex is characterized by the *coordination number* that shows how many atoms, ions or molecules are placed around the central atom. It indicates the total number of σ-type chemical bonds that the central atom forms with the ligands. The coordination number is determined by the nature of the central atom and ligands and may vary from 2 to 12.

The central metal and the ligands bound to it constitute the *coordination (inner) sphere* of the complex compound. The central atom and the internal sphere form the *complex particle*, which restrict by the square brackets in formulas. The complex particle can be neutral, positively or negatively charged, for example, $[Ni(CO)_4]$, $[Mn(H_2O)_6]^{2+}$, $[Fe(CN)_6]^{3-}$. If the complex particle is charged, than compound has an *external (outer) sphere,* because the every charged ion attracts oppositely charged ions, for example, $[Mn(H_2O)_6]Cl_2$, $K_3[Fe(CN)_6]$.

A coordination compound behaves like an electrolyte in water: the complex ion and counter ions separate from each other. But the complex ion behaves like a polyatomic ion: the ligands and central metal ion remain attached. Thus, at dissociation 1 mol of $[Co(NH_3)_6]Cl_3$ yields 1 mol of complex ions $[Co(NH_3)_6]^{3+}$ and 3 mol of Cl^- ions; 1 mol of $K_3[Fe(CN)_6]$ yields 1 mol of complex ions $[Fe(CN)_6]^{3-}$ and 3 mol of K^+ ions:

$$[Co(NH_3)_6]Cl_3 \rightarrow [Co(NH_3)_6]^{3+} + 3Cl^-,$$

$$K_3[Fe(CN)_6] \rightarrow 3K^+ + [Fe(CN)_6]^{3-}.$$

Note, that some coordination compounds such as iron carbonyle $Fe(CO)_5$ do not contain complex ions. In this case we say about *complex particle* not ions. These substances do not capable for dissociation in solution.

The first theory of complex compounds was proposed by the Swiss chemist A. Werner. According to the Werner's theory the central atoms can exhibit both a *primary valence* and a *secondary valence*. The primary valence is the oxidation number of the central ion. The secondary valence is the *auxiliary* valence. According to Werner, the primary valence of the central ion is saturated only by negatively charged ions, but the secondary valence may be filled by both negatively charged ions and neutral molecules.

Naming of complex compounds

1. In naming complexes that are salts, the name of the cation is given before the name of the anion.

2. In naming complex ions or molecules, the ligands are named before the metal. Ligands are listed in alphabetical order, regardless of their charges. Prefixes that show the number of ligands are not considered part of the ligand

name in determining alphabetical order. For example, the $[Co(NH_3)_5Cl]^{3+}$ ion is pentaamminechlorocobalt (III).

3. The names of anionic ligands end in the letter «o», but for electrically neutral ligands ordinarily the name of the molecules are used. Special names are used for several molecules as ligands: water – aqua, ammonia – ammine, and carbon monoxide – carbonyl. For example, $[Fe(NH_3)_2(H_2O)_2(CN)_2]^{2+}$ is the diamminediaquadicyanoiron (III) ion.

4. Greek prefixes (di-, tri-, tetra-, penta-, hexa-) are used to indicate the number of each kind of ligand when more than one is present. If the ligand contains a Greek prefix (for example, ethylenediamine) or is polydentate, the alternate prefixes bis-, tris-, tetrakis-, pentakis-, and hexakis are used and the ligand name is placed in parentheses. For example, the name for compound $[Co(en)_3]Br_3$ (here *en* is ethylenediamine $H_2N–H_2C–CH_2–NH_2$) is tris(ethylenediamine)cobalt (III) bromide.

5. If the complex is an anion, its name ends in -ate. The compound $K_4[Fe(CN)_6]$ is potassium hexacyanoferrate (II), and the ion $[CoCl_4]^{2-}$ is tetrachlorocobaltate (II) ion.

6. The oxidation number of the metal is given in parentheses in Roman numerals following the name of the metal.

The examples for applying these rules: $[Ni(NH_3)_6]Cl_2$ – hexaamminenickel (II) chloride, $[Mn(H_2O)_6]Cl_2$ – hexaaquamanganese (II) chloride, $[Co(en)_2(H_2O)(CN)]Cl_2$ – aquacyanobis(ethylenediamine)cobalt (III) chloride, $K_3[Fe(CN)_6]$ – potassium hexacyanoferrate (III).

Problems

Examples

Problem 1. Classify the following bonds as nonpolar, polar, or ionic: a) the bond in H_2 molecule, b) the bond in CsCl, c) the bond in HBr molecule, d) the carbon-carbon bond in ethane $H_3C–CH_3$.

Solution. Using the information from Appendix (Table on the page 195), gives that electronegativities of the elements are: Cl – 3.0, Br – 2.8, C – 2.5, H – 2.1, Cs – 0.7.

a) The molecule is built from the same atoms only, this gives the nonpolar covalent bonding.

b) In CsCl the difference between the electronegativities of the elements is 3.0 – 0.7 = 2.3, indicating the ionic bond.

c) In HBr molecule the difference between the electronegativities of the elements is 2.8 – 2.1 = 0.7, this corresponds the polar covalent bond.

в) In C_2H_6 the carbon-carbon bond is nonpolar covalent, because these two atoms are identical, and each C atom is bonded to three hydrogen atoms.

Problem 2. For complex compound $[Cr(NH_3)_6](NO_3)_3$ show: central ion, ligand(s) and counter ion. Determine the oxidation number of the central metal atom in the compound. Write equation of electrolytic dissociation of the substance in aqueous solution.

Solution. First it needs to find the complex ion and counter ions that electrically balances the complex ion. This gives the net charge of the complex ion. Next, from the nature of the ligands (charged or neutral species) we can deduce the net charge of the metal and hence its oxidation number. Because each nitrate ion carries +1 charge, and there are three NO_3^- ions, the complex ion is $[Cr(NH_3)_6]^{3+}$. NH_3 is a neutral particle, so the oxidation number of Cr atom is +3.

$$[Cr(NH_3)_6](NO_3)_3 \rightleftarrows [Cr(NH_3)_6]^{3+} + 3NO_3^-.$$

Problem 3. Name the following compound: $[Cr(H_2O)_4Cl_2]Cl$.

Solution. To name the complexes, we need to determine the complex ion and the counter ions, the ligands in the complex and the oxidation state of the central ion. Here the ligands are four water molecules and two chloride ions, this gives tetraaqua and dichloro. The central ion is chromium, the oxidation number of Cr is +3, thus, we have chromium (III). Finally, the chloride ions are counter ions. So, the name of the complex compound is tetraaquadichlorochromium (III) chloride.

Problems for self-solving

1. Determine, which of the following bonds are polar: F – F, H – F, C – S, N – O, Cl – Cl, P – H? Indicate the more electronegative atom in each polar bond.

2. Determine for each case, which bond is more polar: a) B – Cl or C – Cl, b) P – H or P – Cl, c) S – Cl or S – Br, d) C – H or P – H? Also indicate which atom has the partial negative charge.

3. Arrange the bonds in order of increasing polarity for each of the following sets: (a) C–F, O–F, Si–F; (b) O–Cl, S–Br, P–F; (c) Be–Cl, H–Cl, N–Cl.

4. In the given pairs of binary compounds determine which one is a molecular substance and which one is an ionic substance (use table of electronegativities from Appendix): (a) $TiCl_4$ and CaF_2, (b) ClF_3 and VF_3, (c) $SbCl_5$ and AlF_3.

5. Determine and write the oxidation numbers of the central ions in the following compounds: a) $K[Au(OH)_4]$, b) $K_4[Fe(CN)_6]$.

6. Complex ion contains a chromium(III) atom bound to four water molecules and to two chloride ions. Write the formula and the charge of this ion.

7. Name the following complex compound: $(NH_4)_2[CuBr_4]$. Write equation of electrolytic dissociation of this substance in aqueous solution.

8. Structure of complex compound is given by formula $[Pd(NH_3)_3Cl]Cl$. For this substance determine and idicate: central ion, ligand(s), oxidation and coordination numbers of the central ion, inner and outer sphere. Write equation of electrolytic dissociation of the substance in aqueous solution.

9. Indicate the coordination number of the metal ion and its oxidation number as well as the number and type of each donor atom of the ligands for each of the following complexes: (a) $K_3[Co(CN)_6]$; (b) $Na_2[CdBr_4]$; (c) $[Pt(en)_3](ClO_4)_4$, *en* is ethylenediamine $H_2N–H_2C–CH_2–NH_2$; (d) $NH_4[Cr(NH_3)_2(NCS)_4]$.

10. For each of the following polydentate ligands, determine the maximum number of coordination sites that the ligand can occupy on a single metal ion and (ii) the number and type of donor atoms in the ligand: (a) ethylenediamine (en), (b) bipyridine (bipy), (c) the oxalate anion.

THEME 4
SOLUTIONS. ELECTROLYTIC DISSOCIATION

Many of the reagents used in chemical laboratories are in the form of solutions which need to be purchased or prepared.

Solution is a homogeneous mixture composed of only one phase. In such a mixture, a *solute* is a substance dissolved in another substance, known as a *solvent*. The solvent is commonly the major fraction of the mixture. A solution may be gaseous, solid, or liquid. For medical purposes the most important are liquid solutions, in particularly the aqueous solution in which the solvent is water. In this theme we will discuss only aqueous solutions, in which the solute initially is a liquid or a solid.

A solution may be more or less concentrated or diluted. This means, it may contain a large or small amount of dissolved substance in a given amount of solvent. Composition of the solution or *concentration* can be expressed in various ways.

The most common unit of solution concentration is *molarity* (M or mol/L). Molarity of a solution is defined as the number of moles of solute per one liter of solution. Note, that the unit of volume for molarity is liter, not milliliter or some other units. Also note, that one liter of solution contains both the solute and the solvent. Molarity, c, therefore, is a ratio of solute moles, n, and volume of solution, V

$$c = \frac{n}{V} = \frac{m}{M \cdot V}, \tag{4.1}$$

where m is a mass of solute, g; M is a molar mass of solute, g/mol.
The *molality* is another value for the expressing composition of the solutions. It is the number of moles of solute dissolved in 1 kg (1000 g) of a solvent

$$m = \frac{n_{\text{solute}}}{m_{\text{solvent}},\ \text{kg}}. \tag{4.2}$$

The unit of molality is mol/kg.

The *mole fraction* of a component of a solution (solute or solvent) is defined as the ratio of the quantity of the component to the quantity of the substance in solution:

$$x = \frac{n_{\text{component}}}{n_{\text{solution}}}. \qquad (4.3)$$

The mole fraction and the percent by mass (or volume) are unitless values, because they equal to the ratio of two similar quantities.

Mass percent (*w*) of solute in solution is defined as ratio between mass of a solute and mass of solution

$$w = \frac{m(\text{solute})}{m(\text{solution})} \cdot 100\ \% = \frac{m(\text{solute})}{m(\text{solute}) + m(\text{solvent})} \cdot 100\ \%. \qquad (4.4)$$

This value is equal the grams of solute per 100 grams of solution. For example: 20 g of sodium chloride in 100 g of solution is a 20 % by mass solution.

Volume percent (φ) of a component in solution is defined by the equation

$$\varphi = \frac{V(\text{solute})}{V(\text{solution})} \cdot 100\ \%. \qquad (4.5)$$

The φ value may be considered as the number of the solute milliliters per 100 mL of solution. For example: 10 mL of ethyl alcohol plus 90 mL of water gives approximately 100 mL of solution which contains 10 % of ethanol by volume.

Others ways of expressing the solution composition can also be used. For example, *titer*, *T*, is concentration which shows mass of solute per 1 mL of solution, g/mL.

All solutes, that dissolve in water, can be divided in two categories: *electrolytes* and *nonelectrolytes*. An electrolyte is a substance that, when dissolved in water, results in a solution that can conduct electricity. A nonelectrolyte solution does not conduct electricity. For the explanation of this and some other properties of solutions Swedish scientist S. Arrhenius proposed the *electrolytic dissociation theory*. According to this theory molecules of acids, bases or salts undergo dissociation into ions on dissolution in water. The result of this process is the presence of ions in solution. Positively charged ions are called «cations», negatively charged – «anions».

It was found that sometimes only a part of dissolved molecules undergo dissociation. Fraction of the solute molecules, which are dissociated into ions, is called the *dissociation degree*. It equals to the number of dissociated molecules (N) divided to the total number of dissolved molecules in solution (N_o):

$$\alpha = N / N_o . \tag{4.6}$$

Compounds, that completely dissociate, is characterized by $\alpha = 1$ and is called *strong* electrolytes. If the degree of dissociation α is less than 0.03 the electrolyte is called *weak* electrolyte. Electrolyte that characterized by $0.03 < \alpha < 0.30$ is *medium* electrolyte. Degree of dissociation depends on electrolyte concentration and usually decreases with increase in concentration.

In a solution of any electrolyte there is an equilibrium between the free ions, on the one hand, and undissociated molecules, on the other hand, one may write this equilibrium in the form

$$\mathrm{CatAn} \rightleftarrows \mathrm{Cat}^+ + \mathrm{An}^- ,$$

where Cat^+, An^- – cation and anion of the electrolyte. Mass action law for this equilibrium process gives

$$K = \frac{[\mathrm{Cat}^+][\mathrm{An}^-]}{[\mathrm{CatAn}]} , \tag{4.7}$$

where [...] – denotes equilibrium concentration of a particle, K – equilibrium constant, called the *dissociation constant.*

Depending on nature of dissociated compound, one molecule of an electrolyte produces different number of ions:

- *binary* electrolyte gives two ions, for example, NaCl, $CuSO_4$;

$$\mathrm{NaCl} \rightarrow \mathrm{Na}^+ + \mathrm{Cl}^- .$$

- *ternary* electrolyte gives three ions, for instance, Na_2SO_4, $BaCl_2$;

$$\mathrm{BaCl_2} \rightarrow \mathrm{Ba}^{2+} + 2\mathrm{Cl}^- .$$

- *quaternary* electrolyte gives four ions, e.g., NaH_2PO_4, $AlCl_3$;

$$\mathrm{NaH_2PO_4} \rightarrow \mathrm{Na}^+ + 2\mathrm{H}^+ + \mathrm{PO_4}^{3-},\ \mathrm{AlCl_3} \rightarrow \mathrm{Al}^{3+} + 3\mathrm{Cl}^- .$$

It may be shown that for a weak binary electrolyte, e.g. acetic acid, dissociation constant and degree of dissociation are interconnected by the expression

$$K = \frac{\alpha^2 c}{1 - \alpha}, \tag{4.8}$$

where c – total molar concentration of electrolyte in solution. This equation is known as *Ostwald's dilution law*, it is applicable for weak electrolytes only.

Dissociation constant is a measure of electrolyte power: for strong electrolytes $K > 1 \cdot 10^{-2}$, for medium electrolytes $1 \cdot 10^{-4} < K < 1 \cdot 10^{-2}$, for weak electrolytes $K < 1 \cdot 10^{-4}$. It must be remembered that electrolyte strength and its ability for electrolytic dissociation strongly depend on solvent properties. Degree and constant of dissociation decrease with increase in relative permittivity of the solvent, because this leads to rise of coulombic interaction between ions.

Strong electrolytes are considered to be completely dissociated. For example, in solution of hydrochloric acid there are no dissolved molecules but only ions

$$\mathrm{HCl} \rightarrow \mathrm{H}^+ + \mathrm{Cl}^-.$$

Weak electrolytes, for example acetic acid, CH_3COOH, do not ionize completely in solution. This fact is represented as equilibrium between acetic acid molecules and its ions

$$\mathrm{CH_3COOH} \rightleftarrows \mathrm{CH_3COO^-} + \mathrm{H^+}.$$

Here the equation of the ionization process of acetic acid is written with a double arrow to show that it is a reversible reaction. By contrast, in the equation of dissociation of hydrochloric acid a single arrow is used to represent complete ionization process.

It is obvious that dissociation of molecules into ions needs in energy for disruption of chemical bonds. This energy might be quite considerable, for example, energy of crystal lattice of KCl is about 5000 kJ/mol. This energy evolved as a result of interaction of solvent molecules with the ions. This process is called solvation, or in particular case of water, hydration. The dissociation is caused by solute-solvent interactions. This interactions include electrostatic ion-dipole interactions between ions and polar solvent molecules, hydrogen bonding and donor-acceptor interactions.

Problems

Examples

Problem 1. Calculate the mass of solid hydrate $CuSO_4{\cdot}5H_2O$ that is required for the preparation of 100 mL of 0.20 mol/L solution of $CuSO_4$.

Solution. From the given volume and concentration of $CuSO_4$, we can calculate the moles of unhydrous salt $CuSO_4$ required

$$n(CuSO_4) = c(CuSO_4)\cdot V(CuSO_4) = 0.20\times100\cdot10^{-3} = 0.02 \text{ mol.}$$

The formula of crystalline hydrate shows that 1 mole of $CuSO_4{\cdot}5H_2O$ is required for the transferring of 1 mole of $CuSO_4$ into solution. The molar mass of $CuSO_4{\cdot}5H_2O$ is 250 g/mol, thus 250 g of $CuSO_4{\cdot}5H_2O$ brings 1 mol of the salt in solution. If quantity of $CuSO_4$ in solution is 0.02 mol, the required quantity of $CuSO_4{\cdot}5H_2O$ is 0.02 mol too. The mass of $CuSO_4{\cdot}5H_2O$ equals

$$0.02\times250 = 5.0 \text{ g.}$$

So, for preparation of solution we need weigh 5.0 g of $CuSO_4{\cdot}5H_2O$ and transfer it into a 100 mL volumetric flask, dissolve it in some amount of distilled water, then dilute to the mark of the flask.

Problem 2. In a titration experiment, it was found that 24 mL of NaOH solution is needed to neutralize hydrochloric acid in 3 mL of its solution. What is the molar concentration of the analyzed HCl solution if molarity of the titrant solution (NaOH) is 0.1 mol/L?

Solution. Using the molarity of the titrant solution, determine the number of moles of NaOH

$$n(NaOH) = c(NaOH)\cdot V(NaOH) = 0.1\times24\cdot10^{-3} = 2.4\cdot10^{-3} \text{ mol.}$$

In equivalence point of titration the number of moles of NaOH is equal to the number of moles of HCl in analyzed solution

$$n(HCl) = n(NaOH) = 2.4\cdot10^{-3} \text{ mol.}$$

The dividing the number of HCl moles by volume (in liters) of HCl solution gets molarity

$$c(HCl) = n(HCl)/V(HCl) = 2.4\cdot10^{-3}/3\cdot10^{-3} = 0.8 \text{ mol/L.}$$

Problem 3. Commercial concentrated sulfuric acid is labeled as having a density of 1.84 g/mL and being 96 % of H_2SO_4 by weight. Calculate the molarity of this solution.

Solution. This is a typical conversion problem in which we want to go from mass fraction and grams of solution per liter to moles of solute per liter. For the calculation let us take a 100 g of the solution. Here, the mass of the solute is 96 g and the volume of solution is

$$V(\text{solution}) = 100/1.84 = 54.35\ \text{mL} = 0.05435\ \text{L}.$$

The number of moles of H_2SO_4 equals

$$n(H_2SO_4) = 96/98 = 0.98\ \text{mol}.$$

The molarity of the solution is

$$c(H_2SO_4) = n(H_2SO_4)/V(\text{solution}) = 0.98/0.05435 = 18.02\ \text{mol/L}.$$

Problem 4. Calculate the dissociation degree of 0.01 mol/L acetic acid solution. Dissociation constant of CH_3COOH is $1.75 \cdot 10^{-5}$ mol/L.

Solution. Acetic acid in aqueous solution ionizes as a weak monoprotic acid. According to Ostwald's dilution law the initial concentration of the acid, its dissociation constant and dissociation degree are interconnected by equation (4.8). Knowing that the acid is a weak, we may neglect the α value in comparison with the 1 in denominator. Thus, we have

$$K \approx \alpha^2 c \text{ and } \alpha = \sqrt{K / c}\ ,$$

$$\alpha = \sqrt{1.75 \cdot 10^{-5} / 0.01} = \sqrt{1.75 \cdot 10^{-3}} = 0.042.$$

Now we can check our neglection: the value of (1 – 0.042) is really approximately equal to 1. In other case we need to solve the square equation of Ostwald's dilution law for more precise solution.

Problems for self-solving

1. Sodium carbonate, which is known as washing soda, commonly occurs in form of decahydrate $Na_2CO_3 \cdot 10H_2O$. Calculate the mass of solid hydrate that is required for the preparation of 500 mL of 0.1 mol/L solution of Na_2CO_3. *Answer:14.3 g.*

2. Iron (II) sulfate is known since ancient times as «green vitriol», the blue-green heptahydrate with the formula $FeSO_4{\cdot}7H_2O$ is the most common form of this material. Calculate the mass percent of $FeSO_4$ in solution, which is made by dissolution of 2.78 g of solid heptahydrate in 200 mL of water. *Answer: 0.75 %.*

3. What volume of 18 mol/L H_2SO_4 solution is needed for the preparation of 2 liters of diluted H_2SO_4 solution with the molarity of 0.01 mol/L? *Answer:* $V = 11.1$ *mL.*

4. A solution of H_2SO_4 was prepared by diluting of concentrated acid solution. For the determination of the concentration of diluted solution an aliquot of 10 mL was taken and the titration procedure with NaOH solution as a titrant was perfomed. The concentration of NaOH was 0.1 mol/L, the equivalence point was found to be 5.1 mL. Calculate the molarity of the prepared H_2SO_4 solution. *Answer:* $c = 2.55{\cdot}10^{-5}$ *mol/L.*

5. Calculate the percentage of HNO_3 by mass in 21.2 mol/L solution of nitric acid if the density of the solution is 1.48 g/mL. *Answer: 90.24 %.*

6. Calculate the molarity of HCl in solution, if for the neutralization of 10 mL of the solution during titration, 15 mL of 0.1 mol/L NaOH solution was used. *Answer:* $c = 0.15$ *mol/L.*

7. Calculate the dissociation degree of benzoic acid (C_6H_5COOH) for $3{\cdot}10^{-2}$ mol/L water solution. The acid is monoprotic. Dissociation constant of the acid is $6.3{\cdot}10^{-5}$ mol/L. *Answer:* $\alpha = 4.6$ *%.*

8. Calculate the dissociation degree of formic acid (HCOOH) for 0.05 mol/L water solution. The acid is monoprotic. Dissociation constant of the acid is $2.1{\cdot}10^{-4}$ mol/L. *Answer:* $\alpha = 6.5$ *%.*

9. Calculate the percentage of an ionized HF molecules in 0.10 mol/L solution of hydrogen fluoride. Dissociation constant of HF equals $6.8{\cdot}10^{-4}$ mol/L. *Answer: 7.9%.*

10. A solution is made by adding of 0.4 g of NaOH to 50 mL of 0.1 mol/L H_2SO_4 solution. Write a balanced equation for the reaction that proceeds in the solution. Determine whether the resultant solution is acidic, neutral or basic. *Answer: neutral.*

THEME 5

ACID-BASE EQUILIBRIA

Acids and bases

Acids and bases have been defined in a number of different ways. In the simplest form an *acid* can be described as a substance that yields hydrogen ions (H^+) when dissolved in water and a *base* can be described as a substance that yields hydroxide ions (OH^-) when dissolved in water.

Acids commonly used in the laboratory practice are: hydrochloric acid (HCl), nitric acid (HNO_3), acetic acid (CH_3COOH), sulfuric acid (H_2SO_4), and phosphoric acid (H_3PO_4). The first three acids are *monoprotic*. This means *each molecule of the acid yields one hydrogen ion upon ionization*. Sulfuric acid is a *diprotic acid* because *each molecule of the acid gives two hydrogen ions*. Phosphoric acid is *triprotic acid, it yields three* H^+ *ions* upon dissociation. HCl and HNO_3 are strong acids. H_2SO_4 is a strong electrolyte by the first step of dissociation

$$H_2SO_4 \rightarrow H^+ + HSO_4^-,$$

but HSO_4^- is not so strong electrolyte, and we need a double arrow to represent its incomplete ionization

$$HSO_4^- \rightleftarrows H^+ + SO_4^{2-}.$$

Phosphoric acid is a medium electrolyte by the first step of dissociation and a weak acid by the second and third steps

$$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^-,$$

$$H_2PO_4^- \rightleftarrows H^+ + HPO_4^{2-},$$

$$HPO_4^{2-} \rightleftarrows H^+ + PO_4^{3-}.$$

The most commonly used strong bases in the laboratory are: sodium hydroxide (NaOH), potassium hydroxide (KOH) and barium hydroxide ($Ba(OH)_2$). This means that they are completely ionized in solution

$$NaOH \rightarrow Na^+ + OH^-,$$

$$KOH \rightarrow K^+ + OH^-,$$

$$Ba(OH)_2 \rightarrow Ba^{2+} + 2OH^{-}.$$

NaOH and KOH are *monobasic*, $Ba(OH)_2$ is *dibasic*. The most commonly used weak base is aqueous ammonia solution, which is sometimes erroneously called ammonium hydroxide, because here is no evidence that the molecule NH_4OH exists in solution. Ammonia is a weak electrolyte and only a small fraction of dissolved NH_3 molecules react with water to form NH_4^+ and OH^- ions

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-.$$

The «strength» of an acid is a measure of its tendency to lose a proton, and the «strength» of a base is similarly a measure of its tendency to take up a proton.

A point of view on acids and bases that has proved useful in several aspects of physical chemistry is that associated with the names of J. N. Brønsted and T. M. Lowry. According to the Brønsted–Lowry theory of acids and bases, an *acid is a proton donor* and a *base is a proton acceptor*. The proton in this context means a solvated hydrogen ion that presents in solution. Acids and bases in solution are always in equilibrium with their deprotonated and protonated counterparts and hydrogen ion or hydronium (hydroxonium) ions (H_3O^+). According to the foregoing definitions there must be a relationship between an acid and a base; when an acid loses a proton the residue will have some tendency to regain the proton, and hence it will be a base. It is thus possible to write the general expression

$$\underset{\text{acid}}{A} \rightleftarrows \underset{\text{proton}}{H^+} + \underset{\text{base}}{B^-}$$

In its widest sense, a *base has been defined as a substance capable to be donor of electron pair*, while an *acid is a substance capable to accept an electron pair* – according to G. N. Lewis's definition.

Acidity of solutions. Buffer solutions

Quantitative representation of the acidity of solutions, i.e. the content of hydrogen ions in solution, is the pH value that equals to the negative decimal logarithm of hydrogen ions activity

$$\mathrm{pH} = -\log a_{\mathrm{H}^+} = -\log(c_{\mathrm{H}^+} \cdot \gamma_\pm)\,. \tag{5.1}$$

In a diluted solution activities are close to concentrations ($\gamma_\pm \approx 1$), so it is possible to set the pH value of solution equals to analytical concentration of hydrogen ion

$$\mathrm{pH} = -\log c_{\mathrm{H}^+} \text{ or } \mathrm{pH} = -\log[\mathrm{H}^+]. \tag{5.2}$$

In aqueous solution the autoionization of water molecules takes place

$$\mathrm{H_2O} \rightleftarrows \mathrm{H}^+ + \mathrm{OH}^-. \tag{5.3}$$

This process is characterized by equilibrium constant

$$K = \frac{a_{\mathrm{H}^+} \cdot a_{\mathrm{OH}^-}}{a_{\mathrm{H_2O}}}. \tag{5.4}$$

The degree of water dissociation is very small, so the $a_{\mathrm{H_2O}}$ value is constant and equation (5.4) can be represented as follows

$$a_{\mathrm{H}^+} \cdot a_{\mathrm{OH}^-} = K \cdot a_{\mathrm{H_2O}} = K_w. \tag{5.5}$$

Constant K_w is known as *ionic product of water*. At 25 °C the K_w value is equal to $1.008 \cdot 10^{-14}$. Usually this constant is represented as the negative decimal logarithm

$$\mathrm{p}K_w = -\log K_w;\ \mathrm{p}K_w = 14 \text{ at } 25\ °\mathrm{C}.$$

In a dilute solutions the activities of the ions are close to concentrations, in these conditions

$$K_w = [\mathrm{H}^+][\mathrm{OH}^-] \tag{5.6}$$

and

$$\mathrm{p}K_w = \mathrm{pH} + \mathrm{pOH} = 14, \tag{5.7}$$

where

$$\mathrm{pOH} = -\log c_{\mathrm{OH}^-} \text{ or } \mathrm{pOH} = -\log[\mathrm{OH}^-]. \tag{5.8}$$

The value of ionic product of water gives concentrations of ions in pure water at 25 °C

$$[H^+] = [OH^-] = 10^{-7}\,\text{mol/L}.$$

In other words, only very small amounts of H^+ and OH^- ions present in pure water. The concentrations of H^+ and OH^- are interconnected. If an acid is added to the water, the equilibrium of water dissociation shifts to the left and the OH^- ion concentration decreases. If a base is added to water, the equilibrium shifts to the left too, but in this case the H^+ concentration decreases.

If the contents of hydrogen and hydroxyl ions in a solution are equal, than

$$[H^+] = [OH^-] \text{ and pH = pOH = 7},$$

such media is called *neutral*. In *acidic solutions*

$$[H^+] > [OH^-],$$

in *alkaline media*

$$[H^+] < [OH^-].$$

The pH and pOH values of diluted solutions are in range 0–14. But concentrated solutions of a strong acids may have zero or even negative pH values, and concentrated solutions of a strong bases may have pH values more than 14.

The pH value is the theoretical quantitative characteristic of a solution because it is experimentally impossible to determine activity of a single ion. The pH value of a solution, that is determined experimentally, is called as «instrumental» pH value. In the most practical cases we can use pH values calculated according to equation (5.2).

Buffer solutions are solutions with ability to keep constant the pH value at dilution or addition of small amounts of a strong acid or a strong base. Usually buffer solution consists of a weak acid (weak base) and salt of this acid (base) which is strong electrolyte, for example, CH_3COOH and CH_3COONa, NH_4OH and NH_4Cl, etc. In general form it is possible to say, that the buffer solution consists from conjugated acid and base. The pH value of a buffer solution may be calculated using quantities of its components, for example, for acid buffer

$$\mathrm{pH} = \mathrm{p}K - \log \frac{c^{\mathrm{o}}_{\mathrm{HA}}}{c^{\mathrm{o}}_{\mathrm{MeA}}}, \tag{5.9}$$

where pK – negative decimal logarithm of the dissociation constant of the acid; $c^{\mathrm{o}}_{\mathrm{HA}}$, $c^{\mathrm{o}}_{\mathrm{MeA}}$ – initial concentrations of the acid and its salt in the solution. Equation (5.9) is known as *Henderson–Hasselbalch equation.*

Ability of buffer solutions to keep the pH value at addition of a strong acid or base is called *buffer action*. As a measure of buffer action *the buffer capacity*, β, is used. Buffer capacity is an added amount of a strong acid or a strong base, which addition to one liter of a buffer solution changes the pH value to unity. The buffer capacity can be determined as a derivative

$$\beta = \frac{\mathrm{d}b}{\mathrm{dpH}}, \tag{5.10}$$

where $\mathrm{d}b$ is an infinitesimal amount of added base and dpH is the resulting infinitesimal change in pH caused by base addition. Note that addition of $\mathrm{d}b$ moles of an acid will change the pH of the solution by exactly the same value, but in opposite direction.

Acid-base indicators

An acid-base or hydrogen ion indicator is a substance which, within certain limits, varies its color according to the concentration (or activity) of hydrogen ions in solution. It is thus possible to determine the pH value of a solution by observing the color of a suitable indicator when placed in that solution. An acid-base indicator is a substance which can exist in two tautomeric forms in equilibrium with one another, the two forms having different structures and different colors. Color of the indicator solution is determined by the ratio of the concentrations of two forms. It is possible to approximate the actual condition of equilibrium of indicator dissociation

$$\mathrm{HIn} \rightleftarrows \mathrm{H}^+ + \mathrm{In}^-,$$

$$K = \frac{[\mathrm{H}^+][\mathrm{In}^-]}{[\mathrm{HIn}]}, \tag{5.11}$$

where K is the constant of indicator dissociation; the negative logarithm of this constant, i.e., $-\log K$, is represented by pK. For the pH value of solution equation (5.11) gives

$$\mathrm{pH} = \mathrm{p}K + \log \frac{[\mathrm{In}^-]}{[\mathrm{HIn}]}. \tag{5.12}$$

It should be noted that in this equation the pH value refers to the hydrogen ion concentration of the solution containing the indicator, irrespective of whether it is due to the indicator alone or to other substances that may be present in solution. Since two forms of indicator have different colors, for example, A and B for acidic and alkaline media, the actual color exhibited by the indicator will depend on the hydrogen ion concentration of the medium. In an acidic solution, that is, one containing excess of H_3O^+ ions, the equilibrium of indicator dissociation will be displaced to the left; the indicator will thus consist predominantly of the form with color A, and it will exhibit the color A. On the other hand, if the solution is alkaline, containing predominantly OH^- ions, the equilibrium will lie to the right, and the indicator will be largely in the dissociated form; in alkaline, i.e., basic solution, the indicator will consequently have the color B. The equation (5.12) allows to determine the pH value of a solution. If the pK value of indicator is known, and the ratio of concentrations of two forms of the indicator in the given solution is measured, the pH value of the latter can be evaluated. In theory, the ratio of the intensities of color B to color A may have any value, but in practice it is possible to detect the proportions of the two colors in a mixture within certain limits only. For example, if 1 per cent of a blue color is mixed with 99 per cent of red, the eye cannot notice any difference from pure red. In general, it is necessary that there should be a minimum of about 10 per cent of a particular color before it can be exactly detected in the presence of another color. It leads to that indicators might be utilized for determination of the pH value of the solution in the definite range of the pH values. This range is

$$\mathrm{pH} = \mathrm{p}K \pm 1. \tag{5.13}$$

This interval of the pH values is called *the transition or useful range of the indicator*. For example, the pK value of indicator methyl orange equals 3.46. In acidic solutions it has a red color, in alkaline solutions – yellow, in the range of 3.1 to 4.4 an orange color is observed. The pK values and useful ranges of some often used indicators are given in Table 5.1.

Due to the ability of indicators to change a color with pH of solution they are employed for determination of the acidity of solutions. *Universal indicator* is a mixture of several indicators displaying a variety of colors over a wide pH range. Usually it is used as a *test paper* that changes color in accordance with the pH value of the solution. Test papers of universal indicator are used only for an approximate determination of the pH value of solution. Because of the subjective determination of color, acid-base indicators are susceptible to imprecise readings of pH. For precise determination of the pH value, colorimetric and potentiometric methods are used.

Hydrolysis of salts

Generally, *hydrolysis is a process of chemical interaction between water and a substance*. In a hydrolysis reaction, bonds of the substance are broken by their reaction with water or the H^+ and OH^- ions formed after dissociation of water. There are several types of the substances capable for hydrolysis: esters, salts, halogen derivatives, etc.

A particular case of hydrolysis occurs when a salt of a weak acid or weak base (or both) is dissolved in water. Water spontaneously ionizes into hydroxyl anions and hydrogen cations. The salt dissociates too into its constituent anions and cations, and oppositely charged ions interact with one another. Salt hydrolysis usually affects the pH value of a solution. It is true that salts consisting an alkali metal or alkaline earth metal ion and the anion of a strong acid (for example, Cl^-, Br^-, SO_4^{2-}) do not undergo hydrolysis to an appreciable extent, and their solutions are assumed to be neutral.

The solution of a salt formed by a strong base and a weak acid is basic. For example, sodium acetate dissociates in water giving sodium and acetate ions. The acetate ions combine with hydrogen ions to produce molecules of acetic acid, but sodium cations and hydroxyl anions do not react, because NaOH is a strong electrolyte and exists in solution in dissociated form. In this case, the net result is a relative excess of hydroxyl ions, giving a basic solution. The hydrolysis reaction is given by the equation

$$CH_3COONa + H_2O \rightleftarrows CH_3COOH + Na^+ + OH^-.$$

When a salt is formed by a strong acid and a weak base, the solution becomes acidic. For example, consider the process of dissolution of ammonium chloride, in this case the hydrolysis of the NH_4^+ ion proceeds

$$NH_4Cl + H_2O \rightleftarrows NH_3{\cdot}H_2O + H^+ + Cl^-.$$

Because H^+ ions are produced in the reaction, the pH value of the solution decreases.

For salts derived from a weak acid and a weak base, both the cation and the anion hydrolyze. However, whether a solution containing such a salt is acidic, basic, or neutral depends on the relative strengths of the weak acid and the weak base.

Table 5.1. Dissociation constants, useful ranges and solution colors for some indicators at 25 ℃

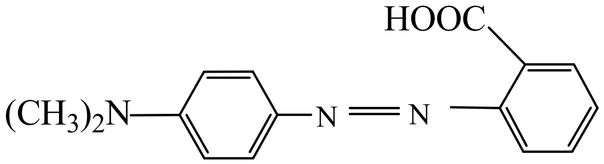
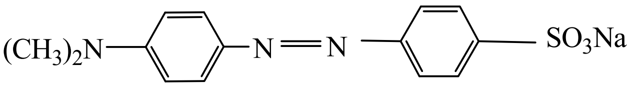
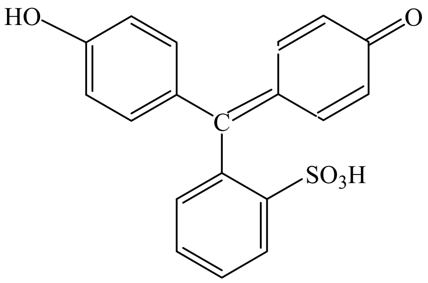
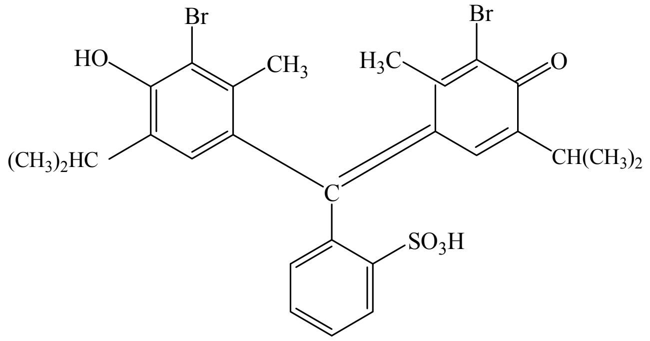
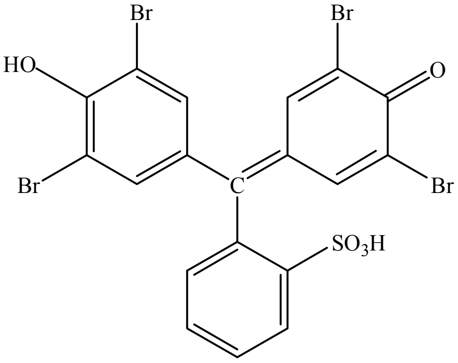
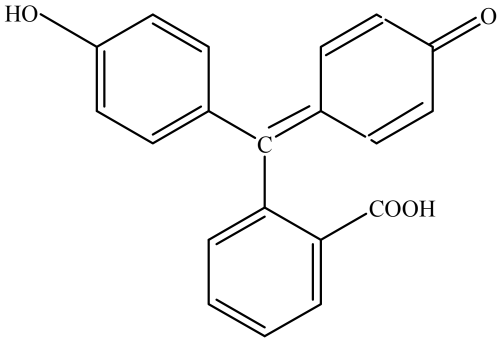
Indicator	**Chemical structure of indicator**	pK	**Useful range and solution color**
Methyl red		5.00	4.2–6.2 red – yellow
Methyl orange		3.46	3.1–4.4 red – orange – yellow
Phenol red		8.00	6.8–8.4 yellow – red

Table 5.1.Continued

Indicator	**Chemical structure of indicator**	p*K*	**Useful range and solution color**
Bromo-thymol blue		7.30	6.0 – 7.6 yellow – blue
Bromo-phenol blue		4.10	3.0 – 4.6 yellow – blue
Phenol-phthalein		9.40	8.2 – 10.0 colorless – crimson
Litmus	Litmus is a mixture of several different dyes. It turns to red color in acidic solutions and red to blue in alkaline solution, the useful range of the indicator is 4.5–8.3 at 25 °C. Acid-base indicators on litmus owe their properties to a 7-hydroxyphenoxazone chromophore.	–	5.0 – 8.0 red – blue

Colorimetric method of determination of the pH value

The pH value of a solution is first determined approximately by means of an universal indicator. This permits the best indicator with appropriate useful range to be chosen from reference data. A definite quantity of this indicator is then added to a certain volume of the test solution. The color produced is compared with those obtained with the same concentration of indicator, in a series of buffer solutions of known pH value. In visual colorimetric method by matching the colors of the given and standard buffer solutions, the pH of the unknown solution may be estimated within 0.05 pH units. When the measurement of the pH value demands high precision it is carrying out by using spectrophotometer or colorimeter for the determination of the ratio of the concentrations of two colored forms of the indicator. If this ratio is known the pH value of solution may be calculated using equation (5.9). Another way for precise determination of the pH is potentiometric method.

Problems

Examples

Example 1. Calculate the pH value of 0.04 mol/L NaOH solution. Assume the base is fully dissociated.

Solution. Because NaOH is considered to be completely ionized, $[OH^-]$ = 0.04 mol/L. The simplest of various alternatives for calculation is to first find pOH value, and then subtract that value from 14 to obtain pH.

$$\mathrm{pOH} = -\log[\mathrm{OH}^-] = -\log 0.04 = 1.4,$$

$$\mathrm{pH} = 14 - \mathrm{pOH} = 14 - 1.4 = 12.6.$$

Example 2. Calculate the pH value for the solution that is resulting if 25 mL of 0.16 mol/L NaOH solution is added to 50 mL of 0.10 mol/L HC1 solution.

Solution. The pH value of the solution is determined by whether an excess of acid or base is used, or whether they are used in exactly equivalent amounts. The first step is to determine this.

$$\text{Moles of NaOH} = c_{\mathrm{NaOH}} \cdot V_{\mathrm{NaOH}} = 0.025 \times 0.16 = 0.004 \text{ mol},$$

$$\text{moles of HC1} = c_{\mathrm{HCl}} \cdot V_{\mathrm{HCl}} = 0.05 \times 0.10 = 0.005 \text{ mol}.$$

Consequently the resulting solution is acidic because there is more acid than base. According to the equation

$$NaOH + HC1 \rightarrow NaC1 + H_2O$$

resulting solution contains salt NaC1 and water. The salt has no effect on the pH value of solution. The excess of the acid is

$$0.005 - 0.004 = 0.001 \text{ mol.}$$

The total volume of the resulting solution is 0.025 + 0.05 = 0.075 liter. The 0.001 mol of HC1 is completely dissociated and concentration of H^+ ions is: $[H^+] = 0.001/0.075 = 0.0133$ mol/L,

$$pH = -\log[H^+] = -\log 0.0133 = 1.88.$$

Problems for self-solving

1. Calculate the pH value of a solution with an HCl molar concentration of a) 10^{-5} mol/L and b) 1 mol/L. Assume the acid is fully dissociated. *Answer: a) pH = 5, b) pH = 0.*

2. Calculate the pH value after adding of 1 mL of 0.01 mol/L HCl solution to 1 liter of distilled water that is initially at pH = 7. *Answer: pH = 5.*

3. What is the pH value of solution that is formed after 100 mL of 0.1 mol/L NaOH solution is added to 900 mL of a solution containing 0.03 mol/L of acetic acid (CH_3COOH, pK = 4.75)? Use Henderson-Hasselbalch equation for calculations. *Answer: pH = 4.52.*

4. «Acetate buffer» solution is made of sodium acetate and acetic acid. Consider such solution contains equal quantities of acid and salt. Calculate the pH value of this solution using Henderson–Hasselbalch equation. Dissociation constant of acetic acid is $1.75 \cdot 10^{-5}$ mol/L. *Answer: pH = 4.76.*

5. Calculate the pH value of «benzoate buffer» using Henderson–Hasselbalch equation. The solution was prepared by mixing of equal volumes of sodium acetate and benzoic acid solution. The concentration of each solution is 0.1 mol/L. Consider dissociation constant of benzoic acid is $6.3 \cdot 10^{-5}$ mol/L. *Answer: pH = 4.20.*

6. The ionic product of water at 40 °C is equal to $3.80 \cdot 10^{-14}$. Calculate the values of molarities of hydrogen and hydroxide ions in distilled water,

and its pH value at 40 °C. *Answer:* $[H^+] = [OH^-] = 1.95 \cdot 10^{-7}$ *mol/L; pH = 6.71.*

7. Determine and write whether aqueous solutions at 25 °C with each of the following ion concentrations are neutral, acidic, or basic: (a) $[H^+] = 1 \cdot 10^{-9}$ mol/L; (b) $[OH^-] = 1 \cdot 10^{-7}$ mol/L; (c) $[OH^-] = 1 \cdot 10^{-14}$ mol/L. *Answer: (a) basic; (b) neutral; (c) acidic.*

8. Calculate the concentrations of a dissolved substances in the following aqueous solutions at 25 °C: (a) KOH for which the pH is 12.0, (b) $Ca(OH)_2$ for which the pH is 11.3. *Answer: (a) 0.01 mol/L; (b) 0.001 mol/L.*

9. The pH value of the 0.10 mol/L formic acid (HCOOH) solution is found to be 2.38. Calculate dissociation constant of formic acid at a given temperature. *Answer:* $1.8 \cdot 10^{-4}$ *mol/L.*

10. Determine whether the pH value of aqueous solutions of the following salts is equal to, greater than, or less than 7: (a) NH_4Cl, (b) Na_2CO_3, (c) KF, (d) KBr. In the cases where the medium is not neutral, write a hydrolysis equation for explanation of your answer.

THEME 6
COLLIGATIVE PROPERTIES OF SOLUTIONS

Colligative properties of solutions are several important properties that for a given solvent depend on the number of solute particles in solution and not on the nature of the solute particles. These particles may be atoms, ions or molecules. It is important to keep in the mind that we are talking about relatively dilute solutions, that is, solutions whose concentrations are less than 0.1 mol/L. The term «colligative properties» denotes «properties that depend on the collection», this means that values of colligative properties depend on the collective effect of the number of solute particles in solution and do not depend on the nature of the particles.

The colligative properties are:

- vapor pressure lowering;
- boiling-point elevation;
- freezing-point depression;
- osmotic pressure.

Vapor pressure lowering

Vapor pressure of a liquid substance is the pressure due to molecules of this substance that would be generated if the gas and the liquid phases of the substance were allowed to reach equilibrium in a closed system.

If a solute is *nonvolatile* (this means, it has a very low, unmeasurable vapor pressure), vapor pressure of the solution is always less than that of the pure solvent and depends on the concentration of the solute. The relationship between solution vapor pressure and solvent vapor pressure was obtained by French chemist F. Raoult and is known as *Raoult's law*. This law states that *the vapor pressure of a solvent over a solution (p_1) equals the product of vapor pressure of the pure solvent ($p_1°$) and the mole fraction of the solvent in the solution (x_1)*

$$p_1 = x_1 p_1°. \tag{6.1}$$

In a solution containing only one solute, than $x_1 = 1 - x_2$, where x_2 is the mole fraction of the solute. Equation of the Raoult's law can therefore be rewritten as

$$(p_1° - p_1)/p_1° = x_2. \tag{6.2}$$

One can see that the *relative decrease in vapor pressure of the solvent is directly proportional to the mole fraction of the solute in solution.*

If both components of a solution are *volatile* and characterized by measurable vapor pressure, the vapor pressure of the solution is the sum of the individual partial pressures. In this case Raoult's law holds equally for all components

$$p_i = x_i p_i°. \tag{6.3}$$

Elevation of boiling point

Because the presence of a solute lowers the vapor pressure of a solvent over the solution, it must also affect the boiling point of the solution. The boiling of a pure liquid or a solution occurs at that temperature at which its vapor pressure becomes equal the external atmospheric pressure. It is known that at any temperature the vapor pressure of the solution is lower than that of the pure solvent, so the vapor pressure of solution reaches atmospheric pressure at a *higher* temperature than the normal boiling point of the pure solvent. This leads to *elevation of boiling point* of solution in comparison with pure solvent. The boiling-point elevation is defined as

$$\Delta T_b = T_b - T_{b,o} > 0, \tag{6.4}$$

where T_b is the boiling point of the solution and $T_{b,o}$ – the boiling point of the pure solvent. Because ΔT_b is proportional to the lowering of the vapor pressure, it must be also proportional to the concentration of the solution. It has been found experimentally that

$$\Delta T_b = K_b m, \tag{6.5}$$

where m is the molality of the solution and K_b is the *molal boiling-point elevation constant.* The units of K_b are $K \cdot kg \cdot mol^{-1}$.

It has been shown experimentally and proved theoretically that K_b is determined only by properties of the solvent

$$K_b = \frac{RT_{b,o}^2 \cdot M_1}{1000 \cdot \Delta H_{vap}^o}, \tag{6.6}$$

here $T_{b,o}$ – boiling temperature of pure solvent, R – universal gas constant, M_1 – molar mass of the solvent, ΔH_{vap}^o – enthalpy change of vaporization of the pure solvent.

The value of boiling-point elevation constant for water is 0.52 K·kg·mol^{-1}, one can see that if the molality of an aqueous solution is 1 mol/kg, the boiling point will be 100.52 °C.

Depression of freezing point

The phenomenon of the depression of the freezing point of a solution is caused by the lowering the vapor pressure of the solution like elevation of boiling point. The pure solvent freezes if its vapor pressures in liquid and solid states are equal. The vapor pressure of a solid solvent depends on temperature only and decreases with the decrease in temperature. This leads the temperature of the freezing of solution is *lower* than the freezing point of the solvent. The *depression of freezing point* is defined as

$$\Delta T_f = T_{o,f} - T_f > 0, \tag{6.7}$$

in which $T_{o,f}$ is the freezing point of pure solvent, and T_f – the freezing point of the solution. The ΔT_f value is proportional to the molal concentration of the solute

$$\Delta T_f = K_f m, \tag{6.8}$$

in which m is the solute molality, and K_f is the *molal freezing-point depression constant*. Like K_b, the K_f has the units of K·kg·mol^{-1} and depends only on properties of the solvent

$$K_f = \frac{RT_{f,o}^2 \cdot M_1}{1000 \cdot \Delta H_{fus}^o}, \tag{6.9}$$

where $T_{f,o}$ – freezing temperature of pure solvent, ΔH_{fus}^o is enthalpy change of fusion of the solvent.

The value of freezing-point depression constant for water is 1.86 K·kg·mol^{-1}, one can see that if the molality of an aqueous solution is 1 mol/kg, the freezing point will be –1.86 °C.

Osmosis

The phenomenon of *osmosis is the spontaneous movement of a pure solvent into a solution separated from it by a semipermeable membrane.*

The membrane is permeable only by the solvent molecules but not by the solute and allows the solvent to pass through. The word *osmosis* originates from the Greek word meaning «push».

The osmotic pressure is the pressure that must be applied to the solution to prevent the osmotic solvent transfer.

For dilute solutions the osmotic pressure is given by the van't Hoff's equation

$$\pi = cRT, \tag{6.10}$$

where T – absolute temperature, c – molar concentration of the solute. If universal gas constant is used as 8.314 J/(mol·K), and molar concentration is expressed in units of mol/m^3, then osmotic pressure is expressed in Pascals.

In chemistry as well as in medicine, if two solutions are of equal concentration and, hence, of the same osmotic pressure, they are said to be *isotonic*. If two solutions are of unequal osmotic pressures, the more concentrated solution is said to be *hypertonic* and the more dilute solution is described as *hypotonic*.

Colligative properties of electrolyte solutions

Colligative properties of electrolytes is characterized by slightly different approach than the one used for the colligative properties of nonelectrolytes. The reason is that electrolytes dissociate into ions in solution, and so one unit of an electrolyte compound separates into two or more particles when it dissolves.

Thus, the colligative properties of binary electrolyte solution should be twice as great as those of an electrolyte solution containing a nonelectrolyte in the same concentration. Similarly, we would expect a ternary electrolyte solution to depress the freezing point by three times as much as a nonelectrolyte solution with the concentration. To account for these effects we must modify the equations for colligative properties as follows

$$(p_1{}^\circ - p_1)/p_1{}^\circ = ix_2, \tag{6.11}$$

$$\Delta T_b = iK_b m, \tag{6.12}$$

$$\Delta T_f = iK_f m, \tag{6.13}$$

$$\pi = icRT\,. \tag{6.14}$$

The variable i is the *van't Hoff's isotonic factor*, which is defined as the ratio of actual number of particles in solution after dissociation and number of molecules (structural units) of initially dissolved substance.

Thus, i should be 1 for nonelectrolytes. For strong binary electrolytes such as NaCl and KNO_3, it should be 2, and for strong ternary electrolytes such as Na_2SO_4 and $MgCl_2$, i should be 3. In reality, the colligative properties of electrolyte solutions are usually smaller than anticipated, because at higher concentrations, electrostatic forces come into play, drawing cations and anions together. A cation and an anion held together by electrostatic forces are called an *ion pair*. The formation of an ion pair reduces the number of particles in solution by one, causing a reduction in the colligative property.

Problems

Examples

Problem 1. The average osmotic pressure of blood is 7.7 atm at 25 $^\circ$C. Calculate the molarity and mass percent of sodium chloride solution that will be isotonic with the blood. This kind of solution is known as a physiological saline solution.

Solution. Sodium chloride is strong electrolyte and gives two ions during dissociation, so its van't Hoff's isotonic factor equals 2. Because we are given the osmotic pressure and temperature, we can solve the equation

$$\pi = icRT$$

for the concentration: $c = \pi/(iRT)$, where we need to use the pressure transferred to SI units: $p = 7.7\times 1.013\cdot 10^5 = 7.8\cdot 10^5$ Pa. Hence,

$$c = 7.8\cdot 10^5/(2\cdot 8.314\cdot 298) = 157.41 \text{ mol/m}^3 = 0.157 \text{ mol/L}.$$

Assuming the dencity of the solution as 1 g/cm^3, we have for mass percent

$$\omega = m(\text{NaCl})/m(\text{solution}) = 0.157\cdot 58.5/1000 = 0.0092 \text{ or } 0.92\ \%.$$

Problem 2. Ethylene glycol, HO–CH_2–CH_2–OH, is a nonvolatile nonelectrolyte. It is used as a main part of automotive antifreeze. Typical antifreeze is an aqueous solution of ethylene glycol containing 25 % by mass of the glycol. Calculate the boiling and freezing points of the antifreeze.

Solution. To calculate the boiling-point elevation and the freezing-point depression we must know the molality of the solution. If the 100 g of the antifreeze is taken, the masses of ethylene glycol and water in the solution are 25 and 75 g, respectively. Using these quantities, we can calculate the molality of the solution

$$molality = n(\text{glycol})/m(\text{water}),\ n(\text{glycol}) = 25/62 = 0.40 \text{ mol},$$
$$molality = 0.40/0.075 = 5.33 \text{ mol/kg}.$$

Using this value and the molal boiling-point elevation and freezing-point depression constants we have

$$\Delta T_f = K_f m = 1.86\times 5.33 = 9.9\ ^{\circ}\text{C},$$
$$\Delta T_b = K_b m = 0.52\times 5.33 = 2.8\ ^{\circ}\text{C}.$$

Finally, the boiling and freezing points of the antifreeze are

$$\text{freezing point} = 0\ ^{\circ}\text{C} - \Delta T_f = -9.9\ ^{\circ}\text{C}.$$

$$\text{boiling point} = 100\ ^{\circ}\text{C} + \Delta T_b = 102.8\ ^{\circ}\text{C}.$$

Problem 3. Arrange the following aqueous solutions in order of their expected freezing points: 0.15 mol/kg KCl, 0.10 mol/kg $BaCl_2$, 0.10 mol/kg HCl, 0.10 mol/kg CH_3COOH, 0.10 mol/kg $C_{12}H_{22}O_{11}$.

*Solution.*We must order these solutions according to expected freezing points, which may be estimated on the total molalities of the dissolved particles in solutions. These values are depended on the initial concentration of the solute, number of ions to be produced during dissociation of the solute and the ability of solute to dissociate. By the first we must determine whether the substance is a nonelectrolyte or an electrolyte and the electrolyte power. $BaCl_2$, KCl, and HCl are strong electrolytes, CH_3COOH is a weak electrolyte, and $C_{12}H_{22}O_{11}$ is a nonelectrolyte. These facts give possibility to say, the molality of solute particles in sucrose is 0.10 mol/kg and that of acetic acid is rather more than 0.10 mol/kg. Potassium chloride and hydrochloric acid after dissociation produce 2 ions, in these cases the total concentration of the ions in solution will be 0.3 mol/kg and 0.2 mol/kg, respectively. The number of ions, formed when barium chloride ionizes, equals 3, this gives the total ion concentration of 0.3 mol/kg. Because the freezing points depend on the total molality of particles in solution, the required order of solutions is: 0.10 mol/kg $C_{12}H_{22}O_{11}$(highest freezing point), 0.10 mol/kg CH_3COOH, 0.10 mol/kg HCl, the lowest freezing point corresponds the solutions 0.15 mol/kg KCl and 0.10 mol/kg $BaCl_2$.

Problems for self-solving

1. Which of the following solutes will produce the largest and the lowest increase in boiling point after dissolution in 1 kg of water: 0.05 mol of barium nitrate ($Ba(NO_3)_2$, strong electrolyte), 0.08 mol of sodiun chloride (NaCl, strong electrolyte), 0.1 mol of acetic acid (CH_3COOH, weak acid) or 0.1 mol of glycerol ($C_3H_8O_3$, nonelectrolyte)?

2. List the following aqueous solutions in order of decreasing of freezing points: 0.01 mol/kg Na_2SO_4, 0.01 mol/kg KBr, 0.01 mol/kg glycerol ($C_3H_8O_3$, nonelectrolyte), 0.01 mol/kg phenol (C_6H_5OH, weak acid).

3. The average osmotic pressure of blood is 7.7 atm at 25 °C. Calculate the molarity of glucose ($C_6H_{12}O_6$) in solution which will be isotonic with the blood. *Answer: c = 0.315 mol/L.*

4. Calculate the osmotic pressure of 0.002 mol/L sucrose ($C_{12}H_{22}O_{11}$) solution at 25 °C. *Answer: p = 4955 Pa.*

5. The osmotic pressure of a solution containing 1.35 g of a protein per 100 mL of solution is found to be 9.12 Torr at 25.0 °C (Torr is a traditional unit of pressure, 1 Torr = 133.3 Pa). Estimate the molar mass of the protein. *Answer:* $M = 4.9 \cdot 10^5$ *g/mol.*

6. The solution is made by dissolving 25 mg of insulin in 5.0 mL of water. The osmotic pressure of this solution equals 2066 Pa at 25°C. Assuming that insulin is nonelectrolyte, and there is no change in volume occurred during its dissolution, calculate the molar mass of the hormone. *Answer: M = 6000 g/mol.*

7. There are two aqueous solutions, namely 0.35 mol/kg of $CaCl_2$ and 0.90 mol/kg of $(NH_2)_2CO$ (urea). Compare the following properties of these solutions: (a) boiling points; (b) freezing points; (c) vapor pressures.

8. A 0.9 percent by mass solution of NaCl is referred to as «physiological saline» or «isotonic saline» because its osmotic pressure is equal to that of the human blood. Calculate the osmotic pressure of this solution at normal body temperature (36.6 °C). The density of the saline solution equals 1.005 g/mL, assume complete dissociation of the solute. *Answer:* $\pi = 796$ *kPa.*

9. Calculate the expected freezing point of a 0.20 mol/kg aqueous solution of $CaCl_2$. Assume complete dissociation of the substance at dissolution. *Answer:* $t = 1.12\ ^oC$.

10. Ethylene glycol, $C_2H_6O_2$, is used for preparation of different antifreeze mixtures. It gives protection against freezing up to –25 °C. How many moles of solute are needed per kilogram of water to ensure such protection? *Answer:* $n(C_2H_6O_2) = 13.44$ *mol.*

Further readings

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