tween the points B and B′ and the data of Table VI indicates the solid phase to be $2CaSO_3 \cdot H_2O$.

Table VII was compiled from the data of Tables III and IV plotted to large scale and shows the values of total, free and combined sulfur dioxide at 50 mm. intervals below atmospheric pressure.

TABLE VII

COMPOSITION OF LIQUID PHASE FOR THE SYSTEM $CaO–SO_2–H_2O$

Total press., mm.	Concn. of sulfur dioxide at 15°, grams per 100 grams H_2O Total	Free	Combined	Concn. of sulfur dioxide at 25°, grams per 100 grams H_2O Total	Free	Combined
50	4.1	2.2	1.9	2.7	1.4	1.3
100	6.8	3.9	2.9	4.7	2.6	2.1
150	8.6	5.1	3.5	6.2	3.6	2.6
200	9.8	5.9	3.9	7.3	4.4	2.9
250	10.9	6.7	4.2	8.3	5.2	3.1
300	11.8	7.4	4.4	9.1	5.7	3.4
350	12.8	8.1	4.7	9.9	6.3	3.6
400	13.8	8.9	4.9	10.6	6.8	3.8
450	14.7	9.6	5.1	11.3	7.3	4.0
500	15.5	10.2	5.3	12.0	7.8	4.2
550	16.3	10.9	5.4	12.7	8.3	4.4
600	17.1	11.5	5.6	13.3	8.7	4.6
650	17.8	12.1	5.7	14.0	9.2	4.8
700	18.4	12.6	5.8	14.6	9.7	4.9
750	19.1	13.2	5.9	15.2	10.2	5.0

Summary

1. The total pressure–composition relationships have been determined for the system $CaO–SO_2–H_2O$ in the acid region up to a total pressure of one atmosphere at 15 and 25°.

2. The solid phase in equilibrium with solution at the pressures investigated has been identified as containing CaO and SO_2 in the molar ratio of 1:1 and the compound $2CaSO_3 \cdot H_2O$ is indicated.

3. The total, free and combined sulfur dioxide has been determined for saturated solutions in equilibrium with solid calcium monosulfite at total pressures of sulfur dioxide and water vapor from the vapor pressure of water to atmospheric pressure for the temperatures 15 and 25°.

4. The temperature–composition relationship has been determined for the total pressure of 761 mm. at temperatures of 15, 25 and 35°.

5. The total, free and combined sulfur dioxide in a solution formed by the reaction of aqueous $Ba(OH)_2$ and SO_2 in which solid was present has been determined for the temperature of 25° and total pressure of 659 mm.

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[CONTRIBUTION FROM THE MEMORIAL HOSPITAL, NEW YORK CITY]

The Swelling of Gelatin in Deuterium Oxide

BY H. Q. WOODARD AND L. C. CHESLEY

Since the discovery of deuterium many investigations have been made of the effect of this isotope of hydrogen on living organisms. Since the hydration of proteins plays an important part in life processes, it seemed desirable to compare the swelling of protein material in deuterium and protium oxides. As the swelling behavior of gelatin is well known from the work of Loeb, Wilson and others, this protein was chosen for study in the present work.

Materials and Method.—Ninety-four per cent. deuterium oxide was obtained through the courtesy of Professor Harold C. Urey of Columbia University. It was purified before each experiment by repeated slow distillation from alkaline permanganate and then from neutral permanganate. In most cases these distillations were preceded by three or more distillations from chromic anhydride. Difficulty was experienced in removing an unidentified volatile impurity which was expelled from the deuterium oxide just below the boiling point and deposited on the walls of the condenser. This material had an acrid odor and an alkaline reaction. It was probably derived from the decomposition of gelatin, since it was necessary to heat the gelatin fragments after each experiment in order to recover the deuterium oxide which they had imbibed. In every case the distillations were repeated until the *p*H of the D_2O, as shown by its color with propyl red indicator, was between 5 and 6, the *p*H range of the laboratory supply of distilled water being 5.3–5.8. Hence, although the deuterium oxide always had a slight odor, it is improbable that it contained the alkaline impurity in significant quantities during any of the experiments.

The gelatin used was "Coignet" sheet gelatin with a *p*H of 5.5.

Because the supply of deuterium oxide available was limited, it was necessary to develop a microtechnique for the swelling experiments. Satisfactory results were obtained when gelatin fragments weighing 8–15 mg. were allowed to swell at 4–6° in 0.10–0.20 cc. of water contained in stoppered 5-cc. test-tubes. After the fragments had swelled for the required time they were removed with forceps, blotted on filter paper, and weighed. The ratio, wt. water/wt. gelatin, could be varied somewhat provided the value of the ratio was kept above 8/1. Results for a given experiment checked to ±3% or better. This is shown in the data for the last experiment in Table I given in detail below. The variation from day to day, as shown by the figures in Table I for the swelling of gelatin in H_2O, is somewhat larger, the difference probably being due to variations in the temperature of the ice box.

LIQUID IMBIBED PER 10 MG. GELATIN

H_2O, mg.	45.4	44.4	44.7	45.3	44.7
D_2O, mg.	47.1	48.6	47.1	50.0	48.5

It will be seen that this technique permits the study only of the type of swelling, in which the Donnan membrane equilibrium is not involved, since the weight of gelatin is large in comparison with the volume of liquid. Under the present conditions, if, for instance, the gelatin were allowed to swell in 0.001 *N* acid or alkali, only about 1% of the gelatin present would be required to combine with all the acid or alkali available. While this would swell according to the Donnan theory, the effect would be masked by that of the remainder, which would swell by imbibition only. For this reason the results are not greatly influenced by the presence of traces of impurities in the water.

This was tested by allowing gelatin fragments to swell in 0.001 *N* NaOH, HCl and NaCl. The degree of swelling in all three types of solution was the same within the experimental error as that in ordinary distilled water, and the final *p*H of all the solutions was 5.5, or that of the gelatin. Similar experiments performed with a solution in ordinary water of the unidentified volatile impurity mentioned above which was recovered from the condenser also showed the swelling to be uninfluenced by this impurity.

Results

As preliminary work indicated that swelling was nearly complete in two days, a comparison was first made of the swelling of gelatin in ordinary water and deuterium oxide in this time. The results are given in Table I, each value being the average of 2 to 5 determinations. The experiments were done over a period of several months during which time the heavy water available became diluted from an initial D_2O concentration of 94% to a final concentration of 42%. For the first three experiments when the concentration of D_2O was about 90%, the averate ratio of mg. 90% D_2O imbibed per 10 mg. gelatin/mg. H_2O imbibed per 10 mg. gelatin is 0.86. For the last two experiments the corresponding ratio for 42% D_2O is 0.93. It therefore appears that gelatin swells 86% as much in 90% D_2O as in H_2O, and 93% as much in 42% D_2O as in H_2O. If the comparison is made on the basis of the calculated volumes of liquid imbibed the corresponding values are 78 and 89%. The difference between the D_2O values and the H_2O values is proportional to the D_2O concentration within the experimental error.

TABLE I

Detns.	Mg. liquid imbibed/10 mg. gela. D_2O	H_2O	Ratio $\frac{\text{wt. } D_2O \text{ per 10 mg.}}{\text{wt. } H_2O \text{ per 10 mg.}}$
2	33.9	39.0	0.87
2	38.1	47.6	.80
2	40.5	44.9	.90
3	38.7	42.9	.90
2	39.2	45.8	.86
5	44.3	48.0	.92
5	43.5	46.2	.94
5	44.9	48.3	.93

The difference in the two-day swelling values might be due either to an actual difference in the equilibrium between the cohesive force of the gel and the attractive force between gelatin and the two types of water, or to a difference in the rate at which this equilibrium is established. To test this, time–swelling curves were obtained, and are given in Fig. 1. The weight of liquid imbibed per 10 mg. of gelatin is plotted against time in hours. Each point represents the average of two determinations. The two curves show no tendency to coincide at the longer swelling periods, the percentage difference between them increasing slightly with time.

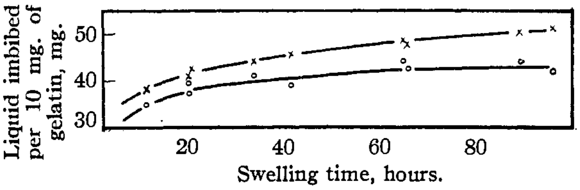

Fig. 1.—×, Gelatin in H_2O; ○, gelatin in D_2O.

Summary

Gelatin swells 86% as much by weight in 90% D_2O, and 93% as much in 42% D_2O, as it does in ordinary water.

The difference is not due to a delay in the establishment of equilibrium between gelatin and D_2O.

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