CHAPTER 1

FORMULATING THE PROBLEM OF THE GEOCHEMICAL MIGRATION OF INCLUDED SUBSTANCES, AND METHODS OF SOLVING IT

§1. Formulating the Problem of Geochemical Migration of Included Substances

In general form, the problem of geochemical migration of included substances may be formulated in the following manner. Let there be a definite configuration of the environment (rock, soil) within which, or at the boundary of which, sources of migrating substances exist. We shall assume that at the moment tentatively adopted as zero \( t = 0 \) the distribution of substances in the medium is known. As a consequence of migration, the distribution changes with time. The problem of the geochemical migration of included substances lies in determining the distribution function of the substances in the medium at any moment of time.

The problem cannot be solved in the general form because of mathematical difficulties. We must therefore seek some simplifications in formulating the problem. First, let us consider the migration of a single dissolved substance or of an individual gas. Second, let us assume that the host rock forms a homogeneous porous medium. This latter assumption means that any volume of the medium substantially greater than the size of the rock grains is characterized by constant averaged physical and chemical properties. Both these assumptions are found only as exceptions in nature. However, without a solution to the problem of migration of a single substance, it is impossible to consider the type of migration that is of most practical interest. The theory may be extended to more complex migration processes, as will be shown below. Setting up the present problem therefore has theoretical and practical interest.

A solution to the problem may be obtained by using the equation of material balance of the moving substance and the equation defining the interaction between the substance and the host rock with time. The latter equation is determined by the physicochemical laws of interaction between substances and the host rocks (sorption, ion exchange, chemical reaction) and is an equation of the kinetics of the corresponding physicochemical process.

§2. Equations of Material Balance and Kinetics of the Processes of Interaction between a Substance and Host Rocks

Let a liquid or gaseous solution, or an individual gas, move through the host rocks at a rate \( \mathbf{u} \) (vector quantity). Let us assume that all the host rocks form a homogeneous porous medium; then the law of interaction between the dissolved substance and the medium is the same for any point in space. The composition of the solution will be characterized by the concentration \( C \), the number of grams of dissolved substance in volume of solution per cm\(^3\) of porous medium.
We introduce the rectangular coordinates (x, y, z) to represent the movement of the solution. The transfer of dissolved substance in the mobile phase is determined by two different mechanisms. First, when the concentration C is not the same throughout the bulk solution, diffusion of the dissolved substance occurs, causing thermal movement of the particles. As a result, the substance is transferred from the zone of high concentrations to a zone of low concentration (diffusion will be examined in more detail in Chap. 2). Second, the particles of dissolved substance are moved at rate $\vec{u}$ of the transporting current. The combination of these processes is normally called convective diffusion of a substance in a solution (gas) [1].

In the process of moving, the substance interacts with the rock: it is adsorbed by the rock and it enters into chemical reactions with the minerals of the rock. Consequently, the migrating substance is present also in an immobile phase, both as a compound identical to that in solution (adsorption) and as a new compound (chemical reaction). We shall use q to designate the number of grams of adsorbed substance or immobile phase through reaction with the rock in each cm$^3$ of porous medium. The substance in the solid phase does not ordinarily lose its mobility, but may diffuse through the volume of host rock [2].

As a result of these processes, the concentration of substance in the mobile and solid phases changes in space and time, so that $C = C(x, y, z, t)$ and $q = q(x, y, z, t)$ are functions of the coordinates and time. The problem of geochemical migration consists in finding these dependent relations.

Let us set up an equation for material balance for an arbitrary volume $V$ of the porous medium. The imaginary surface $S$ surrounding the volume $V$, in the normal case, cuts both free pore space and solid phase. Therefore the current $\vec{J}$ (vector quantity) of the substance, numerically equal to the amount of substance passing through 1 cm$^2$ of the surface $S$ per second, is made up of the current of transport by convective diffusion in the mobile phase and the diffusion current in the immobile phase. The diffusion current $\vec{j}_D$ in the immobile phase, in keeping with the law of Fick (Chap. 2), is equal to

$$\vec{j}_D = -D \text{grad } q,$$

where $D$ is the diffusion coefficient of the substance in the rock.

Since the amount of substance transported by a moving liquid or gas through 1 cm$^2$ of surface per second is equal to $C \vec{u}$, the current $\vec{j}_k$ determined by convective diffusion is equal to

$$\vec{j}_k = C \vec{u} - D \text{grad } C,$$

where $D$ is the diffusion coefficient of the substance in the bulk solution or gas.

Consequently

$$\vec{j} = \vec{j}_D + \vec{j}_k = -D \text{grad } C - \vec{D} \text{grad } q + C \vec{u}.$$

The amount of substance passing through the surface $S$ per second is

$$Q = -\frac{1}{2} \int \vec{j} \cdot d\vec{S},$$

where the integral is taken over the surface $S$ surrounding the volume $V$. The direction from the surface outward was chosen as the positive direction of the vector of the exterior normal. The values $\partial C/\partial t$ and $\partial q/\partial t$ are changes in the amount of substance per second per unit volume of the immobile phases, respectively. Then, the change in amount of substance per volume $V$ per second is