

Lectures on cellulose / C.F. Cross.

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THE
INSTITUTE OF CHEMISTRY
OF
GREAT BRITAIN AND IRELAND.

FOUNDED, 1877.

INCORPORATED BY ROYAL CHARTER, 1885.

LECTURES
ON
CELLULOSE.

By

C. F. CROSS

(Fellow of the Institute).



30, BLOOMSBURY SQUARE, LONDON, W.C.
1912.



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The Lectures were delivered before the Institute of Chemistry, at University College, London, on January 26th (Sir Wm. Ramsay, K.C.B., presiding), and February 23rd, 1912 (Professor J. Norman Collie presiding).

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*The Paper on which the Text is printed has been selected
as conforming with the following specification :—*

*Substantially "rag" (cotton and flax) cellulose free from
esparto, lignocellulose, and mineral loading.*

Lecture I.

In accepting the invitation of the Institute to take a part in the scheme of lectures under which it seeks to extend its constructive work outside and beyond the more fundamental academic influences, I take it that I am expected to address myself chiefly to the younger members, and to give them some of the results, so far as they can be so communicated, of thirty years' experience as a specialist: a record which may be presumed to furnish points of determination, guidance and warning to a younger generation. I am able to presume upon a very general interest in the subject of "Cellulose" arising out of the unique position of the substance itself in the world of things.

As a *chemical individual*, however, it has only a very sectional corner in the fabric of the science; and specialists' investigations of cellulose cannot claim to have contributed matter of any importance to systematic science. Consequently, we may be even thought to be hypercritical if we point out that the sectional treatment of "Cellulose" in the standard text-books is always inadequate and largely inaccurate. As regards the past and the ever-elusive present, we may admit that "it really doesn't matter" that our text-books attach little importance to the subject; but as a subject with a future it claims critical attention.

And here we may note a very common presumption which is on the way to crystallise to a prejudice,—namely, that cellulose is merely an eccentric form of dextrose or carbohydrate matter, and connotes a constitutional problem, ultimately to be elucidated in terms of current systematic chemistry; presenting, therefore, no problems of prospective

scientific importance, though a useful hunting ground for adventurous specialists of an "industrial" turn of mind.

Admitting the humour of this criticism, and further recognising that a sense of humour is a necessary part of the equipment of a chemist about to adventure on the high seas of professional life and trouble, we have nevertheless to propound a more serious view of our subject-matter. It would be out of place to argue the following propositions: we present them for the thoughtful consideration of younger students.

Cellulose is organised matter: "organic" matter in specialised mass forms. As an effect or product of life and in turn the arena of vital processes, we may affirm that no two portions of cellulose are identical; neither is the chemist's cellulose identical with the biologist's cellulose. The former connotes a series of degradation products of the latter, and we have no means of re-ascending the scale.

The total synthesis of carbon-compounds is sometimes confused with quantitative knowledge of the forms of matter so manipulated. This leads to superstition. The synthesis of "organic" compounds is supposed to suggest a potential synthesis of organised matter by laboratory process. As a matter of fact and clear-thinking, this is a subjective creation, a poetic fancy, as little grounded as was the dogmatic assertion of the older chemists that "organic" compounds were exclusively producible by vital force.

In correcting this misconception, and setting free an immense territory for thought and investigation, latter-day chemists are inclined to extend the negation into a dogmatic elimination of the conception of life as a physical or super-physical agency. "*Ils aiment par instinct de faire de la nature morte.*"* In other words it is, or has been, fashionable

* Étude Critique du Matérialisme et du Spiritualisme par la physique expérimentale.—RAOUL PICTET. (Geneva, 1897.)

in "science" to regard life as a property of ultimate matter, organic form as the analogue of crystallisation, and vital effects as a side issue of chemical philosophy.

It is necessary to make passing mention of questions which must arise in the serious study of the problems of the borderland between chemistry and biology, and to enjoin on the young student the duty of serious and clear thinking in this region.

If we now turn from "science," *i.e.*, systematic science, to human industry, cellulose emerges from its sectional corner to a position of predominating importance. A few statistical figures will indicate this predominance (p. 30).

Our cotton manufactures are estimated at the annual gross figure of £125,000,000—at factory cost; hemp, linen and jute goods, products to be ranked as essentially cellulose, at £20,000,000; of this bast-fibre section, jute manufactures may be estimated in terms of imports of the raw fibre at, say, £8,000,000; in the same group are ropes and twines at £4,000,000. Paper and boards are next in order at £14,000,000. These, it must be remembered, are primary products—they are the basis of further manufactures, of which we may mention, for instance, lace and hosiery, books and newspapers, etc.

These more obvious industrial applications of cellulose products by no means exhaust the field.

"Straw" hats which are made from cereal straws, white woods ("chip") and miscellaneous vegetable products, etc., represent an industry approaching £1,000,000 per annum.

The wood and timber trades have to be taken into reckoning—and some guide to their industrial importance is obtained from the statistics of imports of the raw materials; the gross figure of £25,000,000, suggesting a very much larger value for their final manufactured forms.

From these modes of manufacture of vegetable raw

materials, in which their structural and essential chemical characteristics are maintained, and leaving altogether out of account the part played by cellulose as a fundamental constituent of all agricultural and gardening produce, we pass to the group of cellulose derivatives.

As certainly derived in the main from cellulose by processes of regulated destruction, in effect of constructive destruction, we must mention coal, of which our own production reaches the colossal total of 250,000,000 tons per annum, in value, say, £150,000,000.

From such figures and their indirect consequences, upon which we need not dilate, it seems an anti-climax to pass to the nitro-celluloses, which, on the other hand, are direct derivatives. But if coal dominates the productive and constructive life of an industrial community, its powers of offence and defence under modern conditions of life are in an important sense dependent upon nitro-cellulose powders. Without assigning a money value to the industry in explosives, they have an importance *sui generis* and self-evident.

The nitro-celluloses are the essential component of celluloid and xylonite, and in the form of films are indispensable to photography in all departments; these applications of cellulose represent not merely large industrial values, but contributions of useful and æsthetic effects, not to be comprehended in trade returns.

It is quite unnecessary to labour this theme to impress its consequences upon this audience. Summing up our sketch, it is clear that *quâ* productive industries, cellulose occupies a first position and has only one rival in respect of magnitude, which is iron (and steel), with the engineering industries connoted by those comprehensive terms, the gross figures of our production in this sphere approaching £400,000,000.

Even the fermentation industries, at a gross figure of, say,

£70,000,000, with their monstrous load of Excise contributions, fall into quite a secondary category of importance.

Incidentally we may remark that the industries of most direct interest to us as chemists, viz., the manufactures of "heavy chemicals," chemical raw materials, and the highly specialised products of organic synthesis, including dye-stuffs, are of altogether subordinate moment, if not insignificant. Remarkable as is this disproportion, it appears to escape attention in many of the public discussions of the relative progress of chemical industry in England and Germany. (See Diagram, p. 30.) Without touching controversial side issues, we have to complete this aspect of our subject by grouping cellulose in the broadest scheme of classification of industries. Cellulose is a colloidal substance and the prototype of the colloids. In the industrial and widest sense the colloids are useful for their structural qualities, and on this view we group together industries of apparently widely divergent characters: India rubber—oils, paints and varnishes—glass, pottery and bricks, mortars and cements—gelatin, casein and starch—silk, wool, and leather.

Addressing an audience trained in method, both of mind and practice, it would be gratuitous to justify this classification or to follow up in detail the consequences of the organic relations of these heterogeneous spheres of human activity. To an untrained mind the connection between a sheet of glass and a sheet of paper may not be obvious. But a slight transformation of the paper substance—without loss of weight—makes it into a transparent homogeneous coherent sheet, indistinguishable from the vitreous colloid.

Resuming the thread of our exposition, if cellulose is industrially predominant, *à fortiori* the predominance of the industries in colloids is overwhelming. In this order of idea and on this perspective we re-discover the world of nature in our own artificial system.

As chemists we are aware that the beginnings of our science were those of a study of Natural History. We have only to turn for recreative study of this theme to the philosophical works of Robert Boyle, representing the thought of the seventeenth century, or to a work such as "*Elemens d'Histoire Naturelle et de Chimie*" of de Fourcroy, representing the physical conceptions of the eighteenth century, to appreciate the extraordinary divergence of thought and investigation of the nineteenth century. Our pioneers have spent that century in the monastic seclusion of the cloisters—with magnificent result be it confessed—and it is now the calling of the chemist to apply the grammars and dictionaries elaborated during this necessary period of self-contained activity to a new reading of the natural order.

Evidence that such a movement is in active progress is the recognition of the problem of the "Colloidal State" of matter as an abstract subject of investigation, that is, as a problem of pure science and apart from any question of industrial result. This generalised view of the colloidal state as a permanent characteristic of particular forms of matter, and a potential form of an indefinitely wide range of chemical individuals, is well set forth in Wo. Ostwald's "*Grundriss der Kolloidchemie*."

A curious feature of this leading text-book of the subject is that "Cellulose" is not even mentioned, and "Zellstoff" once only!

This observation has led us to remark, in our synopsis, that modern or later specialisation in colloidal phenomena has been mainly characterised by superficial range of treatment; whereas it is in the direction of the third dimension for investigation to move with the greatest promise of progress. Our opinion is that cellulose and cellulose derivations supply an ideal region for the profound and exhaustive application of physical methods directed to the elucidation of the colloidal

state. The fundamental constants are for this, as for any other state of matter: volumes and solution volumes and changes of specific volume with temperature, viscosity (of solutions), elasticity and mechanical properties (of solids), and in the next order the relations of these substances to the various forms or phases of energy, more particularly to heat, but also to electricity and light.

Now we have also to remember that cellulose is the extreme term of the series of so-called carbohydrates, and that this series, cellulose, hemi-cellulose, starch, dextrine, maltose and dextrose, presents a mass of organic relationships which must have their physical correlatives.

We have to remember, too, that the chemist does not lightly rush in to the region of physical measurements. The paradox of the physical laboratory is that the one thing to be positive about is the error of observation, and that the quantification of error is often by far the most exacting, and perhaps interesting, part of an investigation. This quite certainly will be the case in investigating the cellulose, hemi-cellulose, starch series, and may have proved a deterrent to many, otherwise attracted to an obviously fruitful field of work. This discipline of the physicist would have a parallel to the chemist in the rare cases when he has to take a major interest, *not* in the chemical individuals, which are his familiar friends, but in their incidental impurities—a case which arises in investigations of the mechanism of reactions and in determinations of atomic weight. This raises a point in relation to the colloidal state which in process of time may also become a subject of direct investigation. All organic colloids of natural origin present an incidental "impurity" of inorganic matter. Only in certain cases are these investigated or specifically estimated, and chiefly as constituents of agricultural produce. They represent, on the debtor side of the account, exhaustion of the soil; and they indicate on the creditor or positive side special

functions of undoubted moment in the vital processes. It is quite certain that the progress of knowledge of colloids, or rather of the colloidal state, will impose upon us a re-investigation of the inorganic or "ash" constituents of plant colloids, and the co-ordination of a vast amount of material faithfully recorded—that is, "faithfully" in the fuller sense of faith in a scientific meaning and value remaining for future workers to confer upon them.

As a general criticism, therefore, the subject of colloidal matter is presented to the student rather as the play of "Hamlet" with the part of the prince left out.

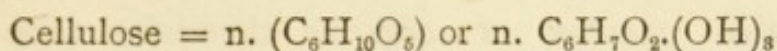
I take it, it is not the function of a lecturer to argue, and I must be allowed to commend the above statement as a subject for an examination essay or a students' debate.

We have now to turn our attention to the central subject of our exposition: cellulose as a chemical individual, that is, in relation to systematic chemistry; and as a necessary preface to the question of a "Normal Cellulose."

The necessity of a definition will be at once evident from the fact that our chemical filter papers are usually supposed to represent a normal cellulose, and are, in fact, frequently taken as a starting point of scientific investigation of cellulose: whereas a very slight knowledge of the technology of paper-making would suggest, *à priori*, the improbability of any of its products reaching this standard; and a chemical examination would soon dispose of any such claim.

To make this clear we must presume a basis of exact knowledge, and we set out the fundamental chemistry of cellulose in the shortest possible compass. Actually, the typical cellulose is the cotton fibre purified by special processes, to which it is assumed to offer complete resistance, whereas the heterogeneous complex of "non-cellulose" constituents of the natural fibre are removed under treatment as soluble derivatives.

Thus isolated and purified, it may be shortly described as follows:—



a saturated compound of unascertained molecular dimensions; insoluble in all neutral solvents; resists action of halogens, of alkaline solutions and oxidants within certain limits; hydrated and dissolved by zinc chloride (50% solution Aq₁) and cuprammonium solutions (15% NH₃, 3% CuO); hydrated with structural changes (mercerisation) by solutions of alkaline hydrates (15% NaOH). Synthetic reactions, mainly those of its alcoholic OH groups:—

(a) With monobasic acids (or anhydrides) giving—

Nitrates: retaining fibrous structure: limit of esterification 3.ONO₂.

Acetates: acetylation usually attended by solution: normal limit 3.OAc: further acetylation of hydrolysed derivatives.

Benzoates: monobenzoate fibrous: dibenzoate (limit) amorphous.

Formates: esters higher than monoformate of doubtful relationship to original. *See Chem. Soc. J.*, 99, 1,450 (1911), Cross and Bevan.

(b) With CS₂ (and NaOH) giving cellulose xanthogenic acid $\text{CS}_2\text{O.C}_{12}\text{H}_{19}\text{O}_9$: alkali salts water-soluble.

Reactions of decomposition:—

(c) With sulphuric acid giving disulphuric esters, but with attack and disintegration of aggregate, the hydrolysis proceeding to extreme limit of resolution to dextrose.

(d) With aqueous acids and oxidants a complex series of products known as hydrocelluloses, oxycelluloses, differing only fractionally in elementary composition from $n.\text{C}_6\text{H}_{10}\text{O}_5$.

In characterising a "normal cellulose," it will perhaps be evident that we have to erect our standard from the inside. It is the paradox of organic chemistry proper — the chemistry of organised matter—that it is a chemistry of which the fundamental relationships are unascertained. Investigation in this region may be compared to living without clocks or time standards, which means that to know where you are in space or time at any stage of investigation you require to take bearings; and, moreover, as the sun and fixed stars are in this region invisible, you are limited to observations of the moon! This analogy is not chosen at random; it represents this fact: while our major appeal is still to the balance, we cannot pass from particular relative weights to the generalised or transcendental relationships of molecular units. We have no fixed point outside the system under observation. Thus, in a series of celluloses, or rather specimens of a particular cellulose, we observe a varying degree of resistance to a certain treatment measured, say, by loss of weight. Thus aqueous sodium hydrate at 15 per cent. strength produces the very characteristic change known as mercerisation. We submit to this treatment specimens all of bleached cotton cellulose, and all ranking with papermakers as a normal product: at the extreme limit in the one direction is a specimen giving up 20 per cent. of its weight to the mercerising alkali; at the other end a specimen containing 2 per cent. of alkali-soluble cellulose. This gradation, quite unmarked by external characteristics, already suggests a cotton cellulose entirely resistant, *quâ* loss of weight, to the alkali. An industrial product fulfilling this requirement is a calico-printer's cotton cloth, prepared by the process of "madder bleaching"; of this we submit a specimen which we have tested.

But this test does not rank with the calico-printer. He requires certain associated properties in his bleached product, and is satisfied if these are fulfilled; they are:

(a) Maximum tensile strength, *i.e.*, full maintenance of the structural properties of the fibre; (b) maximum of non-reactivity as a chemical individual.

The meaning of the "madder bleach" is that the fabric will not take up alizarin from the dye-bath of this colouring matter; the chemical equivalent term is non-reactive. Designs are printed in thickened mordants upon the cellulose fabric, and suitably "fixed." In the dyeing treatment of the whole fabric, the printed portions take up their complement of dye-stuff with calculated modification of shade or hue; the unprinted portion is required to resist, so that when washed up and cleaned from mechanically-adhering colouring matter, it shows the contrast of the pure white ground. A little reflection will show that, whatever view may be taken of the course of dyeing phenomena, we are dealing here with the negative property of non-reactivity or chemical inertness. We may, therefore, add a dyeing test, as a qualitative measure of a normal cellulose. It will be also evident that when cellulose under attack begins to undergo chemical, *i.e.*, constitutional, modification, the first evidence of reactivity is the setting free of CO-groups, of which the familiar Fehling's solution is the simplest test and measure.

Incidentally we have mentioned the fundamental characteristics of cellulose as a structural colloid. These are measured in terms of resistance to rupture, with the associated quality of elongation under strain.

We have now defined three fundamental constants in terms of a "normal cellulose."

- (1) Quantitative resistance to mercerisation;
- (2) Non-reactivity in terms of "Fehling" and dyeing tests;
- (3) Structural integrity measured in terms of resistance to rupture, and of elongation under strain (elasticity).

This is a very firm tripod for the support of a standard of cellulose quality. But as a standard of science we have to remember the limitations of a self-contained standard. In the field of analogy we might consider the case of water and its fundamental properties. What do they know of water who only water know? They may marvel at its aqueosity, but should they find themselves, *e.g.*, disappointed with the Atlantic or Niagara, where is their reserve of emotional suggestion? In the co-ordinate region of science, where would the physicist be in the knowledge of water if he had no critical standpoints external to water, or if temperature were the only measure of heat?

Now the cellulose standard must be established from the standpoint of its limitations—and when this is recognised, we think our schools of technology will find a very useful work to do, to measure in terms, as given, the degree of resistance of cellulose to

Hydrolysis	}	Acid
and		and
Oxidation		Alkaline.†

To our present audience there is no need to argue the matter. Some will see it *presently*, that is at once, in the language of Shakespeare, or at some future date in the latter-day acceptance of the term; but, in either case, none the better or more clearly for our much speaking.

But the *industrial* value of a standard of cellulose may not be so obvious. And here we are really able to touch only the fringe of a large subject. The particular chemical industry which requires for its raw material a cellulose of nearest approach to the normal, is the manufacture of nitro-cellulose explosives. This, for the reason that stability of the nitric esters is essentially conditioned by inertness of the cellulose,

† See *The Chemical World* I., p. 84, 1912.

and undermined by modification in the direction of setting free oxidisable groups. The tests usually adopted are of the same character as those we have sketched, though differing in detail.

But this and others of what we may consider our special or specialised applications of cellulose are of minor importance in regard to industrial value. The industries of more general interest are those of textiles and paper. We have already alluded to the calico-printer's requirements of a specially pure cellulose. We may remark that the exigency and its fulfilment are largely matters of empiricism. We may also remark that the papermaker treats the chemistry of his raw material as a matter of insignificant moment. It is a resistant substance chemically and mechanically, and so long as his bleaching or purifying treatments give the result of sufficiency and efficiency, as judged by external criteria, and the mechanical treatments, the practical and commercial result, he does not invoke the aid of the chemist to teach him his business.

In this neglect we can assure our audience there are elements of tragedy, pathos, and comedy which the student may survey, and in which he may take interest according to his temperament. The tragedy of industrial wealth destroyed and lost, the pathos of so much *avoidable* loss, and the comedy of the really dull person of the play being quite unaware of the possibility of the wrong man being whipped, or why he should laugh under the lash. But we must warn the young student not to take such revelations too seriously. Our humorists have unwittingly spoiled a good deal of fun; and in these days of "many masters" it is better not to attempt a setting in order on the large scale. It is sufficient if we, as chemists, can see and formulate an ideal, and apply it "at home."

Thus the "normal cellulose" is an ideal product and a scientific conception, still perhaps requiring definition by results of investigations, which investigations may well be

undertaken by our schools of technology. It is of practical moment in the cellulose industry, just as a gold standard is essential for regulation of coinage. It is also important as a criterion of processes of isolating or purifying celluloses.

These processes we have to examine in illustration of first principles.

We are limiting ourselves at present to cotton, and the purification or bleaching of cotton is a relatively simple matter. The impurities to be removed are exceptionally low in weight proportion, and readily yield to alkaline saponification, and the residues to oxidation. In industrial work, this means a boiling treatment under pressure with caustic alkali, and oxidation of the coloured residues by weak solution of hypochlorites.

In a "madder bleach," the alkaline treatment is divided into two: a lime boil, followed (after "souring" to clear from residues of basic lime) by pressure-boiling with soda and with addition of rosin.

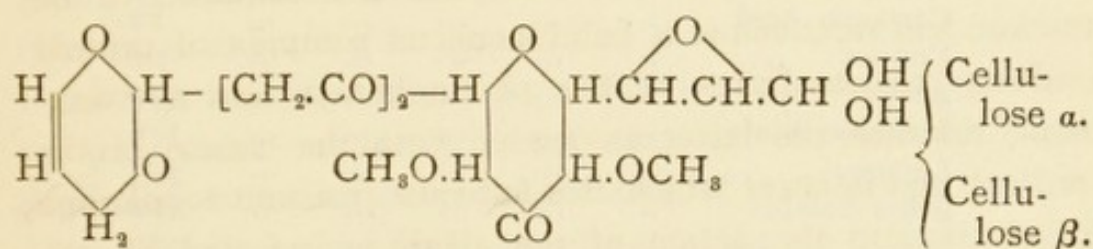
These alkaline treatments, as we shall subsequently and more particularly show, are unsatisfactory to the technologist as they are extremely complex processes and very imperfectly elucidated. In the case of cotton, the non-cellulose to be attacked and removed is a heterogeneous complex of proteid residues, carbohydrates of the pectic group, and a "wax-resin" mixture, the latter associated with the cuticle of the fibre. It is the latter which is relatively resistant to alkaline hydrolysis, and the action of the alkali is impeded by the gelatinisation of "pectic" bodies in the initial stage of the attack. It is also necessary to consider the special physical and mechanical conditions of a mass of cloth in contact with a mass of alkaline liquid from five to seven times its weight only; and, further, the mass of cotton having the structural complications not only of the ultimate fibre, but of the spinners twist and the interlocking contacts of the woven fabric. On

this *exposé* it is not difficult to appreciate the specific advantages of the preliminary lime boil, and the indications of an important general principle of chemical economy, that of division of effect, fairly comparable with division of labour in manual operations.

This leads us to the consideration of a group of processes similarly directed to the isolation of a pure cellulose, but of more distinctive character. These are the industrial treatments of the woods for the preparation of papermaking celluloses or pulp. We can only sketch these very briefly, and as illustrating first principles.

The wood substance is a lignocellulose—a colloidal complex of cellulose and non-cellulose, or lignone, the latter a highly varied though homogeneous complex of groups. This is not an occasion for arguing the controversial theme of the constitution of this lignone complex and its relation to the cellulose. In a work now in the press ("Researches on Cellulose," iii.—Cross and Bevan) we give reasons for adopting the following views for the lignone.

(1) A constitutional schematic formula, that is of general or typical significance as under :—



(See Diagram, p. 31.)

(2) The combination of lignone and cellulose is not of the familiar type of a union of "residues," but an interpenetration of two colloidal systems of such order, and so affecting the ultimate component groups, so that their reactivities are modified similarly to those of groups united by definite chemical bonds.

The lignone complex is reactive in various directions. We demonstrate those which are more obviously characteristic: various colour reactions with aromatic bases and phenols, reactions with the halogens and oxidants demonstrating the unsaturated constitution of its typical groups; and a special reaction with ferric ferricyanide in which, with the unsaturated characteristics of the complex, it shows an exceptional reactivity as a homogeneous colloidal system (*see J. Soc. Chem. Ind.*, 12, 104, 1893).

The isolation of cellulose from the lignocellulose complex is a problem of chemical industry or manufacture.

Industrially, the simplest process is that of boiling or digesting at high temperature, and under pressure, with caustic soda. The lignone is resolved to alkali soluble derivatives. In the case of coniferous woods, the following are the general statistics of the resolution:—

100 of lignocellulose are resolved into

(Insoluble) 35 cellulose ;

(Soluble) 65 lignone products of resolution.

The alkali-soluble derivatives present the following characteristics and quantitative relations:—

Carbonic Acid	1'2
Formic ,,	7'0
Acetic ,,	0'7
Lactonic Acids	32'6
Lignone 	33'3
Ether-Soluble	25'2
						<hr/>
						100'0
						<hr/>

("Chem. Zusammensetzung des Fichtenholzes," P. Klason. Borntraeger, Berlin, 1911).

The proportion of soda neutralised is 20 per 100 parts of the lignone complex. In practice, the caustic soda used is approximately twice this proportion or about 15 to 20 per cent. of the original lignocellulose.

Assuming that the caustic soda thus taken into work is lost, the cost sheet of the process would present the following main features :—

<i>Raw Material</i> for 1 ton "soda" cellulose : pre-					
pared wood	2.5—3.0 tons.
<i>Chemicals</i> (Caustic Soda)	0.5—0.6 ton.
<i>Steam</i> (Coal)	{ Digestion Process		
	{ Mechanical Treatment				
	{ Cylinder drying of Pulp				
<i>Labour and Superintendence</i>	£1 5s. od.—£1 10s. od.

These are the general elementary factors of industrial chemical processes. But there are important qualifying factors which we may roughly set forth.

The *Raw Material* originally is a forest tree. As felled, it contains excess of moisture, and in preparation for treatment it is deprived of bark, sawn, and then chipped, and the chip cleaned. For 2.5—3.0 tons of prepared wood, 4—5 tons of forest wood are required, and the material has to be transported from the forest to the works.

Chemicals—Soda Recovery.—There is, of course, no loss of alkali in the boiling process. The alkaline by-product liquor is evaporated, and at suitable concentration is turned into an incinerating furnace. The dissolved organic matter has a high calorific value. As a useful constant to remember, we may point out that a 12 per cent. solution of cane sugar represents sufficient potential calories for its total evaporation. The lignone by-products represent a higher calorific value proportional to their higher carbon percentage.

Assuming that the wood is digested with twice its weight of original solution, becoming 3.0—4.0 times its weight by condensation of steam, in heating up and compensating for cooling by radiation: the original by-product liquor would represent a solution of 2 tons of by-product in, say, 8—10 tons of soda solution, and obviously an excess of potential calories

for total evaporation. A large proportion of the liquor can obviously be removed at full strength.

But 1 ton of cellulose pulp when drained would retain, say, 2 tons of the liquor. It is obvious that to displace this we have to employ wash water. Washing is carried out to the economic limit as between soda recoverable and water to be evaporated.

Consequently, the item "caustic soda" is the cost of soda in the form of "recovered soda," that is, the cost of evaporation from original liquor plus washings, the cost of furnacing and causticising the ash. To this is to be added the absolute loss of soda, which in a series of operations will amount to 15 per cent.

For a full discussion of the practice of soda-recovery, which is a fundamental problem of chemical engineering, we can refer our audience to the excellent handbook of J. Beveridge, "Paper-Maker's Pocket Book," London, 1911. (McCorquodale.)

A further development of the economy of the alkali process is based upon the deoxidation of sulphate of soda to sulphide by the alkaline by-products of the boiling process. It is evident that the absolute loss of soda can be made up by addition of the equivalent of the neutral salt which in the incineration would be reduced to sulphide—being further in part transformed to carbonate—the sulphide having a hydrolytic efficiency but little inferior to the oxide (hydrate). An extension, however, of this substitution enables us in a cycle of operations to substitute entirely the salt or cheap sulphate as source of alkali.

Taking sulphate of soda at £1 per ton, it is evident that the theoretical value of Sodium Sulphide in this form is 36s. a ton, and under the conditions of its formation from the sulphate by the deoxidising action of the dissolved organic

matter, there is very little additional cost to be reckoned. On the same basis the carbonate represents 27s.

In actual practice the cycle is maintained on a basis of raw materials as follows :—

For 1,000 kilos pulp produced :

8.5 space-metres or 6 solid metres spruce wood.

160 kilos of Na_2SO_4 and 350 kilos quick-lime and the ash from the incinerator.

In the causticised ash liquor the average proportion of active soda compounds is

Na_2CO_3	12	grms.	per	litre.
NaOH	100	"	"	"
Na_2S	26	"	"	"

Consumption of Fuel.—An approximate figure for this important item per ton pulp produced is :—

<i>In steam raising.</i> —For the digestion process for 3 tons steam	lbs.
(1,200 units per lb.) at 90 lbs. pressure	1,000
For drying pulp on cylinders for 1.5 tons steam (1,150 units per lb.) at 25 lbs. pressure	450
<i>For evaporation of liquors.</i> —Additional to heat supplied by combustion of by-products, 8 cwts....	896
	<hr/> 2,346

Labour and Superintendence.—These items complete the skeleton works' cost sheet and may be approximately estimated at £1 5s.—£1 10s. per ton of pulp.

We have introduced these details rather as an illustration of an important part of the work of a technical chemist, and to point out to those who may not have considered such matters from the point of view of a chemist's training, that they are merely an extension of our ordinary practice of quantitative analysis.

Resuming the main theme of our inquiry, we find that the alkaline processes of cellulose isolation fulfil certain technical ideals: yielding a main product of satisfactory quality, and organic by-products which are also utilised in doing chemical

work, and in effect the net result is an industrial process of a high order of economic efficiency.

The objections to those processes are: there is a considerable destruction of cellulose under the action of the alkali, the yields of pulp are considerably below the maximum of laboratory normal processes, and the attack of the active agent or its result may be likened to a chemical *débâcle*. Reverting to our schematic formula for the lignone complex, this ought to suggest to the student that a merely hydrolytic attack must be of the most highly complex order, and as an exercise of imagination, applied to the consideration of the functions of a lignocellulose in nature, he will discover in the complex a paradoxical union of sensitiveness *and* resistance to the chemical influences of our planet. These are notably water and oxygen under the very special conditions of energy equilibrium following from the activity of life on the one hand, and on the other, light, heat and electricity — the forms of energy with which we are familiar. The perennial individual must be endowed with *sensitiveness* to meet the endless chain of adaptations imposed by corporate organic existence, and *resistance* as the obvious condition of permanence.

But the formula is based upon, and therefore might suggest, specific reactions of characteristic groups. Two of these are of especial interest and, though of very opposite characteristics they have certain main features in common.

(1) They are quantitative and invariable; (2) while they specifically modify a particular group, the lignone complex is affected as a whole and converted into derivatives which are soluble. These reactions are:

(1) Chlorination to a quinone chloride; (2) Combination with bisulphite residues, in the first stage to an aldehyde-bisulphite compound, leading, as a second stage, to sulphonation, the entire lignone complex being obtained as a colloidal sulphonate in solution.

The latter reaction is the basis of the now well-known industrial process of preparing cellulose ("bisulphite pulp") from coniferous woods, a process with which we may be said to have grown up.

We only deal with this process in specific contrast to the alkaline or soda processes. The solution employed is a calcium bisulphite solution containing 3 per cent. of SO_2 , of which one-third is combined with CaO (and MgO) in the ratio $\text{M}''\text{O}.\text{SO}_2$. The proportion by weight to the wood is 3.5—5.0, according as the digester is of the rotary or stationary type. It may be assumed that the proportion of SO_2 required for the actual reaction of synthesis is 10 per cent. of the pure wood substance. From the excess of bisulphite solution employed, one-third of the SO_2 is recovered by the simple method of "blowing off" during the digestion and absorbing after cooling, in the freshly-prepared bisulphite liquor.

In comparing the costs of this process with the alkaline processes, it is evident that the main item of difference is the cost of sulphur, which is lost in the form of sulphonated by-product, compared with the cost of recovery of the soda of the alkaline processes, plus the value of the soda beyond the limit of economic recovery.

In the bisulphite process, moreover, the wood requires selection and more careful preparation, the reaction upon which it depends being obviously specific to lignocellulose; whereas the alkaline hydrolysis constitutes a universal attack and decomposes bark, cuticular tissues, even knots, and denser forms of lignocellulose.

The prepared wood for this process may be taken at £3 15s.—£4 per ton of pulp. The cost of sulphur combined in by-product liquor and therefore lost, at 5 per cent. on the wood, say 12.5 per cent. on the pulp, and with incidental costs of conversion into bisulphite, approximately £1 per ton.

Finally, we note that the differences of costs of production are reflected in the market prices of the products, "soda" and "sulphate" pulps ruling at an average of £7 a ton; "sulphite" pulps at £8—£9.

As our concluding illustration we have to consider the first of our characteristic quantitative reactions—that between the lignone complex and chlorine—as the basis of a possible industrial process.

As we are taking an ideal case as distinct from an industrial actuality, we will take the "academic licence" of simplifying the problem in terms of the simplest type of lignocellulose, which is the jute fibre.

This fibre substance reacts in the cold with chlorine, combining with 8 per cent. of its weight as lignone-chloride, and forming an equivalent proportion of hydrochloric acid.

Allowing for unavoidable losses, it appears therefore that 100 parts of jute lignocellulose can be resolved by treatment with 20 parts of chlorine.

Of the products of reaction we may take the lignone chloride as of no value. It is soluble in alkalis and would be so removed from the cellulose, obtained as a pulp, or mass of disintegrated ultimate fibres.

But the hydrochloric acid has a value, and it is one of the paradoxes of chemical industry that evolution brings about a partial inversion of primary values; thus hydrochloric acid comes to have in certain circumstances a value superior to that of the element. In evidence of this point, we refer to a recent paper in the "Chemiker Zeitung," 1912, 36, p. 54, "Zur Herstelling von Salzsäure aus Chlor," which, by the way, sounds like travelling from London to Paris *via* Berlin. Without discussing the complex equilibrium of the alkali industry, it is general knowledge that the displacement of the Leblanc by the Solvay soda process on the one hand—which cuts the production of HCl—and by electrolytic

processes, on the other—which means a relative over-production of chlorine—must involve a modification of the theoretical ratio of values $\text{Cl} : \text{HCl}$. The author of the above paper—O. Nagel—proposes a reaction with water vapour and carbon at high temperature, thus : $\text{Cl}_2 + \text{H}_2\text{O} + \text{C} = \text{CO} + 2\text{HCl}$, for the industrial production of the acid.

It would appear, therefore, that a cellulose process based upon consumption of chlorine, with production of HCl as a by-product, might also contribute to remove an artificial industrial congestion.

Apart from this, in the first place, our present problem is the cost of treating jute fibre with 20 per cent. of its weight of chlorine. What are we to take as the value of chlorine ?

A theoretical maximum value is indicated by the current market price of bleaching powder. Taking this at 92s., and at 37 per cent. "chlorine," the value is $\frac{92 \times 100}{37} = 248\text{s.}$ or £12 8s. The value at the centre of production is obviously less by the costs of conversion into bleaching powder, packing and transport. If, however, we electrolysed sodium chloride we should require to decompose

$\frac{20 \times 58.5}{35.5} = 33$ kilos of common salt to treat 100 kilos of jute fibre, and with the 20 of chlorine we should obtain $\frac{53 \times 20}{35.5} = 30$ of Na_2CO_3 (Hargreaves-Bird process), or 26 of NaOH (Castner-Kellner process).

In an ordinarily efficient electrolyser, steam power, represented by 5 k.w. hours, should produce 1 kilo chlorine, *i.e.*, under favourable conditions, for 2d., together with the equivalent of soda compounds in solution. To this figure we have to add cost of raw material, labour, upkeep of electrolytic plant and general costs.

We now turn to the actual process of resolving the ligno-cellulose. (100 Kilos.)

Taking jute butts or root ends, they require an open boiling with an alkali—say 5 per cent. of their weight of caustic soda. This would be furnished as a fifth of the alternative products of electrolysis.

The fibre—boiled, washed, and squeezed to hold its own weight of water—is exposed to the electrolytic chlorine till fully chlorinated.

The HCl formed is removed by systematic washing. Adding 300 litres of water and removing 300, we recover 6 kilos HCl in 2 per cent. solution, adding 700 litres and removing 700, we obtain 7 kilos HCl in 1 per cent. solution.

Removing the residue of acid at a dilution beyond a useful or economic limit, the chlorinated fibre is then treated with electrolytic alkali in dilute solution, using 10 per cent. of its weight. After washing from the by-products thus dissolved, the cellulose is obtained as a pulp.

A preliminary theoretical cost sheet of materials employed in the treatment is made up as follows:—

To yield 100 kilos of alkali-boiled and purified jute ligno-cellulose, we require 120 kilos of raw material, which at £12 per ton (1,000 kilos) represents 29s.

We have used of electrolytic products costing, say, 4s., the whole of the chlorine, and three-fifths of the alkaline products: to obtain, say, 75 kilos jute (cellulose) half-stuff or pulp.

As a set-off we have 6-7 kilos of HCl in the form of acid liquid, dilute and impure from the presence of some organic matter dissolved from the chlorinated fibre, together with the surplus of electrolytic soda. Presuming a use for such products, and estimating their value at one-half the cost of obtaining them by dissolving or diluting the ordinary commercial products, we might reduce the item of 4s. to 3s. 6d.

To treat 1 ton of boiled raw material, represented by 1,200 kilos of original raw material, the chemicals required are thus in the neighbourhood of 45s. per ton of half-stuff. The further costs are those of steam for the boiling and for power consumed in incidental mechanical operations : and, lastly, labour and superintendence, which would bring the total cost to, say, £24 per ton. With jute at present prices such a cost would be prohibitive. But we have selected jute merely as a chemical type. In our earlier days jute cuttings had a very different market value, viz., £5—£6 per ton, and a process on these lines would have had an industrial outlook.

We must plead the exigencies and limitations of a lecture as our reason for merely sketching the theoretical features of the industrial exploitation of a laboratory reaction. We conclude with an actual demonstration of the operations incidental to the treatment of 120 grams of material, and a very important result of experience, viz., that the cellulose chemist is expected to estimate very closely from observations on 100 grams of material what the factory working will show with 100 tons.

APPROXIMATE STATISTICS.

The following diagrams were used in illustration.

U.K. ANNUAL TRADE IN CELLULOSE PRODUCTS AND
DERIVATIVES.

	Production.
Cotton manufactures	£125,000,000
Linen, hemp jute	19,000,000
Rope, twine, net	3,500,000
Cocoa fibre, straw hat, and miscellaneous ...	2,000,000
Paper and boards	13,500,000
Special industries, cellulose derivatives, explosives, celluloid, and artificial silk	3,000,000
Coal, 260,000,000 tons, say	150,000,000

CHEMICAL MANUFACTURES.

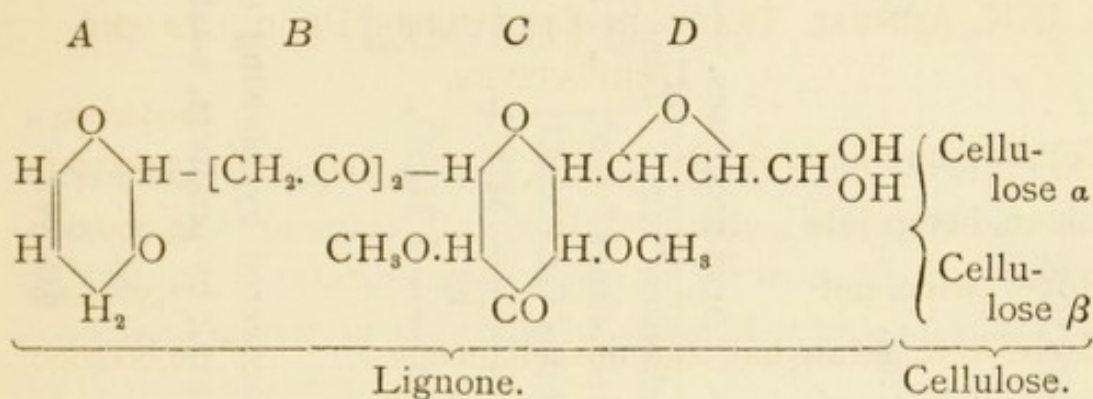
Total production, United Kingdom	£23,740,000
„ „ Germany	62,500,000
Aniline, anthracene dyes & indigo } German exports, total ...	8,000,000
of which to United Kingdom	1,700,000

Percentage-ratio of chemical manufactures to total trade.

	United Kingdom.	Germany.
Imports	1·5	4·5
Exports	4·5	9·5

[E. F. Hooper—"Some Aspects of Chemical Trade"—*J. Soc. Chem. Ind.*,
31, p. 7, 1912.]

Schematic Formula. Lignone complex (jute lignocellulose)
approximately $C_{20}H_{22}O_{10}$.



Constituent Groups.

A Benzenoid

B Ketene

C Pyrone or Hydropyrone

D Side chain : Aldehydic

Methoxyl

Quantitative Diagnosis.

Chlorination to $C_{19}H_{18}Cl_4O_9$
and reactions of Cl: deriva-
tives.

Acetic acid by hydrolysis, oxi-
dation and destructive distil-
lation.

Production of acetone and
maltol; various reactions.

Reaction with bisulphites and
production of lignone sulpho-
nates.

Estimation. Zeisel method.

CELLULOSE FROM CONIFEROUS WOODS.

Forest woods. Barked. Knotted. Chipped.

Digested at high temperatures.

Alkaline processes.

Acid processes.

Temp. 170°. Temp. 180°. Temp. "Mitscherlich" 120°. Time 55 hours.

Caustic Soda.

Caustic Soda

" " Ritter-Kellner " 140°. " 12 "

and Sulphide of Soda.

Bisulphites CaO MgO

% of Wood 17. 20 { 16—Na₂O (NaOH + Na₂CO₃)
4—Na₂S

15 SO₂ { 5 — M"SO₃
10 — H₂SO₃

Incineration—

Loss made up with

Na₂CO₃

Na₂SO₄

Recuperation { Loss made up
with Na₂CO₃

Deoxidised by incineration to Na₂S (and Na₂CO₃)

$\frac{1}{3}$ recovered by blowing off.
 Organic by-products, waste.

[See p. 50.]

Yield of Cellulose =

33—35 %

33—35 %

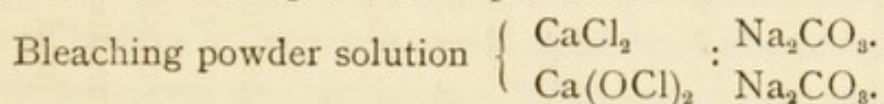
40—42 %

Lecture II.

Having in our first brief survey of the field of cellulose, taken a few prominent examples of industrial problems as illustrations of principles, we revert to our main theme, which is colloidal matter, or the colloidal state, of which cellulose is the obvious prototype.

It will be useful to give a few practical demonstrations of colloids, in their various moods and tenses, not only for their detached interest as striking forms of matter, but to present these types as an evolutionary series in progressive development of properties which culminate in cellulose.

A familiar case of a transitional colloid that is rapidly passing from the colloidal to the crystalline form, is calcium carbonate in its hydrated state, resulting from double decomposition, as in the preparation of sodium from calcium hypochlorite according to the simple reaction:



On mixing solutions of equivalent concentration, solidification takes place. We may assume that we have a complex of all the active groups with very great hydration capacity: a phase of synthesis. Cleavage then asserts itself, with reversion to the simpler molecular forms: the calcium carbonate, as a dehydrated crystalline body, now occupying its normally small volume. It is quite probable that this is a very general characteristic of reaction, and that the colloidal phase represents a synthetic complex with an interior unstable equilibrium of affinities. The colloids we shall consider are

all complex polyhydroxy compounds, and of these compounds, whether inorganic or organic, it is generally true that the OH groups are of variable function, which, at the extreme of divergence, represents a polar opposition, or, in our ordinary terminology, the opposition of base and acid. Alumina is an obvious case; and in silica we can easily demonstrate that one of the OH groups manifests basic properties.

We show the simple experiment of adding to a solution of sodium silicate, hydrochloric acid one-tenth less and one-tenth more than equivalent to the soda. The former sets to a "gel," the latter remains fluid, through formation of a saline chloride or hydrochloride. This observation is due to Prof. Jordis, of Erlangen.

In the carbohydrates, the development of polarity, or amphoteric opposition, may be referred to characteristic constituent groups of Ketene or $\text{CO}-\text{CH}_2$ configuration, this labile and somewhat elusive complex, which appears as a factor of constitution of many groups of carbon compounds. As to the potentialities of this "diatom," we refer our audience to a highly instructive and suggestive paper by our Chairman ["Derivatives of the Multiple Ketene Group." J. Norman Collie—*Chem. Soc. J.*, 91, p. 1806 (1907.)]

Starch, which we have taken as a type of colloid, occupies a unique position, whether considered from the point of view of organic function, industrial utility, which is largely the fulfilment of its organic function in relation to animal life, or its special chemistry. We must presume acquaintance with all that defines its special position in the world of matter and science, since for obvious reasons we can only call attention to certain of its particular characteristics.

Occurring in specialised forms, its colloidal "habit" is particularly manifested in the phenomena of its hydration, the swelling and bursting of the granule in contact with water at specific temperatures to a state of pseudo solution, the

familiar starch paste. This may be regarded as a distension, *ad infinitum*, of the starch granule, presenting in the aggregate a complex of phases; consequently, on drying a starch paste, there is a diversity of reversion phases, producing a discontinuous solid residue, with more or less of the structure of the original granule.

Hence, in many of the industrial uses of starch, *e.g.*, as a "finishing" agent for textiles, there is an evident cause of low efficiency. For it is manifest *per contra* that the true colloid is one that is homogeneous throughout its solution phases, and in reverting, by loss of solvent, maintains that continuity of mass which, in thin layers, produces a transparent film.

It is common knowledge that starch is extremely sensitive to acids, and alkalis, and, even though a "saturated" body, to oxidants; and by various treatments with these reagents, is modified to "soluble starches," in which there is an approximation to the true colloid as above defined. Without attempting to describe or compare these numerous products, we call attention to one with which we are familiar, produced by interaction of dry starch with glacial acetic acid. This action results in partial acetylation and an attack on the starch complex or aggregate, which may be controlled to produce a range of definite variations of the essential colloidal properties. These products known as "Feculose" are employed in industry for various purposes and, in accordance with requirements, they may be prepared so as to yield true solutions of high concentration, *e.g.*, up to 25 per cent., which may be either permanent, or revert to a gel when the originally hot solution is allowed to cool.

Specimens of such Feculose solutions are submitted, comparatively with pseudo solutions of starch produced under similar conditions. It is well known, however, that the limits of fluidity of starch pastes from ordinary starches and modified starches is reached at 5—10 per cent. concentration.

The most important use of Feculose—one of many—is in paper coating, that is, the surface filling of papers to be used as the basis of mechanical prints. In producing these “art papers,” a white inert pigment is suspended in a colloidal medium, *e.g.*, gelatin, or casein solution, and the mixture is applied to the paper surface by rollers, followed by a brushing treatment to complete the even distribution of the coating. The paper thus coated is carried forward and hung in festoons in a drying-room, and is reeled off continuously at the end of its travel, to be finally surfaced by calendering.

Feculose in this industry replaces casein, weight for weight, and gelatin of best quality in the proportion of 5:4, with the advantages (1) of being a colourless and nitrogen-free solid, and (2) that high temperatures can be used in drying.

This is a useful, practical example of the industrial colloid, and the appreciation of colloidal quality by chemical treatment. For the scientific account of these products we refer to: “Die niederen Acetyl-derivate der Stärke und Cellulose”—Cross, Bevan and Traquair, *Chem. Ztg.*, 29 (1905).

Starch is to the biologist the first visible product of assimilation in the plant cell, but its main function is that of reserve material stored in the seed endosperm to supply nutrient material for transformation by the germinating embryo; to the chemist it is a polyhexose anhydride, and by reason of its hydrolysis to sugars, the basis of the fermentation industries,—that government-ridden section of chemical industry!

Proceeding upward in the chemical scale, we have now to mention a group of plant products, also conspicuous and widely distributed as constituents of seed endosperms, which may be classed as hemi-celluloses. This term indicates a genetic relationship of the bodies to cellulose, which may or may not be actual: we are only concerned to demonstrate that their properties are intermediate between those of starch and cellulose.

As a type, we take the endosperms of the locust bean (*Ceratonia Siliqua*), and show specimens of the following stages of treatment: (a) separation of endosperms from cotyledons on the one hand, and external protecting tissues on the other, *i.e.*, the proximate resolution of the seeds into component tissue; (b) digestion of endosperms with water at 90—100°, and progressive hydration to the condition of a “gel,” or pseudo solution, in which, at 3 to 4 per cent. strength, it is an industrial product known as “Tragasol.”

The actual constituents of this “gel,” according to the exhaustive researches of E. Bourquelot, are in the main mannan and galactan, the anhydride form of the hexoses mannose and galactose, in the proportion of 4:1. According to our own observations, the proportion of galactose is usually somewhat lower, *viz.*, from 10 to 15 per cent.

The elementary composition of the complex we have determined as follows:—

(a) Composition of total solids.

(b) Composition of solids precipitated by alcohol.

			(a)		(b)
Carbon	42.40	...	43.50
Hydrogen	5.98	...	5.90

which numbers conform with the general distinction in this group between hydration and hydrolysis: hydration of the anhydrides proceeds to indefinite limits without determining hydrolysis. These hemi-celluloses are in effect resistant to enzyme hydrolysis, but are readily attacked by acids and alkalis.

The industrial uses of tragasol are conditioned by these properties, together with the most important property of reverting to a continuous solid, that is a translucent film. Specimens of the tragasol film are submitted, showing an apparently fibrous structure due to considerable residues of the original cellular structures of the hemi-cellulose, drawn out by manipulation of the viscous “gel.”

The precipitation of these hemi-cellulose hydrates by tannic acid yields a new colloid of remarkable properties.

Taking for the mannan-galactan complex the formula $C_{12}H_{22}O_{11}$, and for tannic acid $C_{14}H_{10}O_9$, combination takes place approximately in the ratio of the formula-weights; the following numbers having been obtained for the elementary composition of the precipitated compound:—

Carbon	47.3
Hydrogen	4.4

The new colloid, termed "Cutiloid," insoluble in cold water, separates as a massive homogeneous curd, representing 5—6 per cent. of solid contents. On slightly raising the temperature, *i.e.*, to 40—50° C., the mass changes from a white coagulum to a transparent homogeneous solution with an enormous increase of viscosity: the change is comparable in sharpness with the bursting point of starch granules at 60—70° C. under similar conditions of heating, but with the difference that the phenomena are reversible.

The properties of the new colloid mark it out for various industrial applications, which will be evident.

Most characteristic are its reactions with gelatin. The reactions of tannic acid with gelatin, and the colloids of animal skin, are well-known: by the previous combination of tannic acid with the complex carbohydrates, its interaction with gelatin is entirely changed. Highly complex colloidal bodies result, but without separation from solution. Hence the application of cutiloid as a tanning agent.

The tanning by "Cutiloid" may be shortly described as a restrained effect, and practical experience has shown that by thus restraining and modifying the attack of tannic acid, it is possible to carry on the tanning process with great rapidity, and without detriment to the product. This is a feature of colloid phenomena which has its parallel in the well-known practice of the silk-dyer. The avidity of silk for colouring

matters is so considerable and general that it would be impossible to dye silk evenly in the skein or mass by the ordinary practice of a dyeing bath, unless the intensity of interaction were restrained. This is effected in practice by using in place of water as the medium, the solution obtained by neutralising the liquors used in degumming the silk. These are soap solutions, and, after boiling with the raw silk, contain its hydrolysable colloids in solution. On neutralising with acid, there is formed a complex colloidal emulsion, and the colouring matters enter into intermediate combination with the components of the emulsion, through which they are taken up by the silk substance at a very much reduced rate, and for obvious reasons.

Before we leave this group of hemi-cellulose colloids we mention another product which has considerable interest.

This is known as "Japanese Isinglass,"* or more generally as Agar-Agar. The preparation of colloids, from edible seaweeds, *e.g.*, *Calidium Lamouroux*, is a characteristic Japanese industry, and occupies about 70 villages on the coast provinces of Yamashiri-Tanba, Setsou, and Shinane. It is a steadily

* There is some doubt as to the identity of this particular specimen, a portion of a large exhibit at the recent Anglo-Japanese Exhibition. Its general characteristics are those of Agar-Agar, which is the Malayan name ("sea-weed") for *Gracilaria lichenoides* (G. Birdwood, *Jour. Royal Soc. Arts*, 60-439). The percentage of galactose estimated is lower than the 33 per cent. usually accepted for Agar-Agar. (König and Bettels, "Chem. Centralblatt": 1905, ii., 1606.) The low yield of furfural (and methyl furfural) appears to exclude celluloses of laminaria. It is also doubtful whether the above description of an industry does not rather apply to the "Nori," a popular foodstuff in Japan, obtained from *Porphyria Laciniata*.

The point, however, is not material, the substance being a typical cellulose of the second group, as distinct from the first, which are those of seed endosperms, and a large Japanese industry in such products actually existing.

For a full account of these characteristic colloids see "Biochemisches Handlexikon" (E. Abderhalden), Vol. 2. Springer, Berlin, 1911.

increasing industry, and the value of the exports for 1910 was 16,000,000 yen (1 yen = 2s. 0½d.). Most of this is exported to China, where it is consumed as food.

Specimens of this product are exhibited, and we demonstrate its characteristic relationships to water. A 2 per cent. solution reverts on cooling to a firm structureless jelly. From this we have prepared the reverted product in transparent film. We have investigated this colloid, with others of the same class, and we may mention its approximate characteristics as follows :—

Moisture (air dry)	22.9
Ash	2.9
Albuminoids	0.91
Furfuroids	2.5 calculated from the yield of furfural 1.2 %

The most characteristic constituent is galactan carbohydrate, which we estimated at 25.0 per cent. It is to be noted that this product has a limited sale in this country, at a wholesale price of 1s. 6d. per lb., c.i.f. London. Its chief consumption is in the preparation of cultural media in bacteriological research.

It will be evident that these are not merely types selected at random, but naturally or artificially selected, each as a basis of industry. It is not to be affirmed that this selection is finally exclusive; it is certainly true that throughout the natural world there are vast numbers of these colloidal substances presenting altogether special properties, and in the future the science will use this material in formally attacking the problem of the causal relationship of structure to constitution, which problem is for obvious reasons more directly suggested and defined by the natural and industrial function of cellulose.

The colloidal characteristics of cellulose are conspicuous in all those reactions which result in a soluble product.

Though we limit ourselves in this exposition to the cellulose-water series, we just note that the higher synthetical derivatives, the cellulose esters, soluble in specific solvents,

present a closely similar range of properties, notably gelatinisation by the solvent as the first stage, then solution to a more or less homogeneous fluid of high but variable viscosity, and a working maximum of filterable solutions at 7—8 per cent. cellulose.

Hence it is immediately clear that the specific colloidal characteristics of cellulose are not bound up with its OH groups, and this gives a first suggestion that these properties have a more deeply-seated cause and origin than the condition of proximate constitution or molecular aggregation.

Cellulose presents us with a bewildering complexity of forms and degrees of hydration, of which we first demonstrate some conspicuous examples, connecting cellulose with the colloids previously described.

Cellulose and Zinc Chloride.—The hydration of cellulose by zinc chloride (50 % ZnCl_2Aq), at 60—70° C., proceeds in unbroken continuity to the maximum represented by solution. The aqueous solution at 1—2 per cent. concentration (cellulose), limpid and viscous at 60°, reverts on cooling to a firm homogeneous gel.

The reactions involved in this series of phenomena are, chemically speaking, obviously of the simplest, and suggest that cellulose interacts as an amphoteric complex, that is, reciprocally, with acid and basic groups of the metallic salt.

Cellulose. Alkaline Hydrate—Carbon Disulphide.—These are stages in the now well known and often described “Viscose” reaction, and we demonstrate an extended series of these products, including those of reversion from the fluid stage by spontaneous decomposition of the xanthogenic ester.

It will be noted that the first product, alkali-cellulose, which has the percentage composition

Cellulose—25 NaOH—12 Water—63

represents considerable hydration of the cellulose, with which are associated large modifications in the structure of the fibre.

After reaction with the bisulphide, the new ester, as Na salt, has a great avidity for water. We demonstrate this combining capacity by the reaction in which we substitute a lignocellulose.

The association of the cellulose and lignone groups somewhat modifies the reaction. It will be noticed that as we proceed to treat with water the reaction product from 5 grams original jute, there is an enormous and progressive distension of the fibres, and we obtain a colloidal sponge occupying some 1,000 c.c. To this we add acetic acid, which at once attacks the coloured alkaline by-products, but which only slowly attacks the xanthate soda. We hasten the reversion, which, to take place spontaneously, requires a lengthened period, and we have a complete restoration of the original fibrous structure. We may regard this extreme distension as the penultimate stage of hydration of cellulose with the structure persisting. It is impossible to draw any line between this phase and the ultimate condition of a structureless solution, if indeed any such can be prepared. The demonstration is an ocular one of the continuity of the solution and reversion phases, which condition the important industrial uses of these derivatives.

Less obvious than these extreme cases are the partial hydrations which accompany and condition the processes of the papermaker.

The mechanical process of "beating" fibrous materials has the two functions, the reduction to uniform and convenient length (2—3 mm.), and the production of a condition of the pulp which affects its suspension in the carrying medium, which is water, and determines a graduated sedimentation as it parts with water, through the sieve or continuously running wire of the papermaking machine. That this condition of the pulp of cellulose is, or involves, hydration, will be easily recognised when the beating process has been prolonged to 24—36 hours. The product then is recognised as a hydrated colloid, and,

when allowed to dry in masses, these finish as a coherent aggregate, to which the term "cellulith" is applied.

In the earlier stages of beating, the effects of hydration are empirically recognised in the terminology of the "beatermen"; the stuff in process develops "wetness" or "greasiness."

The complex of effects produced in the beater are now the object of analytical study, and of inventions designed to separate and control the various factors, notably that of hydration. Mr. H. Jackson, of Garstang, Lancs., papermaker, adopting fundamental views of his raw materials as colloids, and of colloidal quality that it is a variable to be controlled and is measured by hydration capacity, has invented a beating engine designed especially to give maximum hydration effects in minimum time. The mechanical principle of the new beater is a "wet hammering" of the fibres, effected by actual hammers operating centrifugally, so that the force of the blows will vary with the speed of rotation.

We could very well occupy an entire lecture in discussing the problems of this section of cellulose technology. It must suffice to demonstrate a series of products showing the graduated development of the more obvious colloidal characteristics with progressive hydration, up to extreme products in gelatinous forms, which revert on desiccation and dehydration to coherent solids: these can be turned and polished, being, in fact, aggregates of fibrous residues embedded in relatively structureless colloidal cellulose.

These effects of hydration are not only positive factors of the first order of the structural qualities of paper and boards, but they play their part in the process of sizing, by which these products are rendered relatively water and ink-resistant. It would take us too far afield to introduce a technical discussion of the process of "engine sizing" by means of rosin. If we merely state a typical case, we shall direct attention to a technical principle involved in the result.

One hundred parts of fibrous cellulose, beaten with 2,500 parts water, receive, as sizing agent, 2—4 parts rosin in solution as soda-rosin soap, to be decomposed by sulphate of alumina in excess. Now it is assumed in the text-books that the sizing effect produced is the result of double decomposition between the reagents, and deposition of the precipitated resinate as a coating of the fibres—the latter, therefore, a purely mechanical effect, the cellulose being inert. A little consideration will show that this view is superficial; what is involved is a complex equilibrium (1) as between cellulose plus cellulose hydrates, and soda resinate in highly dilute solution, say 1/1000; (2) as between the products of interaction under (1) and sulphate of alumina. That is a final equilibrium as between cellulose—to be regarded as a colloidal hydroxide, of amphoteric character: alumina, which may be described in the same terms, and the resin acid (abietic acid).

This problem is essentially a problem of colloidal chemistry, as, indeed, are all the mill operations of the paper-maker.

The process is the subject of considerable difference of opinion amongst technologists, as to the actual effective sizing compound, and divergent practice as to employing rosin sizes of "neutral" or "acid" composition.

There are in effect several systems of acid sizing, that is, based upon a rosin size containing 20—40 per cent. of free or uncombined resin acid: systems which claim to economise from 20—33 per cent. of the sizing costs, and are industrially exploited on this basis.

But in this controversy the cellulose has been left out of consideration, as the inert recipient of an added effect. The contribution of hydrated colloidal cellulose from the beating operations is also generally ignored.

It is clear to us, and we suggest to our younger technologists, that in these primary and secondary factors

of value of paper and boards, there are margins of value which are largely ignored.

If we can only get our manufacturers to recognise clearly that of the primary group, the values of the fibrous raw materials are the commercial or actual cost, $\frac{\text{minus}}{\text{plus}}$ say 30s. a ton, and in the secondary group, the value of rosin (in sizing) is its commercial cost, $\frac{\text{minus}}{\text{plus}}$ 3s. (per ton of paper), and that it is the function of the trained chemist to use his abilities in this field of margins towards controlling their incidence on the plus side, we shall have done something for technical progress.

On this question of rosin-sizing we refer to a recent experimental investigation of Remington, Bowack and Davidson, printed in *J. Ind. Eng. Chem.*, iii., No. 7 (1911).

The phenomena of engine-sizing thus briefly discussed are of the same order as those processes of dyeing and colouring which in the main are accessory to the textile and paper industries. We have no intention of entering upon this territory further than to point out that for the routine of industrial work in cellulose, a study of the practice and theoretical principles of dyeing is a necessary equipment.

But if beyond this the chemist is attracted as a contributor to the literature of the theories of dyeing, we would enjoin a severely critical programme of research; and above all to be critically selective of really typical cases, whether in the fibre substance taken for experiment, or the colouring matter to be studied.

It is to be observed that, as regards the latter, there always has existed a wealth of material, that is of compounds constitutionally defined; and in the region of "Cellulose," we now have an accumulation of definitely varied derivatives, not only as regards chemical constitution, but also in regard to minute structure and dimensions.

Lastly, there are features in the actual dyeing processes, as in the product which may be selected as typical, such as in the interaction of lignocelluloses and ferric ferricyanide.

These reactions admit of demonstration, and we show the process of dyeing jute with 10—20 and 30 per cent. its weight of the blue cyanides, by simple immersion in the solution of the red cyanide. The typical features of this are—the large proportions of cyanide taken up, without affecting the external characteristics of the fibre; accompanying this unusual combination and interpenetration of two colloids, there is a rearrangement of groups, with transference of oxygen to the unsaturated lignone groups, and production of ferroso ferric cyanides.

It will have been observed that, throughout this brief exposition of the main aspects of "Cellulose," questions of structure are always present. The structural cycle is in fact this: we only know the raw material in the specialised forms of the plant world, fibres and cells; by mechanical devices we can destroy the form more or less with little change of substance; by chemical means, *i.e.*, by reaction, we advance another stage, *viz.*, to that of structureless solution, but with certain constitutional modifications of the cellulose; from these solutions we can revert to the solid form, and by suitable means produce thread, film, or massive solids.

These artificial forms of cellulose in continuous length are of regular or controlled dimensions, and hence it is evident that throughout the entire cycle, structural problems move hand-in-hand with molecular changes which we, of course, can only visualise by theory and imagination. At present the connection between these complementary phenomena is an empirical one, but we cannot doubt that the progress of research will establish the causal relations in quantitative terms.

It is obviously necessary for the chemist entering this field to master the general principles of histological research; questions of minute structure and dimensions are at the root of practice in the textile and papermaking industries, and problems involving measurements even in the *ultra visual* region are as numerous as daisies, in the field of colloids.

The study of structure and minute dimensions in this field has originated and developed rather on an empirical technical basis. The transition to a scientific use of the *data* furnished by these methods is a direct one. Thus, as an illustration: for the artificial fibres considered as regular cylinders, we may take the surface as the product of length by perimeter of sections, *i.e.*, $l \pi D$, and surface varies with diameter. In the finer threads or "silks" the unit filament presents about 1 Cm^2 of surface per metre of length; or the textile thread 14—17 times this surface. Taking a reaction, depending primarily upon surface, an investigation of the rate of combination of the dehydrated product with atmospheric moisture, may therefore be directed to the rate per unit of surface. Threads of any required diameter being prepared may be compared on this basis; and, moreover, the masses of such threads varying as the square of diameter, we can thus establish in numerical terms the mechanism of communication of the hydration effect from the surface inwards. From such *data* it would be possible to arrive at a measure of the exterior surface of natural fibrous celluloses, *e.g.*, cotton, of irregular and variable form.

The ratio of surface to mass is generally assumed to be specifically characteristic of colloids, but the conception is applied in this sense to the unit masses, molecules, or polymolecules of the colloids, *i.e.*, as chemical individuals. A study of the grosser relationships of the visible forms of matter in this order of idea may very well lead to speculative

treatment of the more fundamental constants, and, by means of reactions, to some relative measure of the reacting unit.

But apart from remote speculation, a whole field of work is waiting to be ploughed by standard physical methods, and sown with seed of established ideas and conceptions. Thus, specific volumes, solution volumes, volumes in relation to temperature observed in media with and without presumed interaction with the celluloses, and even the fundamental constants of specific heat, have not been seriously studied in this region of celluloses, cellulose derivatives and compound celluloses.

And, as we have endeavoured to show by demonstrations of allied forms of matter as particular variants of colloidal matter, such physical methods may be extended to include a graduated series of colloids having very definite connecting links with the simpler forms of matter for which physical constants are in effect measures of the reaction unit, or molecule, according to the fully established generalisations of the science.

From cellulose in relation to science, we revert in conclusion to the question of its economic basis and relationships.

The world's supplies of cellulose are divided between : (1) "crop plants," annuals under cultivation primarily for fibre, but yielding secondary products of very great value, of which we need only specify cotton-seed, flax-seed, and (2) perennial woods, which furnish the staple raw material of the paper industry.

In either group there are economic problems of great magnitude, whether in the region of primary supply in relation to consumption, or affecting the secondary element of value in the possible utilisation of waste products.

A concise handling of some of these problems will be found in a recent publication of the U.S. Department of Agriculture, "Crop Plants for Papermaking" (C. J. Brand), 1911.

Of present waste materials potentially available, this brochure mentions,

Corn stalks	30,000,000 tons,
Rice straw	1,500,000 „

also flax straw, megasse or bagasse; the sugar-cane refuse; and cotton-seed hulls, *i.e.*, the residues of the cotton-oil and cake industry retaining a proportion of cotton fibre (20 per cent.) which has resisted the ginning process. Of this latter, the amount available in the United States may be estimated at 1,500,000 tons annually.

The separation and utilisation of this cotton hull fibre as a staple papermaker's cellulose, has been very much advanced by the recent invention of machines which effect a very perfect separation of fibre from shell residues, producing a raw material of 85 per cent. Cellulose concentration. An Anglo-American Corporation (American Cotton Hull and Fibre Co.), exploiting this invention, is already placing a considerable annual tonnage on the European market.

For a general *exposé* of this interesting development, we refer to a paper by Beadle and Stevens, *J. Soc. Chem. Ind.* 28, p. 1015.

As to megasse, which is certainly capable of producing a staple half-stuff, fulfilling many of the requirements of the papermaking industry, the potential supply, estimated on the basis of the world's production of cane sugar, is 9,000,000 tons. Many attempts have been made towards an effective industrial solution of the problem, but so long as wood is able to meet the world's demands, on the present basis of competitive values, it imposes a standard of quality *quâ* cellulose, or fibre,

which competing raw materials have so far been unable to meet. The reasons for this, which are technical and economical, will be found fully dealt with in the standard textbooks. But, with increasing demand, and in absence of general systematic forestry for maintaining the supply of raw material, there may be a serious shifting of the economic equilibrium, and a place made for one or more of the supplies to be derived from present-day waste products.

But the wood cellulose industry cannot be said to have reached its economic basis so long as we have to number the by-products of the bisulphite process amongst the world's wastes. The lignone constituents of the lignocellulose, or wood substance, pass into solution in the cellulose process with little change beyond that of sulphonation. Notwithstanding this, and the high utility of the lignone complex in the natural order, we, that is, industrial we, have no use for it. This is one of the most conspicuous of our economic failures; the waste of organic matter in this form, potentially valuable, is simply colossal.

It must not remain unmentioned that certain directions of utilisation are being exploited, and technically developed; but, it must be confessed, on an insignificant scale. They only serve to emphasise the fact of the general waste and loss of value which eclipse the familiar and historical cases of glycerin and the by-products of coal-gas manufacture.

Given a value of only £5 per ton for this material, obtainable in marketable form at little more than the cost of evaporation, we see that in the wood cellulose industry there is still one of those large margins of unrealised value, which it is difficult to credit in these days of advanced technology.

But the wood industry has yet another colossal waste to bewail, and that is in the familiar form of sawdust, turnings and general waste of mechanical processes.

Here, again, we have certain directions of utilisation, *e.g.*, the mechanical grinding to wood meal and the chemical processes of dry distillation, and fusion with alkalis for the production of oxalic acid. Of minor uses, we may mention the attempts to prepare fermentable sugars by processes of acid hydrolysis, and employing these as the raw material for alcohol, or the entire product as an ingredient of cattle foods.

But sawdust is still a typical "by-word," and if we could knock the sawdust out of the world's dreams of wealth by utilising it on an adequate scale, it could well afford to give up dreams for a season.

There is, in conclusion, no conclusion to this subject, save the formal one dictated by space and time limits! As we said at the outset, it is a subject for the younger generation of chemists; it is just beginning to take definite scientific shape, and may be destined to carry us into regions of natural history which our forefathers loved long since, and we, perhaps, have lost awhile.

EXHIBITS.

The lectures were illustrated by exhibits and a range of special products, more particularly :

Artificial Silk (Viscose Process), full range of specimens, for which we are indebted to Messrs. S. Courtauld & Co., Ltd.

Films of Cellulose (Viscose Process) one metre in width, continuous length. These are manufactured by the Société Blanchisserie et Teinturerie de Thaon, and the Société Française de la Viscose, to whom we are indebted for the specimens.

Feculose, and its applications to coated art papers, confectionery, etc., for which we are indebted to the Feculose Co., of Paisley, N.B.

Tragasol, raw material, industrial forms, films, photographs, and specimens illustrating applications to leather, etc., for which we are indebted to the Gum Tragasol Supply Co., Ltd., of Hooton, Cheshire.

Cotton Hulls, raw material, bleached fibre, and specimens of papers, for which we are indebted to the American Cotton Hull and Fibre Company, Ltd., London.

Jackson Beater specimens of beaten materials, and papers, for which we have to thank Mr. H. Jackson, of Garstang, Lancs.



