

## CHAPTER 2

# Nuclei, Isotopes and Isotope Separation

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According to accepted nuclear models the nucleus is composed of only protons and neutrons. For example, the oxygen atom of mass number 16 has a nucleus which consists of 8 protons and 8 neutrons; since neutrons have no charge but are very similar to protons in mass, the net nuclear charge is +8. There are 8 extranuclear electrons in the neutral atom of oxygen.

### 2.1. Species of atomic nuclei

The term *nucleon* is used to designate both protons and neutrons in the nucleus. The *mass number A* is the total number of nucleons. Thus

$$A = N + Z \quad (2.1)$$

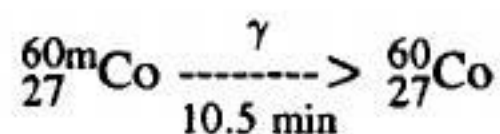
where  $Z$  is the number of protons (= the *atomic number*) and  $N$  is the number of neutrons. The elemental identity and the chemical properties are determined by the atomic number.

As we have seen in Chapter 1, an element may be composed of atoms that, while having the same number of protons in the nuclei, have different mass numbers and, therefore, different numbers of neutrons. Neon, for example, has an atomic number of 10, which means that the number of protons in the nuclei of all neon atoms is 10; however, 90% of the neon atoms in nature have 10 neutrons present in their nuclei while 10% of the atoms have 12 neutrons. Such atoms of constant  $Z$  but different  $A$  are called *isotopes*. The heavy hydrogen isotopes  $^2\text{H}$  and  $^3\text{H}$  are used so often in nuclear science that they have been given special names and symbols, deuterium (D) and tritium (T), respectively.

The word isotope is often misused to designate any particular nuclear species, such as  $^{16}\text{O}$ ,  $^{14}\text{C}$ ,  $^{12}\text{C}$ . It is correct to call  $^{12}\text{C}$  and  $^{14}\text{C}$  isotopes of carbon since they are nuclear species of the same element. However,  $^{16}\text{O}$  and  $^{12}\text{C}$  are not isotopic since they belong to different elemental species. The more general word *nuclide* is used to designate any specific nuclear species; e.g.  $^{16}\text{O}$ ,  $^{14}\text{C}$ , and  $^{12}\text{C}$  are nuclides. The term *radionuclide* should be used to designate any radioactive nuclear species, although *radioisotope* is a common term used for the same purpose.

In addition to being classified into isotopic groups, nuclides may also be divided into groupings with common mass numbers and common neutron numbers. *Isotopes* are nuclides with a common number of protons ( $Z$ ), whereas *isobar* is the term used to designate nuclides with a common number of nucleons ( $A$ ), i.e. the same mass number. Nuclei with the same number of neutrons ( $N$ ) but different atomic numbers are termed *isotones*.  $^{40}_{19}\text{K}$  and  $^{40}_{18}\text{Ar}$  are examples of isobars, while  $^3_1\text{H}$  and  $^4_2\text{He}$  are examples of isotones.

In some cases a nucleus may exist for some time in one or more excited states and it is differentiated on this basis. Such nuclei that necessarily have the same atomic number and mass number are called *isomers*.  $^{60\text{m}}\text{Co}$  and  $^{60\text{g}}\text{Co}$  are isomers; the  $^{60\text{m}}\text{Co}$  nuclide exists in a high energy (*excited*) state and decays spontaneously by emission of a  $\gamma$ -ray with a half-life of 10.5 min to the lowest energy, *ground state*, designated by  $^{60\text{g}}\text{Co}$ .



The symbol m stands for *metastable*, while g (or no symbol) refers to the ground state.

## 2.2. Atomic masses and atomic weights

The *universal mass unit*, abbreviated u (sometimes amu for atomic mass unit), is defined as one-twelfth of the mass of the  $^{12}\text{C}$  atom which has been defined to be exactly 12 u. The absolute mass of a  $^{12}\text{C}$  atom is obtained by dividing the value 12 by the Avogadro number ( $N_A = 6.022\,137 \times 10^{23}$ ). The value for the mass of a  $^{12}\text{C}$  atom, i.e. the nucleus plus the 6 extranuclear electrons, is thus  $1.992\,648 \times 10^{-23}$  g. Atomic masses are expressed in units of u relative to the  $^{12}\text{C}$  standard. This text uses  $M$  to indicate masses in units of u, and  $m$  in units of kilograms;  $m = M/10^3 N_A$ .



In nuclear science it has been found convenient to use the atomic masses rather than nuclear masses. The number of electrons are always balanced in a nuclear reaction, and the changes in the binding energy of the electrons in different atoms are insignificant within the degree of accuracy used in the mass calculations. Therefore the difference in atomic masses of reactants and products in a nuclear reaction gives the difference in the masses of the nuclei involved. In the next chapter, where the equivalence between mass and energy is discussed, it is shown that all nuclear reactions are accompanied by changes in nuclear masses.

The mass of the nucleus can be approximated by subtracting the sum of the masses of the electrons from the atomic mass. The mass of an electron is 0.000549 u. In kilograms, this mass is  $9.1094 \times 10^{-31}$ . Since the neutral carbon atom has 6 electrons, the approximate mass of the nucleus is  $1.992\,648 \times 10^{-26} - 6 \times (9.1094 \times 10^{-31}) = 1.992\,101 \times 10^{-26}$  kg. This calculation has not included the difference in the mass of the 6 extra electrons attributable to the binding energy of these electrons. However, this binding energy has a mass equivalence which is smaller than the least significant figure in the calculation.

The mass of a neutron is 1.008 665 u while that of the hydrogen atom is 1.007 825 u. Since both neutrons and protons have almost unit atomic masses, the atomic mass of a nuclide should be close to the number of nucleons, i.e. the mass number. However, when the table of elements in the periodic system (Appendix I) is studied it becomes obvious that many *elements* have masses which are far removed from integral values. Chlorine, for example, has an atomic mass value of 35.453 u, while copper has one of 63.54 u. These values of the atomic masses can be explained by the effect of the relative abundances of the isotopes of the elements contributing to produce the observed net mass.

If an element consists of  $n_1$  atoms of isotope 1,  $n_2$  atoms of isotope 2, etc., the *atomic fraction*  $x_1$  for isotope 1 is defined as:

$$x_1 = n_1 / (n_1 + n_2 + \dots) = n_1 / \sum n_i \quad (2.2)$$

The *isotopic ratio* is the ratio between the atomic fractions (or *abundances*) of the isotopes. For isotopes 1 and 2, the isotopic ratio is

$$\zeta_1 = x_1 / x_2 = n_1 / n_2; \quad \zeta_2 = x_2 / x_1 = n_2 / n_1 \quad (2.3)$$

The *atomic mass of an element* (or *atomic weight*)  $M$  is defined as the average of the isotopic masses, i.e.  $M_i$  is weighted by the atomic fraction  $x_i$  of its isotope:

$$M = x_1 M_1 + x_2 M_2 + \dots = \sum x_i M_i \quad (2.4)$$

As an example, natural chlorine consists of two isotopes of which one has an abundance of 75.77% and an atomic mass of 34.9689 u and the second has an abundance of 24.23% and a mass of 36.9659 u. The resultant average atomic mass for the element is 35.453. The atomic mass of copper of 63.546 can be attributed to the presence of an isotope in 69.17% abundance with a mass of 62.9296 u and of a second isotope of 30.83% abundance and 64.9278 u. Atomic masses and abundances of some isotopes are given in Table 2.1.

TABLE 2.1. Isotopic data for some elements

| Element   | Z  | N   | A   | Atomic mass<br>(u) | Abundance<br>(%) | Atomic weight | Symbol            |
|-----------|----|-----|-----|--------------------|------------------|---------------|-------------------|
| Hydrogen  | 1  | 0   | 1   | 1.007 825          | 99.985           | 1.00797       | <sup>1</sup> H    |
|           | 1  | 1   | 2   | 2.014 102          | 0.0155           |               | <sup>2</sup> H, D |
|           | 1  | 2   | 3   | 3.016 049          | 0                |               | <sup>3</sup> H, T |
| Helium    | 2  | 1   | 3   | 3.016 030          | ≤ 0.0001         | 4.0026        | <sup>3</sup> He   |
|           | 2  | 2   | 4   | 4.002 603          | 100.00           |               | <sup>4</sup> He   |
| Lithium   | 3  | 3   | 6   | 6.015 121          | 7.42             | 6.939         | <sup>6</sup> Li   |
|           | 3  | 4   | 7   | 7.016 003          | 92.58            |               | <sup>7</sup> Li   |
| Beryllium | 4  | 5   | 9   | 9.012 182          | 100.00           | 9.0122        | <sup>9</sup> Be   |
| Boron     | 5  | 5   | 10  | 10.012 937         | ~19.6            | 10.811        | <sup>10</sup> B   |
|           | 5  | 6   | 11  | 11.009 305         | ~80.4            |               | <sup>11</sup> B   |
| Carbon    | 6  | 6   | 12  | 12.000 000         | 98.892           | 12.0112       | <sup>12</sup> C   |
|           | 6  | 7   | 13  | 13.003 355         | 1.108            |               | <sup>13</sup> C   |
| Nitrogen  | 7  | 7   | 14  | 14.003 074         | 99.635           | 14.007        | <sup>14</sup> N   |
|           | 7  | 8   | 15  | 15.000 109         | 0.365            |               | <sup>15</sup> N   |
| Oxygen    | 8  | 8   | 16  | 15.994 915         | 99.759           | 15.999        | <sup>16</sup> O   |
|           | 8  | 9   | 17  | 16.999 131         | 0.037            |               | <sup>17</sup> O   |
|           | 8  | 10  | 18  | 17.999 160         | 0.204            |               | <sup>18</sup> O   |
| Chlorine  | 17 | 18  | 35  | 34.968 853         | ~75.8            | 35.453        | <sup>35</sup> Cl  |
|           | 17 | 20  | 37  | 36.965 903         | ~24.2            |               | <sup>37</sup> Cl  |
| Uranium   | 92 | 143 | 235 | 235.043 924        | 0.724            | 238.029       | <sup>235</sup> U  |
|           | 92 | 146 | 238 | 238.050 785        | 99.266           |               | <sup>238</sup> U  |

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2.3. Determination of isotopic masses and abundances

2.3.1. The mass spectrometer

The masses and relative abundances of different isotopes occurring naturally in an element can be determined with great exactness using the same technique J. J. Thomson employed to demonstrate the presence of isotopes in neon. The instrument used for this purpose is known as a mass spectrometer. The principles of construction of the electromagnetic *mass spectrometer* are shown in Figs. 2.1 and 2.2.

Let us first consider the movement of an ion in electric and magnetic fields, as shown in Fig. 2.1. The ion of mass *m* is assumed to have a charge *q* (coulomb), which is an integer (*z*) multiple of the elementary charge *e* ( $1.602\ 177 \times 10^{-19}$  C):  $q = ze$ . If it is accelerated from velocity zero to *v* (m s<sup>-1</sup>) by an electric potential *V* (volts), it acquires a kinetic energy *E*<sub>kin</sub> corresponding to

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$$E_{\text{kin}} = \frac{1}{2}mv^2 = qV \tag{2.5}$$

joule (or newton meter). If  $q$  is given in units of the elementary charge, the kinetic energy is in units of *electron volts* (eV). For transformation to other energy units, see Appendix IV.

Figure 2.1 shows the deviations of a positive ion in an electric field  $U$  (newton/coulomb) directed upwards, and a magnetic field  $B$  (tesla) directed into the page. The force  $F$  (newton) acting on the ion due to the electric field is

$$F_e = qU \tag{2.6}$$

The ion would hit the screen at point  $P_1$ . For the magnetic field only, the force is

$$F_m = qvB \tag{2.7}$$

The ion would hit the screen at point  $P_2$ . If the forces balance each other, i.e. when  $F_e = F_m$ , the ion hits the screen at point  $P_0$  with a velocity given by

$$v = U/B \tag{2.8}$$

In either the fields ( $F_e$  or  $F_m$ ) the deviation is counteracted by the centrifugal force  $F_c$ , where

$$F_c = mv^2/r \tag{2.9}$$

and  $r$  is the radius of curvature. In the magnetic field only, the balance between  $F_m$  and  $F_c$  leads to

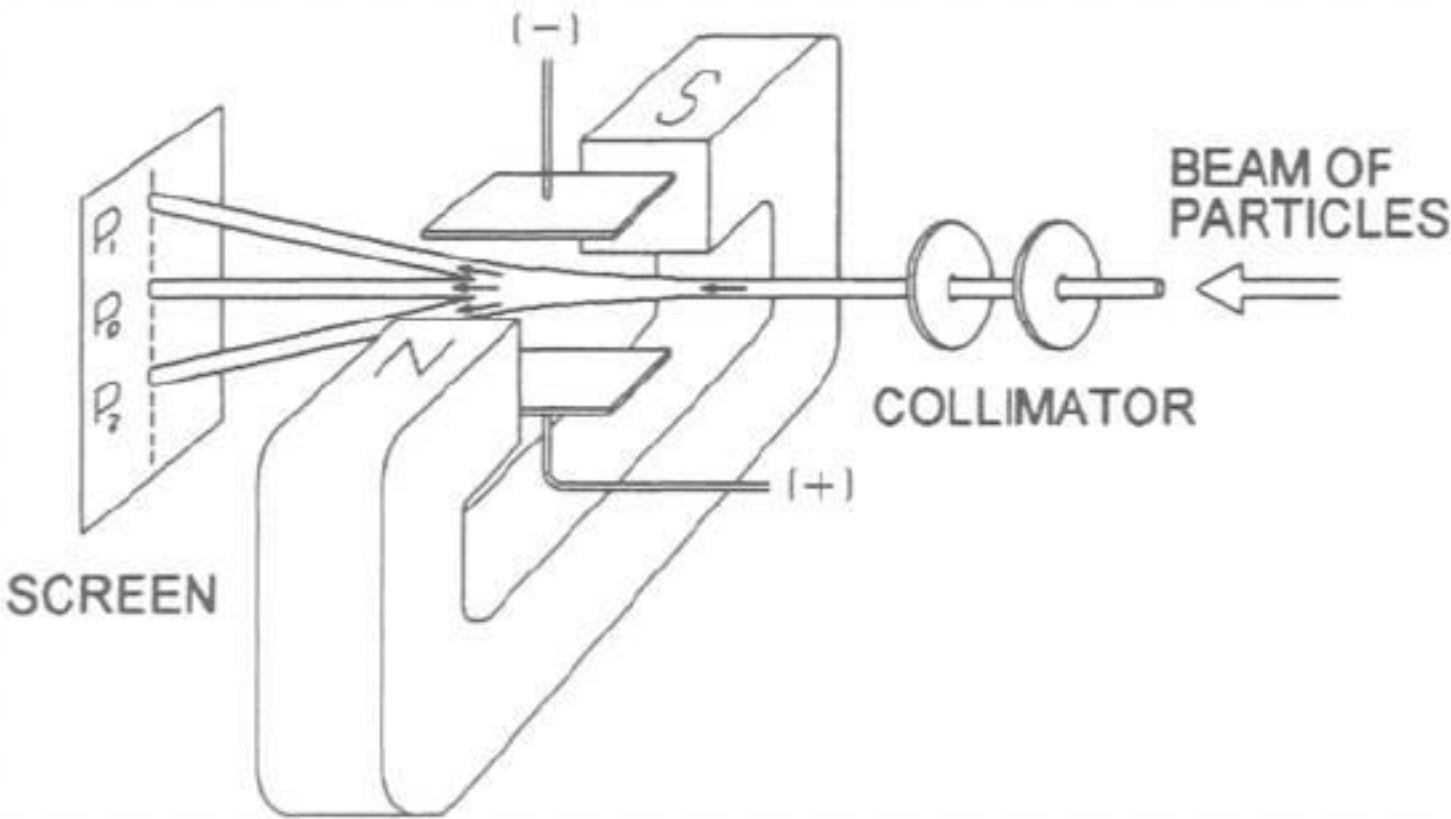


FIG. 2.1. Movement of positive ions in electric and magnetic fields.

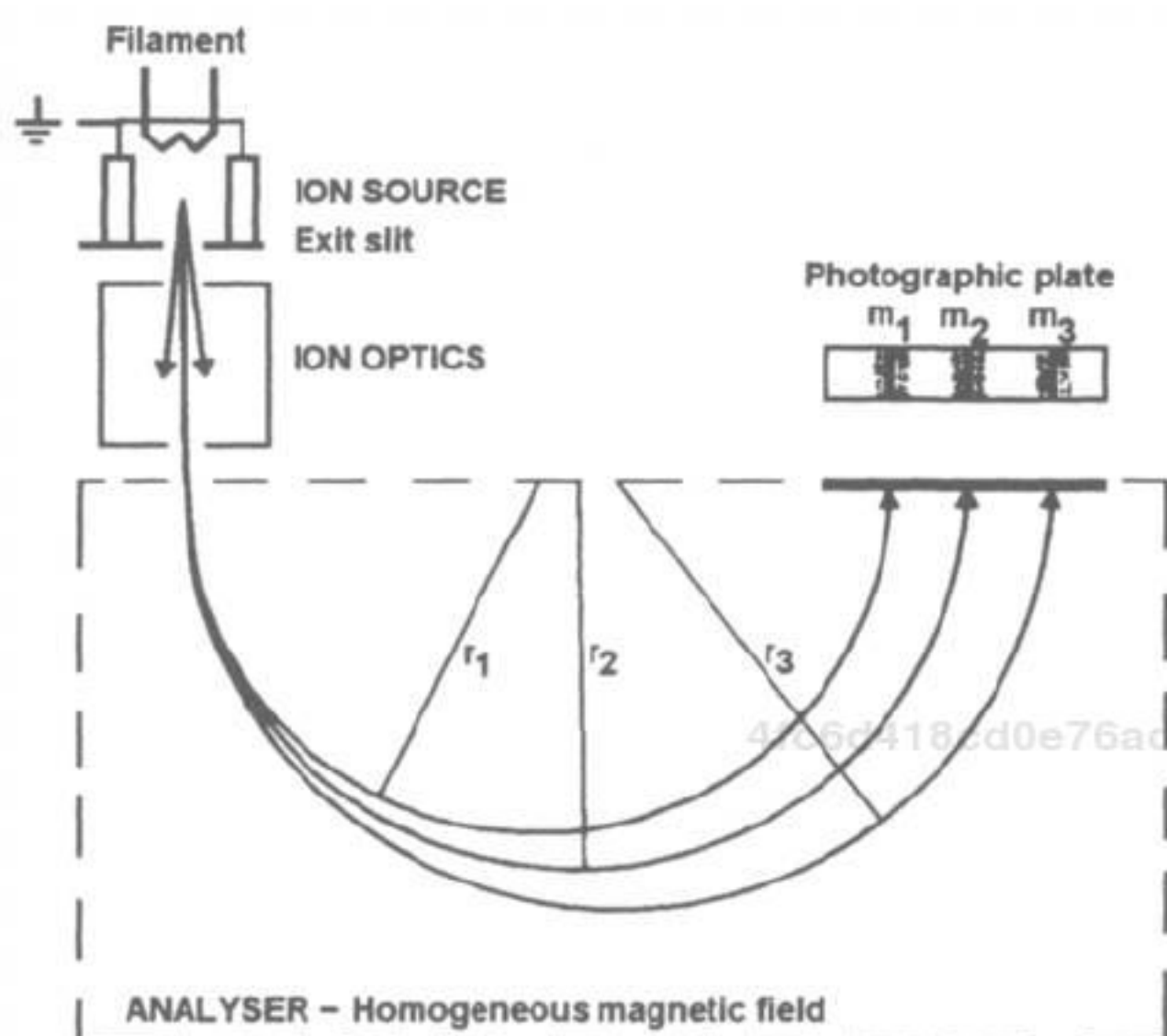


FIG. 2.2. The principle of the mass spectrograph (-meter, if the photographic plate is replaced by an ion current meter).

$$q/m = v/Br \quad (2.10)$$

where  $q/m$  is denoted as the *specific charge* of the ion.

In the mass spectrometer gaseous ions are produced in an *ion source*, e.g. by electron bombardment of the gas produced after heating the substance in a furnace (Fig. 2.2) or by electric discharge, etc. If positive ions are to be investigated, the ion source is given a high positive potential relative to the exit slits. This results in the ions being accelerated away from the source and into the ion optic system. The purpose of the ion optic system is to produce ions of exact direction and of constant velocity, which is achieved through the use of electrostatic and magnetic fields as described; cf. (2.8).

The spectrometer commonly consists of a homogeneous magnetic field which forces the ions to move in circular paths according to (2.10). Combining (2.5) and (2.10) gives

$$m = q r^2 B^2 / 2V \quad (2.11)$$

where  $V$  is the ion acceleration potential. Mass spectrometers are usually designed so that of the three variables  $V$ ,  $B$ , or  $r$ , two are constant and the third variable, which allows ions of different  $q/m$  value to be focused on the detector. The minimum value of  $q/m$  is always  $e/m$  because singly charged ions of the atomic or molecular species are almost always present. In order to avoid collisions between ions and gaseous atoms, which would cause scattering of the ion beam, the system is evacuated. The detector is some charge collecting device (Ch. 8).

A common type of mass spectrometer (A. O. Nier 1940) uses a fixed magnetic field and a fixed radius of curvature for the ion beam. If the acceleration potential  $V$  is varied so that



the masses  $m_1$  and  $m_2$  alternately are registered by the detector, producing ion currents  $I_1$  and  $I_2$ , respectively, the abundance of each isotope can be calculated from the ratios  $x_1 = I_1/(I_1 + I_2)$  and  $x_2 = 1 - x_1$  when only two isotopes are present. The resolution of modern mass spectrometers can be extremely high, as indicated by the values in Table 2.1.

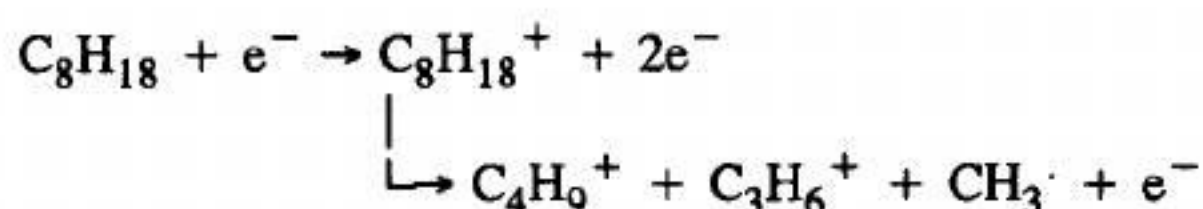
### 2.3.2. Applications

For several decades, mass spectrometers were used primarily to determine atomic masses and isotopic ratios. Now they are applied to a large variety of chemical problems and low resolution mass spectrometers are used for routine chemical analysis. For example, a modern mass spectrometer can easily distinguish between species such as  $^{12}\text{CH}_4^+$  and  $^{16}\text{O}^+$ , having a mass difference of 0.03686 u.

Some uses of mass spectrometry of interest to chemists involved in nuclear science are:

(a) *Molecular weight determination* can be made by mass spectrometry if gaseous ions can be produced with  $M/q$  values not exceeding about 400. This method is of great importance in radiation chemistry (Ch. 7) where often a large number of products are produced which may be quite difficult to identify by other means and in particular for the analysis of organic compounds.

(b) The *study of chemical reactions* directly in the gas phase by mass spectrometry is possible. Using an ion source in which molecules are bombarded by a stream of low energy ( $\leq 100$  eV) electrons, ionization and dissociation reactions can be studied, e.g.



This technique has practical application e.g. in the petroleum industry for determining the composition of distillation and cracking products.

(c) *Isotopic dilution* is a technique for determination of the number of atoms of an element (or isotope) in a composite sample (e.g. rock or biota), from which is difficult to recover the element reproducibly and determine it quantitatively. The technique is simple to use for radioactive nuclides, as described in §9.3, but more complicated and time consuming for stable nuclides. However, the high precision of mass spectrometry makes the latter alternative more accurate, and the technique is widely used for geologic dating.

- 1) Suppose we have a *sample* with *unknown* concentration of a certain element, consisting of the two isotopes 1 and 2, and want to determine the number of atoms,  $N_2$ , of isotope 2 in the sample (which, of course must be of known weight). The number of atoms of each isotope is  $N_1$  and  $N_2$ , thus  $N = N_1 + N_2$ , in unit sample weight. By mass spectrometry we determine the isotope ratio  $\zeta_N = N_1/N_2$ .
- 2) We have a *reference* with the same isotopes, in which the isotopic ratio  $\zeta_P = P_1/P_2$  is known;  $P_1$  is the number of isotope 1, and  $P_2$  of isotope 2 per unit weight.  $P = P_1 + P_2$ .
- 3) The amount  $P$  of the reference (a "spike") is mixed with a known weight of the sample containing the unknown isotope amount  $N_2$ . The mixing must be isotopic, i.e. a complete exchange must take place between the isotopes; this is not a



difficult problem when well planned. A sample is then withdrawn from the mixture, containing  $M_1$  atoms of isotope 1 and  $M_2$  atoms of isotope 2. The sample is measured by the mass spectrometer, yielding  $\zeta_M = M_1/M_2$ .

Since  $M_1 = N_1 + P_1$  and  $M_2 = N_2 + P_2$  simple arithmetic gives

$$N_2 = P(\zeta_P - \zeta_M)/[(\zeta_P + 1)(\zeta_M - \zeta_N)] \quad (2.12)$$

Thus from 3 mass spectrometrically determined isotope ratios ( $\zeta_N$ ,  $\zeta_P$  and  $\zeta_M$ ) and known standard amount  $P = P_1 + P_2$ , the unknown number of atoms  $N_2$  in the sample is determined. The precision of this technique is largest when sample and standard are added in such proportions that  $N \approx P$ . Examples of the use of this technique are given in §5.8 on geologic dating.

Because the variables in these equations often need multiple indexing (e.g. element, isotope and source) the amount of indexing can be reduced by using *italic* element symbols to refer to the specific radioactivity, or concentration, of that nuclide in the sample; e.g.  $^{238}\text{U}$  means  $S_{^{238}\text{U}}$  (radioactivity), or  $N_{^{238}\text{U}}$  (atoms) per unit volume or weight of the sample. Extensive use of this formalism will be found in §5.7ff<sup>1</sup>.

(d) *Analysis of gas purity* (e.g. in plants for separation of  $^{235}\text{U}$  and  $^{238}\text{U}$ ) is done conveniently by mass spectrometry. Not only are the ratios of the uranium isotopes determined, but also the air and water vapor which leaks into the system can be measured. This produces such ions as  $\text{O}_2^+$ ,  $\text{N}_2^+$ ,  $\text{CO}_2^+$ , and  $\text{HF}^+$ , which can be measured easily because mass spectrometry detects the presence of impurities in parts per million (ppm) concentration.

(e) *Instrumental chemical analysis* can be done by using mass spectrometers having ion sources of the inductively coupled plasma type (ICP-MS systems), sometimes as on-line detectors for various chromatographic techniques. Due to the high resolution and sensitivity of this technique it is widely used in analysis of pollutants in the environment.

(f) *Measurement of products from nuclear reactions* can be made with special mass spectrometers on line to the irradiated target. With suitable arrangements both  $A$  and  $Z$  of the recoiling reaction products can be determined.

## 2.4. Isotopic ratios in nature

Mass spectrometric investigations of geologic material has shown that isotopic ratios vary slightly in nature with the largest variations observed for the heaviest and lightest elements.

For the heaviest elements the reason for the variation in the ratio of isotopes in an element can be related directly to the consequence of naturally occurring radioactive decay. For example, in a thorium mineral the decay sequence terminates in the formation of an isotope of lead with mass number 208. By contrast, in a uranium ore, in which  $^{238}\text{U}$  is the most abundant isotope, the primary end product of the decay is an isotope of lead with mass number 206 (see Fig. 1.2). This means that thorium minerals and uranium minerals contain lead with different isotopic composition. In fact, one of the best conformations of the

<sup>1</sup> The Student making notes may have difficulties in distinguishing between italics and normal letters and is therefore recommended to adhere to the use of multiple indexing.



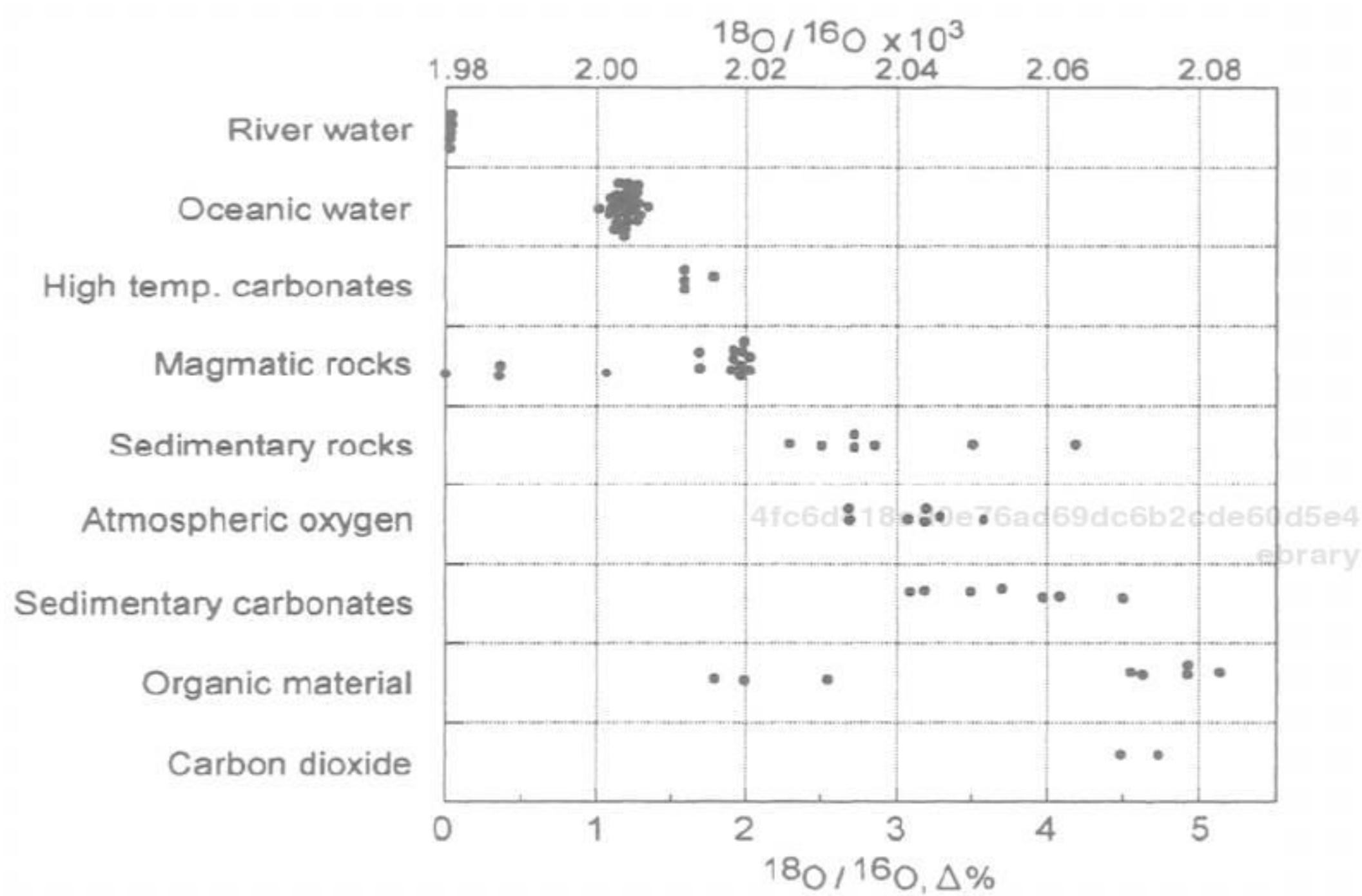


FIG. 2.3. Observed  $^{18}\text{O}/^{16}\text{O}$  isotope ratios. (According to Vinogradov.)

existence of the radioactive decay series came from the proof that lead had different net atomic weights in different minerals.

Because all long natural radioactive decay series end up in lead, Pb made from different ores contain slightly different isotopic abundances of lead isotopes. An unusual use of this fact was made by Andrasko et. al. to identify smears and fragments from lead bullets used in a homicide case, so that the suspect could be bound to the case, as the isotopic composition of lead bullets can be identified not only by manufacturer but also by manufacturing date.

The isotopic ratios for the lightest elements depend on in which natural material they are found. The ratio for  $^7\text{Li}/^6\text{Li}$  varies from 12.20 to 12.48, while that of  $^{12}\text{C}/^{13}\text{C}$  varies from 89.3 to 93.5. The isotopic ratio  $^{18}\text{O}/^{16}\text{O}$  varies by almost 5% as shown in Fig. 2.3. However, since natural oxygen contains only 0.2%  $^{18}\text{O}$ , even a 5% variation in the isotopic ratio has very little influence on the atomic weight of oxygen. The variation of natural isotopic ratios for boron and chlorine causes the uncertainties in their abundances shown in Table 2.1.

## 2.5. Physicochemical differences for isotopes<sup>1</sup>

Although the isotopic variations in the heaviest elements can be attributed to the consequences of radioactive decay, the variations observed in lighter elements are attributable to chemical behavior. The rates and equilibria of chemical reactions depend on the masses of the atoms involved in the reactions as is explained in §2.6 and §2.7. As a consequence, isotopes may be expected to have somewhat different quantitative physicochemical values (the *isotope effect*). As examples of the isotope effect, we may note that the freezing point of H<sub>2</sub>O is 0°C (273.15 K), while that for heavy water D<sub>2</sub>O is 3.82 degrees higher (276.97 K). The boiling point of D<sub>2</sub>O is 1.43 K higher than that of H<sub>2</sub>O. Similarly, while H<sub>2</sub> boils at 20.26 K, D<sub>2</sub> boils at 23.59 K. As a result of these differences in the boiling points, the vapor pressures at a particular temperature for H<sub>2</sub> and D<sub>2</sub> are not the same and distillation can be used to fractionate hydrogen isotopes. Other physical properties such as density, heat of vaporization, viscosity, surface tension, etc., differ similarly.

The optical emission spectra for isotopes are slightly different since electronic energy levels are dependent on the atomic masses. The light emitted when an electron falls from an outer orbit of main quantum number  $n_2$  to an inner orbit of quantum number  $n_1$  ( $< n_2$ ) is given by

$$\tilde{\nu} = R_{\infty} Z^2 m_{\text{red}} (1/n_1^2 - 1/n_2^2)/m_e \quad (2.13)$$

where  $\tilde{\nu}$  is the wave number ( $1/\lambda \text{ m}^{-1}$ ),  $R_{\infty}$  is the Rydberg constant ( $1.097 \times 10^7 \text{ m}^{-1}$ ),  $m_e$  is the electron (rest) mass, and  $m_{\text{red}}$  the reduced mass, according to

$$m_{\text{red}}^{-1} = m_e^{-1} + m_{\text{nuc}}^{-1} \quad (2.14)$$

where  $m_{\text{nuc}}$  is the nuclear mass. For the light hydrogen isotope, the H <sub>$\alpha$</sub>  line (i.e. the transition energy between  $n_1 = 1$  and  $n_2 = 2$ ) occurs at 656.285 nm, while the corresponding line for the deuterium isotope of hydrogen occurs at 656.106 nm. This difference could be predicted from (2.13) and its observation experimentally in 1932 provided the first evidence for the existence of a heavy hydrogen isotope. This spectral difference has practical importance as it can be used for a spectroscopic analysis of the amount of heavy water in light water. Similar *isotopic line shifts* occur in the spectra of all elements, but are rarely as large as the shift of almost 0.2 nm observed for hydrogen. For the isotopes <sup>235</sup>U and <sup>238</sup>U, the isotopic shift is 0.025 nm.

## 2.6. Isotope effects in chemical equilibrium

In a mixture of molecules AX and BX, with a common element X, an exchange of the atoms of the common element between the two molecules may occur. When the two

<sup>1</sup> §§2.5–2.7 outline the scientific basis for isotope effects and isotope separation. This is not essential for the Radiochemistry part of this book.



compounds have different isotopes X and X\*, we may have an *isotope exchange* according to



The equilibrium constant  $k$  in the reaction is given by

$$\Delta G^\circ = -RT \ln k = -RT \ln \{([AX^*][BX])/([AX][BX^*])\} \quad (2.16)$$

where  $\Delta G^\circ$  is the (Gibb's) free energy and  $R$  is the universal gas constant. For values of fundamental constants see Appendix III.

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### 2.6.1. The partition function

It has been shown that  $k$  deviates slightly from 1, giving rise to the isotopic effects observed in nature for the light elements. This deviation can be calculated by methods of statistical thermodynamics. Only the main features of this theory are given here. The equilibrium constant  $k$  can be written

$$k = (F_{AX^*} F_{BX}) / (F_{AX} F_{BX^*}) \quad (2.17)$$

where  $F$  is the *grand partition function*, which for each molecule includes all possible energy states of the molecule and the fraction of molecules in each energy state under given external condition. The grand partition function is defined by

$$F = f_{tr} f_{rot} f_{vib} f_{el} f_{nsp} \quad (2.18)$$

where each term  $f_j$  refers to a particular energy form: translation, rotation, vibration, electron movement, and nuclear spin. The two latter will have no influences on the chemical isotope effect, and can therefore be omitted. It can be shown that each separate partition function  $f_j$  can be described by the expression

$$f_j = \sum g_{j,i} e^{-E_{j,i}/kT} \quad (2.19)$$

where  $E_{j,i}$  is the particular energy state  $i$  for the molecule's energy mode  $j$ ; e.g. for  $j$  = vibration, there may be 20 different vibrational states (i.e. the maximum  $i$ -value is 20) populated.  $k$  is the Boltzmann constant; (2.19) is closely related to the Boltzmann distribution law (see next section).

The term  $g_{j,i}$  is called the *degeneracy* and corrects for the fact that the same energy state in the molecule may be reached in several different ways. The summation has to be made over all energy states  $i$ .

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2.6.2. Kinetic energy and temperature

The kinetic energy of one mole of an ideal gas at temperature  $T$  (K) is given by its translational energy, which according to the kinetic theory of gases is

$$E_{tr} = 3RT/2 \text{ (J mole}^{-1}\text{)} \tag{2.20}$$

Dividing by the Avogadro number  $N_A$  yields the average kinetic energy per molecule (or particle)

$$\bar{E}_{tr} = 3kT/2 \text{ (J particle}^{-1}\text{)} \tag{2.21}$$

where  $k = R/N_A$ . From mechanics we know that the kinetic energy of a single particle of mass  $m$  and velocity  $v$  is

$$E_{kin} = \frac{1}{2}mv^2 \tag{2.22}$$

Summing over a large number of particles, we can define an average kinetic energy

$$\bar{E}_{kin} = \frac{1}{2}m\bar{v}^2 \tag{2.23}$$

where  $\bar{v}^2$  is the mean square velocity. Because (2.21) is the average kinetic energy at temperature  $T$ , it must equal (2.23), i.e.  $\bar{E}_{tr} = \bar{E}_{kin}$ , thus

$$3kT/2 = \frac{1}{2}m\bar{v}^2 \tag{2.24}$$

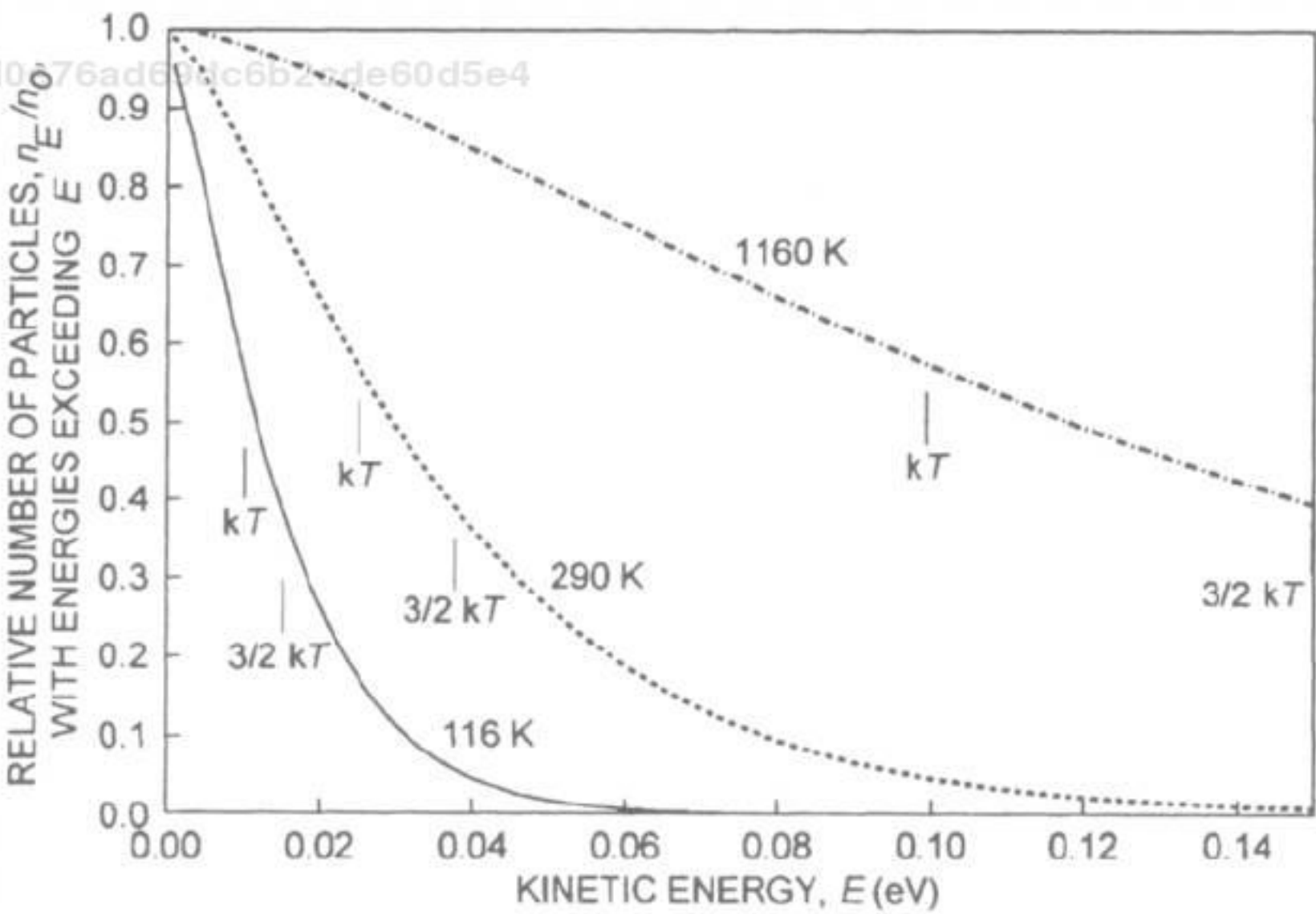


FIG. 2.4. Relative number of particles as function of energy.



Thus for a given temperature there is a corresponding *average particle velocity*. However, the individual particles are found to move around with slightly different velocities. J. C. Maxwell has calculated the velocity distribution of the particles in a gas. For the simplest possible system it is a *Boltzmann distribution*. In a system of  $n_0$  particles the number of particles  $n_E$  that have kinetic energy  $> E$  is given by

$$n_E = n_0 (2/\sqrt{\pi})(kT)^{-3/2} \int_E^{\infty} \sqrt{E} e^{-E/kT} dE \quad (2.25)$$

In Fig. 2.4  $n_E/n_0$  is plotted as a function of  $E$  for three different  $T$ 's. For the line at 290 K we have marked the energies  $kT$  and  $3kT/2$ . While  $3kT/2$  (or rather  $3RT/2$ ) corresponds to the thermodynamic average translational energy,  $kT$  corresponds to the *most probable kinetic energy*: the area under the curve is divided in two equal halves by the  $kT$  line.

In chemistry, the thermodynamic energy (2.21) must be used, while in nuclear reactions the most probable energy  $E'$  must be used, where

$$E' = \frac{1}{2}m(v')^2 = kT \quad (2.26)$$

$v'$  is the *most probable velocity*.

Although the difference between  $\bar{E}$  and  $E'$  is not large (e.g. at 17°C  $\bar{E} = 0.037$  eV and  $E' = 0.025$  eV), it increases with temperature. *The most probable velocity is the deciding factor whether a nuclear reaction takes place or not.* Using (2.25) we can calculate the fraction of particles at temperature  $T$  having a higher energy than  $kT$ :  $E > 2kT$ , 26%,  $> 5kT$ , 1.86%, and  $> 10kT$ , 0.029%. This high-energy tail is of importance for chemical reaction yields because it supplies the molecules with energies in excess of the activation energy. It is also of importance for nuclear reactions and in particular for thermonuclear processes.

### 2.6.3. The partial partition functions

So far there has been no clue to why isotopic molecules such as  $H_2O$  and  $D_2O$ , or  $H^{35}Cl$  and  $H^{37}Cl$ , behave chemically in slightly different manner. This explanation comes from a study of the energy term  $E_j$ , which contains the atomic masses for all three molecular movements: translation, rotation, and vibration.

(a) *Translational energy.* The translational energy, as used in chemical thermodynamics involves molecular movements in all directions of space. The energy is given by the expression (2.21). A more rigorous treatment leads to the expression

$$f_{tr} = (2\pi M k T)^{3/2} V_M h^{-3} \quad (2.27)$$

for the translational partition function, where  $V_M$  is the molar volume and  $h$  the Planck constant. Notice that no quantum numbers appear in (2.27); the reason is that they are not known because of the very small  $\Delta E$ 's of such changes.

(b) *Rotational energy.* Taking the simplest case, a linear diatomic molecule with atomic masses  $m_1$  and  $m_2$  at a distance  $r$  apart, the rotational energy is given by

$$E_{\text{rot}} = I_{\text{rot}} \omega^2 \quad (2.28)$$

where  $I_{\text{rot}}$  is the rotational moment of inertia and  $\omega$  the angular velocity of rotation (radians  $\text{s}^{-1}$ ).  $I_{\text{rot}}$  is calculated from

$$I_{\text{rot}} = m_{\text{red}} r^2 \quad (2.29)$$

where the reduced mass  $m_{\text{red}} = (m_1^{-1} + m_2^{-1})^{-1}$ . Equation (2.28), derived from classical mechanics, has to be modified to take into account that only certain energy states are permitted

$$E_{\text{rot}} = h^2 n_r (n_r + 1) / (8\pi^2 I_{\text{rot}}) \quad (2.30)$$

where  $n_r$  is the rotational quantum number. For transformation of energy in eV to the wave number  $\tilde{\nu}$  or wavelength  $\lambda$  of the corresponding photon energy, the relation

$$\Delta E \text{ (eV)} = 1.23980 \times 10^{-4} \tilde{\nu} \text{ (cm}^{-1}\text{)} \quad (2.31)$$

is used, where  $\tilde{\nu} = 1/\lambda$ . (For blue light of about 480 nm the following relations are obtained:  $480 \text{ nm} = 4.8 \times 10^{-7} \text{ m} = 0.48 \mu\text{m} = 20\,833 \text{ cm}^{-1} = 2.58 \text{ eV}$ .) The rotational energies are normally in the range 0.001 – 0.1 eV, i.e. the wavelength region  $10^{-3} - 10^{-5} \text{ m}$ . The partition function for the rotational energy is obtained by introducing (2.30) into (2.19). More complicated expressions are obtained for polyatomic and nonlinear molecules.

(c) *Vibrational energy.* For a diatomic molecule the vibrational energy is given by

$$E_{\text{vib}} = hc\omega_v (n_v + 1/2) \quad (2.32)$$

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where

$$\omega_v = 1/2 (k' / m_{\text{red}})^{1/2} / (\pi c) \quad (2.33)$$

is the zero point vibrational frequency (the molecule is still vibrating at absolute zero, when no other movements occur) and  $n_v$  the vibrational quantum number.  $k'$  is the *force constant* for the particular molecule.

#### 2.6.4. The isotopic ratio

It is seen from this digression that the mass of the molecular atoms enters into the partition functions for all three modes of molecular movement. The largest energy changes are associated with the vibrational mode, and the isotopic differences are also most pronounced here. Neglecting quantization of translational and rotational movements, one can show that

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$$F = f_{tr} f_{rot} f_{vib} = (2\pi M k T / h^3)^{3/2} V_M 8\pi^2 I_r k T e^{-u/2} / \{h^2 k_s (1 - e^{-u})\} \tag{2.34}$$

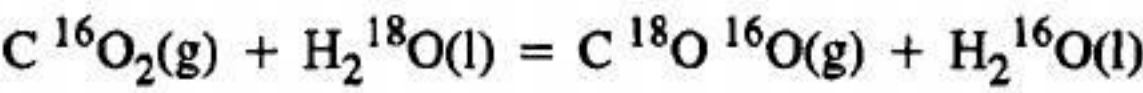
where  $k_s$  is a symmetry constant for rotation and  $u = hc\omega/kT$ . This expression holds for all molecules in (2.15). Thus for the ratio one gets

$$F_{AX}/F_{AX^*} = (M^*/M)^{3/2} k_s I_r^* (1 - e^{-u}) e^{-u^*/2} / \{k_s^* I_r (1 - e^{-u^*}) e^{-u/2}\} \tag{2.35}$$

where the asterisk refers to molecule  $AX^*$ . This relation shows the mass dependency of the equilibrium constant (2.16) (a similar relation holds for the  $BX-BX^*$  combination). (2.35) contains factors all of which can be determined spectroscopically. Consequently, the equilibrium constants for isotope exchange reactions can be, and have been, calculated for many systems.

2.6.5. Paleotemperatures and other applications

Eqn (2.35) contains the temperature in the exponent. Isotope exchange equilibria are thus temperature dependent. A practical use of this fact is the determination of paleotemperatures. In the isotope exchange reaction



the oxygen isotopes in  $CO_2$  exchange with the oxygen isotopes in  $H_2O$ . The value of the equilibrium constant (mole fractions)  $k = 1.046$  ( $0^\circ C$ ) indicates that  $^{18}O$  will be slightly enriched in the  $CO_2$  by the reaction. Thus if carbon dioxide is bubbled through water, the emergent gas will be more enriched in the  $^{18}O$  than the residual water. In this reaction, the *isotope effect* is said to be 4.6%. The following reaction occurs with carbonate ions in water:

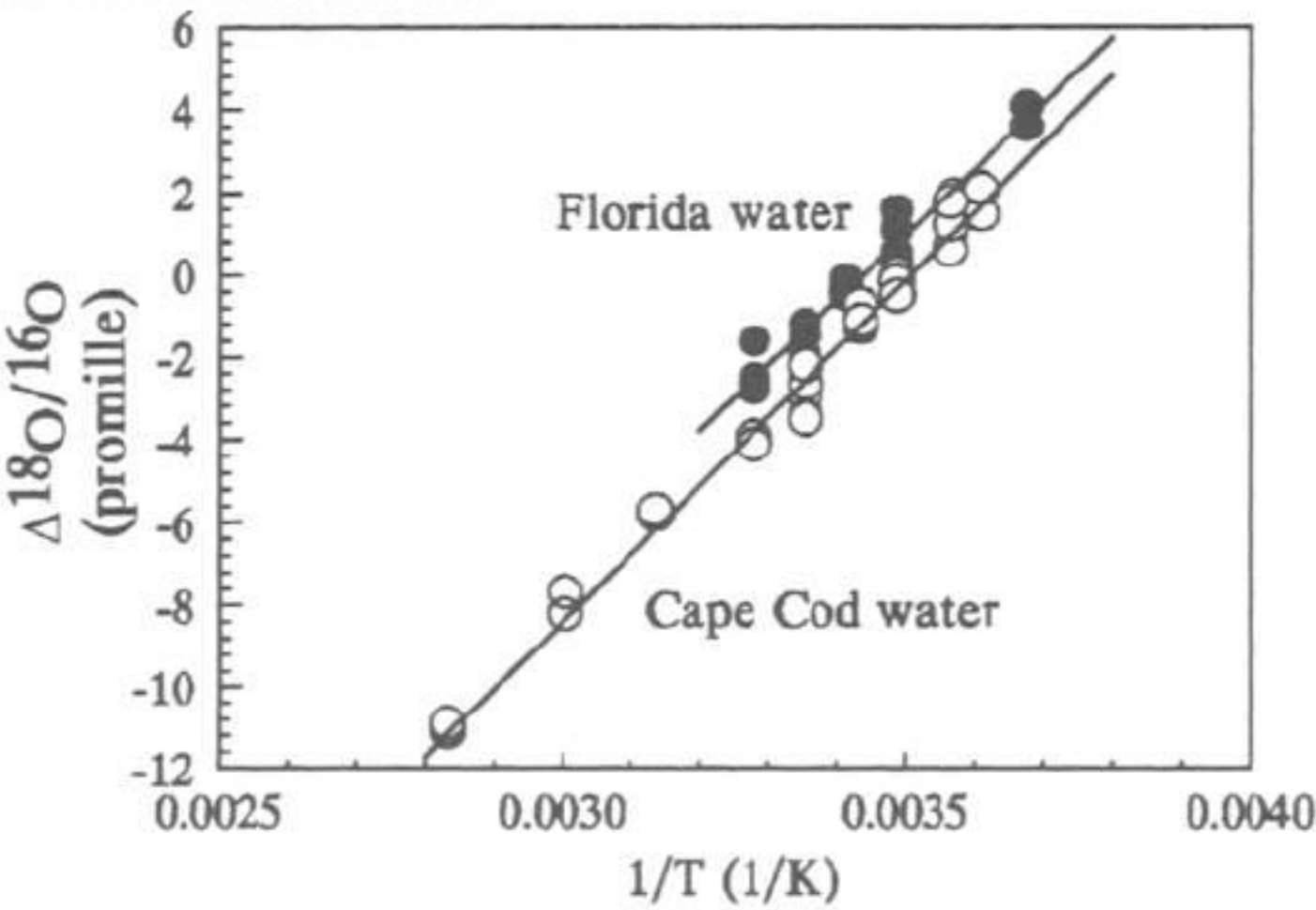


FIG. 2.5. Variation of isotopic composition of  $CaCO_3(s)$  with deposition temperature from water (o-Cape Cod; ●-Florida waters). (From McCrea.)

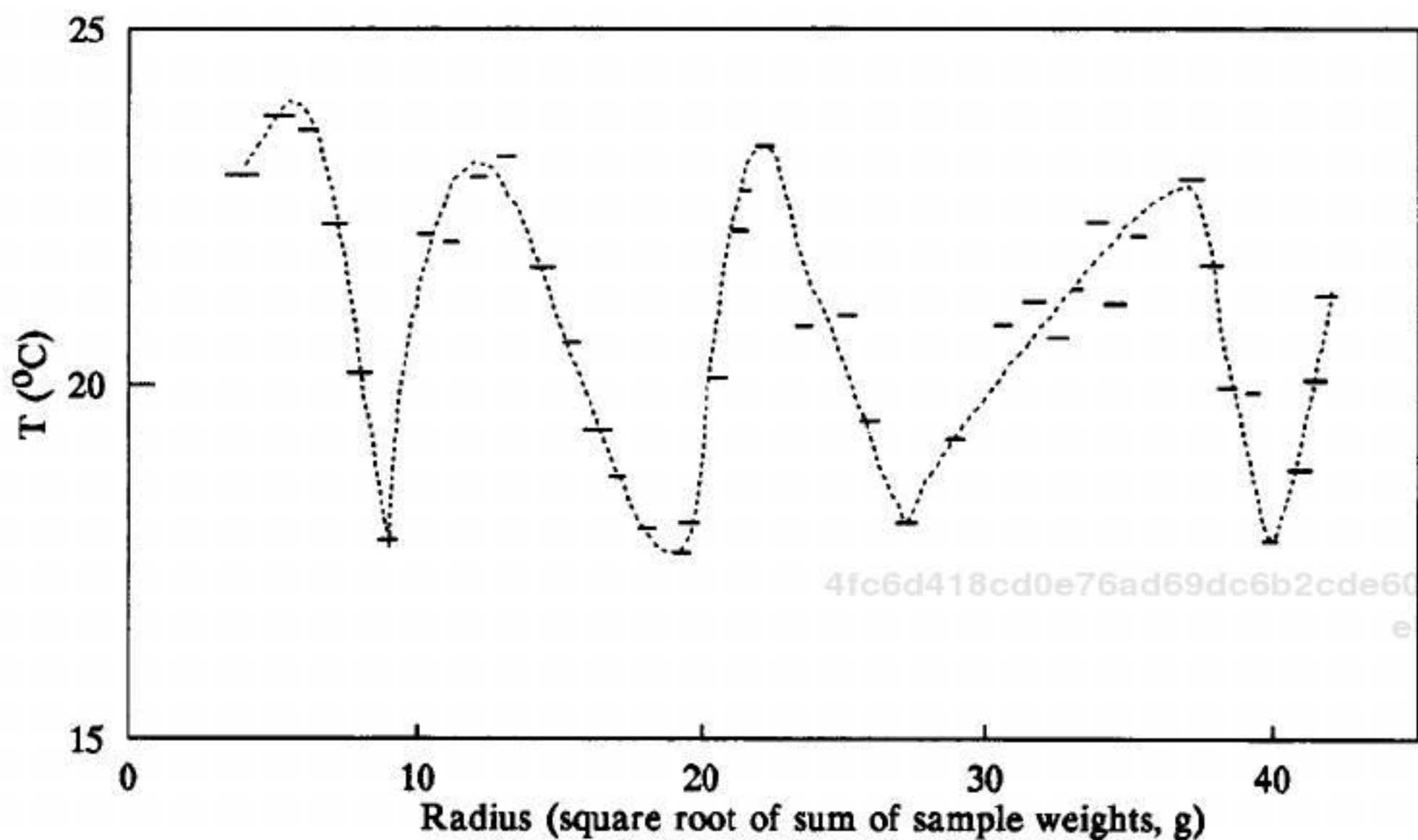
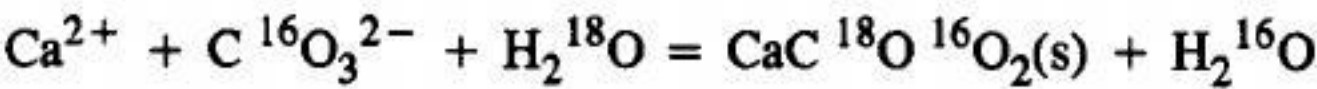


FIG. 2.6. Temperature calculated from the  $^{18}\text{O}/^{16}\text{O}$  ratio in carbonate of a shell from the Jura period as function of the distance from center of the shell. (According to Epstein.)



In this reaction the isotope effect results in enrichment of precipitated carbonate in  $^{18}\text{O}$  compared to dissolved carbonate (Fig. 2.5). The equilibrium constant for this reaction and, hence, the  $^{18}\text{O}/^{16}\text{O}$  ratio, can be calculated to have a temperature dependence according to

$$T(^{\circ}\text{C}) = 18 + 5.44 \times 10^6 (\zeta_T - \zeta_{18})$$

where  $\zeta_{18}$  and  $\zeta_T$  are the isotopic ratios (cf. (2.3)) at  $18^{\circ}\text{C}$  and at temperature  $T$ .

The isotopic ratios for sedimentary carbonate show a variation of  $2.04$  to  $2.07 \times 10^{-3}$  (Fig. 2.3). If it is assumed that these differences are due to the precipitation of the carbonate at different temperatures and that the isotopic composition of carbon in seawater was the same as today, one can use the isotopic ratios to obtain information on geologic temperature. In Fig. 2.6 the data for a shell from the Jura geologic period is shown. The oxygen ratio in the carbonate of the shell has been determined by starting from the center of the shell and measuring the isotopic ratio in each layer of annual growth. The result shows that the temperature at which the carbonate was formed varied during the life of the creature; further, the creature that inhabited the shell must have died during the spring of its fourth year since there was no further growth of the shell after the forth period of increasing temperature.

Chemical isotope effects are particularly large for lighter elements in biological systems. The *chlorella algae* prefers deuterium over hydrogen, and tritium over deuterium. The enrichment factor depends on the conditions of growth; for deuterium to hydrogen an enrichment value of  $1.6 - 3$  has been found, while for tritium to hydrogen the enrichment



factor is about 2.5. Bacteria behave similarly, with *coli bacteria* showing an enrichment factor for deuterium of 3.9.

Inasmuch as some of the hydrogen atoms are not exchanged readily due to the inertness of their chemical bonds, the isotopic fractionation which involves the easily exchangeable hydrogen atoms in these biological processes must have even larger enrichment factors for deuterium and tritium than their measured values would indicate.

The peculiarity of biological material to prefer certain isotopes has led to studies of how biological material behaves in an isotopic environment which differs substantially from that found in nature. Normally it is found that the organisms wither away and lose their ability to reproduce. Carp cannot survive a higher D<sub>2</sub>O concentration than 30%, but, on the other hand, some organisms show a strong growth, and some microorganisms have been found to be able to live in pure D<sub>2</sub>O or H<sub>2</sub><sup>18</sup>O. It has been possible to raise mice with only <sup>13</sup>C in their organism (fed on <sup>13</sup>C algae). Exchanging natural <sup>14</sup>NH<sub>3</sub> for <sup>15</sup>NH<sub>3</sub> seems to have little effect on biological systems.

In all of these investigations it should be noted that even when we characterize an isotopic effect as large, it is still quite small by normal reaction criteria except for hydrogen isotopes. For all but the very lightest elements we can assume in most chemical experiments that there is no isotope effect. This assumption forms a basis of the use of radioactive tracers to study chemical systems.

## 2.7. Isotope effects in chemical kinetics

The reason why higher organisms cannot survive when all light hydrogen atoms are replaced by deuterium is to be found not so much in a shift of chemical equilibria as in a shift in reaction rate leading to a fatal lowering of the metabolic rate when light isotopes are replaced by heavier.

In contrast to chemical equilibria, chemical reaction rates depend on the concentration of the reactants and transition states but not on the product. The concentration of the transition states depends on the activation energy for its formation and the frequency for its decomposition into the products. These factors can be derived from the partition function which, as mentioned above, differ slightly for molecules of different isotopic composition. Let us consider the reaction



The rate constant is given by the expression

$$d[A]/dt = k[A][BC] \quad (2.37)$$

The reaction is assumed to take place over an intermediate compound ABC, usually denoted ABC<sup>#</sup> where the # indicates a short-lived transition state. According to the transition state theory, derived by H. Eyring, J. Biegeleisen, and others, it is assumed that the intermediate complex undergoes internal vibrations, with such an energy  $E_v$  that the bond is broken along the vertical line in the complex AB|C, leading to the fragments AB and C. The rate of reaction is the rate at which the complex ABC<sup>#</sup> decomposes into the products. It can

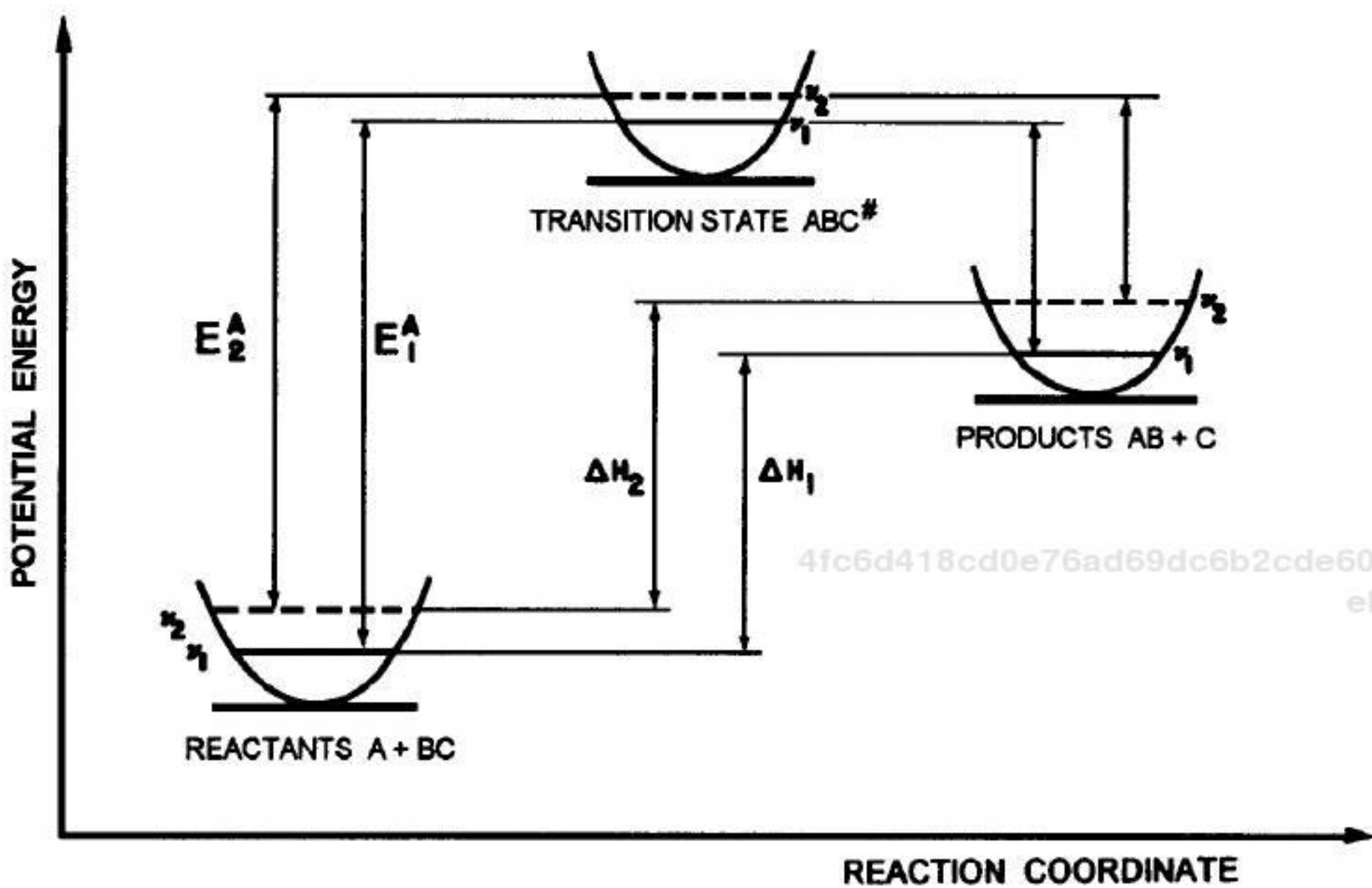


FIG. 2.7. Schematic description of energies in a bimolecular reaction.

therefore also be written

$$d[A]/dt = \nu[ABC^{\#}] \tag{2.38}$$

where  $\nu$  is the frequency at which the complex decomposes.

The reaction can be schematically depicted as in Figure 2.7, where indices 1 and 2 refer to two isotopic reactant molecules (e.g.  $H_2O$  and  $HDO$ ), which must have different zero point energies with frequencies  $\nu_1$  and  $\nu_2$ , respectively. For simplicity only the vibrational ground state is indicated; thus the energy change when going from reactants to products corresponds to the heat of reaction at absolute zero,  $\Delta H_1$  (0 K) and  $\Delta H_2$  (0 K) respectively. Because of the lower vibrational energy of the molecule indexed 1, this must contain the heavier isotope. In general, the difference in activation energy ( $E^{\ddagger}$ ) is greater than the difference in heat of reaction  $\Delta H$  for isotope molecules; thus, generally, isotope effects are larger in the kinetic than in the equilibrium effects.

When the molecule  $ABC^{\#}$  decomposes into  $AB$  and  $C$ , the vibrational energy, given by the Planck relation

$$E_{\nu} = h\nu \tag{2.39}$$

is changed into kinetic energy of the fragments, whose energy is (see §2.6.2)

$$E_{kin} = kT \tag{2.40}$$



Because of the law of conservation of energy

$$E_\nu = E_{\text{kin}}$$

and

$$h\nu = kT \quad (2.41)$$

This development assumes that the vibrational energy is completely converted to fragment translational energy. This assumption is not always valid for polyatomic fragments, in which internal excitation may occur. Introducing (2.41) into (2.38) and equating (2.37) and (2.38) yields

$$k[A][BC] = kT h^{-1} [ABC^\#] \quad (2.42)$$

It is assumed that  $ABC^\#$  is in dynamic equilibrium with the reactants A and BC. Thus

$$[ABC^\#]/([A][BC]) = k^\# \quad (2.43)$$

According to (2.17)

$$k^\# = F_{ABC^\#}/(F_A F_{BC}) \quad (2.44)$$

which with (2.42) yields

$$k = kT F_{ABC^\#}/(h F_A F_{BC}) \quad (2.45)$$

This expression must be multiplied by a factor  $\kappa$ , which is the probability that the complex will dissociate into products instead of back into the reactants as assumed in (2.43). The factor  $\kappa$  is called the *transmission coefficient*. The final rate expression thus becomes:

$$k = \kappa kT F_{ABC^\#}/(h F_A F_{BC}) \quad (2.46)$$

As is shown in §2.6, the grand partition functions  $F_i$  can be calculated from theory and spectroscopic data; because these functions are mass dependent  $k$  is mass dependent. In calculating the  $F_i$ 's, all modes of energy must be included as well as the population of the different energy states.

For isotopes of the lighter elements, the activation energy term makes the main contribution to the reaction rate isotope effect, while for the heavier elements the vibrational frequency causing the decomposition into the products plays the larger role. Because the energy states usually are more separated for the isotopic molecules of the products and reactants than for the transition state, isotope effects are usually larger in reaction kinetics than in equilibria.

Studies of kinetic isotope effects are of considerable theoretical interest, particularly in organic chemistry. The practical applications are still meager, but this will not necessarily be so in the future. An example is the decrease in metabolic rate for  $^{13}\text{C}$  compounds, which has led to the suggestion of its use for treatment of certain diseases, as e.g. porphyria.

2.8. Isotope separation processes

Many fields of fundamental science have found great advantage in using pure or enriched isotopes. The industrial use of nuclear power also requires the enrichment of particular isotopes, primarily of the uranium fuel. The methods which have been developed to achieve isotopic fractionation may be divided into two groups.

(a) *Equilibrium processes* (§2.6). These processes consume little energy, but the size of the isotope effect in normal chemical equilibrium limits their use to the isotope fractionation of very light elements, usually atomic number less than about 10.

(b) *Rate processes* (§2.7). This includes processes which depend on such phenomena as ionic mobility, diffusion, electrolysis, electromagnetic separations, centrifugation, and kinetic processes of a chemical nature. While the isotopic effects in these processes are normally larger than for equilibrium processes, they require a large amount of energy and therefore have economic restrictions.

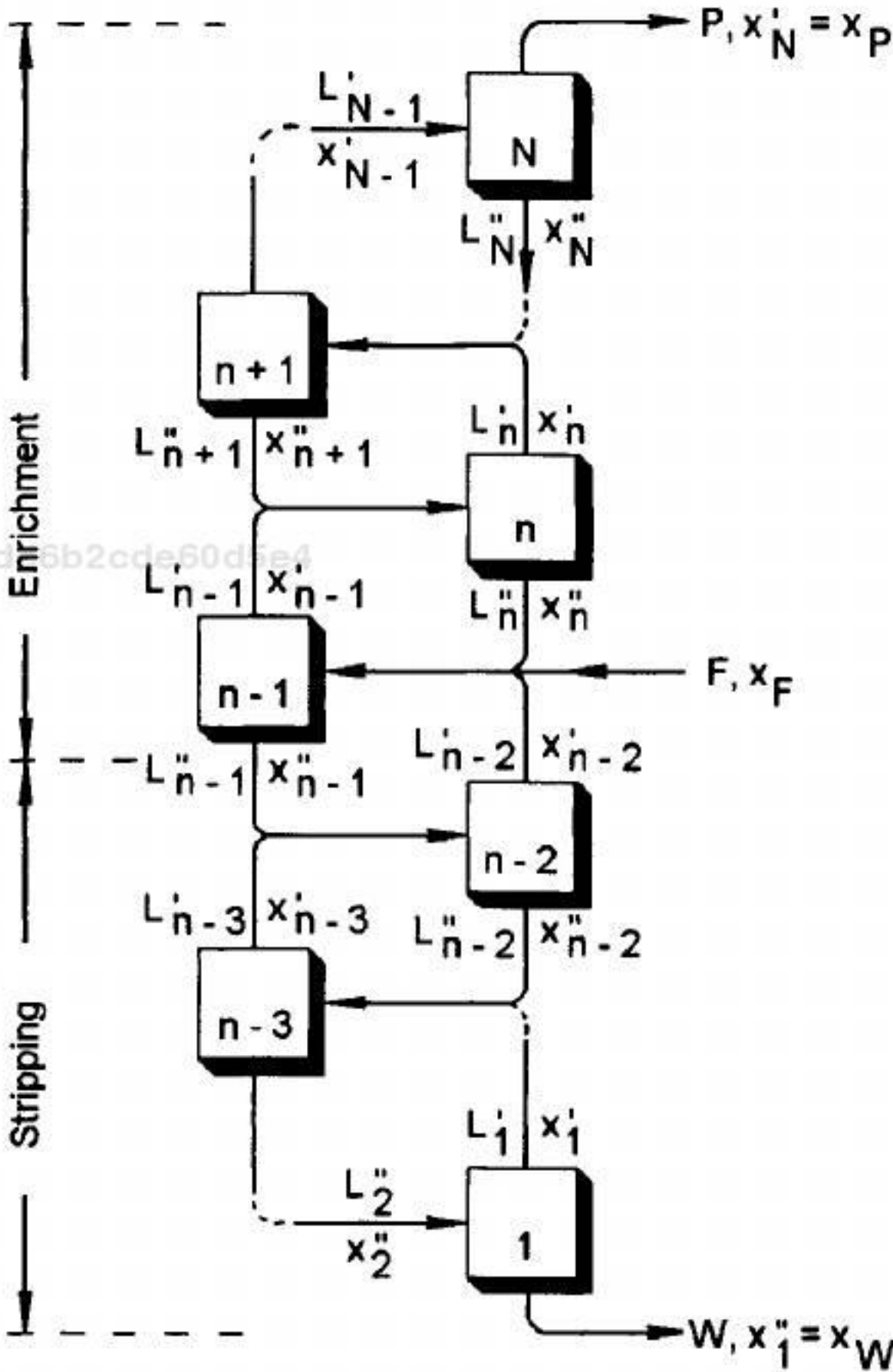


FIG. 2.8. Flow arrangement for an ideal cascade with reflux for isotope separation.



### 2.8.1. Multistage processes

Figure 2.8 shows a flow scheme for an isotopic fractionation process (or isotope enrichment process) based on an  $\alpha$ -value near 1. Each stage consists of a number of cells coupled in parallel; in the Figure only one cell is shown for each separation stage, but in order to obtain a high product flow, the number of cells are usually high at the feed point and then decrease towards the product and waste stream ends. Each cell contains a physical arrangement, which leads to an isotope fractionation. Thus the atomic fraction for a particular isotope is different in the two outgoing streams from a cell; in the *product stream* the isotope is enriched (atomic fraction  $x'$ ), while in the *waste stream* it is depleted (atomic fraction  $x''$ ). The *separation factor*  $\alpha$  is defined as the quotient between the isotopic ratios of the product and waste streams for a single step, thus ((2.2) and (2.3)):

$$\alpha = \zeta'/\zeta'' = [x'/(1-x')]/[x''/(1-x'')] \quad (2.47)$$

In most cases  $\alpha$  has a value close to unity;  $\alpha - 1$  is commonly called *enrichment factor*.

Since separation factors in general are small, it is necessary to use a multistage process to obtain a product with a high enrichment. The number of stages determines the degree of the enrichment of the product, while the number and size of cells in each stage determine the amount of product. This amount ( $P$  moles of composition  $x_p$ ) is related to the amount of feed ( $F$  moles of composition  $x_F$ ) and the amount of waste ( $W$  moles of composition  $x_W$ ) by the equations

$$F = P + W \text{ and } Fx_F = Px_p + Wx_W \quad (2.48)$$

From these equations we obtain

$$F = P(x_p - x_W)/(x_F - x_W) \text{ and } W = P(x_p - x_F)/(x_F - x_W) \quad (2.49)$$

The number of stages required to separate feed into product and waste of specified composition is a minimum at *total reflux*, when  $P = 0$ . For this condition M. R. Fenske has derived a relation, which can be divided into one part for the enrichment:

$$N_p \ln \alpha = \ln[x_p(1-x_F)/\{x_F(1-x_p)\}] \quad (2.50)$$

and one for the stripping part of the cascade:

$$N_W \ln \alpha = \ln[x_F(1-x_W)/\{x_W(1-x_F)\}] \quad (2.51)$$

$N_p$  and  $N_W$  are the minimum number of enrichment and stripping stages, respectively. In isotope separations  $\alpha$  is often very close to one;  $\ln \alpha$  can then be replaced by  $(\alpha - 1)$ . In practice some product flow is desired, the fraction withdrawn at the enrichment stage being known as "*the cut*"  $P/F$ . The number of stages required to produce the composition  $x_p$  then increases. The most economic, and thus also the most common, type of cascade for processes with near unity  $\alpha$  is the so-called *ideal cascade*. In this there is no mixing of streams of unequal concentrations, thus  $x'_{n-1} = x''_{n+1}$  in Fig. 2.8. Although the number of

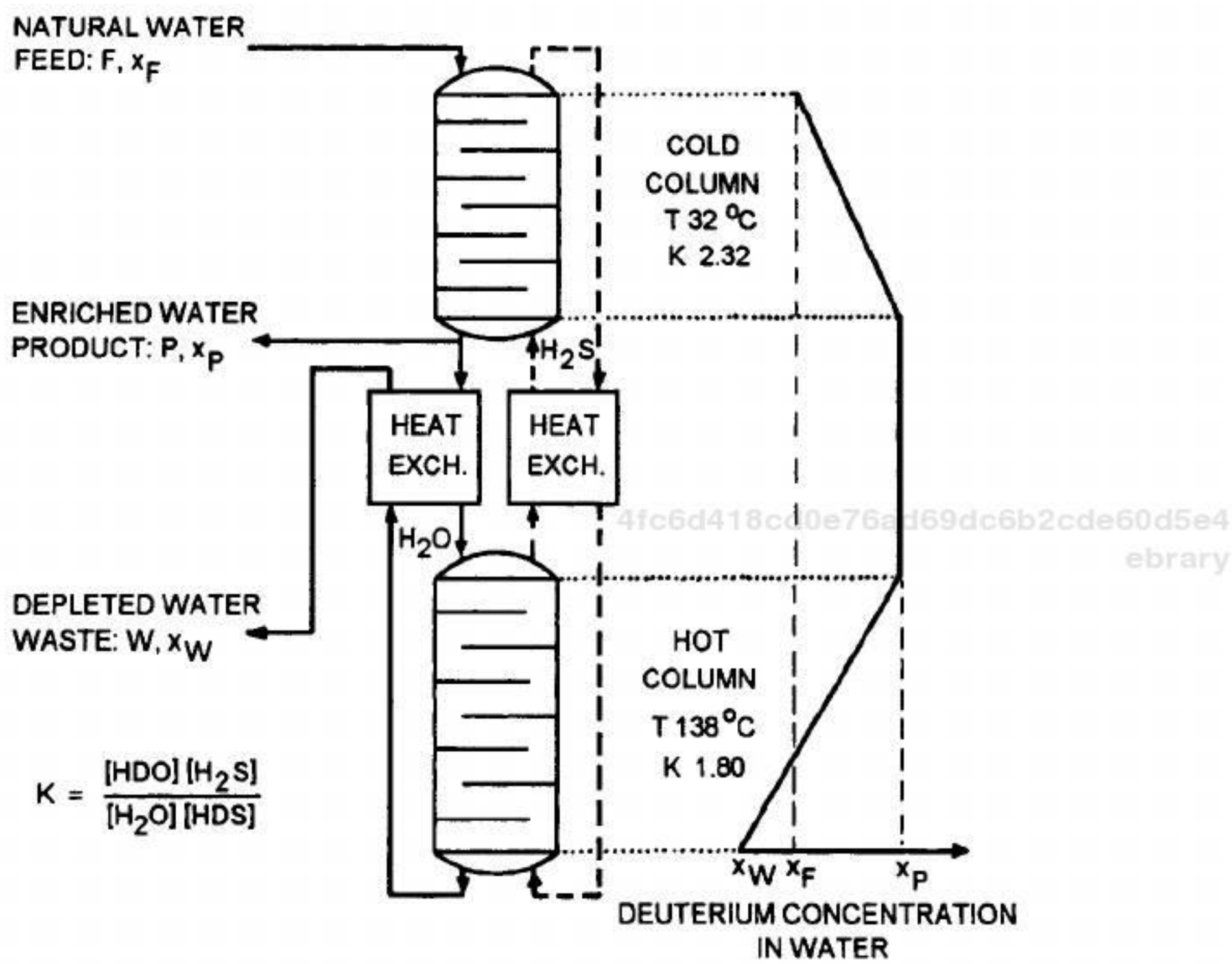


FIG. 2.9. The water-hydrogen sulphide dual-temperature distillation process for enrichment of heavy water.

stages required for a particular product is exactly twice the values given by (2.50) minus 1 and (2.51) minus 1,

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$$N_{\text{ideal}} = 2N - 1 \tag{2.52}$$

the interstage flow becomes a minimum, thus minimizing the inventory and work required. Also for the ideal cascade, the minimum number of stages are obtained at total reflux.

The interstage flow rate  $L_i$  that must be maintained in order that there be any enrichment in the ideal cascade at the point, where the concentration  $x_i$  occurs, is given by

$$L_i = 2P(x_P - x_i) / [(\alpha - 1)x_i(1 - x_i)] \tag{2.53}$$

To obtain the flow rate in the stripping part,  $P$  is replaced by  $W$ , and  $x_P - x_i$  by  $x_i - x_W$ .

For the enrichment of natural uranium (0.71 % in  $^{235}\text{U}$ ) to 80 % in  $^{235}\text{U}$ , the minimum number of enrichment stages is found to be almost 3000 at an enrichment factor of 0.43 %. The flow rate at the feed point becomes about 52 300 times the product flow  $P$ . Isotope separation plants therefore become very large even for small outputs. Isotopic separation on a technical scale using cells with  $\alpha$  near unity thus requires a large number of stages in order to obtain high enrichment and large amounts of materials in order to give a substantial

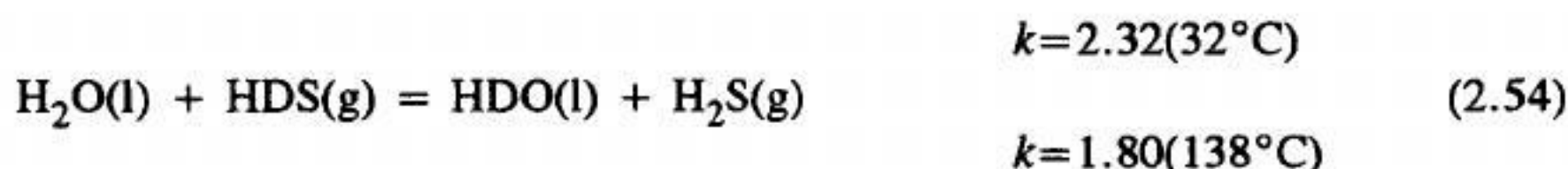
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amount of product. Small changes in  $\alpha$  can have a large economic impact in isotopic separation.

### 2.8.2. Chemical exchange

As an example of an industrial isotope exchange process, let us consider the production of heavy water by the chemical reaction



From the values of the equilibrium constants  $k$  we see that the enrichment of deuterium in water increases with decreasing temperature. Use is made of this property in the two-temperature  $\text{H}_2\text{O}$ - $\text{H}_2\text{S}$  exchange process known as the G-S process (Girdler-Sulphide), which is used in many countries to produce heavy water. A typical plant consists of several units as shown in Fig. 2.9. Through the upper distillation tower natural water flows downward and meets hydrogen sulfide gas streaming upwards. As a result of the exchange between  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$ , heavy hydrogen is enriched in the water. In the lower tower, which is operated at a higher temperature, the equilibrium conditions are such that deuterium is enriched in the hydrogen sulfide and moves with that gas to the upper tower. No catalyzer is required in order to achieve rapid equilibrium in this reaction. The product of the process is water which is enriched in deuterium from the top tower and water which is depleted in deuterium from the bottom tower. The hydrogen sulfide circulates through both towers with no net loss.

Plants capable to produce a total of more than 1200 tons annually are in operation in Canada, India and the US. The largest exchange towers are 60 m high and have a diameter of 6 m. In 5 units (only one unit is indicated in Fig. 2.8) the  $\text{D}_2\text{O}$  concentration is raised from 0.014% to about 15%. The final concentration to 99.97%  $\text{D}_2\text{O}$  is then usually made by distillation of water. The 1990 price for pure  $\text{D}_2\text{O}$  was ~ US \$400 per kg. It is important to recognize in tracer applications that commercially available  $\text{D}_2\text{O}$  always contains some tritium, which is co-enriched with deuterium;  $2 - 7 \text{ kBq kg}^{-1} \text{ D}_2\text{O}$ .

As another example, the lithium isotope  $^7\text{Li}$  (used as  $^7\text{LiOH}$  for pH control in some nuclear power plants because of its small neutron cross-section) is produced in 99.99% purity by countercurrent chemical exchange of lithium between an aqueous solution of  $\text{LiOH}$  and lithium amalgam. A separation factor of 1.06 to 1.07 is reported. Reflux of lithium is obtained at one end by electrolytic reduction of  $\text{LiOH}$  to  $\text{Li(Hg)}$  at a mercury cathode and at the other end by spontaneous oxidation of  $\text{Li(Hg)}$  on graphite by water producing hydrogen gas and  $\text{LiOH}$ .

### 2.8.3. Electrolysis

Electrolysis of water produces hydrogen gas at the cathode, which contains a lower proportion of deuterium than the original water. The isotope effect stems from the

differences in the rates of dissociation of a proton ( $\text{H}^+$ ) and a deuteron ( $\text{D}^+$ ) from water, and the rates of neutralization of these hydrated ions, and thus has a kinetic basis. Depending on the physical conditions  $\alpha$ -values between 3 and 10 are obtained. For  $\alpha = 6$  it is necessary to electrolyze 2700 l natural water (deuterium content 0.014%) to produce 1 l water containing 10% deuterium, mainly as HDO. In a multistage process the hydrogen gas is either burnt to recover energy, or used in a chemical process, e.g. in ammonia synthesis by the Haber-Bosch process. Although this technique was used industrially in Norway to produce ton amounts of pure  $\text{D}_2\text{O}$ , it is no longer considered economic except for final purification of  $\text{D}_2\text{O}$ .

#### 2.8.4. Gaseous diffusion

In a gaseous sample the lighter molecules have a higher average velocity than the heavier molecules. In 1913 F. W. Aston in England showed that the lighter of the two neon isotopes  $^{20}\text{Ne}$ , diffused through the walls of porous vessels somewhat faster than the heavier isotope,  $^{22}\text{Ne}$ . In the gas the average kinetic energy of isotopic molecules must be the same, i.e.  $1/2M_L v_L^2 = 1/2M_H v_H^2$ , where  $M_H$  and  $M_L$  are the masses of the molecules containing the heavy and light isotopes to be separated. The maximum theoretical separation factor in gaseous diffusion is given by

$$\alpha = v_L/v_H = (M_H/M_L)^{1/2} \quad (2.55)$$

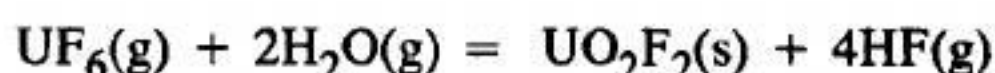
The theory is more complicated, depending among other things upon the mean free path of the gaseous atoms, the pore length and diameter of the separating membrane, and the pressure difference over the membrane. If experimental conditions are carefully controlled, this theoretical maximum can be closely approached.

$^{235}\text{U}$  is enriched through gaseous diffusion using the relatively volatile uranium compound  $\text{UF}_6$ . In addition to its volatility,  $\text{UF}_6$  has the advantage that fluorine consists of only one isotope,  $^{19}\text{F}$ . For the isotopic molecules  $^{235}\text{UF}_6$  and  $^{238}\text{UF}_6$ , a value of 1.0043 is theoretically possible for  $\alpha$  (cf. (2.55)). The following conditions must be considered in the technical application of the separation.

(a) The cells are divided into two parts by a membrane which must have very small pores (e.g. 10 – 100 nm in diameter) in order to obtain isotopic separation. In order that large gas volumes can flow through the membrane, millions of pores are required for each square centimeter. Moreover, the membranes must have good mechanical stability to withstand the pressure difference across them.

(b)  $\text{UF}_6$  sublimates at  $64^\circ\text{C}$ , which means that the separation process must be conducted at a temperature above this.

(c)  $\text{UF}_6$  is highly corrosive and attacks most materials. The membrane must be inert to attack by  $\text{UF}_6$ . Water decomposes  $\text{UF}_6$  according to the equation





This reaction is quite undesirable as HF is highly corrosive and solid  $\text{UO}_2\text{F}_2$  can plug the pores of the membranes. The tubing and cells of a plant are made principally of nickel and teflon to overcome the corrosion problems.

(d) In order to transport the large gas volumes and to keep the proper pressure drop across the membranes, a gaseous diffusion plant requires a large number of pumps. A large cooling capacity is needed to overcome the temperature rise caused by compression of the gas.

The work required to enrich uranium in  $^{235}\text{U}$  increases rapidly with the  $^{235}\text{U}$  content of the product. Because of varying domestic prices on natural uranium, as well as varying content of  $^{235}\text{U}$  in uranium obtained from used reactor fuel elements, so-called *toll enrichment* has been introduced. In this case, the purchaser himself provides the uranium feed into the separation plant and pays for the *separative work* required to make his desired product out of the uranium feed provided. Separative work is defined as

$$\text{Separative work} = W V(x_W) + P V(x_P) - F V(x_F) \quad (2.56)$$

where the *separation potential*  $V(x_i)$  is defined by

$$V(x_i) = (2x_i - 1) \ln\{x_i/(1 - x_i)\} \quad (2.57)$$

As seen from (2.56), separative work has the dimension of mass, and can be thought of as the mass flow rate multiplied by the time required to yield a given quantity of product. The cost of isotope separation is obtained by assigning a value to one separative work mass unit (kgSW or SWU). A 1 GWe nuclear light water reactor station requires about  $180 \times 10^3$  SWU in initial fueling and then  $70 - 90 \times 10^3$  SWU for an annual reload.

In §2.8.1 the number of stages and the interstage flow relative to the product flow was given for enrichment of  $^{235}\text{U}$  from its natural isotopic abundance of 0.71% to a value of 80%. With a waste flow in which the isotopic abundance of  $^{235}\text{U}$  is 0.2%, (2.48) shows that for each mole of product obtained 156 moles of feed are necessary. In more recent designs the concentration of  $^{235}\text{U}$  in the waste is increased to  $\sim 0.3\%$  to minimize cost. Isotope separation through gaseous diffusion is a very energy-consuming process due to the compression work and cooling required. An annual production of 10 MSWU requires an installed capacity of  $\sim 2900$  MW in present plants, or  $\sim 2500$  kWh SWU $^{-1}$ . Improved technology may reduce this somewhat. Gaseous diffusion plants are known to exist in Argentina, China, France, Russia and the United States. The combined capacity of these plants was about 40 MSWU/y at the end of 2000.

### 2.8.5. Electromagnetic isotope separation

During the Manhattan Project of the United States, electromagnetic separation was used to obtain pure  $^{235}\text{U}$ . This process is identical in theory to that described for the mass spectrometer. The giant electromagnetic separators were called *calutrons* (California University Cyclotrons) and were after World-War II used at Oak Ridge National Laboratory to produce gram amounts of stable isotopes of most elements up to a purity of 99.9% or more. Large capacity electromagnetic separators have also been developed and operated in

the former Soviet Union and a few other countries. Gram amounts of electromagnetically separated stable isotopes of most elements are commercially available on the world market in high isotopic purity. Electromagnetic separators are also used for on-line separation of nuclear reaction products (Ch. 15).

2.8.6. Gas centrifugation

Though gas diffusion is the dominating process for  $^{235}\text{U}$  enrichment, its small separation factor, large energy consumption, and secrecy about the technique have encouraged interest in finding other and more advantageous processes. Most effort has been put into developing centrifugal processes because of the large separation factors achievable.

In a gas centrifuge, light molecules are enriched at the center and heavy molecules at the periphery (Fig. 2.10). It can be shown that the ratio of radial concentration to the axial concentration for isotopic molecules under equilibrium conditions and at low pressure (avoiding remixing due to the Brownian movement) is given approximately by

$$x_p/x_F \approx e^{\delta n} \tag{2.58}$$

for  $n$  centrifuges (stages) connected in series. Here

$$\delta = (M_H - M_L) 10^{-3} v_r^2 r^2 / 2RT \tag{2.59}$$

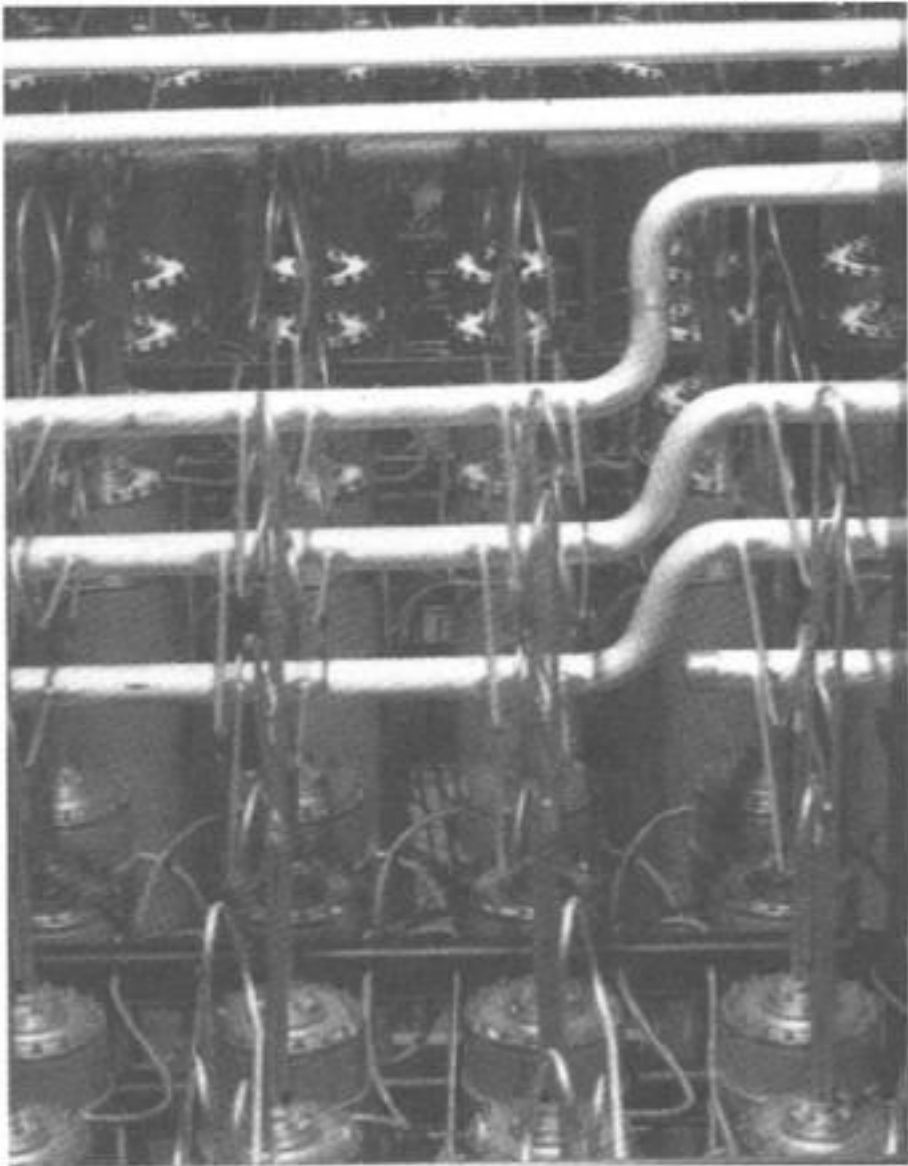
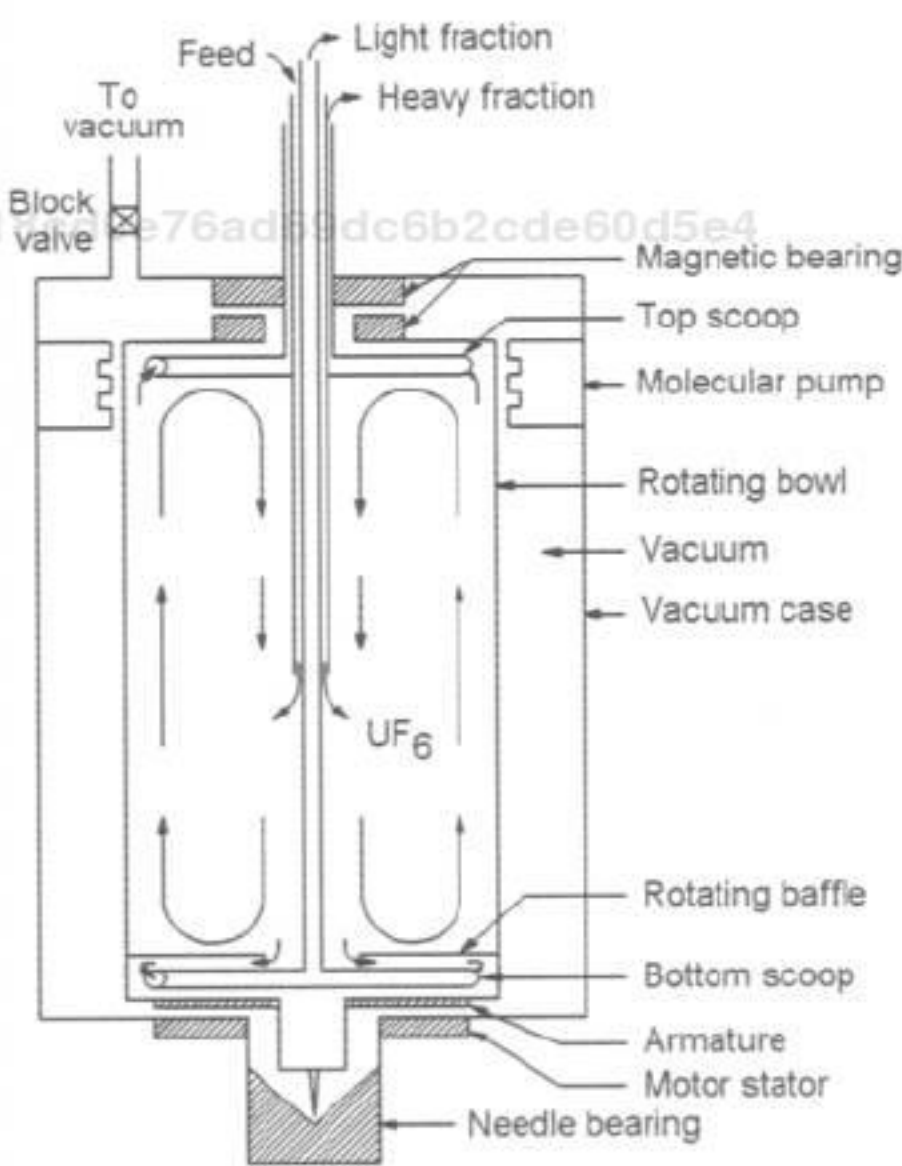


FIG. 2.10. Gas centrifuge for  $^{235}\text{UF}_6$  enrichment. Right shows centrifuge cascade in operation at Almelo.



where  $r$  is the centrifuge radius and  $v_r$  the speed of rotation. The separation factor  $\alpha \approx 1 + \delta$ .

Estimated values for present centrifuges operating on  $\text{UF}_6$  are: length 1 – 2 m; radius 0.2 – 0.4 m; rotational speeds of  $50 - 80 \times 10^3$  rpm. The enrichment obtainable in one stage is limited by the material strength of the centrifuge bowl; the present materials limit  $v_r r$  to  $< 800 \text{ m s}^{-1}$ . Typical separation factors are 1.4 – 3.9 per stage, thus about 10 stages are required to enrich  $^{235}\text{U}$  from 0.72% to 3% with a 0.2% tail. As compared, a diffusion plant would require ~ 1300 stages. The corresponding figures for production of 80%  $^{235}\text{U}$  are ~ 45 and ~ 3600, respectively. Though rather few stages are required to upgrade natural uranium to reactor quality, a very large number of centrifuges are needed to produce large quantities of enriched material.

Current centrifuge technology requires ~ 3% of the power consumed by a diffusion plant, or 50 – 100 kWh  $\text{SWU}^{-1}$ . This makes their environmental impact minimal, as compared to gas diffusion plants, which require substantial electric power installation and cooling towers with large water vapor effluent. Smaller plants of a few MSWU/y are economical, and their output can be readily multiplied by installation of parallel processing lines. The very large number of centrifuges required due to their small size (each having a capacity of  $\leq 15$  SWU/y) and limited life-time does not lead to excessive construction costs due to continuous mass production on-site. On the whole, centrifuge separation now seems to have a lower enrichment cost than large scale diffusion plants. Centrifuge performance has been increased by a factor of ~ 25 since 1980 and is predicted to improve further.

Many plants are now operating, the largest known being near Ekaterinburg (Russia, 9 MSWU/y; Russian centrifuge plants have total capacity of ~ 19 MSWU/y), Almelo (the Netherlands, 1.7 MSWU/y), Capenhurst (United Kingdom, 1.1 MSWU/y) and Gronau (Germany, 1.1 MSWU/y).

#### 2.8.7. Other methods of isotope separation

In theory all physicochemical procedures are capable of isotope separation. Some other methods which have been studied include distillation, solvent extraction, ion exchange, photoionization and photoexcitation.

Tons of  $\text{D}_2\text{O}$  are purified annually in India by cryogenic *distillation* of hydrogen. Tenths of kilograms of pure  $^{13}\text{C}$  and  $^{15}\text{N}$  have been produced at the Los Alamos Scientific Laboratory through distillation of NO and CO at liquid air temperature. At the same time a fractionation between  $^{16}\text{O}$  and  $^{18}\text{O}$  occurs.

A *continuous ion-exchange* isotope separation process for uranium enrichment has been developed in Japan. Few details of this process have been disclosed. However, it is known that "reflux" is obtained by oxidation and reduction of  $\text{U}^{4+}$  and  $\text{UO}_2^{2+}$ . A demonstration plant with a capacity of 2 kSWU/y is in operation at Hyuga.

A method of separation, involving passage of a mixture of  $\text{UF}_6$  and helium or hydrogen at very high velocities through a *nozzle*, as seen in Fig. 2.11, has been developed by E. W. Becker in Germany and in South Africa. The technique is sometimes referred to as "static" or "stationary-walled" gas centrifugation. The separation factor is typically 1.01 – 1.03 per stage, *i.e.* about three times better than in the gaseous diffusion process, and offers great possibilities for further improvements. Thus while the diffusion process requires about 1200



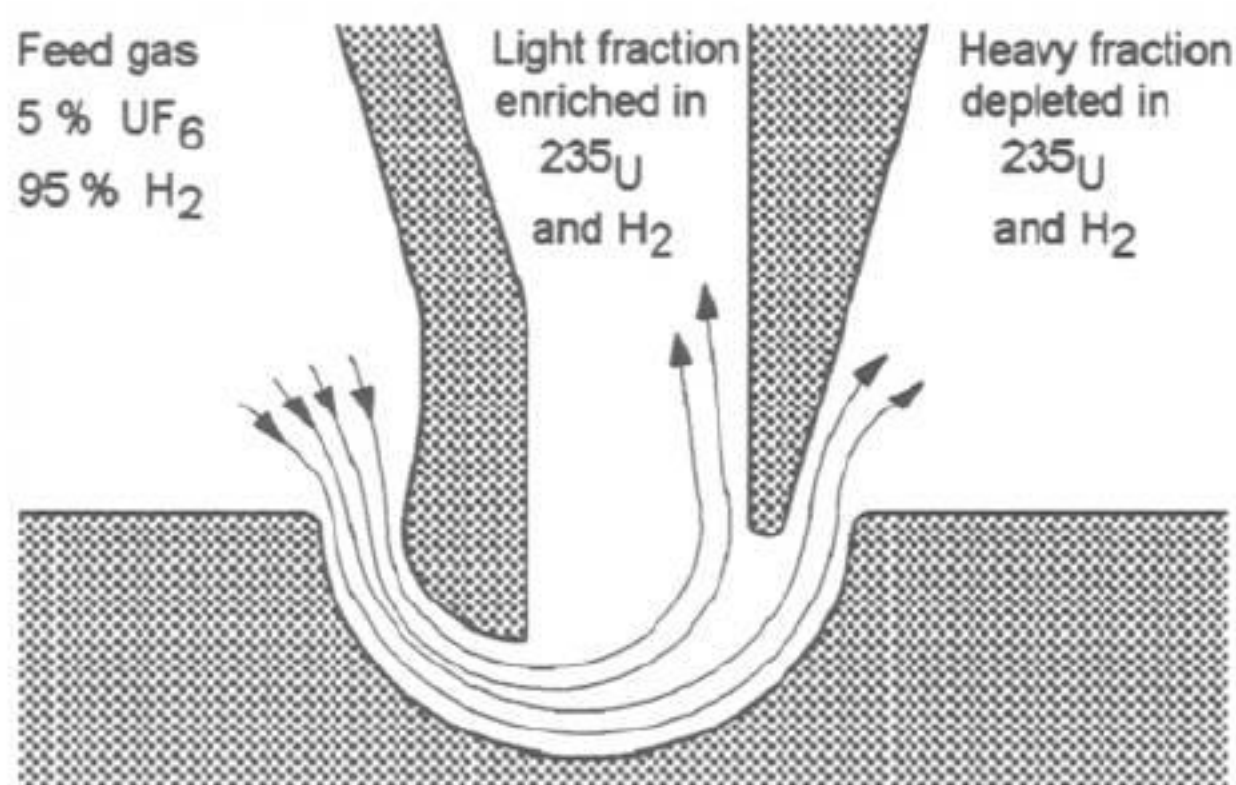


FIG. 2.11. Section through a separation nozzle arrangement showing stream lines.

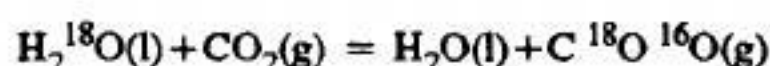
stages for a 3% <sup>235</sup>U enrichment (with 0.2% tails), the nozzle technique will require only about 500 stages. However, the power consumption is said to be larger, ~ 3000 kWh SWU<sup>-1</sup> at a capacity of 10 MSWU/y, as compared to ~ 2500 kWh SWU<sup>-1</sup> for a diffusion plant of the same size. The operating cost is said to be higher than for both the diffusion and the centrifuge methods. A plant based on the original German design is being built in Brazil (10 kSWU/y). A 0.3 MSWU/y separation plant at Valindaba, South Africa, used its own version of the nozzle technique (Helikon process), but is now shut down.

A number of *photoionization* and *photoexcitation* processes are being investigated for isotopic separation, especially of uranium. In one such process UF<sub>6</sub> is irradiated by a laser beam, producing selective vibrational excitation in the <sup>235</sup>UF<sub>6</sub> molecule (cf. §2.5). By irradiation with ultraviolet (possibly, but not necessarily, by laser) light the excited molecule is caused to dissociate, leaving <sup>238</sup>UF<sub>6</sub> undissociated. It is important that the ultraviolet pulse follows quite rapidly after the laser pulse, so that the vibrationally excited <sup>235</sup>UF<sub>6</sub> molecule does not lose its excitation energy through collision with surrounding molecules. It is obvious that this necessitates gas phase reactions. The <sup>235</sup>UF<sub>n</sub><sup>6-n</sup> ion formed through the dissociation (n < 6) is then collected by the action of electromagnetic fields. This technique is not limited to UF<sub>6</sub>; pure uranium metal vapor and plutonium compounds have been separated into their isotopic constituents by two or three photon ionization with laser light (e.g. the US AVLIS process and the French SILVA process). Another alternative is to selectively excite <sup>235</sup>UF<sub>6</sub> molecules by laser light in the presence of a reactive gas (the CRISLA process). The excited molecules then reacts preferentially with the gas forming molecules with lower vapor pressure than UF<sub>6</sub>. Although research in these areas has indicated a large scale feasibility of several similar processes, no predictions can yet be made of their technological value. The energy consumption for the quantum processes discussed above are in the range 10 – 40 kWh SWU<sup>-1</sup>. However, economic estimates indicate that their enrichment cost falls in the same price range as for centrifuge based plants. Hence, the interest in these methods has decreased and development of the ALVIS and SILVA processes has been terminated. Finally, it should be pointed out that the general concept of separative work breaks down for very high separation factors leading to very few units in a cascade (and always for mixtures of more than two isotopes).



## 2.9. Exercises

- 2.1. How many atoms of  $^{235}\text{U}$  exist in 1 kg of uranium oxide,  $\text{U}_3\text{O}_8$ , made of natural uranium?
- 2.2. What is the atomic fraction of deuterium in water with the mole fraction of 0.81 for  $\text{H}_2\text{O}$ , 0.18 for  $\text{HDO}$ , and 0.01 for  $\text{D}_2\text{O}$ ?
- 2.3. The translational energy of one mole of gas is given by  $3/2RT$ , which corresponds to an average thermal molecular velocity  $v$  (the root mean square velocity), while the most probable velocity  $v' = \sqrt{0.67} v$ .
- (a) What is the most probable velocity of a helium atom at  $800^\circ\text{C}$ ?
- (b) What voltage would be required to accelerate an  $\alpha$ -particle to the same velocity?
- 2.4. A Nier type mass spectrometer has a fixed radius of curvature of 5 cm and a magnetic field of 3000 G;  $1 \text{ G} = 10^{-4} \text{ T}$ . At what accelerating voltage will a  $\text{Na}^+$  ion be brought to focus at the ion collector?
- 2.5. In a Dempster type (constant  $B$  and  $V$ ) mass spectrograph utilizing  $180^\circ$  degree focusing, the ions  $^{12}\text{C}^+$  and  $^{11}\text{BH}^+$  are recorded simultaneously, the latter ion having a slightly larger orbit diameter. The separation between the lines recorded on the photographic plate is 0.0143 cm and the orbit diameter for the  $^{12}\text{C}^+$  ion is 20 cm. What is the atomic mass of  $^{11}\text{B}$ ?
- 2.6. When the rotational quantum number  $n_r$  goes from 0 to 1 in  $\text{H}^{35}\text{Cl}$ , it is accompanied by the absorption of light with a wave number of  $20.6 \text{ cm}^{-1}$ . From this it is possible to calculate the interatomic distance between hydrogen and chlorine in the molecules. What is this distance?
- 2.7. In one mole of a gas at STP (standard temperature and pressure, i.e.  $0^\circ\text{C}$  and 1 atm) a small fraction of the molecules have a kinetic energy  $\geq 15kT$ . (a) How many such molecules are there, and (b) what would their temperature be if they could be isolated?
- 2.8. In an investigation the isotope ratio  $^{18}\text{O}/^{16}\text{O}$  was found to be  $2.045 \times 10^{-3}$  for fresh water and  $2.127 \times 10^{-3}$  for carbon dioxide in the atmosphere. Calculate the equilibrium constant (mole fractions!) for the reaction



- 2.9. How many ideal stages in an ordinary cascade are required at an  $\alpha = 6$  to produce water in which 10% of the hydrogen is deuterium?
- 2.10. In a distillation column with total reflux,  $^{10}\text{B}$  is enriched through exchange distillation of  $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$  from the natural value of 20 atom % to a product containing 95%  $^{10}\text{B}$ . The packed column has a length of 5 m and a diameter of 3 cm. What is the approximate height of a theoretical stage if the enrichment factor is 0.026?
- 2.11. A gas centrifuge plant is set up in order to enrich  $\text{UF}_6$  of natural isotopic composition in  $^{235}\text{U}$ . The centrifuges, which each have a length of 100 cm and a diameter of 20 cm, rotate at 40000 rpm. The gas temperature is  $70^\circ\text{C}$ .
- (a) Prove that the separation factor  $\alpha$  in (2.47) can be approximated by  $e^\delta$  according to (2.58) when the product flow is very small compared to the waste flow, and  $\alpha$  is not far from 1.
- (b) Using this approximation, what is the theoretical separation factor for one unit?
- (c) Assuming that the enrichment factor obtained with the centrifuge is only 70% of the theoretical one, what number of units would be required in series in order to achieve  $\text{UF}_6$  with 3%  $^{235}\text{U}$ ?
- 2.12. How much separative work is needed in order to produce 1 kg of uranium containing 4%  $^{235}\text{U}$  from a feed of natural uranium and leaving 0.25% in the tail?

## 2.10. Literature

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