97. *Heat Effects Accompanying the Absorption of Simple Electrolytes by Fully-swollen Alginate and Cellulose Gels. A New Microcalorimetric Method.*

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A microcalorimetric method is described which enables a determination of small heat effects accompanying the interaction of fully-swollen gels with solutions of permeant electrolytes. The results of the measurements enable a comparison to be made between the heat of swelling of alginate or cellulose gels in water and the heat of swelling of the same gels in sodium or calcium chloride solution. The thermochemical reactions here investigated represent typical examples showing the kind of energetic conditions conducive either to salting out or to salting in of colloids as brought about by addition of simple electrolytes.

The measurements here described were carried out in order to estimate small heat changes which accompany the reversible interaction of fully-swollen alginate and cellulose gels with solutions of calcium and sodium chloride. The calorimetric technique employed is a modification of that used by Hill (see, *e.g.*, *Proc. Roy. Soc.*, 1938, *B*, **126**, 136) for a study of heat effects accompanying electrically stimulated contractions of frog sartorii. In our tests a thermopile served as a support for gels of dry weight between 0·0018 and 0·008 g.; the heat to be measured was liberated or absorbed on addition of 0·02—0·04 cm.^{3} of the salt solution. The results of these experiments enable a comparison to be made between the heat of swelling of the gel in water and in the electrolyte solution.

Experimental

The apparatus used is shown in Fig. 1. The thermopile, *G*, constructed by Downing, contained 60 iron–constantan couples in series; the well-insulated wire was 0·1 mm. thick, the resistance being 22 Ω and the sensitivity 3×10^{-3} volt/degree. Alginate gels or ash-free filter-paper strips, *E*, fully swollen with water, were hung over the upper silver electrode and held on to the lower electrode by a spring clip, *F*, made from Perspex. The two glass pipettes contained a solution of calcium or sodium chloride, introduced with the help of a hypodermic needle fitted to a precision micro-syringe. One end of each of the pipettes, *D*, was connected with a flexible tubing, made from Polythene, which contained the same solution as the pipette; there was an air space on each side of the solution in the pipette, to prevent mixing with the solution in the flexible tubing, or a reaction with the gel. The glass vessel, *V*, filled with a paraffin–tetrachloroethylene mixture to the level *I*, was fitted to the rubber stopper, and was immersed in well-stirred water contained in a Dewar vessel. When temperature equilibrium was established, the two pistons, *C*, were pushed into the flexible tubing, thereby moving the solution from the pipettes to the gel on the thermopile. The movement of *C* was adjusted in such a way that the whole solution together with a portion of the air bubble behind it was expelled from the pipette. The heat changes accompanying the interaction of the electrolyte solution with the gel were measured by determining the deflection of a galvanometer connected with the thermopile by means of *A*.

FIG. 1. *Apparatus used for the measurement of heat effects accompanying the absorption of sodium and calcium chloride by fully-swollen alginate and cellulose gels.*

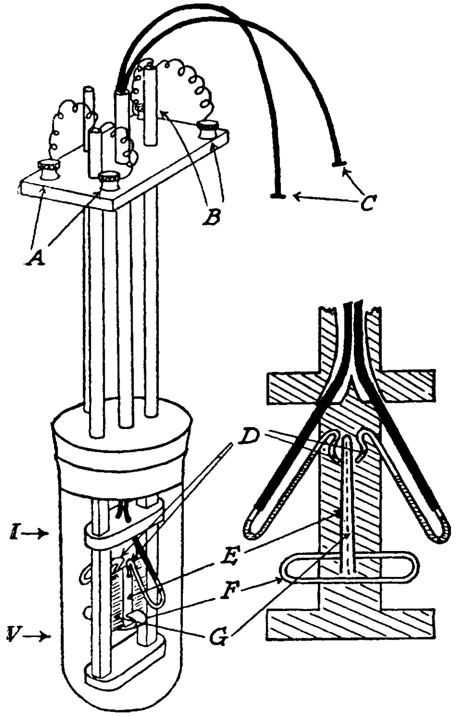
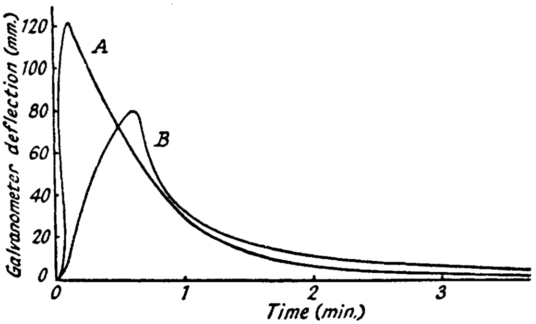


FIG. 2. *Typical galvanometer deflection–time curves at* 19·5°.



(*A*) *Curve relating to heat effect accompanying the addition of* 0·0400 *cm.*^{3} *of* 1N-NaCl *solution to* 0·022 *g. of fully-swollen calcium alginate fibres of* 0·02 *cm. diameter.*

(*B*) *Curve relating to electrically produced heat input of* 2·31 × 10^{-3} *cal.*

The sign of the galvanometer deflection in (*A*) *was opposite to that in* (*B*).

The removal of the solution from the pipettes takes less than 1 sec. Control experiments showed that the heat effect due to the passage of the solution through the jets is negligible. The liquid spread over the gel in a thin layer, the surface tension being sufficient to prevent an accumulation at the lower end, on top of the spring clip, provided the specific gravity of the paraffin–tetrachloroethylene mixture is suitably adjusted. After each experiment a calibration was carried out, by passing an alternating condenser discharge from *B* through the gel, the two silver electrodes serving as points of contact. A battery connected with a commutator, rotating at a rate of 184 r.p.m., charged and discharged a condenser (2 × $10^{-3}\mu$F; 49 volt) four times every revolution. Control tests established that the electrical heat input was proportional to the area under a curve obtained by plotting the time against the galvanometer deflection. Typical curves are shown in Fig. 2: curve *A* represents the deflection produced by the addition of 0·0400 cm.^{3} of 1N-sodium chloride solution to 0·022 g. of fully-swollen calcium alginate fibre of 0·2 mm. diameter; and curve *B* is the calibration curve. The sign of the galvanometer deflection was different in the two runs, heat being absorbed during the interaction of sodium chloride with the gel.

The ratio of the area under the two curves is 1·30; the heat input during calibration was

2·31 × 10^{-3} cal., so the unknown heat effect can be calculated. The method of computation is possible because the galvanometer returns to its original position. If, on the other hand, the vessel, *V*, contained moist air, instead of the paraffin mixture, the initial and final galvanometer positions were markedly different. The effects responsible for the discrepancy are essentially those discussed by Hill (" Adventures in Biophysics," Philadelphia, 1931, Lecture I). Results showing the reproducibility of the micro-calorimetric method are in Table 1, and a summary of the results of the measurements is in Table 2.

The ΔH_d values in Table 2 are heats of dilution, which relate to the reaction between the sodium or calcium chloride solution and water in the absence of the gel, the amount of water used for this dilution process being equivalent to that absorbed by the fully-swollen gels used for these tests. The figure in the first line of col. 9, for instance, is the heat of dilution obtaining on addition of 0·0400 cm.^{3} of 1N-sodium chloride to 0·0202 cm.^{3} of water. It will be seen that the heat changes in cols. 8 and 9 relate to the actual quantities of gel used, while the figures in the last column relate to 1 g. of dry gel. An endothermic process is indicated by the plus sign, and a minus sign indicates that heat is liberated. The various ΔH_d values were calculated from the results published by Richards and Rowe (*J. Amer. Chem. Soc.*, 1921, **43**, 779), Richards and Dole (*ibid.*, 1929, **51**, 794), Robinson (*ibid.*, 1932, **54**, 1311), and Lange and Streek (*Z. physikal. Chem.*, 1931, *A*, **152**, 1). (Some of these authors use signs other than those employed in the present paper in order to indicate whether a reaction is exo- or endo-thermic.) It follows from the results of experiments (*J.*, 1952, 492) that the distribution ratios, ρ, are of the order of unity and that the interaction between calcium alginate and calcium or sodium chloride is wholly reversible, *i.e.*, the permeant electrolyte can be completely removed from the gel. It was also established that the cellulose used for runs 3—5 in Table 2 does not form a water-insoluble addition product with sodium or calcium chloride, and that, on addition of these salts, hydrogen ions are not released.

TABLE 1. *Heat change accompanying the interaction of* 0·0400 *cm.*^{3} *of* 1N-*sodium chloride solution with* 0·022 g. *of fully-swollen calcium alginate fibre of* 0·02 *cm. diameter.* (Temp. 19·6°; heat input during calibration, 2·31 × 10^{-3} cal.)

Area (in cm.^{2}) under curve obtained by plotting galvanometer deflection against time	Run	+53	+44	+50	+52	+66	+64	+49	+55
	Calibration	−43	−35	−40	−36·5	−39·5	−46	−30	−35
Heat of reaction (cal. × 10^{-3})		+3·0	+2·9	+2·9	+3·3	+3·8	+3·2	+3·8	+3·6

TABLE 2. *Results of heat measurements.*

Ref. No.	Gel on thermopile	Dry wt. of gel, mg.	Gel water, mg.	Electrolyte in soln.*	Temp.	No. of runs	$\Delta H_{\text{exp.}}$ (cal. × 10^{-3})	ΔH_d (cal. × 10^{-3})	$\Delta H_{\text{exp.}} - \Delta H_d$ (cal./g. dry gel)
1	Calcium alginate fibre †	1·76	20·2	1·0N-NaCl	19·6°	8	+3·31 ± 0·12	+2·9 ± 0·1	+0·2 ± 0·1
2	Calcium alginate strip ‡	1·76	20·2	1·0N-NaCl	20·0	17	+3·99 ± 0·16	+2·9 ± 0·1	+0·6 ± 0·1
3	Cellulose §	6·0	22·0	1·0N-NaCl	19·9	11	+2·86 ± 0·13	+2·2 ± 0·1	+0·12 ± 0·04
4		6·0	22·0	1·0N-NaCl	12·8	10	+3·83 ± 0·18	+5·5 ± 0·5	−0·28 ± 0·1
5		8·1	29·0	1·07N-CaCl$_2$	23·5	4	−3·5 ± 0·3	−1·9 ± 0·2	−0·20 ± 0·06
6	Calcium alginate fibre †	2·24	30·0	2·13N-CaCl$_2$	20·0	5	−11·1 ± 0·5	−4·0 ± 0·2	− 3·2 ± 0·3
7		2·24	30·0	1·07N-CaCl$_2$	20·0	5	−6·8 ± 0·4	−1·7 ± 0·2	− 2·3 ± 0·3
8		2·24	30·0	0·504N-CaCl$_2$	20·2	3	−2·4 ± 0·3	−0·79 ± 0·08	− 0·7 ± 0·2
9		2·24	30·0	0·106N-CaCl$_2$	23·8	2	−0·4 ± 0·1	−0·14 ± 0·02	− 0·3 ± 0·1
10		2·24	30·0	0·106N-CaCl$_2$	23·8	2	−0·4 ± 0·1	−0·14 ± 0·02	−0·12 ± 0·06
11	Calcium alginate strip ‡	4·3	54·0	1·07N-CaCl$_2$	25·6	3	−5·6 ± 0·6	−3·7 ± 0·1	− 0·4 ± 0·2

* 0·040 cm.^{3} of electrolyte solution were used in all runs except Nos. 3, 4, and 6, for which 0·02 cm.^{3} were used.

† Diameter 0·02—0·03 cm.; surface/volume ratio 100—250 cm.$^{-1}$.

‡ 0·2 cm. wide, 3·6 cm. long; surface/volume ratio 35 cm.$^{-1}$.

§ Whatman No. 41 filter-paper strips 0·2—0·25 cm. wide, 3·6 cm. long; ash content, <0·1%.

DISCUSSION

The reaction between calcium alginate and sodium chloride solution (Ref. Nos. 1 and 2 in Table 2) involves cation exchange, and in the first set of measurements, in which thin fibres were used, a thermal effect due to the axial contraction of the test pieces may also play a role.* It can be shown with the help of a simple thermodynamic cycle that $\Delta H_{\text{exp.}}$, the experimentally determined over-all heat of reaction, is given by

$$\Delta H_{\text{exp.}} = \Delta H_d + \Delta H_s^{\text{salt}} - \Delta H_s^{\text{water}} + \Delta H_i + \Delta H_c \quad . \quad . \quad . \quad (1)$$

where ΔH_d is the heat of dilution of the electrolyte, in the absence of the gel, as defined above, ΔH_s^{salt} and $\Delta H_s^{\text{water}}$ are heats of swelling of the dry gels, the swelling medium being respectively the solution of sodium or calcium chloride and water, ΔH_i is the heat of calcium–sodium ion exchange, and ΔH_c is the heat of contraction of the fibres. The observations mentioned on p. 496 and in the preceding paper make it probable that on replacement of non-permeant calcium by sodium ions and on contraction of an alginate fibre heat is liberated. Numerical values of ΔH_i and ΔH_c, relating to the concentration conditions of the calorimetric measurements, cannot be estimated; it is merely possible to conclude that the difference between $\Delta H_{\text{exp.}}$ and ΔH_d, as listed in the first two lines of the last column of Table 2, is numerically smaller than the difference between ΔH_s^{salt} and $\Delta H_s^{\text{water}}$. The interactions between cellulose and sodium or calcium chloride and between calcium alginate and calcium chloride, on the other hand, are relatively simple, because a significant cation replacement or an alteration of the shape of the gel does not occur. It is justifiable, therefore, to assume that in runs Nos. 3—11 of Table 2 the over-all heat, $\Delta H_{\text{exp.}}$, is given by the first three terms on the right-hand side of (1).

The reactions at 19·6—25·6° can be divided into two groups (*A*) and (*B*), according to whether the gels are brought into contact with sodium chloride or calcium chloride solution. In the former case, the sign of $\Delta H_{\text{exp.}} - \Delta H_d$ is positive, the numerical value of the difference being between 0·1 and 0·6 cal./g. of dry gel; and thus $\Delta H_s^{\text{salt}} - \Delta H_s^{\text{water}}$ is also a positive quantity. By taking into account the specified convention regarding thermochemical signs, it follows that a positive value of $\Delta H_s^{\text{salt}} - \Delta H_s^{\text{water}}$ indicates an interaction between the dry gel and the water which is energetically more favourable than that between the dry gel and the salt solution. In case (*B*), on the other hand, the difference $\Delta H_{\text{exp.}} - \Delta H_d$ is negative, the numerical values ranging from 0·1 to 3·2 cal./g. of dry gel. In these processes $\Delta H_s^{\text{salt}} - \Delta H_s^{\text{water}}$ must also be a negative quantity, and it can be deduced, therefore, that here the swelling in the salt solution is energetically more favourable than the swelling in water.

The two cases (*A*) and (*B*) can be regarded as representing typical examples showing the kind of energetic conditions conducive either for salting out or for salting in of certain colloids, as brought about by simple electrolytes.

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* The change in shape of the alginate strips, used in runs No. 2, is relatively small.