PHYSICAL CHEMISTRY

Academician Vikt. I. SPITSYN, E. A. TORCHENKOVA, and I. N. GLAZKOVA

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Figure 1

Figure 1: Figure 1

Abstract

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THE INFLUENCE OF RADIOACTIVE RADIATION FROM A SOLID ON THE PROCESSES OF ITS DISSOLUTION

A comparatively small number of studies are known in which the influence of radioactive radiation from solids on the charge of their surface (^{1}) and on certain physicochemical properties (^{2}) is noted, including the rate of isotope-exchange reactions in heterogeneous systems (^{3}), catalytic activity (^{4}), and sorption capacity (^{5}).

The authors of the present communication have studied the influence of the radioactivity of barium sulfate labeled with S^{35} on the kinetics of its dissolution in water and on the magnitude of its solubility.

The latter has repeatedly been determined by various methods and is 2.3 mg/l at 18° (^{6}). Many investigators have noted a number of peculiarities in the behavior of $BaSO_4$ during its dissolution, for example, the formation of solutions whose concentration temporarily (for no more than 24 hr) exceeded the normal solubility of the salt by almost a factor of two (^{7}). It was indicated (^{8}) that the solubility of $BaSO_4$ is approximately constant for crystals whose size is not more than 1-2 μ.

Fig. 1. Kinetics of dissolution in water at 20° of $BaSO_4$ preparations of different specific activity.
1—0.7 mCi/g, 2—1.0 mCi/g, 3—9.0 mCi/g, 4—19.9 mCi/g. The salt was prepared by mixing equivalent amounts of 0.1 N solutions of $BaCl_2$ and Na_2SO_4.

Sulfur-35 was introduced into barium sulfate during its precipitation. The $BaSO_4$ preparations were prepared according to (^{9}). Hot 0.1 N solutions of $BaCl_2$ and Na_2SO_4 (in some cases 0.1 N H_2SO_4), containing a definite amount of S^{35}, were mixed at the same rate with stirring. The latter was continued for 1 hr while heating to 70-80°. After this, the precipitate was aged in the mother liquor for 20 hr. The $BaSO_4$ precipitates were washed first with water, then

Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

with ethyl alcohol, and dried at 80-85° to constant weight. The specific surface area of the $BaSO_4$ preparations was determined by visual-microscopic (1200×) and electron-microscopic (12000×) methods. The particle size of $BaSO_4$ was 2.7-8.1 μ. The data obtained agree with the results of (^{9}).

To investigate solubility, 0.5 g of radioactive $BaSO_4$ and 50 ml of bidistilled water were placed in a test tube. Stirring was carried out at $20 \pm 0.5°$. At definite time intervals, samples of the solution were taken, centrifuged three times at a speed of 5000 rpm, and then applied to targets for measurement of activity. From the activity values of the solution sample and the specific activity of the $BaSO_4$ precipitate, the salt content in the solution was calculated (^{10}). Results of the study—

of the dissolution kinetics of $BaSO_4$ of different specific activity, obtained by mixing 0.1 N solutions of $BaCl_2$ and Na_2SO_4, are presented in Fig. 1.

It is noteworthy that, at a specific radioactivity of the preparations of the order of 0.7-1.0 mCi/g, a considerable supersaturation of the solutions is first observed, which is eliminated after approximately 25 h of stirring the liquid with the precipitate. Preparations with a specific radioactivity of 9-20 mCi/g do not show a similar phenomenon: the concentration of $BaSO_4$ in them increases with time.

Fig. 2. Dissolution kinetics in water at 20° of $BaSO_4$ with activity 0.6-0.7 mCi/g (1, 2, 3) and 8-9 mCi/g (4, 5, 6). The preparations were obtained: 1 and 4—by interaction of equivalent amounts of 0.1 N solutions of $BaCl_2$ and Na_2SO_4, 2 and 5—with a 20% excess of Na_2SO_4; 2 and 6—with a 20% excess of $BaCl_2$.

Fig. 3. Dissolution kinetics in water at 20° of $BaSO_4$ preparations of different specific activity. 1—0.13 mCi/g, 2—1.47 mCi/g; 3—8.2 mCi/g, 4—98.1 mCi/g. The salt was prepared by mixing equivalent amounts of 0.1 N solutions of $BaCl_2$ and H_2SO_4.

If one compares the final concentrations of the solutions obtained, it may be concluded that the solubility of barium sulfate prepared by the method indicated above is maximal in the case of a specific radioactivity of the order of 2 mCi/g and decreases both when it increases and when it decreases (Fig. 4, 1). A similar course of the curve is analogous to the regularity noted earlier by one of us for the influence of the specific radioactivity of the solid phase on the kinetics of isotopic exchange of sulfur in the system K_2SO_4—SO_3 (^{3,11}) and of oxygen in the system Na_2SO_4—O_2 at high temperatures (^{2}). It should be noted that the solubility of radioactive $BaSO_4$ in all experiments exceeded the solubility of barium sulfate known from the literature data.

Fig. 4. Effect of the specific radioactivity of Ba^*SO_4 on the magnitude of its solubility in water at 20°. Methods of obtaining Ba^*SO_4: 1 – $BaCl_2 + Na_2{}^*SO_4$, 2 –$BaCl_2 + {}^*H_2SO_4$

Figure 3: Fig. 4. Effect of the specific radioactivity of Ba^*SO_4 on the magnitude of its solubility in water at 20°. Methods of obtaining Ba^*SO_4: 1 –$BaCl_2 + Na_2{}^*SO_4$, 2 –$BaCl_2 + {}^*H_2SO_4$

The solubility of radioactive $BaSO_4$ increases still more if, in preparing its preparations, an excess of one of the reagents is taken. The greatest increase in solubility is observed when an excess of $BaCl_2$ is used (Fig. 2).

For preparations of different specific radioactivity (0.6-0.7 and 8-9 mCi/g), the same character of attainment of equilibrium with the saturated solution is retained, which was already noted above (Fig. 1).

The solubility of radioactive $BaSO_4$ became appreciably lower if the salt was prepared according to the procedure of ([9]), but using a 0.1 *N* solution

${}^*H_2SO_4$ instead of $Na_2{}^*SO_4$ (Fig. 3). However, the dissolution-kinetics curves had the same form as in Fig. 1. Preparations with specific radioactivities of 0.1 and 1.5 mCu/g showed a considerable tendency toward supersaturation phenomena. At activities of the preparations of 8.2 mCu/g and 98.1 mCu/g, such phenomena were not observed. All the studied samples of radioactive Ba^*SO_4 had a higher solubility in water than is indicated for nonradioactive barium sulfate.

The curve of the concentrations of saturated Ba^*SO_4 solutions as a function of the specific activity of the preparations in this case is also characterized by a maximum (Fig. 4, 2), similarly to the solubility curve of preparations obtained by the interaction of $BaCl_2$ and $Na_2{}^*SO_4$ (Fig. 4, 1). However, the magnitude of the maximum for curve 2 is less sharply expressed.

Fig. 4. Effect of the specific radioactivity of Ba^*SO_4 on the magnitude of its solubility in water at 20°. Methods of obtaining Ba^*SO_4: **1** –$BaCl_2 + Na_2{}^*SO_4$, **2** –$BaCl_2 + {}^*H_2SO_4$

The phenomena described above apparently must be explained as a consequence of the continuous emission of β-particles by radioactive Ba^*SO_4 preparations. The electric charges arising at the phase boundary must affect the structure of the double layer and promote additional adsorption of ions by the precipitate. The electric fields that are created evidently exert on dissolution processes an influence analogous to the ionic strength of solutions. It is known that the solubility of sparingly soluble substances depends strongly on this factor ([12–14]). The presence of a maximum on the curves showing the dependence of the solubility of $BaSO_4$ on its specific radioactivity can be explained by a change in the character of the interaction of β-particles with the substance upon a considerable increase in their number ([11]). It should be expected that the influence of the specific radioactivity of precipitates on the magnitude of their solubility will be more pronounced in the case of sparingly soluble compounds and at high radiation energy.

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CITED LITERATURE

1. P. Curie, M. Curie, C. R., **130**, 647 (1900).
2. Vikt. I. Spitsyn, Izv. AN SSSR, OKhN, 1958, No. 11, 1296; Österr. Chem.-Ztg., **60**, 130 (1959).
3. Vikt. I. Spitsyn, I. E. Mikhailenko, DAN, **121**, 319 (1958).
4. A. A. Balandin, Vikt. I. Spitsyn et al., DAN, **121**, 495 (1958).
5. Vikt. I. Spitsyn, V. V. Gromov, DAN, **123**, 722 (1958); Radiokhimiya, **1**, 181 (1959).
6. F. Kohlrausch, Zs. phys. Chem., **64**, 129 (1908).
7. G. A. Hulett, Zs. phys. Chem., **37**, 385 (1901).
8. B. Fischer, Anal. Chem., **23**, 1667 (1951).
9. A. M. Rutgers, W. van den Heuvel, Experientia, **11**, Fasc. 12, 481 (1955).
10. Vikt. I. Spitsyn, P. N. Kochurov et al., *Methods of Work Using Radioactive Indicators*, Publishing House of the Academy of Sciences of the USSR, 1955, p. 234.
11. I. E. Mikhailenko, Vikt. I. Spitsyn, DAN, **131**, 129 (1960).
12. G. Lewis, M. Randall, *Chemical Thermodynamics*, Moscow, 1936, p. 287.
13. E. B. Shternina, Izv. sekt. fiz.-khim. anal. IONKh AN SSSR, **19**, 345 (1949).
14. Vikt. I. Spitsyn, I. A. Savich, ZhNKh, **3**, 1979 (1958).

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