LVII. THE GELATINISATION OF PECTIN IN SOLUTIONS OF THE ALKALIES AND THE ALKALINE EARTHS.

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Pectin substances have been known since the year 1825, when Bracannot¹ extracted from the roots and stems of a number of plants a substance to which he gave the name of pectic acid; about the same time Payen extracted a similar substance from the root of *Ailanthus glandulosa*. This discovery was followed up by other investigators, and Frémy's researches [1848] placed beyond doubt the existence in plant tissues of a class of substances distinct from the celluloses, though strongly resembling them. Frémy shewed that the parent substance, to which he gave the name of pectose, exists together with cellulose in the cell walls of green fruits, as well as in other parts of plants, and passes into solution during the process of ripening; it may also be brought into solution by boiling with acids. To this soluble variety he gave the name of pectin. Pectin undergoes further changes in boiling, and Frémy recognised two distinct varieties, parapectin, which is precipitated by neutral lead acetate, and metapectin, which is produced by boiling pectin or parapectin with acids, and is precipitated by barium chloride. Frémy also discovered the coagulating action of the enzyme pectase. These results have been confirmed and extended by later observers, especially by Mangin [1892, 1893], and a series of pectin substances has been recognised, differing in solubility, coagulable under different conditions, and marked by increasing acidity.

The action of alkalies on pectin was regarded by Frémy and his successors as resulting in the formation of an acid substance to which the name of pectic acid has been given; this being insoluble is precipitated by acids from alkaline solutions of pectin. The insoluble compounds of the alkaline earths

¹ For a résumé of early researches on pectin, see *Science Progress*, 6, 344.

were looked upon as salts of pectic acid, and the action of pectase has been ascribed to the formation of calcium pectate. These conclusions of Frémy have been accepted by later observers; nevertheless the existence of pectic acid, and in particular its action in determining gelatinisation, must be regarded as in the highest degree uncertain. The work of recent years on adsorption compounds has taught us that change of physical properties and state of aggregation frequently occurs without any definite change of chemical composition. Gelatinisation and loss of solubility cannot be regarded as evidence in themselves of chemical change. All that is definitely known of pectin in this connection may be summarised as follows:

(1) Pectin boiled with water and acids becomes increasingly acid in reaction.

(2) It is coagulated reversibly by the alkalis, irreversibly by the alkaline earths; the action of acids on this coagulum leaves in both cases an insoluble residue.

(3) Certain salts, e.g. calcium chloride, in very concentrated solution, bring about a coagulation which is reversible.

(4) Coagulation by pectase is dependent upon the presence of calcium salts [Bertrand and Mallevre, 1894].

Although this last fact can be simply explained by the supposition that pectic acid is produced and is precipitated in the form of its calcium salt, this is quite uncertain, and the identification of this salt with the product of the reaction of pectin with calcium hydroxide is entirely unsupported by evidence.

The chemical composition of pectin has not at present been determined with any certainty. Analyses vary considerably but indicate a composition very near to, if not exactly, that of a carbohydrate; from the fact that pectin substances give furfural on distillation with hydrochloric acid and mucic acid when treated with nitric acid, the presence of galactan and pentosan groups in the complex molecule has been deduced. The analyses indicate that there may be a slight excess of oxygen in the molecule above the carbohydrate percentage, and Tollens [1914] has suggested that this may be explained by the existence of a few carboxyl groups in the molecule; if these are condensed with hydroxyl in the neutral pectin their progressive hydrolysis would account for the increasing acidity of pectin solutions when these are hydrolysed. In conformity with this hypothesis Tollens suggests a formula $6 (\text{C}_{10}\text{H}_{18}\text{O}_9) + \text{O}$ or $5 (\text{C}_{10}\text{H}_{18}\text{O}_9) + \text{C}_{10}\text{H}_{18}\text{O}_{10}$.

The object of the experiments described below was the study of the mechanism of gelatinisation and its dependence upon chemical change in the case of pectin solutions gelatinised by the action of the alkalies and alkaline earths.

Experimental.

The pectin used in the following experiments was prepared principally from limes ; a little lemon pectin was also used. The fruit was cut up and boiled with water for several hours until quite soft ; the liquid was then filtered through muslin and the residue further extracted with boiling water, until the greater part of the pectin had been removed. The liquid was evaporated to a small volume, alcohol was added to precipitate the pectin, and the jelly thus produced was drained through muslin, redissolved in water, and reprecipitated by alcohol many times. No attempt was made to remove calcium salts. The solutions were finally boiled until all alcohol was driven off. With the specimens prepared later solutions were made from the dry powder obtained by washing the pectin jelly with alcohol until most of the water was removed, drying at 100° and powdering. The solutions were distinctly acid and highly viscous, they could be kept indefinitely in the presence of chloroform ; a slight sediment was formed on standing apparently due to the presence of mechanically contained impurities. Pectin prepared in this way is readily precipitated by neutral lead acetate, and therefore consists largely, if not entirely, of the variety distinguished by Frémy and Mangin as parapectin ; barium chloride gives no precipitate but concentrated solutions form a jelly on standing.

The following are particulars of the different pectin solutions used :

(a) Prepared from limes ; concentration (determined by evaporating 5 cc. at 100°) 0.48 g. in 100 cc.

(b) Prepared from limes ; concentration 0.25 g. (dry powder) in 100 cc.; ash 2.72 per cent.

Acidity 10 cc. = 0.5 cc. N/25.

(c) Prepared from lemons ; concentration approx. 0.25 g. (dry powder in 100 cc.); determined by evaporating 5 cc. at 100° = 0.31 g. in 100 cc.

Acidity 10 cc. = 0.3 cc. N/25.

The weight of residue left by evaporating solution (b) to dryness was not determined ; the concentrations of (b) and (c) were nearly the same, (b) being slightly the more concentrated.

MEASUREMENTS OF THE RATE OF PRECIPITATION OF PECTIN BY
THE ALKALIES AND ALKALINE EARTHS.

If solutions of the alkaline earths are added to a solution of pectin containing 1 per cent. or even less, a stiff jelly is produced; concentrated solutions of potassium hydroxide produce a similar effect. If the pectin solution is very dilute, a gelatinous precipitate is formed, resembling in appearance a small precipitate of aluminium hydroxide; if the alkali is also sufficiently dilute, the rate of precipitation becomes measurable. In very dilute solutions, if the mixture is allowed to stand without shaking, a very attenuated jelly is formed; this is very unstable; a slight movement causes rifts to form in the jelly, and precipitation takes place almost instantaneously. From this it appears that the first action of barium hydroxide or other alkali is the formation of a continuous jelly, which being mechanically unstable is readily broken up in dilute solution; with a larger excess of hydroxide the mechanical instability is so great that precipitation takes place immediately. That a jelly is formed in the first place is confirmed by the more or less sudden change which takes place in the appearance of the mixture in all cases previous to precipitation. With potassium hydroxide the action is very similar, but very much higher concentrations are necessary for gelatinisation and precipitation, and the precipitate forms less sharply; the rate of precipitation is consequently less easily measured.

The following method was employed for the measurement of the rates of precipitation: the solution of alkali or of alkaline earth was measured into a small flask and diluted to a volume such that with the addition of pectin solution it measured 50 cc. During the experiment the temperature was kept constant (usually at 15°) by immersing the flask in a glass trough filled with water. To ensure immediate precipitation the flask was constantly shaken. The time was measured from the moment at which the addition of pectin solution was made to the moment of precipitation; it was found possible to measure to within a quarter of a minute, and the results obtained usually agreed to within half a minute or less. The pectin solution used for all rate measurements was the solution (a) unless otherwise mentioned.

Precipitation by the hydroxides of the alkaline earth metals.

It was found that in all cases the rate of precipitation was nearly proportional to the square of the concentration; in the following tables the product $\text{time} \times (\text{concentration})^2$ is given for comparison.

In the diagram (Fig. 1) the reciprocals of the times are plotted against the squares of the concentrations.

The effect of change of temperature has not been measured, but the rate increases very rapidly with a small increase of temperature.

Fig. 1. Rate of precipitation of pectin by the alkaline earths (Tables II B, III and IV).

TABLE I.

Rate of precipitation of pectin by barium hydroxide.

Conc. of BaO_2H_2 mg. equiv. per litre c	A. 2 cc pectin in 50 cc.		B. 1 cc. pectin in 50 cc.		C. 0.5 cc. pectin in 50 cc.	
	t (mins.)		t (mins.)		t (mins.)	
	c^2t		c^2t		c^2t	
	1 measurement		1 measurement		2 measurements	
2	35	140	30	120	34	136
3	—	—	—	—	16 ¹	144
4	8.5	136	9	144	9.25	148
6	4	144	4	144	5	180
8	2.5	160	3	192	3	192
10	1.5	160	2	200	2	200

¹ 1 measurement.

Another series gave the following results :

TABLE II.

Rate of precipitation of pectin by barium hydroxide.

Conc. of BaO_2H_2 mg. equiv. per litre c	A. 3 cc. pectin in 50 cc.		B. 2 cc. pectin in 50 cc.	
	t (mins.)		t (mins.)	
	c^2t		c^2t	
	1 measurement		2 measurements	
2	47.5	190	41.9	167
3	17 ¹	153	16.25	146
4	9.25	148	9.1	146
5	—	—	6.0	150
6	4	144	4.1	148
8	2.5	160	2.4	152
10	1.75	175	1.6	162

¹ 2 measurements.

The series in Table II is the more accurate; in the most dilute pectin solutions the precipitate does not form very sharply.

TABLE III.

Rate of precipitation of pectin by strontium hydroxide.

Conc. of SrO_2H_2 mg. equiv. per litre c	2 cc. pectin in 50 cc.	
	t (mins.)	c^2t
	2 measurements	
4	17.25	276
5	10.0	250
6	7.6	274
8	4.6	296
10	3.4	337

TABLE IV.

Rate of precipitation of pectin by calcium hydroxide.

Conc. of CaO_2H_2 mg. equiv. per litre c	A. 2 cc. pectin in 50 cc.		B. 1 cc. pectin in 50 cc.	
	t (mins.)	c^2t	t (mins.)	c^2t
	2 measurements		2 measurements	
2.6	37.4	253	30.9	209
3.5	19.25	236	16.9	206
4.4	11.5	223	11.0	213
5.3	8.1	228	7.9	222
6.2	6.0	231	6.5	250
7.0	4.5	220	4.75	233
7.9	3.6	226	3.9	242

A direct comparison was made of the rates of precipitation by barium, strontium, and calcium hydroxides in equivalent quantities. The following results were obtained:

TABLE V.

mg. equiv. per litre c	3 cc. of pectin solution (c) in 50 cc.					
	t (mins.)					
	Ba		Sr		Ca	
4	14		18		17	
3.8	6.5		9	9.75	7.5	8
9.9	2.5	2.5	3.75	4	3.25	3.25

In comparing the foregoing results, it must be remembered that the time measured is that necessary for precipitation, and not that which is required for the formation of the jelly. As soon as the jelly forms absorption of hydroxide takes place, and this causes the framework of the jelly to stiffen and contract, so that spontaneous precipitation takes place at all but very

small concentrations ; at these concentrations precipitation can be brought about by shaking, but it is probably necessary in this case also for a certain amount of absorption to take place in the jelly before it can be precipitated. This amount will obviously vary with the character of the jelly, and is probably less for barium, which gelatinises very readily, than for strontium or calcium. The rate of absorption will depend upon the concentration of the hydroxide and the absorption capacity of the jelly ; the latter factor is markedly greater for calcium than for the other hydroxides.

The abnormality of the strontium curve in position and character is probably due to the influence of the absorption factor in precipitation, which

TABLE VI.

Rate of precipitation of pectin solutions of varying concentrations by barium hydroxide (conc. 4 mg. equiv. per litre).

Conc. of pectin cc. solution (a) in 50 cc.	t (mins.)			
	I.		II.	
1	16.5	16.5	14	15.5
2	13	10.5	13.5	—
3		10		10.75
4		9.5		—
5		9.5		9.5
10		9		8.5
15		9		—
20		9		—
25		—		—
30		10		9.5
40		—		—
50		—		10.5

becomes unimportant for barium on account of the insolubility of the jelly, and for calcium on account of the rapidity with which absorption takes place. The effect will be that a quantity will be added to the time required for gelatinisation, which will decrease as the concentration increases, but will increase relatively to the total time of precipitation, thus causing the precipitation constant to increase. A slight increase of the precipitation constant is to be observed in the barium curves also. This increase in the precipitation constant cannot be ascribed to changes in the degree of dissociation, even where, as for barium hydroxide, the change would be of a corresponding order of magnitude in the two cases, for the conductivity curve shews that at the concentrations employed barium hydroxide dissociates according to the equation

no non-ionised hydroxide being present, and it will be evident from the results and conclusions to be given below that the formation of BaOH^+ ions is unlikely to affect the rate of precipitation. These remarks anticipate results and conclusions which will be given in detail at a later stage.

The effect of varying the quantity of pectin is shewn in Tables VI and VII.

TABLE VII.

Rate of precipitation of pectin solutions of varying concentrations by strontium hydroxide (conc. 5 mg. equiv. per litre).

Conc. of pectin cc. solution (a) in 50 cc.	<i>t</i> (mins.)
1	10.25
3	10.25
4	10.50
5	11.75

These tables shew that for very dilute solutions the rate of precipitation increases with increase in the quantity of pectin present; for larger concentrations an opposite effect is produced and the rate of precipitation gradually decreases.

The effect of salts on precipitation.

Potassium chloride added to a solution of barium hydroxide retards the precipitation of pectin; this is to be expected as double decomposition will take place to some extent.

TABLE VIII.

Rate of precipitation of pectin by barium hydroxide in the presence of potassium chloride.

2 cc. of pectin solution in 50 cc.	
Conc. of BaO_2H_2 4 mg. equiv. per litre.	
Conc. of KCl mg. mols. per litre	<i>t</i> (mins.)
0	9.1
10	10.75
20	11.5

The effect of salts having a common ion is to increase the rate of precipitation; it has been possible to measure the accelerating effects for both ions, since potassium hydroxide in dilute solution has itself no precipitating action on pectin.

TABLE IX.

Rate of precipitation of pectin by barium hydroxide in the presence of salts having a common ion.

A. 2 cc. of pectin solution in 50 cc.
Conc. of BaO_2H_2 4 mg. equiv. per litre.

Conc. mg. equiv. per litre	<i>t</i> (mins.)		
	BaCl_2		KOH
	I. (1 measurement)	II. (2 measurements)	(1 measurement)
2	7	7.25	6.25
4	6	5.75	4.75
6	5	4.75	3.5
8	4	4.25	3.25
10	3.5	3.75	3.00

B. 2 cc. of pectin solution in 50 cc.
Conc. of BaO_2H_2 2 mg. equiv. per litre.

Conc. mg. equiv. per litre	<i>t</i> (mins.)	
	BaCl_2 (2 measurements)	KOH (1 measurement)
2	21.4	17.5
4	16.4	11.75
6	13.4	10
8	11.75	8
10	9.5	—
12	9.25	—
20	—	3.25

C. 0.5 cc. of pectin solution in 50 cc.
Conc. of BaO_2H_2 4 mg. mols. per litre.

Conc. mg. equiv. per litre	<i>t</i> (mins.)	
	BaCl_2 (1 measurement)	KOH (1 measurement)
2	8.5	7
4	7	5.5
6	6.5	5
8	5.5	4.5
10	5.5	3.5
20	4.5	—

The corresponding measurements for calcium chloride were found to be partially invalidated by impurities in the calcium chloride and are therefore omitted; the results were however similar. Tables of the effect of strontium chloride and nitrate on strontium hydroxide and of potassium hydroxide on calcium hydroxide are given.

TABLE X.

Rate of precipitation of pectin by strontium hydroxide in the presence of strontium salts.

2 cc. of pectin solution in 50 cc. Conc. of SrO_2H_2 4 mg. equiv. per litre.		
Conc. (mg. equiv. per litre) $\text{Sr}(\text{NO}_3)_2$ and SrCl_2	<i>t</i> (mins.)	
	$\text{Sr}(\text{NO}_3)_2$ (3 measurements)	SrCl_2 (1 measurement)
2	10.75	12
4	8.6	10
6	7.6	9.25
8	6.9 ¹	—
10	6.25	7.75
14	5.25	6.25
20	4.65	5.25

¹ 2 measurements.

TABLE XI.

Rate of precipitation of pectin by calcium hydroxide in the presence of potassium hydroxide.

2 cc. of pectin solution in 50 cc. Conc. of CaO_2H_2 3.5 mg. equiv. per litre.	
Conc. of KOH (mg. equiv. per litre)	<i>t</i> (mins.) (2 measurements)
2	13.1
4	9.9
6	8.75
8	7.1
10	6.4
12	6.0
20	4.5

It will be observed from these tables that the rate of precipitation is accelerated both by potassium hydroxide and by the salts of the alkaline earth metals; the effect of the latter is less than that of potassium hydroxide. It is of course possible that the anion exerts an inhibitory effect; but this is an unlikely supposition since, as is shewn later, the effect of potassium salts on the rate of precipitation by potassium hydroxide is nearly identical, and since chloride ions are not appreciably absorbed by the pectin jelly. The absorption of other anions has not been determined, but there is no reason to suppose the chloride ion in any way exceptional. A large part of the difference in the rates for barium chloride and potassium hydroxide is certainly due to the incomplete dissociation of the former; the uncertainty

as to the dissociation of divalent salts makes it difficult to say whether the whole difference can thus be accounted for, but the similarity of the two curves (see Fig. 2) makes this very probable; it is possible however that a small part of the discrepancy may be due to absorption effects. The conductivity curves for strontium chloride and nitrate are very uncertain at great dilutions; they however indicate that the dissociation of strontium chloride falls off with considerably greater rapidity than that of the nitrate as concentration increases, and this difference probably suffices to account for the small differences in the rates measured.

Fig. 2. Rate of precipitation of pectin by barium hydroxide in the presence of barium chloride and potassium hydroxide (Table IX A, B).

Since the rate of gelatinisation of pectin is proportional to the square of the concentration of the hydroxide added, and is accelerated by the addition of either ion, it is concluded that the rate of gelatinisation is proportional to the product of the concentrations of alkaline earth metal and hydroxyl; the following table gives the value of this product for equal times in the case of:

- (1) barium hydroxide (C_1),
- (2) barium hydroxide and barium chloride (C_2),
- (3) barium hydroxide and potassium hydroxide (C_3),

assuming complete dissociation; the values of the concentrations for equal times are obtained by interpolation from the results in Table II B and Table IX A.

TABLE XII.

Value of the product $Ba \times OH$ for equal values of t .

t	BaO_2H_2 C_1^2	$BaCl_2 + 4$ mg. equiv. BaO_2H_2 per litre $4(C_2 + 4)$	$KOH + 4$ mg. equiv. BaO_2H_2 per litre $4(C_3 + 4)$
3	52	—	56
4	36	46	35
5	29	37	30
6	23	30	20
7	18	21	—

Fig. 3. Rate of precipitation of pectin by potassium hydroxide and by mixtures of potassium hydroxide and potassium salts.

(a) c = conc. of potassium salts in the presence of 290 mg. equiv. per litre of potassium hydroxide.

(b) c = conc. of potassium ions above 244 mg. equiv. per litre.

As will be seen the values for additions of potassium hydroxide correspond very closely with those for barium hydroxide alone; for barium chloride the percentage difference decreases as the concentration decreases.

Precipitation by Potassium Hydroxide.

TABLE XIII.

Rate of precipitation of pectin by potassium hydroxide.

2 cc. of pectin solution in 50 cc.		
Conc. (c) mg. equiv. per litre	t (mins.) 2 measurements	$(C - 310) t$
319	15.15	186
348	5.75	218
377	3.1	209
406	2.25	216
464	1.4	212

The values of $1/t$ plotted against the concentration (Fig. 3 (a)) give a straight line cutting the x axis at the concentration 310; the values of the constant $(C - 310) t$ are given in the table.

The following table shews the effect on the rate of precipitation of additions of various potassium salts to potassium hydroxide.

TABLE XIV.

Rate of precipitation of pectin by potassium hydroxide in the presence of potassium salts.

2 cc. of pectin solution in 50 cc.
Conc. of KOH 290 mg. equiv. per litre.

Conc. mg. equiv. per litre	KCl t (mins.) 2 measurements	KNO ₃ t (mins.) 2 measurements	K ₂ CO ₃ t (mins.) 2 measurements	K ₂ SO ₄ t (mins.) 2 measurements
40	9.5	9.0 ¹	14	10.75
60	6.0	5.75	—	7.50
80	4.5	5.0	7.25	6.0
120	2.6	3.0	4.50	3.4
160	1.6	1.9	3.25	2.9
200	1.1	1.75	2.4	2.4

¹ 1 measurement.

Fig. 3 (a) shews these results graphically, the reciprocals of the values of t being plotted against the concentrations; the curves thus obtained only diverge slightly from a straight line, except in the case of potassium chloride.

If however the values of $\frac{1}{t}$ are plotted against the concentrations of the potassium ion, a different result is obtained; the curves for KCl, KNO₃ and K₂SO₄ fall together at the lower concentrations, though they diverge slightly as the concentration increases, and the curves for KCl and KNO₃ for which

the measurements extend further than those for the salts of the dibasic acids shew marked curvatures towards the y axis. For the sake of clearness the mean curve for the three salts is given in the figure (Fig. 3 (b)); the curve for potassium carbonate is shewn separately. The discussion of these results is deferred until later.

The calculation of the ionic concentrations was made on the assumption that for salts of monobasic acids $C_3 = C_2 (C_1 + C_2)$ and of dibasic acids $C_3 = C_2 (C_1 + C_2)^2$, where

C_1 = concentration of KOH,

C_2 = concentration of salt,

C_3 = that concentration at which the salt in pure solution is equally dissociated.

If the square root or cube root of the product of the ions be taken to represent the effective ionic concentration, we have

$$C_3^2 \alpha_3^2 = C_2 (C_1 + C_2) \tau_1 \sigma_2$$

and

$$C_3^3 \alpha_3^3 = C_2 (C_1 + C_2)^2 \tau_1^2 \sigma_2,$$

where α_1 represents the mean dissociation of the mixture of salt and potassium hydroxide; for salts of monobasic acids $\alpha_1 \alpha_2 = \alpha_3^2$ approximately; the formula will therefore enable the degree of dissociation of the salt in the mixture to be calculated with fair accuracy; for salts of dibasic acids $\alpha_1^2 \alpha_2 > \alpha_3^3$, the value found for C_3 will therefore be too small and the degree of dissociation too high; for small concentrations however the percentage error is not very great.

The following table gives the data for the calculation of the degree of dissociation of the various salts between the concentrations 40 and 200 mg. equiv. per litre in the presence of potassium hydroxide at a concentration of 290 mg. equiv. per litre.

TABLE XV.

Salt	Concentration (c)	C_3	λ	λ_∞	α
KCl	40	115	1040	1240	84
	200	313	985	—	79.5
KNO ₃	40	115	970	1180	82
	200	313	875	—	74
K ₂ CO ₃	40	163	850	1300	65.5
	200	363	775	—	59.5
K ₂ SO ₄	40	163	855	1310	65.5
	200	363	780	—	59.5
KOH	290	290	1905	2270	84
	319	319	1895	—	83.5
	464	464	1853	—	81.5

The concentrations of dissociated salt (C) corresponding to the concentrations in Tables XIII and XIV and the product of these concentrations with α are therefore as follows :

TABLE XVI.

A. KOH.				
	C		αC	
	290		244	
	319		266	
	348		289	
	377		311	
	406		334	
	464		378	
B. Salts.				
	KCl	KNO ₃	K ₂ CO ₃	K ₂ SO ₄
C	αC	αC	αC	αC
40	34	33	26	26
60	50	49	39	39
80	66	64	51	51
120	98	94	75	75
160	129	122	98	98
200	159	148	119	119

The decrease in the dissociation of KOH with increasing salt concentrations has been disregarded.

The following table shews the action of potassium chloride on varying quantities of potassium hydroxide :

TABLE XVII.

5 cc. of pectin solution (c) (from lemons) at 20°.		
Conc. mg. equiv. KOH per litre	Conc. mg. equiv. KCl per litre	t (mins.) 1 measurement
686	0	1.5
343	200	2.5
171	300	5.25
103	340	14

ABSORPTION OF THE ALKALINE EARTHS BY GELATINISED PECTIN.

The process of gelatinisation is accompanied by absorption ; in dilute solution the precipitate can be easily filtered off, and it was possible therefore to determine by titration the quantity of hydroxide that had been absorbed. Since the change of volume on gelatinisation is inappreciable, the following method was adopted for the estimation of the amount of hydroxide absorbed.

A mixture of alkaline earth, pectin and water was made in a flask of known volume and was allowed to stand for a definite time, usually half an hour.

It was then filtered, the first part of the filtrate was rejected and a part of the remainder, usually one-half of the original volume, was titrated with standard acid.

To avoid absorption of carbon dioxide the filtering funnel was fixed in a bell jar, through which passed a funnel provided with a stopcock; a little potash was placed inside the bell jar, and all communications to the outer air were closed with soda lime tubes. After standing, the contents of the flask were emptied rapidly into the stoppered funnel; the first part of the filtrate was then allowed to run through, after which the whole apparatus was removed, so that the filter drained into a dry flask. To ensure constant temperature the whole apparatus, together with the water and solutions, used for the mixture, was kept in a zinc cupboard, maintained at a constant temperature by means of a thermoregulator. A variation of 5° did not affect the results appreciably.

Absorption takes place rapidly, and, except in the case of the most dilute solutions, apparent equilibrium is established in less than half an hour; the following measurements shew the variation in the rate of absorption in very dilute solution.

TABLE XVIII.

Rate of absorption of barium hydroxide in dilute solution by gelatinised pectin.

Final conc. of BaO_2H_2 100 cc. = cc. $\text{N}/25$	Absorption		
	0.5 hr.	1 hr.	2 hrs.
5	1.7	2.0	2.3
	1.8	2.1	2.2
	1.7	—	—
11	2.1	2.2	2.3
	2.1	—	—
38	2.8	—	2.6
	2.6	—	—

It will be noticed that, except at extreme dilution, equilibrium was established within the half hour; the variations for the concentrations 11, though these probably indicate a slight increase, are within the errors of experiment. This however was not true equilibrium, as a slow absorption continued to take place even after several days; this slow absorption may be due to chemical action, but is more probably caused by slow diffusion of hydroxide into the interior of the jelly. A similar effect was observed by Morawitz [1910] in his experiments on the absorption of salts by charcoal,

and was ascribed by him to diffusion. In the case of calcium, which is much more strongly absorbed than either barium or strontium, the increased absorption is appreciable after 4·5–5 hrs. The following measurements for calcium and strontium are given for comparison.

TABLE XIX.

Absorption after 4·5–5 hrs.

Vol. 100 cc. 10 cc. of pectin solution (C).

A. *Strontium Hydroxide.*

Final conc. 100 cc. = cc. N/25	Absorbed	
	after 0·5 hr.	after nearly 5 hrs.
11	2·1	2·2
36	2·9	2·9
90	3·6	3·8

B. *Calcium Hydroxide.*

	after 0·5 hr.	after 4·5 hrs.
8	2·5	2·7
	2·5	—
	2·5	—
27–29	3·1	3·5
	3·2	after 24 hrs.
		4·8

In these experiments the absorption was determined by titrating with N/25 HCl and phenolphthalein in the cold; the alkaline earth solution was added from a pipette, which was washed out into the flask; water and pectin were then added, and the flask was filled to the mark and thoroughly shaken. In all the absorption experiments the water used was boiled to free it from carbon dioxide. The order in which the mixture was made—whether it was diluted before or after the addition of pectin—was found to be without effect. The concentration of hydroxide was determined for each measurement by a blank titration in which pectin was absent. The mixture was allowed to stand half an hour, and the amount of absorption was then measured by the difference in the value given by the titration of 50 cc. in the two cases, the mixture having been filtered as described above. The absorption at this point was assumed to have attained a definite state, probably by saturation of the outer layer of the jelly-forming substance; that this assumption is justified is confirmed by the regularity of the absorption curves obtained. Differences between two titrations giving the amount absorbed usually agreed within less than 0·1 cc.; the greatest variations amounted to 0·15. These are doubled in the table which expresses the absorption for the total volume.

TABLE XX.

*Absorption of the alkaline earths by gelatinised pectin.*Vol. 100 cc. 10 cc. pectin solution (C). T 20°–25°.

BaO ₂ H ₂ 2 measurements		SrO ₂ H ₂ 1 measurement		CaO ₂ H ₂ 2 measurements	
Final conc. 100 cc. = cc. N/25	Absorbed cc. N/25	Final conc. 100 cc. = cc. N/25	Absorbed cc. N/25	Final conc. 100 cc. = cc. N/25	Absorbed cc. N/25
11	2.1	11	2.1	8	2.5
38	2.7	36	2.9	30	3.15
66	3.0	—	—	51	4.05
94	3.2	90	3.6	73	4.55

Fig. 4. Absorption of alkaline earths by pectin (Tables XX. XXI).

It will be seen (Fig. 4) that these points lie on converging straight lines which nearly meet on the y axis; if Table XVIII be referred to it will also be noticed that, even at very great dilutions, the amount of barium hydroxide absorbed coincides with the corresponding line, if sufficient time be allowed for equilibrium to be established. Strontium and calcium do not gelatinise pectin so readily, and in consequence absorption cannot be determined at equally great dilutions; this is especially the case for strontium.

It was unfortunately impossible to extend these results as material was lost during an interruption of the work, and the concluding experiments were made with a very limited quantity of pectin; some earlier measurements are however given, made with a different specimen of pectin, which shew the effect on the absorption of increasing the concentration of the pectin. The measurements are not quite so accurate as the preceding, the method

employed being slightly different ; the concentration of the calcium hydroxide was in this case determined by titration of the original solution, and a measured volume of this solution was added from a pipette. This method had two defects, which were avoided by the method described above ; the amount of carbon dioxide absorbed during the mixing process was unchecked, and the delivery of calcium hydroxide solution from the pipettes was not quite regular, this being due to a tendency of the solution to behave towards glass as to a greasy surface, in consequence of which drops were liable to adhere to the pipette. The flasks and pipettes used were carefully calibrated. In a given series the greatest differences between two measurements of the absorption was 0.3 c.c.

TABLE XXI.

*Absorption of calcium hydroxide by gelatinised pectin.*Vol. 100 cc. T 18°–20°.

A. 20 cc. of pectin solution (b).

Final conc. 100 cc. = cc. N/25	Absorbed cc. N/25		Mean
	Series I (2 measurements)	Series II (2 measurements)	
24	6.3	6.15	6.25
33	(7.3)	6.55	6.55
43	6.9	6.8	6.85
52	7.45	7.65	7.55
62	7.65	7.95	7.8

B. 10 cc. of pectin solution (b).

Final conc. 100 cc. = cc. N/25	Absorbed cc. N/25 (2 measurements)
16	3.55
26	3.8
35	4.5
45	4.65
65	4.85

The mixture was left for half an hour as in the preceding measurements, and equilibrium was tested by measuring the absorption after 1 hour at low and high concentrations. The corresponding curves are shewn in Fig. 4 I, II.

Absorption in the presence of calcium or barium chloride.

A fairly concentrated solution of calcium chloride was necessary to increase the absorption by a measurable amount ; the following table shews the increase in absorption for different concentrations of calcium hydroxide ; 30 cc. or 70 cc. of approximately N/25 calcium hydroxide were mixed with 20 cc. of pectin and varying quantities of calcium chloride, and the volume was made up to 200 cc.

TABLE XXII.

Absorption of calcium hydroxide by gelatinised pectin in the presence of calcium chloride.

Vol. 200 cc. 20 cc. of pectin solution (b). T 18°–20°.

A. 70 cc. CaO_2H_2 added : final conc. 200 cc. = 62–66 cc. N/25.

cc. N/25 CaCl_2	Absorption			
	(1)	(2)	(3)	Mean
0	7.25	7.25	7.25 ¹	7.25
10	7.7	7.7	7.45	7.62
50	8.4	8.25	8.35	8.33

B. 30 cc. CaO_2H_2 added : final conc. 200 cc. = 23–26 cc. N/25.

0	5.8	5.8	5.85 ¹	5.82
10	(6.9)	6.15	—	6.15
50	6.7	6.7	—	6.7

¹ After standing 1 hour.

In order to determine whether or not chloride ions were absorbed, 10 cc. of the filtrate from the mixtures A and B of the preceding table, each containing 50 cc. CaCl_2 in 200 cc., were neutralised and titrated with N/10 AgNO_3 , potassium bichromate being used as indicator; 5 cc. of the original CaCl_2

TABLE XXIII.

Absorption of barium hydroxide by gelatinised pectin in the presence of barium chloride.

Vol. 100 cc. 20 cc. of pectin solution (b). T 17°–18°.

A. Final conc. of BaO_2H_2 : 100 cc. = 67–69 cc. N/25.

cc. N/2 BaCl_2	Absorbed		
	(1)	(2)	Mean
0	6.6	6.5	6.55
10	8.2	7.9	8.05
30	8.0	—	8.0

B. Final conc. of BaO_2H_2 : 100 cc. = 9–10 cc. N/25.

5	5.0	4.7	4.85
40	5.1	4.8	4.95

solution required 23.95 AgNO_3 . The equivalent quantities of the solutions to which pectin had been added required :

A. 23.8 cc.

B. 24 cc.

It appears therefore that pectin does not absorb chloride ions.

Table XXIII shews the absorption of barium hydroxide in the

presence of varying quantities of barium chloride; the concentration was determined for each measurement by a blank test in the absence of pectin; titrations were made by adding 20 cc. of N/2 HCl to the mixture where necessary, and titrating with N/25 HCl in the presence of phenolphthalein. In this case the solutions were boiled to eliminate carbon dioxide, but this was found to be without effect upon the result.

Theoretical.

It has been shewn that the rate of precipitation of pectin by the alkaline earths is very nearly proportional to the product of the concentrations of hydroxyl and metallic ion, and that this product may, with great probability, be taken as a measure of the rate of gelatinisation; the theoretical implications of these results remain to be considered.

(1) The fact that both anions and kations are concerned in the precipitation excludes the possibility that the alkali acts by a process of diffusion into the suspended pectin complex, since in this case the rate of diffusion and consequently of precipitation also, would be dependent upon the rate of diffusion of the more slowly moving ion; i.e. the rate of precipitation would be determined in general by the metallic ion alone.

(2) It is also improbable that precipitation is due to surface adsorption. This usually takes place with great rapidity and it is quite unlikely that the process of adsorption would be prolonged through a considerable interval, as in this case; moreover when adsorption occasions precipitation this has been found to be generally due to the adsorption of an ion having a charge opposite to that of the adsorbent [see especially Morawitz, 1910]. Since both positive and negative ions are concerned in the precipitation of pectin, this cannot be due to any change of potential brought about by adsorption.

(3) A third possibility is that the rate of gelatinisation is a measure of the rate of chemical change.

It may be seen from the measurements of absorption that the amount of alkaline earth which combines with pectin is small, therefore the concentrations of alkaline earth may be taken as constant throughout the time t , and we have on this assumption

$$\frac{dx}{dt} = RC_1C_2(a-x)^p,$$

where a is the initial quantity of pectin present; x is the amount transformed in time t ; C_1 , C_2 the concentrations of metallic ion and hydroxyl.

Putting $p = 1$ we have

$$RC_1C_2 = \frac{1}{t} \log \frac{a}{a-x}.$$

Now $\frac{a}{a-x}$ is constant for all the measurements of a series since it must be presumed that gelatinisation occurs when a definite quantity of pectin has undergone change.

Hence

$$C_1C_2t = K.$$

It is therefore possible to express the rate of gelatinisation of pectin as determined by the velocity of a chemical change in which pectin reacts with barium, strontium or calcium and hydroxyl ions ; the reaction equation will probably be of the form

It may be observed in Tables I-IV that the value of the constant c^2t is usually too high for the first measurement of the series, and that the error is greater, the greater the quantity of pectin present ; this may be accounted for not only by the slight acidity of the pectin but also by the fact that when the value of c is very small, an appreciable error is made in taking c as constant throughout the time t .

It has been shewn that the rate of precipitation of pectin by potassium hydroxide is conditioned by the concentration of potassium ions ; it is to be remarked, however, that gelatinisation does not take place below a definite and fairly high concentration. Since above this concentration the rate of gelatinisation increases proportionately to the increase of concentration, it may be assumed that hydrolysis takes place, and that the reaction may be represented by the equation

which takes place in both senses ; the pectin cannot be itself dissociated since the reaction takes place slowly, and therefore could only take place between ions if it were dependent upon a process of diffusion, which has been shewn to be extremely improbable. The equation shews that the rate of reaction for a given concentration of hydroxyl will be determined by the concentrations of the potassium ions.

The hypothesis of chemical change affords therefore a partial explanation of the character of the curves shewn in Fig. 3. These curves indicate, however, that while for small additions of salt the rate of precipitation is nearly pro-

portional to the increase of the potassium ions, for larger additions the rate of precipitation increases more rapidly, the effect being ultimately greater than that produced by an equal quantity of potassium hydroxide ; moreover the specific character of the salt begins to assert itself. This appears to point to a molecular reaction between salt and pectin, and this reaction as is to be expected is more evident in the case of the salts of monobasic than in that of those of dibasic acids. The curve for potassium carbonate suggests that the error in the calculation of the degree of dissociation is preceptibly greater in this case than in that of potassium sulphate, which is probable since the ordinary solution of potassium carbonate contains hydrolysed salt, whereas in the present case hydrolysis is prevented by the excess of potassium hydroxide.

The hypothesis of a reaction between salt molecules and pectin is supported by the general analogy between the reactions described here and those of the sugar group. The constitution of the so-called saccharates and the analogous glucose compounds with the alkaline earths is doubtful, but formulae of the type assumed here for the pectin compounds, in which CaOH or its analogues replace a hydrogen atom, e.g. $\text{C}_{12}\text{H}_{21}(\text{CaOH})\text{O}_{11}$, $\text{C}_6\text{H}_{11}(\text{CaOH})\text{O}_6$, are not improbable, and have been strongly supported by some investigators [see especially Lippmann, 1904, p. 1701]. Compounds with the alkalis are similarly formed, e.g. $\text{C}_{12}\text{H}_{21}\text{KO}_{11}$ [Tollens, 1914, p. 400]. The sugars are also known to form molecular compounds with sodium chloride and many other salts [Tollens, 1914, p. 401 ; Lippmann, 1904, p. 1323].

In the ordinary notation the equation

$$\frac{dx}{dt} = KC_1C_2(a-x)$$

represents the reaction of one molecule of pectin with e.g. the ions Ba and OH . Now the molecule of pectin is certainly large, and is made up, at least to a very great extent, of condensed carbohydrate groups ; these groups will be largely independent of one another, and therefore it is probable that for the purposes of this equation they may be regarded as independent molecules. The equation will therefore represent the rate of reaction of a carbohydrate group with the ions Ba and OH , rather than that of the whole complex molecule.

The rate of reaction of pectin with barium hydroxide (Table VI) increases with the concentration of the pectin while this is very small ; at higher concentrations the rate becomes stationary, and it finally decreases. There is probably more than one cause for this behaviour. The fact that the rate

of reaction decreases much more rapidly for strontium than for barium suggests that absorption plays an increasing part, and that for the reason given on page 558, gelatinisation and precipitation become less and less coincident as the concentration of pectin increases. But besides this other factors may be brought into play; unchanged pectin probably acts to impede gelatinisation, and there is good reason to believe that the degree of dispersion of pectin decreases with the concentration, so that the active mass will increase less rapidly than the concentration; the importance of this latter factor in dilute solution is however entirely problematical.

Turning now to the absorption compounds which gelatinised pectin forms with the alkaline earths, it must be remarked that the term "absorption compound" has been used in its most general sense to denote a compound of continuously varying composition. Reference to the curves in Fig. 4 shews that the absorption curves are straight lines cutting the y axis at varying points. The simplest explanation of a straight line absorption curve is that of solid solution. Surface adsorption is precluded both by the character of the curve and by the slowness with which the condition of equilibrium is reached at small concentrations, which again favours the hypothesis of a solid solution. If surface adsorption occurs at all it must be to a very small extent.

If V be the volume of the jelly; A the amount of alkaline earth absorbed; N the partition coefficient of alkaline earth between jelly and solution, we have for a solid solution at concentration C

$$\frac{CV + A}{CV} = N, \quad \text{i.e. } A = CV(N - 1),$$

which gives a straight line when V is constant.

It has been shewn that a true equilibrium is not reached under the conditions of the experiments, and that absorption continues for days, probably owing to a slow process of diffusion. This has been taken to mean that the apparent equilibrium is due to saturation at the surface; V will consequently be a function of the surface area. Now $V(n - 1) = \tan \theta$ if θ is the angle the absorption curve makes with the axis of x , and it will be seen by comparing curves I and II Fig. 4 that $2 \tan \theta_2$ is greater than $\tan \theta_1$; accordingly $\frac{V_2}{2}$ is greater than V_1 , i.e. the specific surface increases as the concentration of the pectin decreases.

The absence of surface adsorption is important, since in this case the point at which the straight line cuts the y axis will give the composition of

the compound of alkaline earth and pectin. This is confirmed by the convergence of the curves for calcium, strontium and barium (Fig. 4 III, IV, V) which approximately meet at a point on the y axis. These curves give the absorption for 10 cc. of pectin solution (c) in 100 cc.; the solutions were therefore very dilute, and the convergence to a point is to be attributed to this fact. At higher concentrations it is most unlikely that this occurs, and some experimental evidence was obtained on this point, but it needs further investigation.

Taking 1.9 (2.2 – 0.3 for the acidity) as combining with 10 cc. of pectin solution containing approximately 2.5 grms. of dry pectin per litre, we have 330 as the weight of pectin combining with the equivalent of alkaline earth. This figure is certainly too high since the specimen of pectin was not pure, and no allowance was made for the weight of ash. It may be compared with the formula $6(C_{10}H_{18}O_9) + O$ suggested by Tollens. The weight of the $C_{10}H_{18}O_9$ group is 282.

It is well known that the alkaline earths are easily soluble in sugar solution, and cane sugar has been shewn to form a series of solid solutions with lime [Cameron and Patten 1911], so that in this case again the resemblance of pectin to the members of the sugar group is preserved. It has been shewn that calcium chloride as such is not absorbed by pectin; it merely serves to increase the absorption of the calcium hydroxide, and a similar effect is obtained with barium chloride and barium hydroxide. This may be a salting out process, due to decreased dissociation; but it seems more probable, at any rate in the case of calcium, that the chloride increases the solubility of the hydroxide in pectin as it does in water [Cameron and Bell 1907], but to a greater extent, thus increasing the value of the partition coefficient n .

Theory of gelatinisation of pectin.

References to the theory of gelatinisation have been hitherto avoided, and it has been assumed that alterations of physical or chemical properties may suffice to bring this process about, without reference to the mechanism of the change. This now remains to be considered, and it will be necessary, as a preliminary, to discuss shortly the current theories of gelatinisation [see the historical introduction, Bachmann 1912].

Until very recently jellies have been almost universally supposed to consist of two phases separated by a process of desolution during the solidification of the original sol. According to this theory where desolution results in

gelatinisation the one phase separates in droplets, which remain suspended in the continuous phase, and afterwards cohere, and in most cases solidify, forming the framework of the gel. Hardy [1900] observed this process for mixtures of alcohol, water and gelatin, and he found it possible, by suitably varying the conditions of experiment, to obtain droplets of almost ultra-microscopic size.

Hardy's work gave fresh confirmation to the widely accepted honeycomb theory of gel structure due to Bütschli's classical researches on the structure of gelatin [1898], a theory which was also supported by Quinke's theoretical investigations, and by the authority of van Bemmelen, who used it for the interpretation of his later work ; it was however adversely criticised in some quarters ; notably by Pauli [1902] who regarded the structure observed by Bütschli in coagulated gelatin as a secondary structure due to the coagulation, and not as preexisting in the uncoagulated jelly. To establish this point he investigated the action of the coagulating agent, and arrived at the conclusion that essential differences exist between the processes of gelatinisation and coagulation, a conclusion very important for the theory of these processes. He shewed that the one process could be accelerated by means which caused retardation in the other ; that e.g. grape sugar added to gelatin accelerates gelatinisation and raises the temperature of solidification, while it hinders precipitation ; and that the independence of the two processes was also proved by the fact that coagulation could take place as well in solid as in liquid gelatin. He also pointed out certain discrepancies between the results of Bütschli's theory and experiment, and he concludes that the " species of coagulation " worked by chromic acid, alcohol, etc. in solidified gelatin must be regarded as a true coagulation, essentially different from the preceding process of solidification, that the honeycomb structure observed in the coagulation is secondary, and that those appearances in uncoagulated gelatin which Bütschli regarded as due to this structure must be looked upon rather as the result of imperfect homogeneity.

Pauli's conclusions did not meet with general acceptance, and the theory of Bütschli held its ground until the introduction of ultra-microscopic methods of research allowed the application of a conclusive test. By this means Bachmann [1912] has shewn that gelatin jellies possess a far more complicated structure than the theory of Bütschli would allow, being built up of microns, sub-microns, and probably still finer elements. Bachmann points out also that the jellies prepared by Hardy are of a very different character from those of gelatin, being soft, white and opaque, rather than clear and stiff. Such

difference in character may well denote an altogether different method of formation.

The continuity of properties which has so often been observed between sol and gel has led some investigators to regard gels as sols of greatly increased viscosity, but viscosity alone cannot account for their properties. Hatschek [1911] has pointed out that gels differ from highly viscous substances, such as pitch, in their inability to flow, as do these, however slowly. Any theory of gels must take account of this rigidity, as also of the heterogeneity of structure which they exhibit, which is usually of the same order as that of the sol from which they are derived.

Bütschli's theory of the structure of gels replaced an older theory due to Nägeli; this "micellar theory" contemplated the gel as consisting of molecular aggregations or *micelle* of varying degrees of complexity, separated by films of water and attracted together more or less strongly according to the thickness of the intervening film. The breakdown of Bütschli's theory has brought about a return to more or less similar conceptions [cf. Zsigmondy 1912, p. 72]. These afford a fairly satisfactory explanation of the coagulating effect of change of potential on inorganic sols, but are less successful where organic sols are concerned, the gelatinisation of which takes place at much smaller concentrations, and appears to be largely independent of electrical conditions, and there is some tendency at present to regard gelatinisation in these as due to the properties which organic sols share with true solutions, rather than to those which they possess in common with the suspensoids, i.e. as a process akin to crystallisation, rather than as a process of aggregation due to a change in the conditions of suspended particles. It must be recognised however that our present ignorance of the nature of aggregation processes makes this a somewhat provisional distinction. Procter [1911] regards the sol of gelatin in this light, and considers its gelatinisation to be due to the formation of a molecular network, while the work of Pauli [1913] on protein solutions has shewn the relationship of the aggregation processes which take place in these to the phenomena of crystallisation.

It has been shewn that the rate of gelatinisation of pectin solutions may be regarded as determined by rate of chemical combination; this at once suggests a crystallisation process. It is of course to be expected that chemical change in suspended particles might cause aggregation and precipitation, but it is difficult to conceive that the rate of aggregation would be directly proportional to the rate of chemical change. Those aggregation processes, the rates of which have been studied, have been shewn to depend upon the

adsorption of oppositely charged ions [cf. Freundlich and Ishizaka, 1913 : Paine, 1912], and in these cases the rate of precipitation shews no simple relation to that of adsorption ; also where aggregates separated by films of water are concerned, rate of diffusion must determine rate of chemical action, and moreover, in the present case, the extreme dilution at which pectin gelatinises in alkaline solution makes any but a molecular hypothesis difficult of acceptance. Therefore here also the "crystallisation" hypothesis affords the simplest explanation of the facts.

During the last few years von Weimarn's [1911] work has thrown much light on the theory of gelatinisation, and since his theory is the most complete expression of the "crystallisation" theory, an attempt will be made to outline this in order to compare with it the results obtained for pectin jellies.

Von Weimarn regards inorganic jellies as concentrated highly disperse suspensoid solutions. He has himself prepared jellies from barium sulphate and other inorganic substances, and he has shewn that in general any substance under suitable conditions may be prepared in this form, the requisite conditions being to combine a sufficiently high degree of dispersion with a sufficiently high concentration. His theory of crystallisation, which is on the lines of the preceding theories of Lehmann and Tammann but permits of wider application, shews the relation of these jellies to substances in ordinary crystalline form. He regards crystallisation as the result of two independent processes (1) the formation of molecular aggregates by sudden concentration, and (2) the growth of centres by diffusion, either of molecules or of small aggregates. The first process gives rise to a suspensoid solution, and from this crystals are formed by the second process of diffusion. The rate of the first process, which von Weimarn takes as proportional to the relative supersaturation (i.e. the ratio of the quantity of substance capable of separating out to the solubility), determines the degree of dispersion ; where this is great the degree of dispersion will be high. Now if the second process is impeded or inhibited, stable suspensoid solutions will arise, and this will evidently take place when the degree of dispersion is so high that the greater part of the substance present separates during the first process in the form of small molecular aggregates, for these will neither diffuse rapidly nor combine readily with one another, since their vector properties will be small. A stable suspensoid solution is therefore formed, when a substance separates from a solution whose relative supersaturation is very high ; the greater the solubility the greater the relative supersaturation, and the higher the degree

of dispersion necessary for stability ; concentrated suspensoid solutions will take the form of a jelly.

As a test of his theory von Weimarn prepared a number of disperse solutions by the admixture of solutions containing substances which mutually precipitate one another ; e.g. barium sulphate was obtained at different degrees of dispersion by mixing solutions of barium chloride and magnesium sulphate at various concentrations. At the highest concentrations jellies of cellular structure were produced, since the reaction took place at the surface where the two solutions were in contact, and by maintaining the same degree of relative supersaturation with a lesser solubility (by alteration of the solvent) a jelly of network structure could be obtained.

In the application of this theory to organic sols, von Weimarn points out that between true solutions and disperse solutions an absolute continuity of properties exists, and that " the properties peculiar to the solutions of simple substances decrease in intensity as the molecular complexity increases." These complex solutions gelatinise readily because their molecules diffuse with difficulty, and with increase of concentration form groups practically incapable of overcoming the internal friction of the solvent, while cohesion is weak since the energy of the molecule is exhausted in its complicated internal structure. They form in fact disperse solutions, in which at small concentrations diffusion and vectorial cohesion are as much suppressed as in the highly concentrated disperse solutions of inorganic substances, and with a similar result. A lattice work is thus formed, the particles of which are bound together by vectorial forces, and which may therefore be entitled crystalline, but which will be soft and weak, and will be penetrated by the solvent, and greatly deformed [von Weimarn 1912].

The size and nature of the particles of which pectin solutions are formed have not been determined, but there is some reason to believe that the degree of dispersion decreases with increase of concentration, since the difficulty of filtration increases ; only very dilute solutions can be filtered through hardened filter paper without separation of the dissolved pectin. The characteristics are those of an emulsoid, and the solutions may very probably consist of a suspension of aqueous pectin in a dilute pectin solution. In this case the reaction with the alkalis and the alkaline earths will take place in the solution and at the surface of the particles. As the reaction proceeds a supersaturated solution will be formed ; this, as has been shewn, will solidify to a jelly at any concentration at which a molecular network can be produced. At very small concentrations where suspended pectin must be almost entirely

absent, the solution will remain supersaturated until practically the whole of the pectin present has been transformed, for the presence of a foreign substance will greatly impede both diffusion and cohesion, and will thus hinder the formation of a continuous network. As concentration increases the relative supersaturation previous to gelatinisation will increase, while the fraction of pectin transformed will decrease; the amount separating out will thus increase with the concentration, but in a smaller ratio. These considerations afford an explanation of the positions of the points at which the curves in Fig. 4 cut the y axis, as also of the rate measurements in Table VI.

SUMMARY.

(1) The rate of gelatinisation of pectin is not determined by the rate of diffusion nor by the rate of surface adsorption of the alkali or alkaline earths producing gelatinisation.

(2) It can be expressed as a velocity equation determined by the concentration of the reacting substances, when the initial concentration of pectin is constant.

(3) It is therefore regarded as determined by the rate of a chemical reaction—the substitution of H by BaOH, K etc.

(4) That a reaction of this kind takes place is supported by the fact that the constitution deduced for compounds of the alkalies and alkaline earths is strikingly analogous to that of the corresponding compounds of the mono- and di-saccharides. Similar molecular compounds with salts are probably also formed.

(5) Gelatinised pectin forms solid solutions with the alkaline earths which may be compared with the solid solutions of lime and cane sugar.

This investigation was carried out at King's College for Women, Kensington Square. I am glad to have this opportunity of expressing my gratitude to Mr H. L. Smith for his help and advice in the early stages of the work, which was begun in his laboratory, and to the authorities and those members of the staff to whom I am indebted for the facilities which they have given me during its progress.

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