Chapter 2
Isotope Geochemistry of Natural Waters

2.1 Some Properties of Waters and Solutions

From the physical point of view, all natural waters are solutions of various inorganic and organic compounds. They also contain gases, colloidal and suspended particles of organic and inorganic origin, and many species of microorganisms. Thus, when studying the dynamics and phase transition of natural waters which result in their isotopic fractionation, one should not use the physicochemical constants for distilled water but rather those for solutions of given composition and concentration, which are features of the given type of natural water.

In a general sense, phase transitions in a one-component system are represented by the Clapeiron–Clausius equation

$$\frac{\partial p}{\partial T} = \frac{\Delta H}{T \Delta V} \tag{2.1}$$

where T and p are temperature and pressure of the phase transition; ΔV is the molal change in volume for this; ΔH is the molal heat of this transition (i.e., melting, vaporization, etc.).

Equation 2.1 is valid only for the reversible processes. Plotted on the (p, T)-diagram, the equation describes the two-phase equilibrium (Dreving and Kalashnikov 1964). For most of the phase transitions, we have $\partial p/\partial T > 0$. The only exceptions are the phase transition for the ice–water system and also those for a small number of other substances (such as bismuth, gallium, and germanium). The schematic thermodynamic diagram of water in terms of the p and T variables is given in Fig. 2.1.

The curves TA and TC corresponds to the pressure of vapor which is in equilibrium with water and ice respectively and the curve TB shows the dependence of ice melting temperature on pressure. The curve TB has a negative gradient, which means that the melting temperature decreases with an increase in pressure ($\partial p/\partial T < 0$). The point T is called the triple point of the thermodynamic equilibrium. It corresponds to the pressure and temperature at which coexistence of the three phases (solid–water–vapor) is possible. For water, the triple point pressure is equal to 609 Pa and the temperature is +0.0076°C; the ice melting temperature under pressure 1.013×10^5 Pa

Fig. 2.1 Schematic
thermodynamic diagram of
water (p and T-diagram): *I* is
the domain of water existence
in the liquid phase; *II* is the
domain of ice existence;
III is the domain of water
existence in the gaseous phase
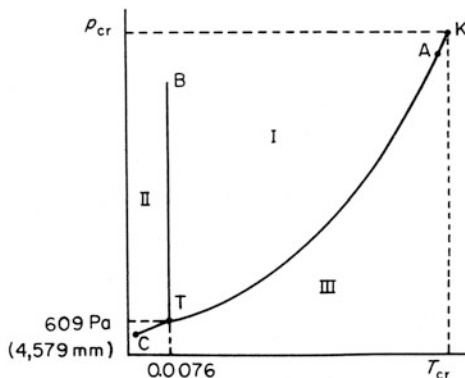
is 0°C. The dash represents the thermodynamic equilibrium between vapor and super-cooled water since ultra-distilled water permits super-cooling down to −50°C.

The point K in the diagram is called the critical point. It corresponds to the critical values of temperature and pressure. For water, the critical value of pressure is $p_{cr} = 2.21 \times 10^7$ Pa and the critical temperature is $T_{cr} = 374.2$°C. At these values, the water has density of 0.324 g/ml (the critical density). The critical point on the graph TK corresponds to the temperature and pressure at which the difference between the liquid and the vapor completely disappears. The critical point for liquids was discovered by Mendeleev in 1860. At the critical point, the graph TK pictured in the p and T coordinates breaks down. Indeed, putting the values $T = T_{cr}$, $H_{gas} = H_{liquid}$, and $V_{gas} = V_{liquid}$ into Eq. 2.1, we see that the left-hand side of the equation becomes indeterminate, which indicates that there is a discontinuity of the function $p = f(T)$. All the properties of the coexisting phases are the same at the critical point. Moreover, for temperatures $T > T_{cr}$, water cannot exist in a liquid and vapor state simultaneously at any pressure. In contrast to the liquid phase, the solid phase (ice) can theoretically exist at temperature $T > T_{cr}$, but the phase transition of vapor into solid for these temperatures can occur only at much distilled water, that is for a one-component system.

Natural waters from the thermodynamic point of view are complicated multi-component solutions. Therefore, the coexistence of water in the liquid phase in equilibrium with vapor (more precisely with the abovementioned critical phase) is possible in groundwater at depths of scores of kilometers. Figure 2.2 is a thermodynamic diagram of water at high pressures.

Fractionation, migration, and accumulation of the stable and radioactive isotopes which are components of water molecules—and also those of substances—contained in water solutions are dependent on the properties of the water solutions. These properties are in turn functions of the chemical composition of the given solution, its temperature and pressure.

A solution is a homogeneous system (in solid, liquid, or gaseous state) which consists of two or more substances (Karapetyan 1953). From the thermodynamic viewpoint, all the components of a solution are equivalent and therefore the division of the components into solvent and solute is relative.

Fig. 2.2 Water state diagram at high (**a**) and superhigh (**b**) pressures for ice modification densities (in g/ml): **I** corresponds to 0.92; **II** corresponds to 1.12; **III** corresponds to 1.03; **V** corresponds to 1.09; **VI** corresponds to 1.13; **VII** corresponds to 1.46; *G* is the domain of liquid water existence
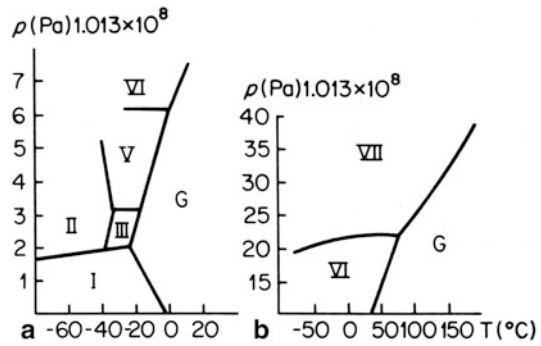
2.1.1 The Notion of Activity and the Activity Coefficient

The notion of activity in thermodynamics of real solutions was introduced by Lewis in 1905–1908. When calculating the thermodynamic state of real systems, the analytical concentration of a given component is replaced by its activity equal to the concentration of this component in an ideal system. The introduction of the value of activity makes it possible to describe the behavior of the real solutions using the thermodynamic equations obtained for ideal system. In this case, the functional dependence between the parameters remains unchanged after the replacement of the substance concentration in the solution by its activity. This made it possible to apply the ideal solution relationships to the real systems.

The activity is a function of the concentration c and differs from it by some factor γ which is called the activity coefficient:

$$a = \gamma c. \tag{2.2}$$

It is known from the theory of solutions that the chemical potential of a substance in an ideal solution can be given by the following equation:

$$\mu_{\text{ideal}} = \mu_0 + RT \ln c, \tag{2.3}$$

where μ_{ideal} is the chemical potential of the ideal solution; μ_o is the standard chemical potential; T is the absolute temperature; R is the gas constant.

For the real system, Eq. 2.3 must be rewritten so that the value of the concentration is replaced by the activity

$$\mu_{\text{sol}} = \mu_0 + RT \ln \gamma c = \mu_0 + RT \ln a, \tag{2.4}$$

where, μ_{p} is the chemical potential of the real solution.

It is evident from Eqs. 2.3 and 2.4 that the activity can be considered as a function of the thermodynamic properties of the solution:

$$\ln a = \frac{\mu_{\text{sol}} - \mu_0}{RT} \tag{2.5}$$

Here the activity coefficient can be defined as a function of the difference between the chemical potentials of the substance in real and ideal systems.

In fact, from Eq. 2.4, it is evident that

$$\mu_{sol} = \mu_0 + RT \ \ln \gamma c = \mu_0 + RT \ \ln \gamma + RT \ \ln c = \mu_{ideal} + RT \ln \gamma. \quad (2.6)$$

Then

$$RT \ln \gamma = \mu_{sol} - \mu_{ideal}, \quad (2.7)$$

$$\ln \gamma = \frac{\mu_{sol} - \mu_{ideal}}{RT} \quad (2.8)$$

or

$$\gamma = \exp\left(\Delta\mu / RT\right). \quad (2.9)$$

Since the activity coefficient is a function of the thermodynamic properties of a system, the arbitrary standard thermodynamic state can be used for their estimation. One should keep in mind that during the calculations, all the values must be referred to the one standard thermodynamic state both for the solvent and for the solute.

2.1.2   The Relationship between Solvent and Solute Activity

It is known (Izmaylov 1966) that the total differential of the isobaric–isothermal potential G (Gibbs' free energy) is equal to

$$dG = -Sdp + VdT + \sum \mu_i dn_i, \quad (2.10)$$

where, S is the entropy of the system; T, V, p are the temperature, volume, and pressure respectively; μ_i is the chemical potential of the ith component of the system; n_i is the molar quantity of the ith component.

At constant p and T, the equation has the form

$$dG = \sum \mu_i dn_i.$$

For the system in equilibrium, $dG = 0$, so $\sum \mu_i \ dn_i = 0$. The total differential of the function G for constant p and T and variable μ_i and n_i is

$$dG = \sum n_i d\mu_i + \sum \mu_i dn_i. \quad (2.11)$$

When the system is in equilibrium, the right-hand equation is equal to zero and since

$$\sum \mu_i dn_i = 0,$$

then

$$\sum n_i d\mu_i = 0. \tag{2.12}$$

Equation 2.12 is called the Gibbs' equation and for binary systems it can be written as

$$n_1 d\mu_1 + n_2 d\mu_2 = 0. \tag{2.13}$$

Subscripts 1 and 2 denote the solvent and the solute, respectively. Dividing Eq. 2.13 by $n_1 + n_2$, we obtain an expression related to the molar fractions of substance

$$N_1 d\mu_1 + N_2 d\mu_2 = 0. \tag{2.14}$$

Substituting in Eq. 2.14, the expression for the chemical potential $\mu = \mu_0 + RT \ln c$, we get the equation for the ideal solutions, which is called the Duhem–Margules

$$N_1 d \ln c_1 + N_2 d \ln c_2 = 0.$$

Substituting the activity $a = \gamma c$ for c, we finally derive the Gibbs–Margules–Lewis equation

$$N_1 d \ln a_1 + N_2 d \ln a_2 = 0, \tag{2.15}$$

where a_1 is the activity of the solvent; solutions; a_2 is the activity of the solute.

Equation 2.15 describes the relationship between the activities of the solvent and the solute. It is commonly used in physical chemistry for determining the activity coefficients of components of real solutions by indirect methods.

2.2   Water Vapor Pressure over the Water and Solution

In practice, the decisive role in the processes of fractionation of the isotopic species of water (molecules with different masses) is played by the phase transitions in the ice–water–vapor system, but for the quantitative analysis of the process of vaporization one should take into account that the vapor pressure of water (the solvent) over solutions is unequal to the pressure of the pure aqueous vapor at the identical temperature value T. For ideal solutions, at constant temperature, the vapor pressure of the solvent for all concentrations follows Raule's law which is:

$$p_1 = p_1^0 N_1, \tag{2.16}$$

where p_1 is the vapor pressure over the solution; p_1^0 is the vapor pressure over the distilled water; N_1 is the concentration of solvent (the molar fraction).

For real solutions, one should replace N_1 in Eq. 2.16 by the value of the solvent activity $a = \gamma N_1$. Then Raule's law for real solutions is represented by the equation
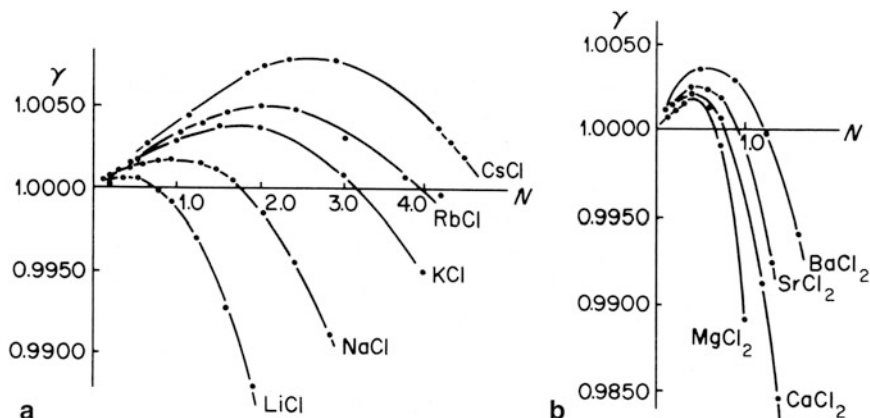
$$p_1 = p_1^0 a_1. \tag{2.17}$$

Fig. 2.3 The dependence of the activity coefficient of water γ in some aqueous electrolytes on the molality concentration of the solution N for cations Li–Cs (**a**) and Mg–Ba (**b**)

From Eq. 2.17, it is evident that the activity of water in the solution can be expressed by the ratio of water vapor pressure over the solution p_1 and the vapor pressure over distilled water p_1^0 (at the same temperature T):

$$a_1 = \frac{p_1}{p_1^0},$$

or,

$$\gamma N_1 = \frac{p_1}{p_1^0}. \tag{2.18}$$

Here γ is said to have a negative deviation from Raule's law if, in the real solution, $\gamma < 1$, and it has positive deviation if $\gamma > 1$.

The dependence of the activity coefficient of water in some aqueous electrolytes on the molal concentration of the solution[1] is shown in Fig. 2.3.

It can be seen from the diagrams that the aqueous electrolytes exhibit both positive and negative deviations from Raule's law depending on concentration of the solutions. It is typical that in the series of cations Li→Cs and Mg→Ba, there is a tendency towards positive deviations from Raule's law (the curves' maxima are shifted to the domain of greater values of concentration). Samoilov (1957) explains this phenomenon in terms of the difference in hydration of the ions in water solutions. According to his theory, ions of electrolytes affect the translational motion of the surrounding molecules of water in the solution. Ions with great heat of hydration (Li, Na, Mg, Ca) weaken the translational motion in the hydrate shells, which results in the decrease of activity coefficient. In contrast, the ions with negative hydration

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[1] The molality of the solution is the quantity of gram-molecules of the substance dissolved in 1,000 g (55.55 moles) of water

Table 2.1 Vapor pressure decrease (in Pa) over water solutions of some salts

Salts	Concentrations (in moles/l of water)						
	0.5	1.0	2.0	3.0	4.0	5.0	6.0
$CaCl_2$	2,261	5,293	12,635	22,158	32,120	42,495	–
K_2CO_3	1,915	4,123	9,044	14,032	20,216	27,787	34,384
KCl	1,523	3,245	6,384	9,855	13,420	17,091	20,243
$MgCl_2$	2,234	5,187	13,367	24,379	36,841	50,141	–
Na_2CO_3	1,902	3,631	7,116	10,667	14,763	–	–
NaCl	1,636	3,352	6,929	10,640	14,763	19,019	23,475
Na_2SO_4	1,676	3,325	6,504	9,863	–	–	–

(with loss heat hydration), disturbs the water structure in the hydration shells, which intensifies the translational motion of water molecules and results in an increase in the activity coefficient (such ions are K, Rb, Cs, Ba) .

It is noteworthy that the process of cation hydration in water solution leads to the isotopic fractionation of hydrogen and oxygen in their hydrated shells (Sofer and Gat 1972, 1975). For instance, ^{18}O is concentrated in the hydrated shells of ions with great heat of hydration (fractionation coefficient $\alpha \geq 1$) and those with negative hydration (using Samoylov's notation) with, as a rule, $\alpha \leq 1$ (Sofer and Gat 1972; Taube 1954).

The isotopic fractionation of hydrogen and oxygen upon the hydration of ions is of some importance to the isotopic fractionation of natural waters.

Table 2.1 shows the data on decreases in vapor pressure over water solutions of some salts contained in natural waters. The amount of vapor pressure decrease over solutions of given concentrations at 100°C is given and can be compared with the pressure of pure water vapor (1.01×10^5 Pa) at the same temperature.

In studying the fractionation of hydrogen and oxygen isotopes in the process of the vaporization of water of different salinity, it is necessary to take into account the decrease of pressure of the saturated vapor over the salt solution. In fact, the change of the salinity in surface reservoirs during the vaporization process will lead to decreases in the saturated vapor pressure over their surface. However, the total pressure of water vapor, as a rule, depends not only on the total area of vaporization in the given region but also on the atmospheric moisture which is transported from the other regions. In this case, the isotopic equilibrium in the closed basin will depend on the salinity of its waters, temperature of evaporation, the humidity, and the isotopic composition of the water in the basin and of the atmospheric vapor.

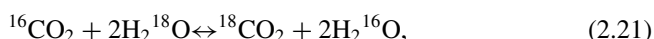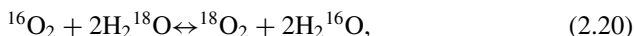## 2.3   Physicochemical Foundations of Isotope Separation

In considering the environmental phenomena and processes of geochemistry and cosmochemistry based on studies of isotopic composition of chemical elements, one makes the assumption that the initial isotopic composition of any chemical element is a natural constant (Rankama 1963). Then, as a result of natural physicochemical processes, the isotopic composition of any element changes through geological history.

If the chemical properties of individual elements depend mainly on their electronic configurations, then the differences observed in the physicochemical processes, where the isotopes and the isotopic varieties of molecules take part, are due to the differences in the masses of the isotopes and their nuclear properties. As an illustration, consider the typical reaction of the isotopic exchange which can be written in the form (Godnev 1956):

$$aC_1 + bD_2 \leftrightarrow aC_2 + bD_1, \qquad (2.19)$$
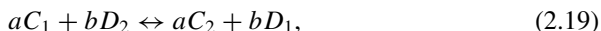
where C_1, C_2, D_1, D_2 are molecules of different isotopes of the same element.

The following exchange processes serve as an example of such reaction:

$$^{16}O_2 + 2H_2{}^{18}O \leftrightarrow {}^{18}O_2 + 2H_2{}^{16}O, \qquad (2.20)$$

$$^{16}CO_2 + 2H_2{}^{18}O \leftrightarrow {}^{18}CO_2 + 2H_2{}^{16}O, \qquad (2.21)$$

The thermodynamic expression for the equilibrium constant of these reactions is

$$K = \frac{Q_{C_2}^a Q_{D_1}^b}{Q_{C_1}^a Q_{D_2}^b} = \frac{(Q_{C_2}/Q_{C_1})^a}{(Q_{D_2}/Q_{D_1})^b}, \qquad (2.22)$$

here Q_{c1}, Q_{c2}, Q_{D1}, Q_{D2} are partition functions of isotopic molecules.

According to quantum, statistics for thermodynamic functions, the expression for the partition function of the individual molecules is, in slightly simplified form:

$$Q = Q_1 Q_r Q_v \exp \frac{E_0}{kT} \qquad (2.23)$$

where Q_1 is the translational partition function of the molecule; Q_r is the rotational partition function of the molecule; Q_v is the oscillation partition function of the molecule; $\exp(-E_0/kT)$ is a factor of the zero-point energy of the molecule.

The partition function of the molecule's translational motion during the isomolar reactions is given by

$$Q_1 = \frac{(2\pi MkT)^{3/2}}{h^3}, \qquad (2.24)$$

where M is the mass of the molecule; K is the Boltzmann's constant; h is the Plank's constant; T is the Kelvin's temperature.

A simplified expression for the partition function of the rotational motion of molecules is

$$Q_K = \frac{8\pi^2 IkT}{\sigma h^2}, \qquad (2.25)$$

where I is the moment of inertia, that is the sum of the products of the individual atom masses constituting the molecule and its squared distances up to the axis of rotation of the molecule; σ is the symmetry number; other notations are as in Eq. 2.24.

The partition function of the oscillation motions of the molecule can be written in the following simplified form:

$$Q_v = \left[1 - \exp\left(-\frac{hv}{kT}\right)\right]^{-1} \tag{2.26}$$

where v is the frequency of the atom oscillation in the molecule.

It follows from Eq. 2.22 that the equilibrium constant of the reaction expressed by Eq. 2.19 is determined by the ratio of the partition function of the isotopic molecules C_2C_1 and D_2D_1. If we denote the partition function for each isotopic molecule pair by Q_1 and Q_2 then (at average temperatures) we obtain

$$\frac{Q_2}{Q_1} = \exp\left(-\frac{\Delta E_0}{kT}\right)\frac{(Q_1)_2(Q_r)_2(Q_v)_2}{(Q_1)_1(Q_r)_1(Q_v)_1}$$

$$= \exp\left(-\frac{\Delta E_0}{kT}\right)\frac{\sigma_1}{\sigma_2}\frac{I_2}{I_1}\left(\frac{M_2}{M_1}\right)^{3/2}\left(\frac{1 - \exp\left(-hv_1/kT\right)}{1 - \exp\left(-hv_2/kT\right)}\right), \tag{2.27}$$

where σ_1, σ_2, I_1, I_2, M_1, M_2, v_1, v_2 are the symmetry numbers, moments of inertia, masses (molecular weights), and frequencies of the internal oscillations of the isotopic molecules, respectively.

The factor $\exp\left(-\Delta E_o/kT\right)$ takes into account the difference in the zero-point energies of the two isotopic molecules C_2C_1 and D_2D_1.

The difference in the zero-point energies of oscillations may be given

$$\Delta E_0 = \frac{hv_2}{2} - \frac{hv_1}{2}. \tag{2.28}$$

If we introduce the new oscillations

$$u_1 = \frac{hv_1}{kT} \tag{2.29}$$

and

$$u_2 = \frac{hv_2}{kT}, \tag{2.30}$$

then Eq. 2.27 can be rewritten in the form

$$\frac{Q_2}{Q_1} = \frac{\sigma_1}{\sigma_2}\frac{I_2}{I_1}\left(\frac{M_2}{M_1}\right)^{3/2}\left(\frac{\exp\left(-u_2/2\right)}{1 - \exp\left(-u_2\right)}\right)\left(\frac{1 - \exp\left(-u\right)}{\exp\left(-u_1/2\right)}\right). \tag{2.31}$$

For polyatomic molecules, the expressions for the partition functions have the same form as of Eqs. 2.24 and 2.25, but all the moments of inertia and frequencies of the molecules' oscillations should be taken into account. In this case, Eq. 2.27 can be written as

$$\frac{Q_2}{Q_1} = \exp\left(-\frac{\Delta E_0}{kT}\right)\frac{\sigma_1}{\sigma_2}\prod_n\left(\frac{I_{2n}}{I_{1n}}\right)^{1/2}\left(\frac{M_2}{M_1}\right)^{3/2}\prod_i\frac{1 - \exp\left(-hv_1/kT\right)}{1 - \exp\left(-hv_2/kT\right)}, \tag{2.32}$$

where $I_{11}, I_{12}, \ldots, I_{1n}$ and $I_{21}, I_{22}, \ldots, I_{2n}$; $v_{11}, v_{12} \ldots v_{1i}$ and $v_{21}, v_{22} \ldots v_{2i}$ are, respectively, the moments of inertia and the oscillation frequencies of the first and second isotopic molecules.

The difference in zero-point oscillation energies can be introduced in the form

$$\Delta E_0 = \sum_i \frac{hv_{2i}}{2} - \sum_i \frac{hv_{1i}}{2}. \tag{2.33}$$

Substituting Eq. 2.33 into Eq. 2.32, one obtains

$$\frac{Q_2}{Q_1} = \frac{\sigma_1}{\sigma_2} \prod_n \left(\frac{I_{2n}}{I_{1n}}\right)^{1/2} \left(\frac{M_2}{M_1}\right)^{3/2} \prod_i \left(\frac{\exp\left(-hv_{2i}/kT\right)}{1 - \exp\left(-hv_{2i}/kT\right)}\right) \left(\frac{1 - \exp\left(-hv_{1i}/kT\right)}{\exp\left(-hv_{1i}/kT\right)}\right) \tag{2.34}$$

Introducing the variables in Eq. 2.29 and 2.30, with substituting of hv_{1i} and hv_{2i} for hv_1 and hv_2, and putting them into Eq. 2.34, an analogy with Eq. 2.31 is obtained:

$$\frac{Q_2}{Q_1} = \frac{\sigma_1}{\sigma_2} \prod_n \left(\frac{I_{2n}}{I_{1n}}\right)^{1/2} \left(\frac{M_2}{M_1}\right)^{3/2} \prod_i \left(\frac{\exp\left(-u_{2i}/2\right)}{1 - \exp\left(-u_{2i}\right)}\right) \left(\frac{1 - \exp\left(-u_{1i}\right)}{\exp\left(-u_{1i}/2\right)}\right) \tag{2.35}$$

Using the Teller–Redlich rule (Redlich 1935), which relates the ratio of the products of the frequencies for each symmetry type of the two isotopes to the ratio of their masses and the moments of inertia, Eq. 2.35 can be rewritten as

$$\frac{Q_2}{Q_1} = \frac{\sigma_1}{\sigma_2} \left(\frac{M_2}{M_1}\right)^{3/2} \prod_i \frac{u_{2i}}{u_{1i}} \left(\frac{\exp\left(-u_{2i}/2\right)}{1 - \exp\left(-u_{2i}\right)}\right) \left(\frac{1 - \exp\left(-u_{1i}\right)}{\exp\left(-u_{1i}/2\right)}\right), \tag{2.36}$$

which, in the case of the diatomic isotopic molecule, may be simplified to the form

$$\frac{Q_2}{Q_1} = \frac{\sigma_1}{\sigma_2} \left(\frac{M_2}{M_1}\right)^{3n/2} \frac{u_2}{u_1} \left(\frac{\exp\left(-u_2/2\right)}{1 - \exp\left(-u_2\right)}\right) \left(\frac{1 - \exp\left(-u_1\right)}{\exp\left(-u_1/2\right)}\right), \tag{2.37}$$

where n is the number of isotopic atoms exchanged; M is their mass.

Equations 2.36 and 2.37 are used to calculate equilibrium constants for the isotopic exchange reactions of isotopic molecules. In order to carry out the calculations, the experimental data on the oscillation spectra frequencies, the molecules' masses, and their symmetry numbers are required. The theory for approximating equilibrium constants of isotopic exchange reactions was developed by Bigeleisen and Mayer (1947), Urey (1947), Tatevsky (1951), and other authors.

In calculating the equilibrium constants for such isotopic exchange reactions as in Eq. 2.19, the following function is introduced:

$$f = \frac{Q_2}{Q_1} \left(\frac{M_1}{M_2}\right)^{3n/2}. \tag{2.38}$$

Using Eq. 2.38, the expression for the equilibrium constant, Eq. 2.22 can be written in the form

$$K = \frac{(Q_{C_2}/Q_{C_1})^a}{(Q_{D_2}/Q_{D_1})^b} = \frac{[f(M_2/M_1)^{3n_1/2}]^a}{[f(M_2/M_1)^{3n_2/2}]^b}. \tag{2.39}$$

Let the number of exchangeable isotopic atoms in both molecules be equal, that is $n_1 = n_2$. Then

$$K = f_C^a/f_D^b. \tag{2.40}$$

Using the Bigeleisen–Mayer function and corresponding experimental data, an approximate value of the function is obtained

$$\ln f = \ln \frac{\sigma_1}{\sigma_2} + \sum_i \left(\frac{1}{2} - \frac{1}{u_i} + \frac{1}{e^{u_i} - 1} \right) \Delta u_i = \ln \frac{\sigma_1}{\sigma_2} + \sum_i G(u_i) \Delta u_i, \tag{2.41}$$

where $G(u) = 1/2 - 1/u_i + 1/(e^{u_i} - 1)$ is the Bigeleisen–Mayer function.

The value of the function $G(u)$ have been given in a number of studies (Bigeleisen and Mayer 1947; Godnev 1956).

The following is an example of a calculation of the equilibrium constant for the isotopic exchange reaction according to the method described by Godnev (1956).

Let us determine the equilibrium constant at $T = 600\,K$ for the following reaction of isotopic exchange,

$$C^{16}O_2 + 2H_2{}^{18}O \leftrightarrow C^{18}O_2 + 2H_2{}^{16}O.$$

Using Eq. 2.39, we can write

$$K = \frac{(Q_{C^{18}O_2}/Q_{C^{16}O_2})}{(Q_{H_2{}^{18}O}/Q_{H_2{}^{18}O})^2} = \frac{f_{CO_2}}{(f_{H_2{}^{16}O})^2} \tag{2.42}$$

With the help of the data on the function $G(u)$ (Godnev 1956) and for the corresponding values of the oscillating frequency of the molecules $C^{16}O_2$, $C^{18}O_2$, $H_2{}^{16}O$ and $H_2{}^{18}O$ for symmetry numbers of all the molecules $\sigma_1 = \sigma_2 = 2$, we may determine the parameters u_i and Δu_i (Table 2.2).

Putting the data given in Table 2.2 in Eq. 2.41, one obtains

$$f_{CO_2} = 1.076; f_{H_2O} = 1.026.$$

Finally, making use of the Eq. 2.42, one obtains the unknown isotopic exchange equilibrium constant for the system under investigation at $T = 600\,K$

$$K_{(600K)} = 1.023.$$

Similar methods to those developed for calculating equilibrium constants, based on the spectroscopic data, and are widely used for calculating the fractionation factors of the stable isotopes of light elements in reactions between the gaseous molecules

Table 2.2 Parameters of the isotopic exchange reactions of CO_2 and H_2O

v_i, cm^{-1}	$v_i + \Delta u_i$	v_i, cm^{-1}	u_i	Δu_i	G_i
$C^{16}O_2$		$C^{18}O_2$		$C^{18}O_2$	
1,342	3.219	1,266	3.037	0.182	0.22128
667	1.600	657	1.576	0.024	0.12649
667	1.600	657	1.576	0.024	0.12649
2,355	5.650	2,320	5.566	0.084	0.32435
$H_2{}^{16}O$		$H_2{}^{18}O$		$H_2{}^{18}O$	
3,650	8.756	3,642	8.737	0.019	0.38574
1,595	3.826	1,590	3.814	0.012	0.26018
3,756	9.011	3,740	8.972	0.039	0.38864

(Richet et al. 1977) and in heterogenic systems (Urey 1947; Bigeleisen and Mayer 1947).

When u ranges from 0 to ∞, the value $G(u)$ ranges from 0 to 0.5. At high temperatures Δu tends to zero. Therefore, in Eqs. 2.38–2.41, we have $Q_2/Q_1 \approx \sigma_1/\sigma_2$ and

$$K = K_0 = \frac{(\sigma_1/\sigma_2)_C^a}{(\sigma_1/\sigma_2)_D^b}. \tag{2.43}$$

The limiting value of the equilibrium constant of the isotopic exchange reaction $K = K_0$ corresponds to the equally probable distribution of isotopes between the molecules of the system and is determined by their symmetry numbers. Further, in this case, the separation of the isotopes in the exchange reactions does not occur. In some studies (Bowen 1966; Galimov 1968a) concerned with the application of isotope techniques in geology, it is stated that the equilibrium constants for individual isotopic exchange reactions tend to unity with increasing temperature. This is not true if we consider general case of isotopic exchange, which may be represented by such a reaction as Eq. 2.19.

Thus, the limiting value of the equilibrium constant is equal to 2 for the isotopic exchange reaction $DCl + H_2O \leftrightarrow HCl + HD$. In fact, the symmetry numbers of the molecules DCl, HCl, HD are equal to unity and $\sigma_{H_2} = 2$, and hence $K_0 = 1 \times 2/1 \times 1 = 2$. For this reaction the equilibrium constant K increases with temperature and tends to the limiting value $K_0 = 2$ (Brodsky 1957). But the isotopic fractionation factor between the molecules of hydrochloric and hydrogen actually tends to unity with an increase in temperature.

As a second example, let us consider the reaction of isotopic exchange between ammonia and hydrogen:
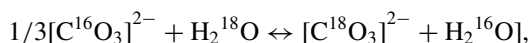
$$NH_3 + HD \leftrightarrow NH_2D + H_2.$$
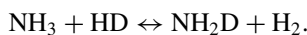
The limiting value of the equilibrium constant for this reaction is $K_0 = 1.5$. In fact,

$$K_0 = \frac{(\sigma_{NH_3}/\sigma_{NH_2D})}{(\sigma_{H_2}/\sigma_{HD})},$$

$\sigma_{NH_3} = 6, \sigma_{NH_2D} = 2, \sigma_{HD} = 1$, and hence $K_0 = (6 \times 1)/(2 \times 2) = 1.5$.

For the isotopic exchange reaction between carbonate-ion and water (Bowen 1966) written in a general form as

$$1/3[C^{16}O_3]^{2-} + H_2{}^{18}O \leftrightarrow [C^{18}O_3]^{2-} + H_2{}^{16}O],$$

where the value of K_0 is equal to unity since, in this case, the symmetry numbers of the molecules do not change. The process of equilibrium isotopic fractionation occurring due to the energy state difference of the isotopic molecules is sometimes called the thermodynamical isotopic effect.

In a series of physicochemical processes occurring at non-equilibrium conditions, the isotopic fractionation can be the result of kinetic effects.

In the case when the initial concentrations of the isotopic molecules are equal, the reaction rate constant and the true rate of the process according to the theory of the absolute rates of reactions can be given by the equation (Glasstone et al. 1941):

$$K_v = k \frac{kT}{h} \frac{Q^*}{Q_1 Q_2} \exp(-\Delta E_0 / RT), \tag{2.44}$$

where K_v is the reaction rate constant; k is the Boltzmann's constant; T is the absolute temperature; h is the Plank's constant; Q^* is the oscillation-rotational partition function of the activated complex of reacting substances; R is the gaseous constant; ΔE_0 is difference between zero of energy activated complex and reacting matter (energy of activation of the reaction at $0°K$); κ is the constant for a given reaction (coefficient of the transmission coefficient by Glesstone).

It follows from the Eq. 2.44 that the differences in the rates of processes involving reacting substances, containing both heavy and light isotopes of an element, are due to the differences in the molecular weights of the isotopic species of molecules (as was shown earlier, the partition function of each molecule includes the mass and the moment of inertia of the molecule) and also to the change in activation energy ΔE_0.

Hence, for the light isotopes (such as deuterium and protium) the difference in the rates of reaction on which the isotopic molecules are participating is influenced both by the difference in the mass of the molecules and by the difference in the activation energy. If both molecules are heavy, then the isotopic composition has little effect on their masses. In this case the difference in kinetics is practically completely dependent on the change in the activation energy of the activated complex formation.

The isotope separation, carried out in non-equilibrium conditions and provided by difference in the rate of reactions of the isotopic molecules, is called isotopic kinetic effect.

It has been shown by Varshavsky and Veisberg (1955) that the total distribution of deuterium (D) between the hydrogen-bearing substances should depend on individual distribution, characterizing each of the reactions involved. Under such circumstances, the total α can be found by calculating the partial values of α_i for all the reactions and taken proportional to the mass of the D concentration. Varshavsky and Veisberg assumed that the values of α_i for all the exchange reactions between given substances are equal to each other and to the total α. This assumption is equivalent to the assumption that there is a statistical distribution between the different D-bearing

molecules of the same substance. As Varshavsky and Veisberg have shown, this assumption is true with an accuracy of 5% (at 25°C) for water and ammonia. The exception is molecular hydrogen, for which this assumption is true with an accuracy of about 20%. Taking this assumption into account, one can estimate α of any reaction of the hydrogen isotope exchange. In practice, it is more convenient to use that expression for the total α which contains all the oscillation frequencies of the molecules containing D atoms and those which do not contain them:

$$\alpha = \frac{\left[\prod (v_n/v_0) \frac{1-\exp(-hv_0/kT)}{1-\exp(-hv_n/kT)}\right]^{1/n} \exp\left\{(-h/2kTn)\left[\sum v_n + Z_n - \sum v_0 - Z_0\right]\right\}}{\left[\prod (v_m/v_0') \frac{1-\exp(-hv_0/kT)}{1-\exp(-hv_m/kT)}\right]^{1/m} \exp\left\{(-h/2kTm)\left[\sum v_m + Z_m - \sum v_0' - Z_0'\right]\right\}},$$

where v_n, v_0, v_m, v'_n are the fundamental frequencies of the corresponding molecules; m, n are numbers of hydrogen atoms in the molecules of the corresponding substances; Z_n, Z_0, Z_m, Z_0' are the total corrections, accounting for the effect of anharmonicity of oscillations.

In the given expression, the numerator contains the oscillation frequencies of one substance only and the denominator contains those of the other one. Therefore, α may be expressed by any of the two quantities β, each one representing an individual substance and being independent of the other substance in the isotopic exchange reaction. Varshavsky and Veisberg called these quantities the β-factors:

$$\beta = \left[\prod (v_n/v_0) \frac{1 - \exp(-hv_0/kT)}{1 - \exp(-hv_n/kT)}\right]^{1/n}$$
$$\exp\left\{(-h/2kTn)\left[\sum v_n + Z_n - \sum v_0 - Z_0\right]\right\}.$$

It follows from this expression that the β-factor depends on temperature. For small temperature ranges, the dependence of the factor appearing before the exponent can be neglected. Then the expression for the β-factor becomes

$$\beta = a \exp(-b/T),$$

where

$$a = \left[\prod (v_m/v_0) \frac{1 - \exp(-hv_0/kT)}{1 - \exp(-hv_m/kT)}\right]^{1/m} \approx \text{const},$$
$$b = (-h/2kTn)\left[\sum v_n + Z_n - \sum v_0 - Z_0\right] \approx \text{const}.$$

Varshavsky and Veisberg have calculated and tabulated the values of a and b and also of the β-factor at 20, 50, and 75°C, for some of the hydrogen-bearing substances (Table 2.3). The anharmonicity of the oscillation has not been taken into account and the observed frequencies were substituted for the zero-point ones.

It has been shown that β-factors of hydrides (compounds and radicals) vary with increase in the atomic number of an element bounding hydrogen (Fig. 2.4). Here

Table 2.3 a, b and β-factors for some hydrogen-bearing substances. (After Varshavsky and Veisberg 1955)

Compounds	a	b	β_{20}	β_{50}	β_{75}
H_2	0.8484	418.7	3.54	3.10	2.83
CH_4	0.5971	894.5	10.74	8.09	6.63
C_2H_6	0.4640	932.8	11.20	8.33	6.77
C_2H_4	0.4632	936.8	11.33	8.42	6.84
C_6H_6	0.4128	984.7	11.89	8.70	6.99
NH_3	0.5611	889.4	11.68	8.81	7.23
H_2O	0.6344	852.1	11.62	8.87	7.34
HF	0.7340	757.3	9.73	7.66	6.47
H_2S	0.6291	633.1	5.46	4.47	3.88
HCl	0.7245	572.1	5.11	4.26	3.75
HBr	0.7192	517.3	4.20	3.57	3.18
HI	0.7178	453.7	3.38	2.93	2.64
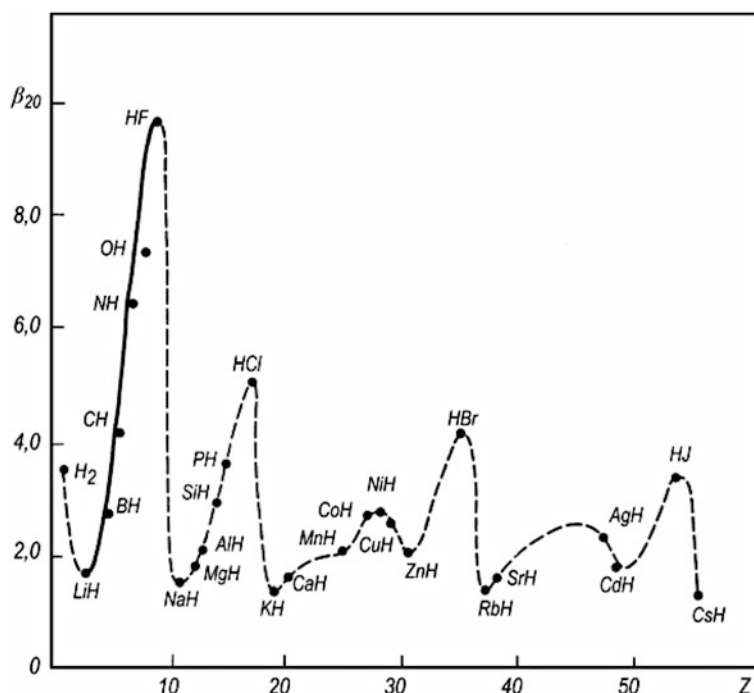
Fig. 2.4 Dependence of β-factors of two-atomic hydrides on the atomic number of element bounding hydrogen. (After Varshavsky and Veisberg 1955)

values of the β-factors of the diatomic hydrides, in contrast to the polyatomic ones, increase sharply within each period. The authors explained this in terms of the number of electrons in the outer shell of an atom linked to the hydrogen one. An examination of the resultant data shows that the maximum possible factor of D distribution

($\alpha = 8.0 - 8.5$ at 20°C) should correspond to the isotopic exchange reaction between hydrogen and a hydride of the most heavy alkaline metal and also that of the compound containing non-metal of the first period. The utilization of the β-factors makes it possible to estimate α-factors of the D distribution between the hydrogen-bearing compounds without complicated calculations.

The fractionation of isotopes, under non-equilibrium conditions and caused by differences in the rates of the exchange reactions, is referred to as the kinetic isotope effect.

It is obvious that in general the same physicochemical process (e.g., phase transitions, isotopic exchange reactions, biochemical processes, etc.) may occur in natural conditions both exchange under equilibrium and non-equilibrium conditions.

On one hand, this complicates the clear interpretation of the observed facts. On the other hand, it enables an estimation of the degree of equilibrium of this—or the other natural process—to be made.

For a quantitative estimation of the isotopic fractionation effect in a physicochemical process the fractionation factor α is used (Brodsky 1957):

$$\alpha = \frac{N/(1-N)}{n/(1-n)} = \frac{R_1}{R_2}, \tag{2.45}$$

where $N/1 - N = R_1$ is the atomic part of the isotope in the enriched fraction (component); $n/(1-n) = R_2$ is the atomic part of the isotope in the depleted fraction (compound).

In the case of a minimal content of the component being enriched which is the case, for example, during the fractionation of a natural mixture of isotopic species of water, one might assume that $1 - N \approx (1 - n) = 1$ and hence,

$$\alpha = \frac{N}{n}. \tag{2.46}$$

If the process of fractionation is successively repeated k times, then the total isotopic fractionation factor will be α^k.

2.4   Hydrogen and Oxygen Isotope Separation at Phase Transition of Water

During the fractionation of isotopes in a liquid–vapor system, the content of the isotopic components in liquid is N and $1 - N$ and their vapor pressures in a pure form will be p_1^0 and p_2^0. According to Raule's law for ideal liquid mixtures (Rabinovich 1968), the vapor pressure of each component above the mixture can be expressed as

$$\rho_1 = N\rho_1^0; \rho_2 = (1 - N)\rho_2^0. \tag{2.47}$$

Then

$$\frac{p_1}{p_2} = \frac{p_1^0}{p_2^0}\frac{N}{1 - N} \tag{2.48}$$

The partial pressures of the isotopic species of molecules of liquid in the vapor phase are proportional to the ratio of their molar ratios n and $(1-n)$. Hence, Eq. 2.45 can be rewritten in the form

$$\frac{n}{1-n} = \frac{N}{1-N}\frac{p_1^0}{p_2^0}.$$

or

$$\alpha = \frac{p_2^0}{p_1^0} \tag{2.49}$$

If subscript 2 corresponds to the light (more volatile) isotopic component, then $\alpha > 1$.

The vapor pressure is a function of temperature and is described by Eq. 2.1. If one uses Mendeleev–Klapeiron's equation $pV = RT$ for the saturated vapor, then, neglecting the volume of the condensed phase for one mole of the vapor, it follows that

$$\frac{dp}{dT} = \frac{\Delta H p}{RT^2} \quad \text{or} \quad \frac{d(\ln p)}{dT} = -\frac{\Delta H}{RT^2}. \tag{2.50}$$

With sufficient accuracy one can assume that the value of ΔH is a constant over a narrow range of temperatures. Then integration of Eq. 2.50 yields

$$\ln p = -\frac{\Delta H}{4.576T} + \text{const}, \tag{2.51}$$

that is a linear relationship between the logarithm of vapor pressure and the inverse temperature holds

$$\ln p = A - \frac{B}{T}. \tag{2.52}$$

For the ideal liquid mixture of the two isotopic species of molecules (e.g., H_2O and HDO), the logarithm of the vapor pressure ratio, corresponding to more and less volatile components, follows the equation

$$\ln \frac{p_2}{p_1} = A' - \frac{B'}{T} = \ln \alpha, \tag{2.53}$$

where p_2 is the pressure of the saturated vapor of H_2O; p_1 is the pressure of the saturated vapor of HDO; A', B' are constants.

It is easy to show that $B' = \Delta H' R$, where $\Delta H'$ is the change in heat of vaporization for the liquids H_2O and HDO.

It follows from Eq. 2.53 that below some fixed temperature, one has $\ln \alpha > 0$ and $\alpha > 1$. At a certain temperature the value of $B'/T = A'$ and $\alpha = 1$, and above this temperature $\alpha < 1$. In this case the enrichment of the vapor phase with respect to the heavy isotope occurs. The temperature at which $\alpha = 1$, is called the temperature (point) of intersection (Rabinovich 1968).
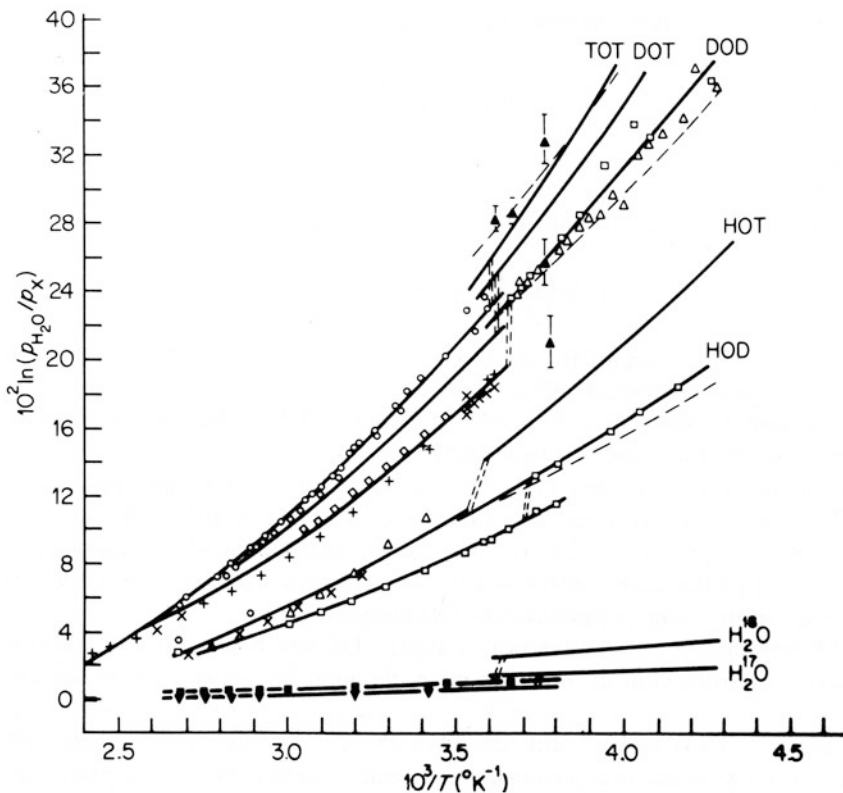
Fig. 2.5 Experimental relations between vapor pressure of the heavy and light water molecules and the temperature. Solid lines are obtained by calculations. (After Van Hook 1968)

The Eq. 2.53 is shown in Fig. 2.5, which illustrates the influence of isotopic substitutions in the water molecule upon the pressure of the saturated vapor.

Equation 2.53 satisfactorily describes the dependence of the fractionation factor on temperature over a comparatively narrow temperature range. Over a wide temperature range, the experimental data, as one can see from Fig. 2.5, does not conform to the straight line expressed by Eq. 2.53, since the enthalpy of the reaction is, in turn, a function of temperature.

Sometimes the experimental data can be linearized successfully with the help of the polynomial

$$\ln \alpha = A + \frac{B}{T^2}. \tag{2.54}$$

More exactly, the experimental dependence $\ln \alpha = f(T)$ may be described using more complicated polynomial function of the form:

$$\alpha = A + \frac{B}{T} + \frac{C}{T^2} C/T^2. \tag{2.55}$$

Table 2.4 Values of the fractionation factors α for the water hydrogen and oxygen isotopes in liquid–vapor systems. (From Brodsky 1957; Rabinovich 1968)

t, °C	$\alpha_{D_2O} = \dfrac{P_{H_2^{16}O}}{P_{D_2O}}$	$\alpha_{HDO} = \dfrac{P_{H_2^{16}O}}{P_{HDO}}$	$\alpha_{H_2^{18}O} = \dfrac{P_{H_2^{16}O}}{P_{H_2^{18}O}}$	$\alpha_{T_2O} = \dfrac{P_{H_2^{16}O}}{P_{T_2O}}$	$\alpha_{HTO} = \dfrac{P_{H_2^{16}O}}{P_{HTO}}$
1.0	–	1.104	–	–	–
3.815	1.215	1.000	–	–	–
10	1.190	1.091	–	1.265	1.125
20	1.162	1.080	1.0092	1.230	1.110
30	1.139	1.070	1.0084	1.198	1.096
40	1.116	1.060	1.0071	1.182	1.076
50	1.100	1.051	1.0068	1.145	1.065
60	1.090	1.046	1.0061	1.105	1.056
70	1.079	–	1.0054	1.098	1.049
80	1.066	1.032	1.0050	1.083	1.041
100	1.050	1.027	1.0040	1.059	1.030
140	1.029	1.012	1.0021	–	–
180	1.012	1.006	1.0000	–	–
220	1.000	1.000	–	–	–
240	0.997	0.998	–	–	–
260	0.994	0.996	–	–	–

Thus, according to the data of Bottinga (McKenzie and Truezdell 1977), the relationship $\ln \alpha = f(T)$ for the liquid–vapor system and isotopic species of water molecules $H_2^{18}O$ and $H_2^{16}O$ over the range of temperatures from 3 to 360°C can be expressed by

$$10^3\ln \alpha = -3.494 + 1.205(10^3/T) + 0.7664(10^6/T^2).$$

The values of the factor α for the binary liquid–vapor system consisting of various isotopic species of water are given in Table 2.4, taken from the study of Rabinovich (1968).

The equations obtained by Bottinga and Craig (1968) expressing the dependence of the fractionation factor on temperature in the liquid–vapor system gives slightly different values of α_D and α_{18_O} from those shown in Table 2.4, in the range of temperatures 100–300°C. Since these values are applied by different researchers while studying the conditions of hydrogen and oxygen isotopic fractionation in hydrothermal systems and are used for calculating base temperatures, we introduce them in Table 2.5 based on calculations of Arnason (1977a).

The values of the coefficients α_D and α_{18_O} are given for the range of temperatures from −20 to +100°C, which were obtained by Merlivat and by Zhavoronkov, respectively, and summarized by Dinçer (1968).

As can be seen from a comparison of the values of α_D and α_{18_O}, given in Tables 2.4 and 2.5, the accuracy of experimental determinations of the above is likely to be ~0.005 for α_D and ~0.0005 for α_{18_O}.

Table 2.5 Values of the fractionation factors α_D and α_{18_O}

t, °C	$\alpha_D = \dfrac{P_{H_2{}^{16}O}}{P_{HDO}}$	$\alpha_{18_O} = \dfrac{P_{H_2{}^{16}O}}{P_{H_2{}^{18}O}}$
Arnason (1977a)		
100	1.0256	1.0053
120	1.0212	1.0045
140	1.0166	1.0039
160	1.0118	1.0034
180	1.0074	1.003
200	1.0035	1.0025
220	1.0004	1.0022
240	0.9981	1.0018
260	0.9966	1.0015
280	0.9958	1.0012
300	0.9957	1.0009
Dinçer (1968)		
−20	1.1469	1.0135
−10	1.1239	1.0123
0	1.106	1.01119
20	1.0791	1.00915
40	1.06	1.00746
60	1.046	1.00587
80	1.037	1.00452
100	1.029	1.0033

2.5 Relationship Between the Isotope Reaction Change Constant and the Fractionation Factor

As demonstrated above, the isotopic exchange in the system under equilibrium conditions may be described both by the equilibrium constant K and the fractionation factor α.

For such a reaction as $Ax + Bx^* = Ax^* + Bx$, where there is only one atom of exchangeable isotopes x and x^* in each molecule of the reacting substances, the equilibrium constant is equal to the fractionation factor

$$\alpha = \left(\frac{x^*}{x}\right)_{Ax} : \left(\frac{x^*}{x}\right)_{Bx} = \frac{[Ax^*]}{[Ax]} : \frac{[Bx]^*}{[Bx]} = K. \tag{2.56}$$

In more complicated reactions, where several atoms of exchangeable isotopes in each molecule are involved, $\alpha \neq K$.

For example, let us consider the isotopic exchange of oxygen in the carbon dioxide–water system

$$C^{16}O_2 + H_2{}^{18}O \leftrightarrow C^{16}O^{18}O + H_2{}^{16}O.$$
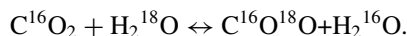
The equilibrium constant of this reaction is

$$k = \frac{[C^{16}O^{18}O][H_2{}^{16}O]}{[C^{16}O_2][H_2{}^{18}O]} \tag{2.57}$$

and the isotopic fractionation factor is equal to

$$\alpha = \left(\frac{^{18}O}{^{16}O}\right)_{CO_2} : \left(\frac{^{18}O}{^{16}O}\right)_{H_2O}. \tag{2.58}$$

Symbols ^{18}O and ^{16}O denote here the atomic ratios of oxygen-18 (^{18}O) and oxygen-16 (^{16}O). For water, the molecule of which contains one atom of oxygen, it follows that

$$\left(\frac{^{18}O}{^{16}O}\right)_{H_2O} = \frac{[H_2{}^{18}O]}{[H_2{}^{16}O]}. \tag{2.59}$$

For carbon dioxide, one should take into account that the molecule $C^{16}O_2$ contains two atoms of ^{16}O. Besides, the molecule $C^{16}O^{18}O$ also contains an atom of ^{16}O. Then

$$\left(\frac{^{18}O}{^{16}O}\right)_{CO_2} = \frac{[C^{16}O^{18}O]}{[C^{16}O^{18}O] + 2[C^{16}O_2]}. \tag{2.60}$$

Putting the values of $^{18}O/^{16}O$ from Eqs. 2.58 and 2.59 into Eq. 2.60 and multiplying both numerator and denominator by $C^{16}O_2$ one obtains

$$\alpha = \frac{[C^{16}O^{18}O][H_2{}^{16}O]}{[C^{16}O_2][H_2{}^{16}O]} \frac{[C^{16}O_2]}{[C^{16}O^{18}O] + 2[C^{16}O_2]}, \tag{2.61}$$

or

$$K = 2\alpha \frac{[C^{16}O^{18}O] + 2[C^{16}O_2]}{2[C^{16}O_2]}. \tag{2.62}$$

If the atomic ratio of ^{18}O in the carbon dioxide after equilibrium is reached is denoted by R_2, then

$$2[C^{16}O_2] = 1 - 2R_2, \tag{2.63}$$

$$[C^{18}O^{16}O] + 2[C^{16}O_2] = 1 - R_2. \tag{2.64}$$

Substituting Eq. 2.63 and 2.64 into Eq. 2.62, we obtain expressions for K and α

$$K = \frac{2\alpha(1 - R_2)}{(1 - 2R_2)}, \tag{2.65}$$

$$\alpha = \frac{K(1 - 2R_2)}{2(1 - R_2)}. \tag{2.66}$$

If $R_2 \ll 1$, which remains the same for natural concentrations of ^{18}O, then $K \approx 2\alpha$, or $\alpha \approx K/2$.

The relationship between α and K for isotopic exchange reactions was studied by Brodsky (1957), who demonstrated theoretically that, in general

$$a = (K/K_0)^{1/ab},$$

where a and b are the stoichiometric coefficients of the reaction.

Thus, for the isotopic exchange reaction between carbon dioxide and water $a = b = 1$ the symmetry numbers; σ_{H_2O} for both isotopic molecules of water are equal to σ_b (the substitution of ^{16}O for ^{18}O does not change the symmetry of the molecules); the symmetry number $\sigma_{C^{16}O_2}$, and $\sigma_{C^{16}O^{18}O} = 1$.

Hence,

$$K_0 = \frac{\sigma_b x_2}{\sigma_b x_1} = 2.$$

From this, the importance of the 2 in the denominator of Eq. 2.66 becomes apparent. It is the limiting value of the factor K of the isotopic exchange reaction. One can easily find from Eq. 2.66 that the factor α depends on the concentration (atomic factor) of the isotope in the exchange system. The value of α does not depend on concentration only when $R_2 \rightarrow 0$. This condition is satisfied in particular while considering the reactions of exchange in the system with natural concentrations of D and ^{18}O.

The above-mentioned oxygen isotopic exchange reaction between water and carbon dioxide, which is in common use for the mass spectrometric measurement of isotopic ratios of oxygen in water applying the isotopic equilibration method at 25°C (Epstein and Mayeda 1953; Craig 1957), has been proposed in the following form by Urey (1947):
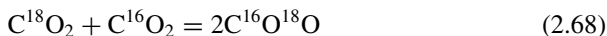
$$1/2C^{16}O_2 + H_2{}^{18}O \leftrightarrow 1/2C^{18}O_2 + H_2{}^{16}O.$$

In this case, the equilibrium constant K is equal to the isotopic fractionation factor α. In fact,

$$K = \frac{[C^{18}O_2]^{1/2}}{[C^{16}O_2]^{1/2}} : \frac{[H_2{}^{18}O]}{[H_2{}^{16}O]}. \tag{2.67}$$

The expression for the coefficient α can be written as

$$\alpha = \left(\frac{^{18}O}{^{16}O}\right)_{CO_2} : \left(\frac{^{18}O}{^{16}O}\right)_{H_2O} = \frac{2C^{18}O_2 + C^{16}O^{18}O}{2C^{16}O_2 + C^{16}O^{18}O} : \frac{[H_2{}^{18}O]}{[H_2{}^{16}O]}.$$

The equilibrium constant of the reaction

$$C^{18}O_2 + C^{16}O_2 = 2C^{16}O^{18}O \tag{2.68}$$

can be given in the form

$$\sigma_1 \sigma_2 : \sigma_{12}{}^2,$$

where σ_1, σ_2, σ_{12} are the symmetry numbers of the isotopic species of the carbon dioxide molecules $C^{18}O_2$, $C^{16}O_2$, $C^{16}O^{18}O$. It is obvious that $\sigma_1 = \sigma_2 = 2$ and $\sigma_{12} = 1$. Therefore, the limiting value of the equilibrium constant will be equal to 4.

Equation 2.68 can be written now as

$$\frac{[C^{16}O_2]}{[C^{16}O_2]^{1/2}[C^{18}O_2]^{1/2}} = 2.$$

After simple transformations, we get

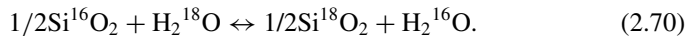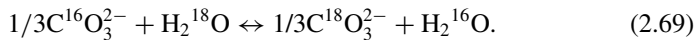$$\alpha = \frac{[C^{16}O_2]^{1/2}}{[C^{16}O_2]^{1/2}} : \frac{[H_2{}^{18}O]}{[H_2{}^{18}O]}.$$

One can see that the right-hand side of last expression and the right-hand side of Eq. 2.67 are same.

On the basis of the theoretical calculation of Urey (1947), carried out for the CO_{2gas}–H_2O_{liq} system, taking into account the isotopic fractionation factor of oxygen between vapor and liquid water ($\alpha = 1.009$), the value $\alpha_{H_2O-CO_2} = 1.038$ has been obtained at 25°C. Later on, this value was determined experimentally with a higher degree of precision by Compston and Epstein (1958) and it was found that $\alpha_{H_2O-CO_2} = 1.0407$. Since 1975, most of the studies on isotopes of oxygen use the value $\alpha_{H_2O-CO_2} = 1.0412 \pm 0.0001$, obtained by O'Neil et al. (1975).

2.6   Hydrogen and Oxygen Isotope Fractionation at Interaction Between Water and Gases and Rocks

In the hydrological cycle, the process of interaction in rock-water and water-gas systems are important for the isotopic fractionation of oxygen and hydrogen. We shall now consider the experimental results of determining the isotopic fractionation factors for various natural systems, obtained by different researchers.

The isotopic exchange reactions in the water–carbonate or silicate rocks may be written (Urey 1947) in a general form as

$$1/3C^{16}O_3^{2-} + H_2{}^{18}O \leftrightarrow 1/3C^{18}O_3^{2-} + H_2{}^{16}O. \tag{2.69}$$

$$1/2Si^{16}O_2 + H_2{}^{18}O \leftrightarrow 1/2Si^{18}O_2 + H_2{}^{16}O. \tag{2.70}$$

For such a presentation of isotopic exchange reactions, the symmetry numbers of the molecules with exchangeable isotopes do not change. Therefore, according to Eq. 2.56, the fractionation factor will be equal to the equilibrium constant, that is

$$\alpha \equiv K. \tag{2.71}$$

In this case, the dependence of the equilibrium constant K on temperature in the water–mineral system over a wide range of temperatures can be described with a sufficient degree of accuracy by Eq. 2.54, that is

$$\ln \alpha = A + B/T^2. \tag{2.72}$$

At high temperature $\alpha \to 0$ and $\ln\alpha \to 0$, therefore, the constant $A \to 0$. Thus, the dependence of the equilibrium constant on temperature plotted with $\ln \alpha - 1/T^2$ coordinates can be approximated by a straight line passing through the origin.

On the other hand, according to Eq. 2.45, the isotopic fractionation factor between the two phases a and b can be written in general form as

$$\alpha = \frac{R_a}{R_b}, \tag{2.73}$$

where R_a and R_b are the isotopic ratios of each isotope in a corresponding phase.

Let us use the generally accepted expression for reporting isotope data in a given phase versus some standard:

$$\delta = \frac{R_{\text{sample}} - R_{std}}{R_{std}} \times 1000\text{‰}. \tag{2.74}$$

where R_{sample} and R_{std} are isotopic ratios for sample and standard, respectively.

Using Eq. 2.74, the Eq. 2.73 can be written as:

$$\alpha = \frac{1 + \delta_\alpha/1000}{1 + \delta_b/1000}. \tag{2.75}$$

Taking logarithms of Eq. 2.75, we obtain

$$\ln \alpha = \ln (1 + \delta_\alpha/1000) - \ln (1 + \delta_b/1000). \tag{2.76}$$

As $\ln(1+x) \approx x$, if $x \ll 1$, we obtain the approximate relationship

$$10^3 \ln \alpha \approx \delta_\alpha - \delta_b = \Delta. \tag{2.77}$$

With the help of Eq. 2.77, the isotopic fractionation factor can be expressed by the difference of the δ-values for corresponding phases or compounds if their isotopic compositions have been measured relative to some standard.

For graphical presentation of the $\ln \alpha$ dependence on temperature it is convenient to use Eq. 2.72 in the form

$$10^3 \ln \alpha = A + B \left(10^6/T^2\right), \tag{2.78}$$

or with the help of the more complicated polynomial

$$10^3 \ln \alpha = A + B \left(10^3/T + C(10^6/T^2)\right). \tag{2.79}$$

For the solution of practical problems, it is important to have reliable values of the fractionation factors of the oxygen and hydrogen in water—principal rock formation minerals. The experiment consists of mixing the finely crushed sample of the mineral (approximately 0.2 g) together with water, in an ampoule at a known temperature, before soldering it. After equilibrium is attained and mass spectrometric

measurements are taken, the fractionation factor can be calculated by the formula

$$\alpha_{18_O} = \frac{[^{18}O/^{16}O]_M}{[^{18}O/^{16}O]_B} = \frac{(1000 + \delta^{18}O)_M}{(1000 + \delta^{18}O)_B},$$

$$\alpha_D = \frac{[D/H]_M}{[D/H]_B} = \frac{(1000 + \delta D)_M}{(1000 + \delta H)_B}.$$

However, as experimental study has shown (Nortrop and Clayton 1966; Suzuoki and Epstein 1976), the isotopic equilibrium between the exchangeable phases for silicate, carbonate, and clayey minerals, even at high temperatures (700–800°C), requires 300–400 hours to settle. To avoid continuous laboratory experiments, Nortrop and Clayton (1966) used the so-called method of partial isotopic exchange. This method is based on the kinetics of the isotopic exchange reactions in heterogeneous system and permits determination of the fractionation factor by interpolating experimental data. This method was employed for the first time by Nortrop and Clayton while studying oxygen isotope exchange in the dolomites-water system and later on the method was modified by Suzuoki and Epstein (1976) to study the hydrogen isotopic exchange between water and hydroxyl-bearing minerals. The method consists of placing pre-weighed amounts of crushed mineral into gold soldered ampoules together with water of varying isotopic composition. After the corresponding mass spectrometric measurements have been taken the value of the fractionation factor α_e is calculated by the graphical method of least squares from the equation

$$10^3(\alpha_i - 1) = 10^3(\alpha_e - 1) + A(\alpha_f - \alpha_i),$$

where α_i is quotient of division of isotopic ratios in the sample of the mineral and in water before the experiment starts; α_f is the same after a period of time t; α_e is equilibrium fractionation factor at $T°\kappa$.

The slope A in the equation is dependent on the time of exchange, that is a function of the isotopic exchange completeness. The equation is given in the form convenient for calculations, since, as a first approximation,

$$10^3(\alpha - 1) \approx \delta_{mineral} - \delta_{water} \approx 10^3 \ln \alpha.$$

2.7   Isotope Geothermometry

Equations 2.78 and 2.79 are in common use for calculating modern and paleotemperatures of the formation of minerals and also for determining the base temperatures of the hydrothermal systems.

Thus, Clayton (1961) has determined experimentally the oxygen isotope fractionation factor for a calcite-water system at high temperatures. He employed the parameters of the paleotemperature scale drawn up by Epstein et al. (1951) and plotted the curve describing the equilibrium in the calcite-water system, in the

range of temperatures of approximately 1,000°C. This dependence in the range of temperatures 0–750°C can be described by the following empirical equation

$$10^3 \ln \alpha_{18_O} = 2.73(10^6/T^2) - 2.56.$$

Clayton et al. (1972) determined experimentally the dependence of the fractionation factor on temperature in the quartz-water system in the range of temperatures. However, this dependence, as Knauth and Epstein (1976) have pointed out, requires correction for real geological temperatures in the low-temperature range. Interpolating Clayton's data in the low-temperature range and using the value $\alpha = 1$ at 0°C they reported the following relationship for the quartz-water system, suitable for temperatures 0 − 100°C:

$$10^3 \ln \alpha_{18_O} = 3.09(10^6/T^2) - 3.29.$$

In the case of the water-quartz system, Kawabe (1978) obtained by thermodynamic calculations the following values of the parameters in Eqs. 2.78 and 2.79 for temperatures below 100°C:

$$10^3 \ln \alpha_{18_O} = -5.533 + 3.2763(10^6/T^2),$$
$$10^3 \ln \alpha_{18_O} = -18.977 + 8.582(10^3/T) + 1.9189(10^6/T^2).$$

Numerical values of the fractionation factor in Eqs. 2.78 and 2.79 for the quartz-water system have been determined by several researchers. Some results are shown in the range of temperatures from 0 to 100°C in Fig. 2.6.

In the narrow ranges of temperatures used for the paleotemperature analysis of the ancient ocean, the obtained empirical relationships differ from those expressed by Eqs. 2.78 and 2.79.

Urey et al. (1951) and Epstein et al. (1951, 1953) found experimentally the following dependence of temperature upon the isotopic composition of oxygen in the sea carbonates:

$$t = 16.5 - 4.3\delta^{18}O + 0.14(\delta^{18}O)^2,$$

where the $\delta^{18}O$ values in this case are expressed versus the PDB-I standard, which is 30.6‰ heavier than the standard of the ocean water (SMOW).

Later on, Epstein and Mayeda (1953) proposed a more general form for a paleotemperature scale:

$$t = 16.5 - 4.3(\delta - A) + 0.14(\delta - A)^2,$$

where A is parameter describing the isotopic composition of water in which the shell of a mollusk grew up. The value of A is equal to the $\delta^{18}O$ value of the sea water, obtained on the basis of the isotopic analysis of carbon dioxide equilibrated with the examined water at 25°C and measured relative to the PDB-I standard. However, as Bowen (1966) has pointed out, it is impossible to determine the value of A for

Fig. 2.6 Temperature dependence of the oxygen isotopes for quartz–liquid water system: (*1*) Shiro and Sakai (1972); (*2*) Labeyrie (1974); (*3*) Backer and Clayton (1976); (*4*) Knauth and Epstein (1976); (*5*) Kawabe (1978). (After Kawabe 1978)
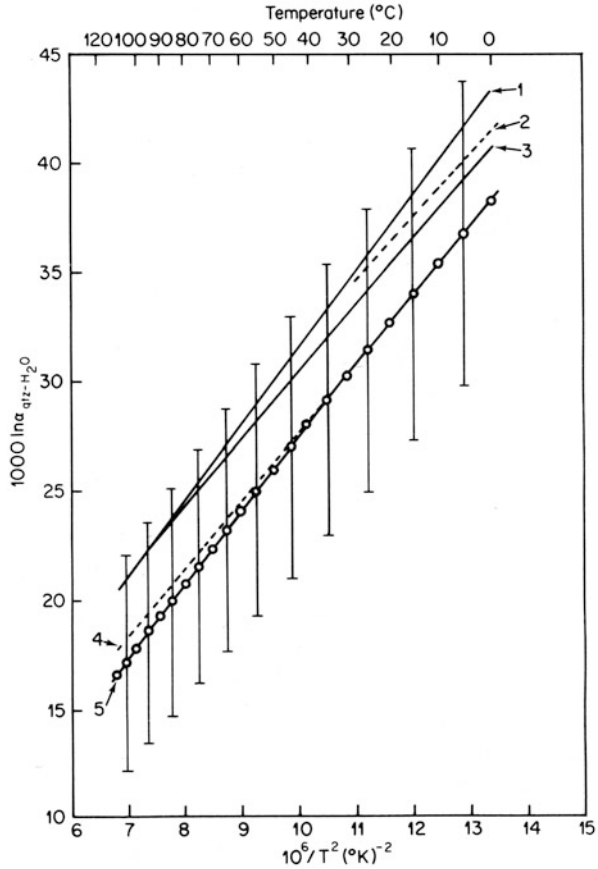
paleooceans using only the carbonate thermometer. This means that all measurements made for the oxygen isotopes in the carbonate shells of fossil mollusks will only give relative temperatures. The absolute temperatures would be imprecise. More precise results seem to be obtained by eliminating the parameter A, for example, simultaneously using data for phosphate paleothermometry (Longinelly and Nuty 1965). Thus, one obtains

$$t = -90 - 4.8 \left(\delta_p - \delta_w\right),$$

where δ_p is the oxygen isotopic composition of the phosphates; δ_w is the isotopic composition of water from which sedimentation of the phosphates occurred.

Analyzing the formula of Epstein, Mayeda and Craig (1965) have shown that several corrections should be involved, taking into account the systematic errors of the oxygen isotopic composition analysis on the mass spectrometer when the ionic source is being filled in with the carbon dioxide. In this case, the formula of Epstein and Mayeda should be rewritten in the corrected form

$$t = 16.5 - 4.3 \left(\delta_c^o - \delta_w^o\right) + 0.14 \left(\delta_c^o - \delta_w^o\right)^2,$$

where δ_w^o is the oxygen isotopic composition in the investigated carbonates, measured relative to the PDB-I standard in the carbon dioxide which was extracted from the carbonate sample by reaction with 100% phosphoric acid; δ_w^o is the oxygen isotopic composition of water measured in relation to the PDB-I standard of the carbon dioxide, equilibrated with water from which the precipitation of the carbonates had occurred.

The corrected δ_c' and δ_w' values, according to Craig, can be obtained from the expressions

$$\delta_c' = f_c\delta_c^o + 0.009\delta^{13}C_c,$$
$$\delta_w' = f_w\delta_w^o + z,$$
$$z = 0.009\delta^{13}C_t - (\alpha/\rho)\,\delta^{18}O_t,$$

where $\delta^{13}C_c$ is the isotopic composition of the carbon in a sample of precipitated sea limestone; f_c is the correction coefficient of experimentally measured δ_w^o value of the carbon dioxide extracted from the sample being investigated while taking into account apparatus errors (for apparatus of mean resolution $f_c = (1.028 - 1.029)$; f_w is the correction coefficient of experimentally measured δ_w^o value of the carbon dioxide being in equilibrium with water while taking into account the systematic and apparatus errors (f_c); $\delta^{13}C_t$ is the carbon isotopic composition of the carbon dioxide used for equilibration purposes; $\delta^{18}O_t$ is the isotopic composition of oxygen of the same gas; α is the isotopic fractionation factor of oxygen in the CO_2–H_2O system, which can be assumed to be 1.04; ρ is the ratio of atoms (gram-atoms) of oxygen in water to atoms (gram-atoms) of oxygen in carbon dioxide in the equilibrium flask. All the values are taken in ‰.

As Craig (1965) has shown $f_w \approx 1.04$, and $z \approx -0.09‰$.

The difference between the measured values ($\delta_c^o - \delta_w^o$) is related to those corrected by

$$\delta_c^o - \delta_w^o = \frac{\delta_c' - \delta_w'}{f_c} + \left(\frac{f_w}{f_c} - 1\right)\delta_w^o + \frac{z}{f_c}.$$

The sum of the last two terms on the right-hand side of this equation is approximately equal to $-0.092‰$. Substituting ($\delta_c - \delta_w$) from the difference ($\delta_c' - \delta_w'$) Craig obtained from the last relationship, the corrected carbonate-water isotopic temperature scale equation is in the form

$$t = 16.9 - 4.2\left(\delta_c' - \delta_w'\right) + 0.13\left(\delta_c' + \delta_w'\right)^2.$$

Here δ' is the corrected $\delta^{18}O$ value, which is measured in the carbon dioxide extracted from the carbonates by reaction with 100% H_3PO_4 (δ_c^o) and is measured in CO_2 equilibrated with water at 25°C (δ_c).

The equation is applicable for any laboratory standard on condition that measurements of the oxygen isotopes of CO_2 extracted from the carbonates and equilibrated with water are made relative to the same standard.

Note that the correction factor f_c and f_w for the modern mass spectrometers can be different from those given above for the old instruments such as M-86 (Atlas-Werke) or MI-1305 (SCB APS Academy of Sciences of the USSR).

For the carbonate paleotemperature measurements, the PDB-1 standard is obtained by crushing and grinding the belemnite (mollusk of the Belemnitela Americana type) taken from Peedee formation of South Carolina (Upper Creteaceous, Maastrichtian). At present, this standard is completely exhausted but in 1957 Craig compared the PDB-1 standard with the etalon isotopic specimen No. 20 from the National Bureau of Standards, USA. The NBS-20 standard is a $CaCO_3$ specimen of Solenhofen limestone, for which the corrected value of $\delta^{18}O = 4.14‰$ has been found (Bowen 1966).

The isotopic composition of sample X in relation to the PDB standard $\delta_{(x-PDB)}$ can be calculated if one takes some other standard B whose $\delta_{(x-B)}$ value is (Craig 1957). Then

$$\delta_{(x-PDB)} = \delta_{(x-B)} + \delta_{B+PDB} + 10^{-3}\delta_{(x-B)}\delta_{(x-PDB)},$$

where all δ values are expressed in terms of per mile.

Craig (1965) has calculated the $\delta^{18}O$ value of the PDB-1 standard on the SMOW scale. A comparison of oxygen isotopic composition of the carbon dioxide, obtained from the PDB-1 standard and from the analogous La Jolla standard, with the isotopic composition of CO_2 equilibrated with the ocean water at 25°C, has shown that on the SMOW scale the oxygen isotopic composition of the carbon dioxide extracted from the PDB-1 standard and from the La Jolla standard are $0.22‰$ and $0.18‰$ heavier than the oxygen isotopic composition of the carbon dioxide equilibrated with SMOW at 25°C. In this case, as Craig has demonstrated, the following relation exists:

$$R_{(PDB-CO_2)}/R_{(SMOW-CO_2)} = 1.00020,$$

where $R_{(PDB-CO_2)}$ and $R_{(SMOW-CO_2)}$ are the $\delta^{18}O/\delta^{16}O$ isotopic ratios in the carbon dioxide obtained from the PDB-1 carbonate by the acid extraction with 100% H_3PO_4 and another sample of CO_2 equilibrated with the ocean water (SMOW) at 25°C.

It is also known that during the CO_2 extraction from $CaCO_3$ with 100% H_3PO_4 isotopic fractionation between liquid and gaseous phases occurs. The value of $\alpha_{CaCO_3-CO_2} = 1.01000$ (Clayton 1961) has been accepted, that is the extracted carbon dioxide is enriched by approximately 10‰ with ^{18}O in relation to the $CaCO_3$ sample. According to Craig, the value of fractionation factor is $\alpha_{H_2O-CO_2} = 1.0407$ (25°C). If both fractionation factors are known, one can write

$$\frac{R_{(H_2O-CO_2)}}{R_{(CaCO_3-CO_2)}} = \frac{\alpha_{(H_2O-CO_2)}R_{H_2O}}{\alpha_{(CaCO_3-CO_2)}R_{CaCO_3}} = 1.03040\frac{R_{H_2O}}{R_{CaCO_3}}.$$

Combining the last equation with the previous one, we obtain

$$\delta_{(PDB-SMOW)} = (1.00020 \times 1.03040) \times 10^3 = +30.6‰,$$

that is the oxygen isotopic composition in the PDB-1 standard is 30.6‰ heavier than the SMOW one.

Using the new value of $\alpha_{H_2O-CO_2} = 1.0412$ (O'Neil et al. 1975), one obtains

$$\delta_{(PDB-SMOW)} = 31.1‰,$$

which is likely to be more precise value than which was obtained earlier (+30.6‰). It follows that the oxygen isotopic composition of any carbonate sample on the SMOW scale will be related to the PDB-1 scale by the equation

$$\delta_{SMOW} = 1.031\delta_{PDB} + 31.1‰.$$

If the values of the fractionation factors $\alpha_{CaCO_3-CO_2}$ and $\alpha_{H_2O-CO_2}$ are corrected in the future, then the constant factor in the last expression will be different from those obtained.

The above paleotemperature scales are in common use in paleotemperature analysis (Bowen 1966; Teys and Naydin 1973).

Labeyrie (1974) derived an equation applicable to the determination of surface water temperature using the oxygen isotopic composition of water and that of silica of the diatomic silt which has the form

$$t = 5 - 4.1(\delta_{SO_2} - \delta_{H_2O} - 40).$$

In the range of low temperatures, this equation gives the value of temperatures which are close to those for the fractionation factor related to the equation obtained by Knauth and Epstein (1976).

For the study of the base temperatures of the hydrothermal systems, the scale which is dependent on the fractionation factor of oxygen isotopes in the sulfate-water system is often used. According to Lloyd's (1968) evidence, this dependence, in the case of the dissolved sulfate-water system, is

$$10^3 \ln \alpha_{18_O} = 3.251(10^6/T^2) - 5.6.$$

Mizutani and Rafter (1969) and Mizutani (1972) have reported the same relationship for slightly different initial conditions:

$$10^3 \ln \alpha = 2.88(10^6/T^2) - 4.1.$$

McKenzie and Truesdell (1977) have employed these relationships for determining base temperature of hydrothermal systems in the range of 100 to 400°C. They noted that the equations of Lloyd and Mizutani and Rafter must be corrected for the following considerations. For the experimental determination of the corresponding $\delta^{18}O$ values, the isotopic composition of water was analyzed by the method of water equilibration with CO_2. The fractionation factor in the carbon dioxide-water system being used was equal to $\alpha_{25°C} = 1.0407$. However, the new experimental evidence, obtained by O'Neil et al. (1975), has shown that a more precise value of the factor is $\alpha_{25°C} = 1.0412$. If we take this into account then the numerical values obtained for the base temperatures at corresponding conditions deviate slightly from those given above:

$$10^3 \ln \alpha = 3.251(10^6/T^2) - 5.1.$$
$$10^3 \ln \alpha = 2.88(10^6/T^2) - 3.6.$$

However, the obtained corrections do not considerably affect the temperatures being calculated. Sakai (1977) reported the equation for the barytes-water system which was obtained earlier by Kusakabe and Robinson in the range of temperatures 100–500°C:

$$10^3 \ln \alpha = 3,01(10^6/T^2) - 7.3.$$

In the case where notable differences occur in the fractionation factor of oxygen isotopes in coexisting phases on the basis of $\delta^{18}O$ values of mineral pairs, the temperatures of the mineral formation are calculated as well as the isotopic composition of the coexisting water phase. As Degens has pointed out, studies of systems such as calcite–apatite, syenite–magnetite, calcite–dolomite, calcite–quartz, or other oxygen-bearing minerals are essential (Becker and Clayton 1976).

In a similar way to oxygen isotopic fractionation in rock-water systems, the hydrogen isotopic fractionation occurs during the formation of cristallohydrates, clay minerals, and in hydrothermal processes during serpentinization and chloritization of silicate minerals of primary magmatic rocks. All these processes are directed so the OH-hydrogen in slightly depleted in D in relation to the equilibrated water phase. By the opinion of Hamza and Epstein (1980), in perspective, the direction of the isotope geothermometry is the study of oxygen isotope distribution between different oxygen-bearing groups of a mineral and its OH-groups.

For example, according to data obtained by Fontes and Gonfiantiny (1967) for the water-gypsum system, the fractionation factors are $\alpha_{18_O} = 1.004$ and $\alpha_D = 0.98$. Therefore, during crystallization of gypsum, its bounded water becomes enriched in ^{18}O by 4‰ and depleted in D by 20‰ compared to the solution.

In the process of the formation of clay minerals, the isotopic fractionation of hydrogen and oxygen occurs between water and hydroxide ions of minerals, for example, those of kaolinite $Al_4(OH)_8[Si_4O_{10}]$ or montmorillonite $Mg_3(OH)_4[Si_4O_8(OH)_2] \cdot nH_2O$. In the process of clay mineral formation from mountain rocks weathered with the help of precipitation, when the conditions of the reaction in the water-rock system are close to those at equilibrium, these minerals, as a rule, are enriched in ^{18}O by approximately 27‰ and depleted in D by 30‰ compared with the water participating in their formation (Savin and Epstein 1970a; Sheppard et al. 1971; Lawrence and Taylor 1971; Suzuoki and Epstein 1976; Sofer 1978). In Table 2.6, the corresponding fractionation factors are presented according to various authors.

It is most likely that the hydrogen fractionation factor in the mineral-water system undergoes insignificant change in the range of temperatures from normal up to 400°C. This conclusion can be drawn from the summarized data reported by Taylor (1974) and also from the results of Suzuoki and Epstein (1976) who have studied the isotopic fractionation of hydrogen between hydroxide-bearing minerals and water. These authors determined that in the kaolinite-water system at 400°C, the fractionation factor $\alpha_D = 0.977$. This α_D value is close to the value of the fractionation factor given in Table 2.6 for normal temperatures of the hypergenic zone (Savin and Epstein 1970a; Taylor 1974). Hence, when the temperature increases to more than 300°C kaolinite, being in isotopic equilibrium with water, becomes depleted in D by $\sim$ 10‰

Table 2.6 Hydrogen and oxygen isotope fractionation factors for water-clay minerals and water-gypsum systems at $t = 10$–$20°C$

Mineral	$\alpha_D = \frac{(D/H)_{mineral}}{(D/H)_{water}}$	$\alpha_{18_O} = \frac{(^{18}O/^{16}O)_{mineral}}{(^{18}O/^{16}O)_{water}}$	Reference
Montmorillonite	0.94	1.027	Savin and Epstein (1970a)
Kaolinite	0.97	1.027	Savin and Epstein (1970a)
Glauconite	0.93	1.026	Savin and Epstein (1970a)
Quartz (Si$-$OH), 0°C	0.92	1.039	Kolodny and Epstein (1976)
Gypsum	0.98	1.004	Sofer (1978); Fontes and Gonfiantini (1967)

Table 2.7 Hydrogen and oxygen isotope fractionation factors for water–hydroxide-bearing mineral systems (After Suzuoki and Epstein 1976)

Mineral	t, °C	$\alpha_D = \frac{(D/H)_{mineral}}{(D/H)_{water}}$
Muscovite	750	1.000
	650	0.992
	550	0.988
	450	0.976
Biotite	850	0.981
	650	0.972
	550	0.965
	450	0.957
	400	0.955
Phlogopite	650	0.990
	575	0.985
Hornblende	670	0.982
	570	0.974
	450	0.963
	400	0.961
Lepidolite	650	1.015
Serpentinite	400	0.980
Kaolinite	400	0.977
Boehmite	400	0.936

compared with kaolinite at equilibrium with water of the same isotopic composition at normal temperature (at 20°C). In Table 2.7, referring the data of Suzuoki and Epstein (1976), the hydrogen isotopic fractionation factors are given in the system of water-hydroxide-bearing minerals for temperatures above 400°C (Suzuoki and Epstein 1976).

In the range of temperatures 450–800°C, Suzuoki and Epstein (1976) obtained the following dependence of the fractionation factors on temperature for oxygen-bearing minerals:

$$10^3 \ln \alpha_{muscovite\text{-}water} = -22.1(10^6/T^2) + 19.1,$$

$$10^3 \ln \alpha_{biotite\text{-}water} = -21.3(10^6/T^2) + 2.8,$$

$$10^3 \ln \alpha_{hornblende\text{-}water5} = -23.9(10^6/T^2) + 7.9.$$

Suzuoki and Epstein also obtained the general equation for amphiboles and micas taking into account the cation substitution on the minerals' crystal grating:

$$10^3 \ln \alpha_{mineral\text{-}water} = -22.4(10^6/T^2)) + 28.2(2X_{Al} + X_{Mg} + X_{Fe} = 1).$$

where X_{Al}, X_{Mg}, X_{Fe} are the molal ratios of the corresponding $(X_{Al} + X_{Mg} + X_{Fe} + 1)$.

It is obvious that this equation can be applied to other oxygen-bearing minerals such as serpentine and kaolinite.

The data on the temperature dependence of the fractionation factor for the serpentine-water system obtained by Suzuoki and Epstein are in accordance with those obtained by Sakai and Tsutsumi (1978). In the range of temperatures 100–500°C and at water pressure of 2 *Kbar*, they have obtained the following relationship:

$$10^3 \ln \alpha_{serpentine\text{-}water} = 2.75(10^7/T^2) - 7.69(10^4/T) + 40.8.$$

This relationship contradicts the semi-empirical evidence of Wenner and Taylor (Taylor 1974). According to these, serpentines become progressively depleted in D, compared to water being in isotopic equilibrium with them, if the temperature decreases from 500 to 100°C. According to the experimental evidence of Suzuoki and Epstein (1976) and also that of Sakai and Tsutsumi (1978), the opposite process takes place (Fig. 2.7).

Figure 2.8 show the graphical dependence of the equilibrium fractionation factors of oxygen isotopes for natural mineral-water systems based on data obtained by various authors (Taylor 1974). The figure shows that practically all the oxygen-bearing rocks are enriched with ^{18}O compared with the equilibrated water. With increase in temperature, the difference in ^{18}O values for water and rock decreases. At high temperatures, under natural conditions, this effect results in ^{18}O enrichment of the groundwaters compared with ^{18}O content in precipitations. This effect is often called 'the oxygen shift'.

For isotopic investigations of natural waters, some isotopic fractionation curves for liquid and gaseous reacting components are of great hydrologic interest. Figure 2.9 and 2.10 are graphs of experimental and calculated dependences of oxygen and hydrogen isotopic fractionation factors at equilibrium for such systems. These graphs are based on data from various authors and are taken from the work of Taylor (1974).

It is evident from Fig. 2.9 that in the CO_2–H_2O gas system, the carbon dioxide is enriched with ^{18}O by about 50‰ compared to the water vapor with which it is isotopically equilibrated at 20°C. In the range of temperatures 100–300°C, this equilibrium can be calculated with the help of an equation obtained by Bottinga (1969):

$$10^3 \ln \alpha = -10.55 + 9.284(10^3/T) + 2.561(10^6/T^2). \qquad (2.80)$$

Interaction of carbon dioxide with groundwaters takes place in nature, for example, in regions of modern volcanic activity where it leads to the depletion of ^{18}O in the groundwaters. An analogous phenomenon has been observed by Ferrara et al. (1965) in thermal waters of the Larderello region.

Equation 2.80 can be used in the calculation of isotopic base temperatures in hydrothermal systems based on the oxygen isotopic composition data in water vapour and carbon dioxide. This study was done in the Larderello region (Panichi et al. 1977, 1979).
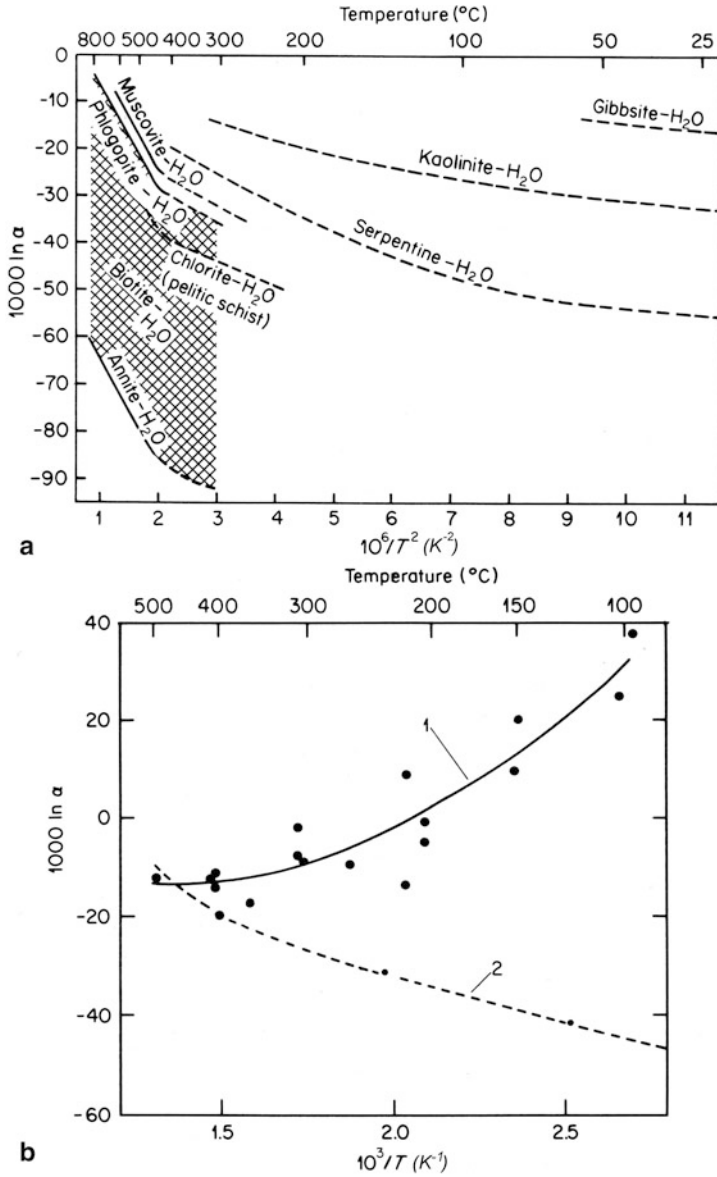
Fig. 2.7 Temperature dependences of the hydrogen isotope fractionation factor for a mineral-water system (**a**) are obtained by various authors (from Taylor 1974) and for a serpentine-water system (**b**). (*1*) experimental results of Suzuoki and Epstein (1976) and by Sakai and Tsutsumi (1978); (*2*) empirical curve of Wenner and Taylor. (From Taylor 1974)
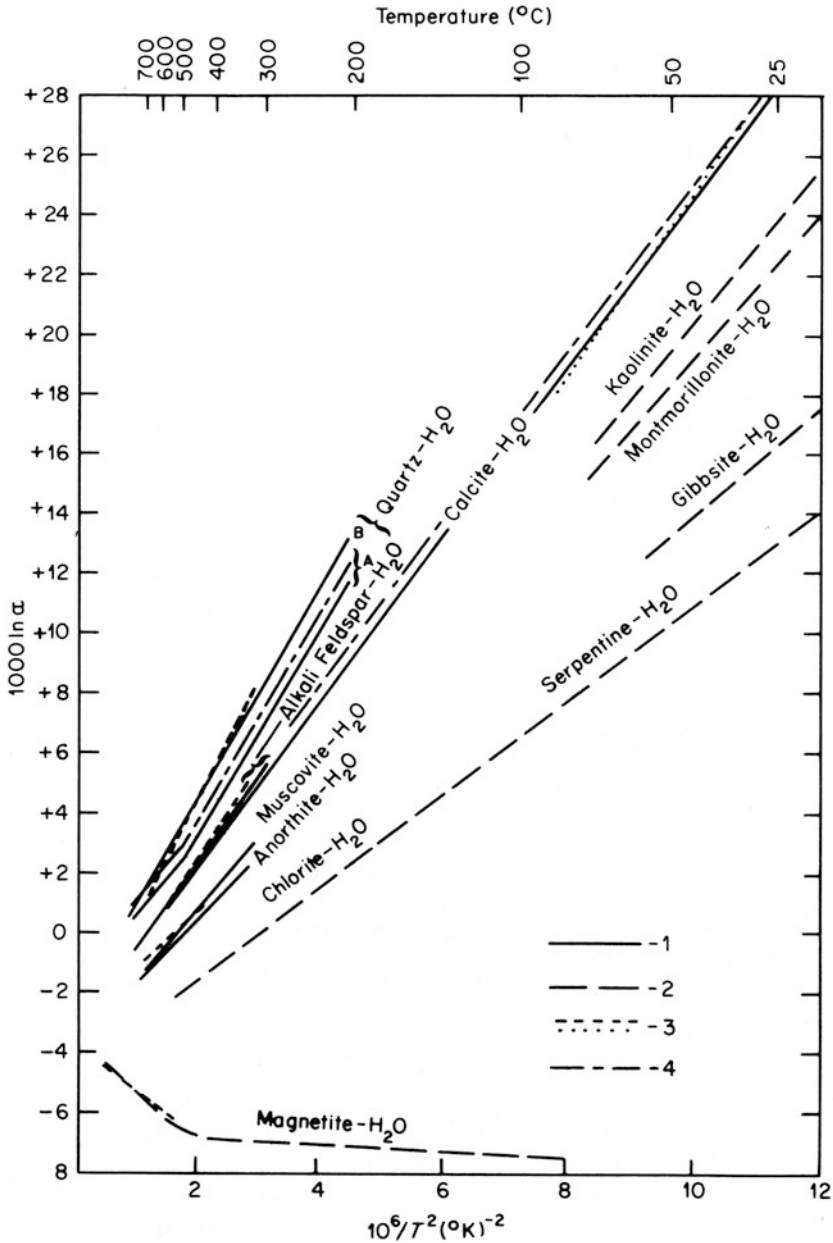
Fig. 2.8 Equilibrium oxygen isotope fractionation curves for natural mineral-water systems are obtained by various authors. (*1*) experimental curves (A—'complete' isotopic exchange; B—'patrial' isotopic exchange); (*2*) empirical curves; (*3*) calculated curves; (*4*) experimental curves based on changing the CO_2–H_2O liquid fractionation factor at 25°C from 1.0407 to 1.0412. (From Taylor 1978. © IAEA, reproduced with permission of IAEA)

Fig. 2.9 Calculated equilibrium oxygen isotope fractionation factors as a function of temperature for CO_2–H_2O and CO_2–calcite and experimentally determined curve for liquid water–vapor water. (From Taylor 1974. © IAEA, reproduced with permission of IAEA)
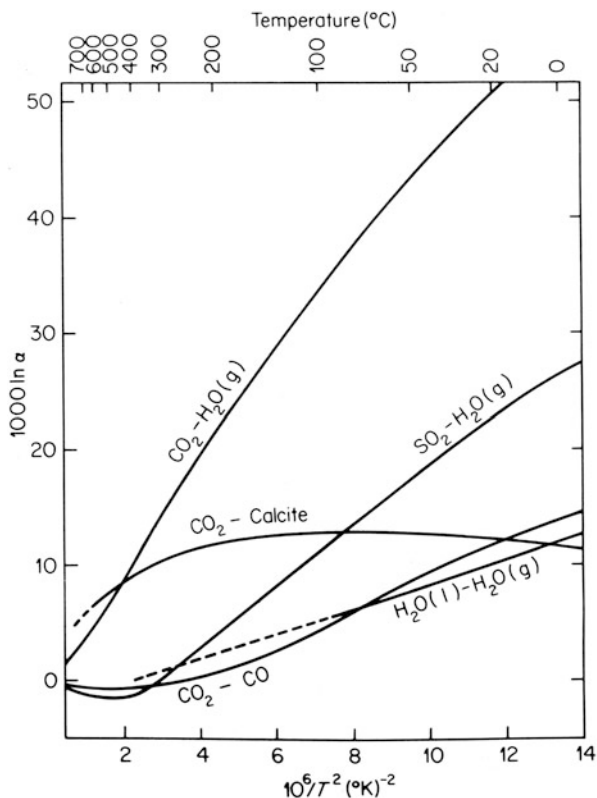

Figure 2.10 shows several curves calculated for the isotopic fractionation of hydrogen, which are of interest from the geological viewpoint. From the plotted curves, one can see that under equilibrium at 400°C water will be enriched in D by 400‰ compared to the gaseous hydrogen.

Hence, if some water is reduced to gaseous hydrogen in the hydrothermal system, then, knowing the initial isotopic composition of water and the hydrogen fractionation factor in the system H_2O–H_2, the isotopic composition of the remaining water can be calculated. Let the initial value of deviation $\delta D_{H_2O} = -70‰$. Suppose 5% of the gaseous hydrogen is released after heating the water above 400°C, then for hydrogen, $\delta D_{H_2} = -470‰$. One can find the $\delta D^*_{H_2O}$ value of the heated water from the condition of normalization of the total quantity of molecules (or molal fractions) of H_2O and H_2 per unit as

$$\delta D^*_{H_2O} = \frac{\delta D_{H_2O} - 0.05\delta D_{H_2O}}{0.95} = \frac{-70 - 0.05(-470)}{0.95} \approx -50‰.$$

The approximate calculations show that exchange processes in the water-hydrogen system in principle may lead to the enrichment of water with D, but it is unlikely that the processes considered play a decisive role in the hydrogen isotopic change of

Fig. 2.10 Calculated equilibrium hydrogen isotope fractionation factors as a function of temperature for H_2O–H_2, CH_4–H_2 (experimental data) and H_2O–CH_4 (calculated values). (From Taylor 1974. © IAEA, reproduced with permission of IAEA)
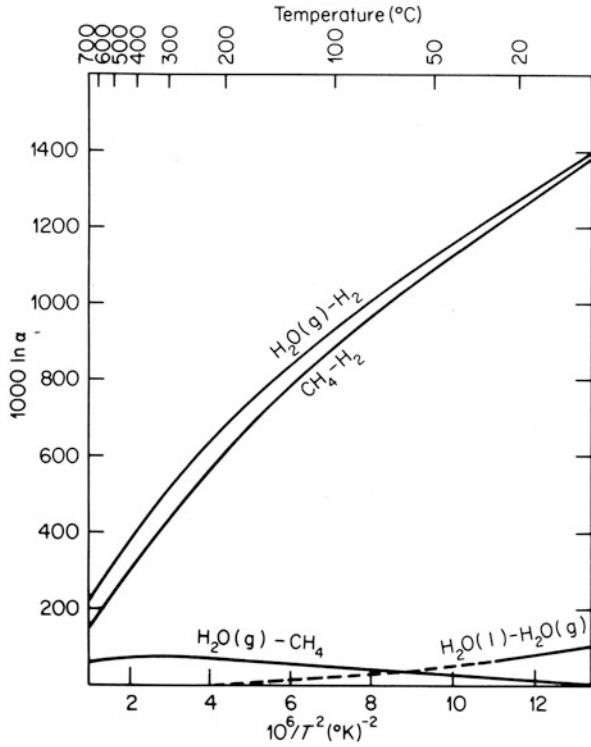
groundwater since, under the changed conditions methane will be formed. However at real temperatures, as shown by Taylor (1974), the hydrogen fractionation in the H_2O–CH_4 system does not exceed 70‰ (see Fig. 2.9). In order to change the isotopic composition of water by 20‰, as in the previous case, 30% of the hydrothermal solution must react with carbon-bearing components to produce methane. As Taylor pointed out, this reaction might only occur in systems which contain carbon in large amounts (graphite, coal, and oil). It is not likely to occur under natural conditions.

The reactions of this isotopic equilibrium in such systems as water-hydrogen and water-methane can be used for determining water temperature in hydrothermal systems. For example, Arnason (1977a) has used the data on hydrogen isotopes of water and the dissolved hydrogen in water for determining base temperatures in the hydrotherms of Iceland.

The formation of the isotopic composition of oxygen and hydrogen in natural waters and the influence of different natural factors on isotopic separation processes are considered below.