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Hydrogeochemistry Fundamentals and Advances

Mass Transfer and
Mass Transport

Viatcheslav V. Tikhomirov

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Volume 2: Mass Transfer
and Mass Transport

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To my beloved women, to my mother, wife and daughter dedicated!

Contents

Abstract	xi
Preface	xiii
Spontaneous Processes and Mineral Equilibrium	xv
1 Chemical Reactions	1
1.1 Real Water Solution	2
1.1.1 Properties of Water Solution	3
1.1.2 Composition of Water Solution	7
1.1.3 Structure of the Water Solution	13
1.1.4 Basis Components of a Solution	18
1.2 Spontaneous Processes	21
1.2.1 Energy of Spontaneous Processes	25
1.2.2 Direction of the Spontaneous Processes	27
1.2.3 Chemical Potential	28
1.2.4 Thermodynamical Concentration	32
1.2.4.1 Activities in Ideal Solutions	33
1.2.4.2 Activities in Real Solutions	37
1.3 Chemical Reactions	48
1.3.1 Restrictions of Spontaneous Reactions	49
1.3.2 Law of Mass Action	52
1.3.3 Equilibrium Constants of Reactions	55
1.3.4 Direction of Reactions	61
1.3.5 Reaction Rate	65
1.3.5.1 Elementary Reactions	66
1.3.5.2 Complex Reactions	72
1.3.6 Dependent and Independent Reactions	77

2	Hydrogeochemical Processes	81
2.1	Homogenous Processes	82
2.1.1	Electron Exchange	82
2.1.1.1	The Mechanism of Redox Processes	84
2.1.1.2	Oxidation Potential	88
2.1.1.3	Determination of Oxidation Potential	91
2.1.1.4	Oxygen Fugacity	97
2.1.2	Proton Exchange	98
2.1.2.1	Mechanism of Acid-based Reactions	99
2.1.2.2	Hydrogen Parameter	100
2.1.2.3	Buffer Systems	103
2.1.2.4	Determination of Solution's pH	105
2.1.3	Complexation	107
2.1.3.1	Mechanism of Complexation	108
2.1.3.2	Stability of Complex Formations	115
2.1.3.3	Complexation Function	119
2.1.4	Real Composition of Water	125
2.1.4.1	Rates of Homogenous Processes	126
2.1.4.2	Ionic Equilibrium in the Solution	127
2.1.4.3	Models of Water Solution's Composition	130
2.2	Heterogeneous Processes	134
2.2.1	Phase Rules	136
2.2.2	Mass Transfer by Mineral Components	140
2.2.2.1	Mineral-salt Complex of Rocks	142
2.2.2.2	Adsorption and Desorption	146
2.2.2.3	Ion Exchange	161
2.2.2.4	Surface Complexation	187
2.2.2.5	Adsorption and Desorption Rate	201
2.2.2.6	Dissolution and Minerogenesis	207
2.2.3	Mass Transfer of Nonpolar Components	304
2.2.3.1	Mass Transfer with Underground Gas	312
2.2.3.2	Mass Transfer with Nonpolar Substances	325
2.2.3.3	Distribution of Nonpolar Components	341
2.2.4	Equilibrium of Heterogeneous Processes	343
2.3	Bio-geochemical Processes	347
2.3.1	Biogeochemical Cycle	348
2.3.2	Niches of the Detrital Trophic Chain	354
2.3.3	Biodegradation of Organic Matter	370
2.3.3.1	Reactions of Biodegradation	372
2.3.3.2	Digestion	377
2.3.4	Rates of Biochemical Processes	383
2.3.5	Redox Geochemical Zoning	392

2.4	Isotopic Processes	399
2.4.1	Radioactive Decay	400
2.4.1.1	Primordial Radionuclides	400
2.4.1.2	Cosmogenic Radionuclides	403
2.4.2	Balanced Fractionating	407
2.4.3	Isotopic Mixing	414
2.4.4	Ground Water Chronometry	416
3	Migration of Elements	421
3.1	Migration forms	422
3.1.1	Subsurface Transporters	423
3.1.2	Aquaphiles	426
3.1.2.1	Estimates of Migration Capability	427
3.1.2.2	Properties of Aquaphilic Migration Forms	451
3.1.3	Organophiles	480
3.1.3.1	Amphiphilic Organophiles	481
3.1.3.2	Nonpolar Organophiles	486
3.1.4	Gasophiles	487
3.2	Mixing and Mass Transport	494
3.2.1	Hydrodynamic Dispersion	496
3.2.1.1	Diffusion Mixing	496
3.2.1.2	Advective Mixing	502
3.2.1.3	Dynamic Dispersivity and Methods of its Determination	505
3.2.2	Advection-dispersion Mass Transport	510
3.2.2.1	Equation of Advection-dispersion Mass Transport	511
3.2.2.2	Analytical Solution of Mass Transport Equations	513
4	Hydrogeochemical Forecasting	541
4.1	Methods of Forecasting	541
4.2	Model Forecasting Method	545
4.2.1	Problem Identification	547
4.2.2	Construction of Mathematical Models	548
4.2.2.1	Types of Hydrogeochemical Models	550
4.2.2.2	Selection of a Computation Process	559
4.2.2.3	Input Data	565
4.2.2.4	Selection of the Program Software	569
4.2.3	Reliability of Model Forecasting Results	570

Symbols	581
References	593
Normative Publications	608
Appendices	609
I Thermodynamic Properties of Mineral Forms of Migration	609
II The Partition Coefficients of the Gas Components	609
III Physical and Chemical Properties of Organic Compounds	609
APPENDIX I Thermodynamic Properties of Mineral Forms of Migration	611
A. Cation Generating Elements	611
B. Complex Generating Elements	627
C. Ligand Generating Elements	668
D. Salt and Minerals	677
APPENDIX II The Partition Coefficients of the Gas Components	685
A. Underground Gases of Methane Composition	685
B. Underground Gases of Nitrogen Composition	695
C. Underground Gases of Carbon dioxide Composition	697
APPENDIX III Physical and Chemical Properties of Organic Compounds.	698
A. Physical and Chemical Properties of Organic Carbon Compounds	698
B. Physical and Chemical Properties of Pesticides	709
Index	715

Abstract

This book is the second part of a course, “Fundamentals of Hydrogeochemistry.” It reviews spontaneous processes responsible for the formation of ground water composition and properties. It includes four major sections. The first section introduces the basics of thermodynamics and provides the concept of properties of chemical reactions. The second section is devoted to basic processes of the formation of natural waters properties and composition in the geological environment. The main attention is devoted to the water mass exchange with rock, subsurface gas, non-polar liquids and biochemical processes. The third section reviews processes of mass-transfer in the geological medium. In the fourth section methods of hydrogeochemical forecasting are described.

The textbook is intended for students specializing in geology, geochemistry, hydrogeology and ecology, and also may be of use to hydrologists and oceanologists.

Reviewer

Doctor of Geology, Prof. M.V. Charykova (S.-Petersb. State Univ.)

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Preface

This book is part II of a textbook *Fundamentals of Hydrogeochemistry*, part I of which was published in 2012. Whereas part I dealt with methods of study and description of the hydrochemical state of the geological medium, part II mostly touches upon spontaneous processes, which occur in ground waters. The processes are studied in consideration of the complexity of the geological environment in order to give an idea of their numerical modeling methods. In this connection the book contains four main sections.

Chapter one gives general ideas of the water solution's thermodynamical state and spontaneous reactions in it, their laws, energy, direction and kinetics.

Chapter two reviews main processes of spontaneous formation composition of ground water as an aggregate of many similar reactions between a multitude of components in the water composition. In this connection is introduced a concept of homogenous processes (redox, acid-base, complex formation, etc.) and mass exchange between water and rock, subsurface gas and non-polar liquids (ion exchange, surface complex formation, dissolution and mineral formation, physical absorption, etc.), as well as of biochemical and isotope processes.

Chapter three is about the element or compounds migration in the process of mixing and flow of ground water.

And lastly, chapter four gives an idea of hydrogeochemical forecasting and modeling methods.

The publication of this textbook was made due to the help by P.K. Konasavsky, A.A. Potapov and M. Gorfunkel who took upon themselves the ungrateful labor of reading the manuscript and gave helpful advice.

The author will appreciate any comments and advice about the textbook content and requests that comments be sent to:

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Spontaneous Processes and Mineral Equilibrium

No density or weight and no size.
They are just functions of varying rate.
All in existence due to pressure delta,
Temperature, mass, potential.
The stream of time is terribly uneven,
The space is just variety of shapes.
There is not one but many mathematics...
Maximilian Voloshin. Cosmos (1923)

Evolution of properties and composition in the geological medium is first of all change in properties and composition of ground water as a result of their reaction to the action of external factors. Cosmic, climatic, hydrological, biology-soil, anthropogenic and other factors disrupt both energy and material equilibrium of the medium, and the medium's resistance to this action and tendency to restore the equilibrium are the substance of ***spontaneous processes*** subordinated only to the laws of thermodynamics, physics and chemistry.

Before reviewing spontaneous processes, we must have a concept of the laws of thermodynamics, physics and chemistry, which control them. At the base of hydrogeochemical processes are the multitude of elements in the composition of water solutions and chemical reactions between them. For this reason familiarity with processes should begin with familiarity with the laws of conversion of one substance in the water composition into another one.

1

Chemical Reactions

Ground water, thermodynamically, is part of a complex heterogeneous system called the geological medium. This medium includes, beside ground water, rocks and often also underground gas or complex non-polar liquids (oil, oil products, etc.).

Rocks as aggregate of various minerals compose the largest part of the geological medium. Each mineral may be considered as an individual solid phase of the phase of constant composition. Minerals may be solid solutions and may contain substitutional impurities, which affect their chemical properties. However, hydrogeochemists more often ascribe to them permanent composition. This allows minerals to be viewed as elements of a single compound i with a molar fraction $C_i = 1$. The presence of impurities is usually ignored.

Ground water in its substance is a mixture of micro-particles of various size and composition poorly bonded between themselves. In terms of size these particles are drastically dominated by molecular size (less 1 nm), which in aggregate form *real solution*. In smaller amounts are present uniformly distributed micelles (1 to 100 nm). With the growth of their content the solution becomes colloid solution (sols), and sometimes even forms gels. Even larger particles (greater than 100 nm) form

suspensions and emulsions. Poly-molecular particles of similar properties and composition (for instance, all grains of the same mineral, gas bubbles or liquid drops) may be considered as individual homogenous substances: minerals, non-polar liquids or underground gases. In such case it is convenient to merge suspended mineral particles and enclosing rock into one medium. Lastly, ground water may be treated also as a live *ecosystem*. The aggregate of its live organisms (plants, animals, micro-organisms and fungi) form *biocenose*, which defines the nature of biochemical processes and plays an important role in the formation and its composition.

Overall liquid ground water is also a complex heterogeneous system, in which should be discerned: 1) real solution; 2) inert suspended substance; 3) biocenose (live dispersed matter).

1.1 Real Water Solution

Real solutions where individual components are visually indistinguishable compose most of the ground water volume and define its properties and composition. As a rule, it is identified with ground water in hydrogeochemistry studies.

Properties and composition parameters of this solution are called *thermodynamic state parameters*. They are subdivided into extensive and intensive ones. The *extensive* parameters include those which depend on the size of the medium or system, are proportionate with them and, therefore, are additive. Such are mass – m , volume – V , amount of the matter, heat, energy, etc. The *intensive* parameters include parameters, whose value does not depend on the size of the system or phase, namely, pressure – P , temperature – T , density – d , concentration – C , etc. They reflect change in the state of water.

Extensive and intensive parameters are tied between themselves. Change in any of them results in changes in the other ones. The ideas of cause and effect interrelation between these parameters define the *model of solution state*, and the mathematical expression of a given interrelation is the *equation of state of the solution*. It is sufficient to know some minimum number of its parameters for the complete description of the solution properties. As a rule, as such parameters of state serve first of all most easily measured, namely: volume, pressure, temperature and composition (V, P, T, C_i). Equations of state for the complex solutions are constructed based on equations of state of pure substances, which make its composition. For this are needed additional parameters, associated with the mixing

processes (mixing proportions, interaction coefficients, etc.). Parameter values and their interrelation are determined both theoretically, i.e., according to logic, and experimentally. For this reason, equations of state for the solutions, as a rule, include semi-empirical functional interrelations.

1.1.1 Properties of Water Solution

Solutions have special properties, which identify them among other substances. Real water solution is no exception.

1. First of all, it has variable composition, and the concentration of its substances are not constant. H_2O , as the dominant substance – solvent has most stable concentration, the others are present as admixtures. Their content varies within a very wide range and is usually quoted in values of concentration (molarity, molality, molar fraction, etc.).
2. Any solution is a medium with ***distributed parameters***. This means that within its limits composition and properties may change, but gradually. For this reason, specific stable boundaries between the waters of different composition are absent. On the contrary, concentration and property changes within the space coordinate of a single solution display gradients, i.e., values of parameter changes attributed to a unit of distance.
3. Real water solutions are capable of mixing with one another in unlimited proportions. At mixing, their extensive parameters are summed up whereas the intensive ones are levelling off.

If we treat mixing of different water solutions as a purely physical process, with no consideration of their chemical interaction, the mixture composition may be easily calculated.

Let us assume that mixed are only two solutions with salinities m_0 and m_1 and concentrations of component i respectively $C_{0,i}$ and $C_{1,i}$. If the fraction of one of them in unit volume of the mixture is equal to α , then the corresponding fraction of the other one will be equal to $1 - \alpha$, a salinity and concentration of the component i in the mixture will be the sum of the two addends:

$$m = \alpha \cdot m_0 + (1 - \alpha) \cdot m_1, \quad (1.1)$$

$$C_i = \alpha \cdot C_{i,0} + (1 - \alpha) \cdot C_{i,1}. \quad (1.2)$$

If mixed are two waters with known content of the component i , which does not enter chemical interaction, then from the composition of the mixture it is possible to determine proportions of the mixed waters:

$$\alpha = \frac{C_i - C_{i,1}}{C_{i,0} - C_{i,1}} \quad (1.3)$$

The value α , which may range between 0 and 1, is often called **fractional mixture concentration**. If the component i is not present in one of mixed waters ($C_{i,i} = 0$), the fractional concentration is equal to the ratio $C_i/C_{i,0}$.

To determine the fractional concentration of mixing are used, as a rule, strong acids or bases, which poorly form insoluble salt. For instance, to study the fraction of sea or fresh water in their mixture are used Cl^- or Na^+ but not sulphates, varbonates, Ca^{2+} or Mg^{2+} . In particular, the fraction of sea water in such mixture is determined from the following equation:

$$\alpha_{\text{sea}} = \frac{C_{\text{water,Cl}} - C_{\text{water,Cl,fresh}}}{C_{\text{water,Cl,sea}} - C_{\text{water,Cl,fresh}}} \quad (1.4)$$

where $C_{\text{water,Cl}}$, $C_{\text{water,Cl,sea}}$ and $C_{\text{water,Cl,fresh}}$ are weight contents of Cl^- , correspondingly, in mixtures, sea and fresh waters. If the chlorine content in fresh water is negligibly low and may be disregarded ($C_{\text{water,Cl,fresh}} \approx 0$), then

$$\alpha_{\text{sea}} = 0.00177 \cdot C_{M,\text{Cl}} \quad (1.5)$$

where $C_{M,\text{Cl}}$ is Cl^- concentration in millimoles per 1 liter.

In the absence of chemical interaction value α_i does not depend on the nature of the component. That is why the mixture composition may be calculated if the composition's mixed solutions are known. For this it is necessary to equate Equations (1.4) for two different components (or one component i and salinity) and to unfold the obtained equation as a function of interrelation between their concentrations in the mixture:

$$C_i = m \frac{(C_{i,1} - C_{i,2})}{m_1 - m_2} + \frac{m_1 \cdot C_{i,2} - m_2 \cdot C_{i,1}}{m_1 - m_2}. \quad (1.6)$$

Equation (1.6) shows that at mixing of two waters concentration of their components, which do not take part in chemical reactions are not removed from the solution, are tied between themselves in direct linear relation. For this reason the discovery of such linear interrelation in the ground water composition may indicate the participation in their formation of the mixing process.

- All solution parameters are tied between themselves by the equation of state. The most important component of such an equation is the connection between intensive and extensive parameters. This interrelation has a complex, not fully studied nature. However, it noticeably simplifies and is amenable to experimental studies in ideal double-component solutions with dominance of one component – solvent.

For characterization of the interrelation between the composition and extensive properties of the solution the outstanding American physicochemist Gilbert Newton Lewis (1875–1946) introduced additional intensive parameters under the common name **partial molar quantity**. Among them are partial molar volume, partial molar heat capacity, chemical potential, *etc.*

If we add to a water solution ΔN_i moles of any component i , its volume, heat, energy and other extensive properties will change by some value Δg . Such change of an extensive parameter, related to one mole solved component i , is called **mean partial quantity**

$$\bar{g}_i = \left(\frac{\Delta g_i}{\Delta N_i} \right)_{P,T,N_1,N_2,\dots,N_k}, \quad (1.7)$$

where \bar{g}_i is mean partial molar value of any extensive property, for instance volume ($\text{cm}^3 \cdot \text{mole}^{-1}$) or heat capacity ($\text{cal} \cdot \text{mole}^{-1} \cdot \text{deg}^{-1}$). It depends on concentration. That is why the derivative of this interrelation should be considered:

$$\bar{g}_i = \left(\frac{\partial g_i}{\partial N_i} \right)_{P,T,N_1,N_2,\dots,N_k}, \quad (1.8)$$

Which characterized real partial molar values. Thus, **true partial quantity** of a component i is partial derivative of any extensive property of its ideal solution (g_i) over its concentration at constant temperature and pressure.

The partial molar values per se are intensive properties as they do not depend on the total amount of solution and may be both positive and negative. If the solution pressure and temperature do not change, any of its extensive property is a function only of its composition:

$$g = f(N_1, N_2, N_3, \dots, N_k).$$

Let us assume that to a solution are added sequentially all its components by infinitely small amounts at constant pressure and temperature. At

each addition any extensive parameter changes by values $\partial g_1, \partial g_2, \dots, \partial g_k$, which respectively are equal:

$$\partial g_1 = g_1 \partial N_1, \partial g_2 = g_2 \partial N_2, \dots, \partial g_k = g_k \partial N_k. \quad (1.9)$$

In which case the derivative of the change of any extensive property at the addition of one component i may be represented as the sum of two addends:

$$\partial g_i = g_i \partial N_i + N_i \partial g_i, \quad (1.10)$$

And at the addition of all components total value of the extensive properties G will change by

$$\partial G = \sum g_i \partial N_i + \sum N_i \partial g_i. \quad (1.11)$$

If the amounts $\partial N_1, \partial N_2, \partial N_3, \dots, \partial N_k$ have the same proportions as in the initial solution, the composition of the latter does not change. This is the same as mixing two solutions of the same composition: the solution amount increases, and its composition does not. In this case the very partial molar values g_j also do not change, and $\sum N_i \partial g_i$ in the second addend in Equation (1.11) are equal to 0. Then

$$\partial G = \sum g_i \partial N_i. \quad (1.12)$$

Integrating Equation (1.12), on condition of constancy median partial molar values \bar{g}_i we obtain Equation

$$G = \sum_{i=1} \bar{g}_i N_i, \quad (1.13)$$

Which is called the **first Gibbs-Duhem equation**. It shows that any extensive property g , for instance volume, heat capacity or energy of the solution, may be determined from its composition, if corresponding median partial molar values of its components are known. For instance, if the mole amount of individual components in the composition of a solution and their partial molar volumes are known, then the volume of the entire solution will be equal to the sum of their products.

At the addition of not all components or all but in other proportions, the composition of the source solution noticeably changes, but the addend in the equation (1.11) $\sum N_i \partial g_i \neq 0$. Equating equations (1.11) and (1.12), we obtain **the second Gibbs-Duhem Equation**:

$$\sum N_i \partial g_i = 0 \quad (1.14)$$

It describes the association between partial molar values of different components in one solution at constant temperature and pressure. It follows from it that if content of only one component changes, the partial molar values of all components change, but so that

$$N_i \left(\frac{\partial g_1}{\partial N_1} \right)_{P,T,N_i} = - \left[N_2 \left(\frac{\partial g_2}{\partial N_1} \right)_{P,T,N_i} + N_3 \left(\frac{\partial g_3}{\partial N_1} \right)_{P,T,N_i} + \dots + N_k \left(\frac{\partial g_k}{\partial N_1} \right)_{P,T,N_i} \right]. \quad (1.15)$$

In other words, an increase in an extensive parameter of a solution due to addition of a component i is compensated by a decrease of median partial molar values of the remaining components in its composition.

If both parts of Gibbs-Duhem equation is divided by $\sum N_i$, i.e., if they are related to 1 mole of the solution, the equations (1.13) and (1.14) will assume the form:

$$G_M = \sum_{i=1} \bar{g}_i C_i, \quad (1.16)$$

$$\sum_{i=1} C_i \partial g_i = 0, \quad (1.17)$$

where G_M is median extensive parameter (volume, mass, heat capacity, etc.) of 1 mole of the solution.

Equations (1.13), (1.14), (1.16) and (1.17) are very important for further understanding of the effect of change in water composition of solutions on their extensive properties, first of all on volume and energy. In this connection very significant are median partial molar values of the components in water solutions, which are determined experimentally in pure solutions of individual components at an increase of concentration by 1 mole. The obtained results may be found in reference literature (Naumov *et al.*, 1971; Wagman *et al.*, 1982; CRC Handbook of Chemistry and Physics, 2004–2005, etc.).

1.1.2 Composition of Water Solution

Real composition of ground water is much more complex than the analytical one. It is a whole and very brittle formation created by the forces of

inter-atomic and inter-molecular interactions. Participants in it are almost all elements of Mendeleev's table, whose chemical properties are defined first of all by the number and potential energy of outer valence electrons. Only elements in the eighth group of the Mendeleev's table, the so-called *inert gases*, have completely occupied outer electron shells and refuse either to incorporate or give away electrons. As a result they are chemically most passive and are present in water only in atomic state. All other elements interact between themselves. For this reason the overwhelming majority of atoms in natural water are in a bonded state.

Such bonds may be *interatomic* (*interatomic bonding*) and *intermolecular* (*intermolecular bonding*). Forces of interatomic interaction are very strong (on the order of 10^2 kJ·mole⁻¹) and form the strongest chemical bonds, namely, molecules and ions. Forces of intermolecular interaction are weaker (0.1–1 kJ·mole⁻¹) and control bonds between molecules and ions. Among them are noticeably identified hydrogen bonds, which hold an intermediate position with energy close to 10–50 kJ·mole⁻¹. The less energetic bonds are, the weaker they are and the easier destroyed, so it is more difficult to discover and analytically study them. Most methods of chemical analysis destroy intermolecular and hydrogen bonds and determine the content of components with the strongest interatomic bonds. However, weak bonds are most common and play an important role in the formation and real properties of ground water in static conditions of the geological medium.

Interatomic chemical interactions are most energetic. Their multitude, according to quantum theory, may be boiled down to three major types: *covalent*, *polar* and *ion*. In the absence of differences in electric negativity, the bond between atoms has non-polar covalent nature, at very large difference (more than by 1.7 times) – ion and in the intermediate case – polar.

Covalent and polar bonds form due to communization of one or several electrons. Covalent bonding is typical of atoms with identical or similar properties, mostly non-metals. If these atoms are positioned symmetrically, molecules with covalent bonding have no charge or polarity. Such non-polar compounds, as a rule, have no inter-molecular bonds, and they are chemically very passive. Molecules with covalent bond poorly interact with H₂O and are poorly soluble in water. They are mostly numerous organic (C₃H₁₂, C₆H₆, etc.) and gas components (N₂, CH₄, C₂H₆, etc.).

The polar bonding is a covalent bonding where the atoms are positioned asymmetrically relative to the electron orbits, causing thereby the molecule polarity. Such molecules form dipoles with positively and negatively charged ends. They form when interacting atoms are too different in their electric negativity to be able to form only a covalent bond insufficiently

Table 1.1 Dipole momentums of individual molecules in gas (Debye units, $1\text{D} = 3.34 \cdot 10^{-30} \text{Kl}\cdot\text{m}$) (CRC Handbook of Chemistry and Physics, 2004–2005).

Molecule	Dipole momentum, $\mu \cdot 10^{18}$	Molecule	Dipole momentum, $\mu \cdot 10^{18}$
CO_2, CH_4	0	SO_2	1.63
CO	0.11	$\text{C}_2\text{H}_6\text{O}$	1.68
NO	0.16	CH_4O	1.70
NO_2	0.32	H_2O	1.85
O_3	0.53	$\text{C}_3\text{H}_6\text{O}$	2.88
H_2S	0.98	NaCl	9.00
NH_3	1.47		

different to convert it to an ion bond. The polar bond is resident first of all in H_2O , and also HCl , NH_3 , SO_2 , etc. Their properties depend on values of *dipole momentum*, which is equal to the product of their positive charge and distance between the charges (Table 1.1). Substantial dipole momentum is intrinsic in H_2O and ammonia (NH_3), alcohols, organic acids, ethers. But the main dipole in water solutions composition is obviously H_2O , which determines main water properties. Other polar chemical compounds are sufficiently active and relatively well soluble in water.

In a case of ion bonding one or more electrons is/are lost by some atoms or their groups, and acquired by other atoms or their groups. A result is the formation of particles with electrostatic charge – ions. The distinguishing feature of such ions is that the bond between them and their behaviour to a substantial extent is determined by forces of the electrostatic field. By the sign of the charge are distinguished cations (positively charged) and anions (negatively charged). By the size they may be monoatomic (K^+ , Mg^{2+} , Cl^- , etc.) and polyatomic (HCO_3^- , SO_4^{2-} , etc.), by the charge values – mono- (Na^+ , Cl^- , etc.) and poly-charged (Cu^{2+} , Al^{3+} , S^{2-} , etc.). The capacity of these ions to interact between themselves and with other compounds to a substantial extent depends on their size and charge, and also on the *charge density* (ion potential), i.e., the ratio of ion z_i charge and the values of its radius r_i . Ions are well soluble in natural water and are main among the analysed components.

Intermolecular interaction has mostly an electrical nature and depends on the distances between molecules. At very large distances molecules do not interact but on approach they first are pulled to each other, and then repel. Depending on the type of a molecule, three major

types of their interaction are distinguished: the dispersion, induction and orientation ones.

The dispersion interaction is observed between non-polar neutral molecules. It occurs only at the moment of the approach of these molecules due to the appearance in them of a short-time induced dipole momentum. In natural waters composition so interact mostly gas or organic components at encounter. This interaction is relatively rare, brief and too weak. For this reason its effect on ground water composition is insignificant.

Inductive interaction occurs between polar and non-polar compounds. At the moment of their approach under the influence of the dipole charge occurs inductive polarization of non-polar molecules. In water, most common inductive interaction is established between dipoles H_2O and electrically neutral gas and organic compounds. But this interaction is also relatively weak and does not form firm super-molecule bonds. Moreover, non-polar molecules rather obstruct stronger orientation interactions between H_2O dipoles. Non-polar molecules of a large size increase the distance between H_2O dipoles, weaken hydrogen bonds between them and therewith decrease internal pressure. The greater the size of non-polar molecules, the smaller their solubility in water whereas its invasion of tetrahedral structure of water requires additional energy proportionate to the values of external pressure. That is why solution of non-polar compounds facilitates decrease of the density of a water solution and increase of its compressibility factor and freezing temperature.

Orientation interaction is observed between charged particles and is most important in the formation and composition of water properties. Three major types of such interaction are distinguished: 1) between dipoles, 2) between ions and dipoles, 3) between ions.

The first type is linked mainly with interaction of H_2O molecules between themselves and much more rarely with dipoles of organic compounds. Dipoles, when they meet, orient to one another by opposite charges and interact. Exactly at inter-dipole interaction often arise hydrogen bonds, strengthening supra-molecule formations.

The second type is typical of interaction between H_2O and ions. When they meet, water dipoles orient in the electrostatic field of ions, pulled in by the end with the opposite charge and become less mobile. This way form super-molecule associations of the aquatic complex type $[\text{ion}(\text{H}_2\text{O})_n]$. Such process is called **hydration**, and formed complexes – **hydrates**. Diluted solutions are dominated by saturated aquatic complexes where each ion is surrounded by water molecules, for instance, $\text{Cu}[\text{H}_2\text{O}]_6^{2+}$, $\text{Ni}[\text{H}_2\text{O}]_6^{2+}$. Even ions of hydrogen H^+ and hydroxyl OH^- do not exist in water

individually but form complexes $\text{H}[\text{H}_2\text{O}]^+$ (hydroxonium) and $\text{OH}[\text{H}_2\text{O}]^-$ (hydroxide hydrate).

The third type is associated with interaction of ions between themselves. A water solution with high relative dielectric permeability substantially weakens forces of electrostatic attraction between oppositely charged ions, which prevents them from interaction between themselves. Because of this cations and anions coexist in water separately. Only at very high their concentration and deficit of water they are capable of interacting with one another forming more complex associations, often joined by donor-acceptor bonds, i.e., at the expense of undivided pair of electrons from the donor-atom and free orbital of acceptor-atom.

That is exactly the competition between different forms of orientation interaction, which determines the composition and chemical properties of ground water. In very fresh water dominates orientation interaction between H_2O dipoles. As salinity and concentration of the *dissociated ions*, i.e., the simplest anions and cations (Na^+ , Ca^{2+} , Cl^- , CO_3^{2-} , etc.) grows, also increases the role of interaction between water and ions. At relatively high salinity ions have to interact between themselves, forming more complex *associated ions* (CaHCO_3^+ , NaHCO_3^- , HSiO_3^- , HCO_3^- , etc.), capable of decomposing into simpler ones with freshening water. At this, the number of associated ions increases. Thus form complex super-molecular compounds with relatively weak bonds (PbCl_3^- , AlF_6^{3-} , $\text{Fe}_2\text{OH}_4^{2+}$, etc.). Moreover, one and the same dissociated ion may be part of the composition of different associated ones. For instance, calcium in the sea water may exist simultaneously as Ca^{2+} , $[\text{CaHCO}_3]^+$, $[\text{CaCO}_3]$, $[\text{CaSO}_4]$, etc.

The simplest associated ions, which include only two ions (for instance, FeOH^+ , AlF_6^{3-} , NaSO_4^- , CaCO_3 , etc.), are called *ion pairs*. Associated formations from a large number of cations and anions are called *complex* or *coordination compounds*. Cations (Al^{3+} , Cu^{2+} , Fe^{3+} , NH_4^+ , H_3O^+ , etc.) are positioned in the venter of these complex formations and are called *central atoms* or *central groups*. Anions (OH^- , Cl^- , CO_3^{2-} , SO_4^{2-} , etc.) and more rarely polar compounds (H_2O , NH_3 , etc.) are positioned around cations and are called *ligands* or *addends*. Central atoms and their closest ligands form an internal sphere of complex compounds. Outside of this sphere may be additional ligands, which are called off-spherical. In writing the composition of complicated complexes it is customary to include the compound of the central atom with ligands of internal sphere in square brackets, and with ligands of the external sphere – in squiggle brackets ($\{[\text{Cu}(\text{H}_2\text{O})_6]^{2+}\text{Cl}^-\}$, $\{[\text{Mn}(\text{H}_2\text{O})_6]^{2+}\text{SO}_4^{2-}\}$, $\{[\text{Al}(\text{H}_2\text{O})_6]^{3+}\}$, etc.).

The nature of bonds in complex compounds may be diverse – inter-dipole, ion-dipole, sometimes hydrogen but most common is *donor-acceptor*,

which is covalent with some polarity. At that, ligands play a role of *donor* and the central atom – of *acceptor* of electrons.

The number of donor atoms in the composition of an individual ligand determines its denticity (toothiness). If a ligand have only one such atom (OH^- , Cl^- , F^- , etc.), it is called *monodentate*, i.e., single-toothed. A ligand with several such atoms is called *polydentate*, i.e., multi-toothed. Polydentate ligands have 2 and more bonds with one and the same central atom, clamping up on it like a claw. That is why such complexes with polydentate ligands are especially strong and are called *cyclical* or *chelate*, i.e., claw-like. They are often called simply *chelates*. To the polydentate are attributed ligands of the type CO_3^{2-} , SO_4^{2-} , PO_4^{2-} and many organic acids. Complex formations may include various ligands. Then they are called *mixed complexes* ($[\text{AlF}_2(\text{OH})]^0$, $[\text{BF}_2(\text{OH})]^0$, $[\text{BeF}(\text{OH})_2]^-$, etc.). At incomplete utilization of their donor capacity the ligands can have coordination tie with the second cation. Then ligands serve as a bridge. Such complexes with several central atoms are called *polynuclear complexes*. The bridges are capable of forming both monodentate and polydentate ligands. In particular, in the formation of such bridges quite often participates OH^- . Various polynuclear hydroxide complexes are typical for metals Zr, Hf, Nb, Ta, Sc, Pb, Zn, Th ($\text{Th}_2(\text{OH})_2^{6+}$, $\text{Th}_4(\text{OH})_8^{8+}$, $\text{Th}_6(\text{OH})_{15}^{9+}$, etc.). Polynuclear complexes with various central atoms are called *heteropolynuclear complexes*.

Ligands are positioned around the central cations in a certain order. The number of ligands which can append the central cation is called the *coordination number*, which in interrelation with and depending on the size of interacting ions has the values 2, 4, 6 and greater. The charge of a complex formation is equal to the sum of charges of intertied cations and anions and may be positive, negative and neutral. At that, neutral complexes may have analogue minerals. For instance, $\text{Al}(\text{OH})_3^0$ and gibbsite, BaSO_4^0 and barite, CaCO_3^0 and calcite, CaSO_4^0 and anhydrite, etc.

The appearance of polynuclear complexes sometimes facilitates polymerization and formation of large macromolecules, which are capable of making solution into colloid. For instance, at hydrolysis of oxide iron Fe^{3+} may form a complex compound $\text{Fe}(\text{OH})_3^0$, which polymerizes and forms large colloid molecules $[\text{Fe}(\text{OH})_3]_n$. In such solutions precipitates mineral of iron hydroxide – the limonite. Similar colloid forms occurrence are typical of many chelate complex compounds with organic ligands.

Overall real composition of ground water is a result of complex mostly orientation inter-molecular interactions. Their role increases with a decrease in solution particle mobility, i.e., lowering of temperature and