On the Different Filtration Rates of Anions and Cations When Solutions Percolate Through Fine-Porous Filters

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On the Different Filtration Rates of Anions and Cations When Solutions Percolate Through Fine-Porous Filters

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At present, attention in geochemistry is being drawn to the hypothesis of acid-base hydrothermal differentiation advanced by D. S. Korzhinskii (^{2}). According to this hypothesis, the change in the acidity of solutions, which is the decisive factor in the evolution of postmagmatic solutions, occurs as a result of the different filtration rates of anions and cations when hydrothermal solutions percolate through fine-pored rocks, i.e., as a result of the acid-base filtration effect.

We undertook an experimental study of the acid-base filtration effect in 0.1-0.001 N solutions of chlorides and sulfates of copper and iron. Previous experimental studies of the filtration effect (^{3}-^{5}) could not be used in this direction, since changes in the concentration of solutions during filtration were estimated by indirect methods (from changes in electrical conductivity).

In studying the filtration effect, phenomena of sorption of the solution components by the filter material must first of all be excluded and evaluated. Therefore, as the filter material we chose thoroughly purified quartz and carried out experiments to determine the sorption of solution components on crushed quartz. The sorption experiments gave a negative result. They showed that, at the sensitivity and accuracy of the methods we used, sorption of copper, iron, chlorine, and sulfate on quartz from dilute solutions (0.1-0.001 N) is not detected.

We carried out more than 100 experiments on the filtration of 0.1-0.001 N solutions of chlorides and sulfates of copper and iron through fine-pored filters made of crushed quartz under room-temperature conditions (18-22°) and normal pressure. Filtration was carried out in a quartz tube filled with quartz powder. The conditions of the standard experiments were as follows. Tube size: $D =$ 22-23 mm, $l =$ 280-300 mm. The filter was quartz powder with particle sizes: 1) 0.020-0.025 mm; 2) 0.015-0.019 mm; 3) 0.009-0.014 mm. The height of the filter column was 160 mm. The height of the solution column above the filter was kept constant and was 110-120 mm. The solution above the filter was stirred.

The entire volume of filtrate that had percolated during definite time intervals was collected as samples. The sample volumes ranged from 0.5 to 3.5 ml. De-

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pending on the composition and concentration of the solution, the following analytical methods were used: 1) the colorimetric diethyldithiocarbamate method for determining copper; 2) the colorimetric rhodanide method (in the absence of copper) and the salicylate method (in the presence of copper) for determining iron; 3) the colorimetric method with barium chromate and diphenylcarbazide for determining the sulfate ion; 4) the volumetric mercurimetric method for determining the chloride ion. The error of the determinations did not exceed 2–3% with samples of 0.3–1.0 g per determination.

Two series of experiments were carried out. In the first series of experiments, filtration of the solutions was performed through an initially dry filter.

In all experiments an unambiguous change in concentration is observed as the solutions are filtered: (a) the concentration of cations (Cu^{++}, Fe^{+++}) in the first samples is lower than in the initial solution; (b) the concentration of anions (Cl^{-}, SO_4^{--}) in

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Experiment No.	Solution	Ion	Filter particle size, mm	Porosity, %	Initial conc., 10^{-3} mg/ml	φ_i	Points
21	$0.001\,N$ $FeCl_3$	Fe^{+++}	0.015 – 0.019	41.6	15.9	0.90	1
21	$0.001\,N$ $FeCl_3$	Cl^{-}	0.015 – 0.019	41.6	38.2	1.04	2
22	$0.001\,N$ $FeCl_3$	Fe^{+++}	0.015 – 0.019	45.6	15.6	0.78	3
22	$0.001\,N$ $FeCl_3$	Cl^{-}	0.015 – 0.019	45.6	38.3	1.23	4
124	$0.001\,N$ $CuCl_2$	Cu^{++}	0.015 – 0.019	39.3	35.1	0.73	5

Experiment No.	Solution	Ion	Filter particle size, mm	Porosity, %	Initial conc., 10^{-3} mg/ml	φ_i	Points
124	0.001 N $CuCl_2$	Cl^-	0.015–0.019	39.3	39.5	1.07	6
125	0.001 N $CuCl_2$	Cu^{++}	0.015–0.019	43.4	35.9	0.81	7
125	0.001 N $CuCl_2$	Cl^-	0.015–0.019	43.4	38.8	1.11	8
128	0.001 N $CuCl_2$	Cu^{++}	0.020–0.025	38.9	32.0	0.69	9
128	0.001 N $CuCl_2$	Cl^-	0.020–0.025	38.9	40.9	1.30	10

the first samples is greater than or equal to their concentration in the initial solution; (c) as the solutions are filtered, the concentration of cations increases, while that of anions decreases and becomes equal to the concentration of the initial solution; the curve of the dependence of C on v, or of C on t, initially has a diffusion-like form; (d) the effect of the change in concentration in the first samples is more clearly expressed in more dilute solutions and differs for different components. As a criterion

example, Fig. 1 shows the results of several experiments on the filtration of 0.001 N solutions.

The observed changes in the concentration of the filtrate are a consequence of the different filtration rates (filtration effect) of cations and anions, which differ from the filtration rate of the solvent. When the solution enters the fine-pored medium of the filter, the continuous flow of the solution is disrupted; differential motion of the solution takes place, in which the solvent and each dissolved component move at different velocities.

Fig. 2. Experimental C—v curves for experiments on filtration of 0.01 and 0.001 N solutions of $FeCl_3$ and $CuCl_2$ through a filter saturated with water. Concentration in hundredths and thousandths of a gram-equivalent: 10^{-2} and 10^{-3} g-eq.

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Experiment No.	Solution	Ion	Filter particle size, mm	Porosity, %	Initial conc., g-eq	φ_i	Points
25	0.01 N $FeCl_3$	Fe^{+++}	0.015 – 0.019	46.7	10^{-2}	0.89	1
25	0.01 N $FeCl_3$	Cl^{-}	0.015 – 0.019	46.7	10^{-2}	0.91	2
26	0.01 N $FeCl_3$	Fe^{+++}	0.015 – 0.019	47.2	10^{-2}	0.94	3
26	0.01 N $FeCl_3$	Cl^{-}	0.015 – 0.019	47.2	10^{-2}	1.00	4
27	0.001 N $FeCl_3$	Fe^{+++}	0.015 – 0.019	54.0	10^{-3}	0.80	5
27	0.001 N $FeCl_3$	Cl^{-}	0.015 – 0.019	54.0	10^{-3}	1.02	6
129	0.001 N $CuCl_2$	Cu^{++}	0.015 – 0.019	45.0	10^{-3}	0.78	7
129	0.001 N $CuCl_2$	Cl^{-}	0.015 – 0.019	45.0	10^{-3}	1.30	8

rates. The cations move more slowly than the solvent, which leads to a lowering of their concentration in the first samples. The anions move simultaneously with, or somewhat faster than, the solvent; as a result, the concentration of anions in the first portions is equal to or higher than the concentration in the original solution.

The different rates of motion of anions and cations are especially clearly seen in the second series of experiments, in which filtration of the solution was carried out through a filter preliminarily saturated with water. The results of these experiments are shown in Fig. 2. It is not difficult to see that the greater rate of motion of the anions leads to their overtaking the cations during filtration.

The change in the concentration of the filtrate observed in the experiments is not only a consequence of the different filtration rates of the ions, but is complicated by accompanying diffusion phenomena. The totality of the processes occurring during filtration of a solution through a fine-pored inert filter is described by the equation

$$\partial C_i/\partial t + w_0\varphi_i\partial C_i/\partial x + w_0 C_i\partial\varphi_i/\partial x - D_i\partial^2 C_i/\partial x^2 = 0,$$

where C_i is the concentration of some component i in the solution; w_0 is the filtration rate of the solvent; x is distance; t is time; D_i is the diffusion coefficient; φ_i is the coefficient of the filtration effect, equal, as shown by D. S. Korzhinskii (^{1}), to $\varphi_i = w_i/w_0$; w_i is the filtration rate of the component.

An investigation of this equation shows that when a solution enters a medium with differing φ_i, at first there occurs a general nonstationary

flow of the solution, in which C_i changes in each cross section. As filtration tends toward the stationary state, which is characterized by $C_i = C^0/\varphi_i$, $(\partial x/\partial t)_{C_i} = \omega_i$, and $\omega_i = \varphi_i\omega_0$, the nonstationary flow is localized in the front zone of the solution, where, owing to the difference between ω_i and ω_0, a concentration gradient arises and diffusion will occur. Diffusion will counteract the differentiation of the substance that occurs as a result of the different filtration rates. Thus, naturally, the lower the diffusion rate, the more clearly expressed the filtration effect.

The different filtration rates of cations and anions are best evaluated by means of φ_i, the coefficient of the filtration effect. For the experimental conditions there are the following equivalent expressions for φ_i: $\varphi_i = \omega_i/\omega_0 = t_0/t_i = v_0/v_i$, where ω_0, ω_i are the filtration rates of the solvent and of component i; t_0, t_i are the filtration times of the solvent and component i through a given filter; v_i is the volume that has seeped through before the appearance of the dissolved component; v_0 is the volume of solvent in the filter (equal to the pore volume of the filter).

The values of t_i and v_i can be obtained from the experimental curves, conditionally excluding the influence of diffusion considered above.

Then

$$v_i = v_0 - \left(\sum_1^n \Delta C_n \Delta v_n\right)/C_0,$$

where $\Delta C_n = (C_n - C^0)$ is the difference between the concentrations in the sample (C_n) and in the initial solution (C^0), and $\Delta v_n = v_n - v_{n-1}$ is the size of the sample up to C_n, v_n being the concentration and volume value in the last sample differing from the initial solution.

The value of φ_i can also be calculated from the material balance during filtration, i.e., assuming that the deficiency (excess) of substance in the first samples is compensated by the opposite change in the concentration of the solution in the filter. Then

$$\varphi_i = C^0 v_0 / \left(C^0 v_0 - \sum_1^n \Delta C_n \Delta v_n \right).$$

The results of calculating the values of φ_i corresponding to the experiments, carried out by the two methods with complete agreement of the results, are given in the tables accompanying the figures.

The experimental investigations carried out show that when a solution seeps through fine-pored filters a filtration effect takes place, i.e., differential flow of the solution occurs, in which each dissolved component has its own filtration rate. Cations ($\mathrm{Cu}^{++}, \mathrm{Fe}^{+++}$) move more slowly than the solvent; the magnitude of φ_i differs for different cations: $\varphi_{\mathrm{Cu}^{++}} = 0.70$–$0.96$, $\varphi_{\mathrm{Fe}^{+++}} = 0.80$–$0.96$. Anions move simultaneously and somewhat faster than the solvent, the chloride ion moving faster than the sulfate ion: $\varphi_{\mathrm{Cl}^-} = 1.00$–$1.30$, $\varphi_{\mathrm{SO4}} = 1.00$–$1.04$. The value of φ_i depends on the concentration of the solution and the characteristics of the filter (density, pore size, etc.).

Of particular interest is the different filtration rate of anions and cations; the difference $\Delta\varphi = \varphi_a - \varphi_k = (\omega_a - \omega_k)/\omega_0$ reaches 0.4-0.6 in $0.001N$ solutions. This shows that, in the filtration of solutions through fine-pored media, an acid-base filtration effect occurs, in which the more rapid filtration of anions causes a coupled displacement (change in concentration) of hydrogen ions, leading to an increase in acidity at the head of the flow.

The investigations carried out serve as experimental confirmation of D. S. Korzhinskii' s hypothesis on acid-base hydrothermal differentiation.

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Note: Figure translations are in progress. See original paper for figures.