

from a single one by a suitable multiplication of the scale of the  $r$  and  $P_r$  co-ordinates.

It is not possible to derive any simple expression for the value of  $r$  at which the maximum occurs in the  $rP_r$  against  $r$  curve, but it is possible to derive such a relationship for the occurrence of a maximum in the  $r^{(2\beta-1)/(\beta-1)} P_r$  against  $r$  curve by simple differentiation. The maximum occurs at

$$r = \frac{M_0}{\alpha_0 \beta} \frac{3\beta - 2}{(M/M_0)^\beta - 1 - 1} \ln (M/M_0). \quad (4)$$

Comparison of the calculated value of  $r$  from equation (4) with that derived from the experimental values of Evans gives  $9.2 \times 10^3$  calculated compared with  $10 \times 10^3$  experimental. The agreement is rather better than the fit of the experimental and calculated curves from equation (3) as measured by the maximum in the  $rP_r$  against  $r$  curve, which occurs at  $4.5 \times 10^3$  (experimental) and at  $3.0 \times 10^3$  (calculated).

Thus it can be seen that by adopting the earlier general treatment, not only can the integration be expressed in terms of the well-tabulated incomplete gamma function, but also the variation of distribution with concentration of monomer and initiator can readily be derived. Further, this approach enables an additional test between theory and experiment to be made.

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<sup>1</sup> Baxendale, Evans and Kilham, *Trans. Farad. Soc.*, **42**, 668 (1946).

<sup>2</sup> Baxendale, Bywater and Evans, *Trans. Farad. Soc.*, **42**, 675 (1946).

<sup>3</sup> Herington and Robertson, *Trans. Farad. Soc.*, **38**, 490 (1942).

<sup>4</sup> Pearson, "Tables of the Incomplete Gamma Function" (H.M. Stationery Office, 1922).

### Ionic Exchange and Fibre Contraction

A 0.2 *N* aqueous solution of sodium alginate (molecular weight  $\sim 10^5$ ) was extruded into 1 *N* hydrochloric acid, thus producing alginic acid fibres, which were converted into calcium alginate by immersion in *M*/10 calcium acetate. The well-washed calcium alginate threads, fully swollen with water, contained  $0.37 \times 10^{-3}$  gm.-equiv. calcium per gm., the ratio of equivalent calcium to equivalent water-insoluble acid was 1.0, and the dry weight was about 8 per cent. These fibres were opaque, slightly elastic, birefringent and capable of heterogeneous cation exchange reactions in which a replacement of the calcium by other cations takes place.

During the study of this ion exchange under continuous flow conditions<sup>1</sup>, it was observed that on replacement of the calcium by sodium or potassium a striking change of shape of the fibres takes place. An experiment of this kind was as follows. A calcium alginate thread, fully swollen with water, and 0.4 mm. in diameter, was hung over a hook and rinsed with 1 *N* sodium carbonate, at a rate of flow of 2.0 cm.<sup>3</sup>/sec. During this treatment an initial contraction of the fibre, followed by a lengthening, took place, as shown below:

Time from start of flow (sec.)	0	5	10	20	30	40	50	60
Length of fibre (cm.)	14.0	13.4	13.0	12.6	12.2	12.5	13.3	14.6
Contraction (%)	0	4.5	7	10	13	11	5.5	-5

After 60 sec., the experiment was interrupted in order to weigh the fibre; there was an increase of weight of about 20 per cent. In a control experiment, analyses were carried out after 30 sec., when the maximum contraction had occurred, and it was found that 29 per cent of the calcium had been converted into calcium carbonate, with simultaneous formation of sodium alginate. In estimating the calcium carbonate formed in this double decomposition, the fibre was immersed in water, and carbon dioxide was bubbled through the suspension; the calcium carbonate was thus quantitatively converted into the soluble calcium bicarbonate, while the undecomposed calcium salts were treated with 1 *N* hydrochloric acid, the calcium thus liberated being separately determined.

A similar shortening of various alginate fibres is also brought about by solutions of alkali phosphates, fluorides, oxalates or citrates. In some of these experiments, the contraction was as large as 20 per cent of the original fibre-length, and the weight of the fibre did not change during the shortening. The birefringence of the fibre decreased during the contraction, while the elasticity and the transparency increased. A few preliminary tests were also done under isometric conditions, when a force of at least 3 gm./mm.<sup>2</sup> was observed.

In attempting to explain these effects, it is assumed that the bivalent calcium ions form salt bridges between adjacent alginate chains, thereby building up a three-dimensional network in which the chains formed by repeating *d*-mannuronic acid residues must be relatively straight. On replacing some of the calcium by alkali ions, gel segments will be liberated, which are more flexible than the completely 'vulcanized' structure. The segments will be able, therefore, to take up configurations which are statistically more probable and in which the chains are curled up to a certain extent; this will lead to a shortening of the fibre as a whole. The results obtained with other alginate fibres can be explained along similar lines, but it is not always possible to specify the nature of the inter-molecular cross-links.

In general, the contraction is regarded as a partial gel-sol transition, an interpretation which is also in accordance with the observed change of birefringence, transparency and elasticity. An important condition for fibre contraction appears to be that the replacement of calcium by alkali ions occurs rapidly. A number of experiments, to be described elsewhere, indicate that on slow replacement of the calcium by alkali ions no appreciable contraction of the fibres occurred, which is probably due to a predominating influence of plastic flow. The latter effect is perhaps mainly responsible for the lengthening of the fibres after contraction, but other reactions may also play a part during this stage of the ionic adsorption.

This investigation is being continued and extended to the study of protein and nucleoprotein fibres.

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<sup>1</sup> This technique is similar in principle to that used in chromatographic adsorption analysis, and has also been used for an investigation of the cation exchange properties of the Brown Alga from which the sodium alginate is extracted. See Wassermann, paper submitted to *Proc. Roy. Soc.*