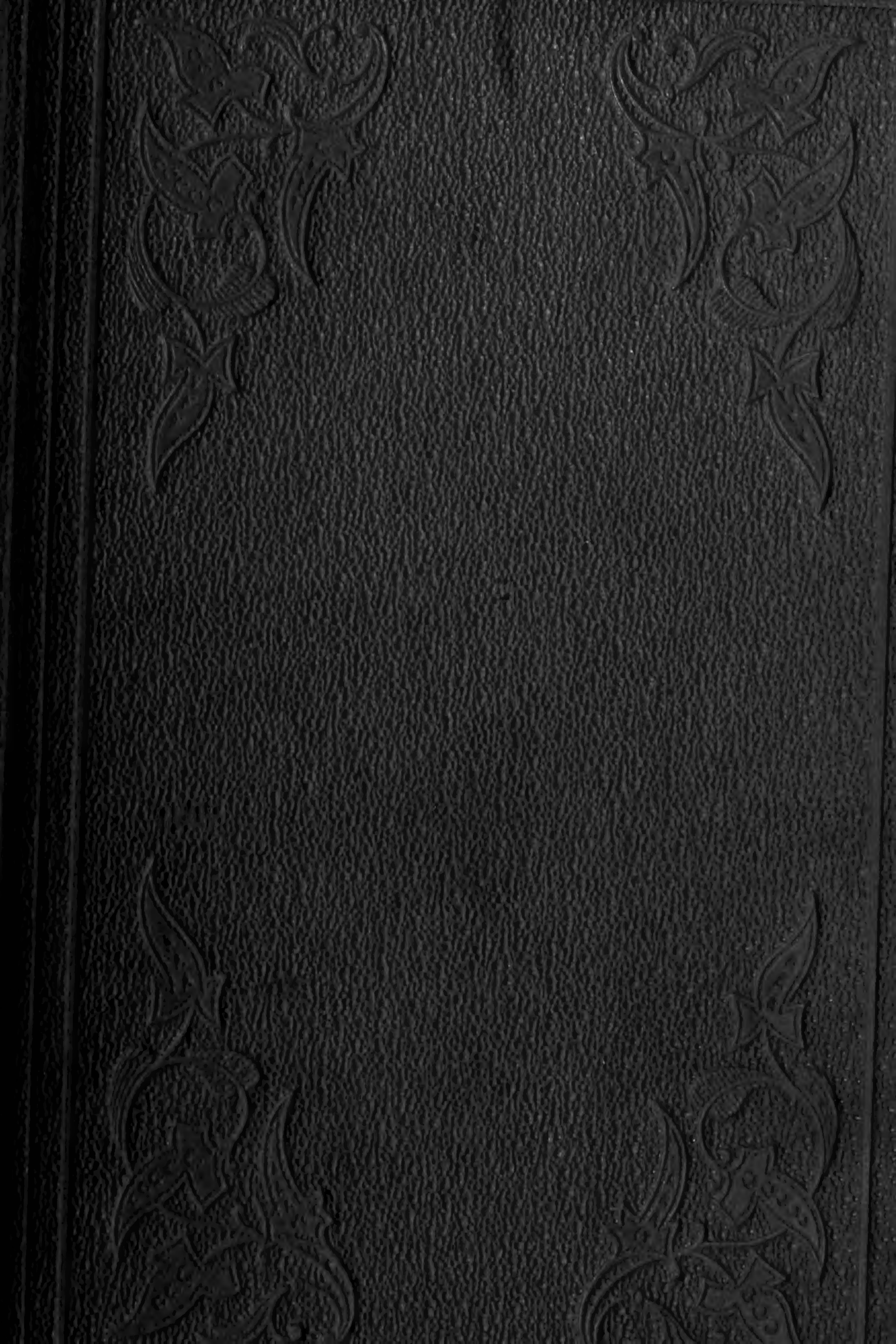

REPORT

OF THE

BRITISH ASSOCIATION

FOR THE ADVANCEMENT OF SCIENCE

1918.

LONDON
JOHN MURRAY, ALBEMARLE STREET
1919

Office of the Association: Burlington House, London, W. 1.

PREFACE.

THE Annual Meeting of the British Association in 1918 was cancelled, for the second year in succession, under circumstances described in the Report of the Council included in this volume.

As in 1917, the Organising Committees of the Sections, having been empowered by the Council to do so, held in the early part of the summer such meetings as were necessary to transact such business as was essential in spite of the cancellation of the Annual Meeting, including the forwarding to the Committee of Recommendations of proposals for the appointment or reappointment of Research Committees, and for grants of money to some of them. The Organising Committees were also empowered to receive Reports from Research Committees, and to recommend for printing in the Annual Report such of these Reports as it was thought undesirable to delay.

On July 5, 1918, in the rooms of the Linnean Society, meetings were held of:—

The Council, at 11.30 A.M., to approve the Report of the Council to the General Committee, and for other business;

The General Committee, at 12 noon, to receive the Reports of the Council and of the General Treasurer, to confirm the arrangements made in connection with the cancellation of the Annual Meeting, and for other business;

The Committee of Recommendations, at 2.30 P.M., to make recommendations to the General Committee concerning the appointment of, and grants of money to, Research Committees, etc.;

The General Committee, at 4 P.M., to receive the Report of the Committee of Recommendations.

The present volume contains, as usual, the Reports of the Council and of the General Treasurer, and the list of Research Committees appointed by the General Committee. The usual lists and other records referring to previous meetings are omitted. For the rest, the volume contains only the Reports of Research Committees, referred to above, of which the General Committee, on the advice of the other committees concerned, decided that it would be undesirable to delay the issue. The Report of the Meeting of the Conference of Delegates of Corresponding Societies, which was held in the rooms of the Geological Society on July 4, is also included.

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REPORTS ON THE STATE OF SCIENCE, ETC.

OFFICERS AND COUNCIL, 1918–19.

PATRON.

HIS MAJESTY THE KING.

PRESIDENT.

SIR ARTHUR EVANS, D.LITT., LL.D., PRES.S.A., F.R.S.

PRESIDENT ELECT.

The Hon. Sir CHARLES A. PARSONS, K.C.B., Sc.D., F.R.S.

GENERAL TREASURER.

Professor JOHN PERRY, D.Sc., LL.D., F.R.S., Burlington House, London, W. 1.

GENERAL SECRETARIES.

Professor W. A. HERDMAN, D.Sc., LL.D., F.R.S. | Professor H. H. TURNER, D.Sc., D.C.L., F.R.S.

ASSISTANT SECRETARY.

O. J. R. HOWARTH, M.A., Burlington House, London, W. 1.

CHIEF CLERK AND ASSISTANT TREASURER.

H. C. STEWARDSON, Burlington House, London, W. 1.

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BONE, Professor W. A., F.R.S.
BRABROOK, Sir EDWARD, C.B.
CLERK, Sir DUGALD, K.B.E., F.R.S.
DENDY, Professor A., F.R.S.
DICKSON, Professor H. N., C.B.E., D.Sc.
DIXEY, Dr. F. A., F.R.S.
DYSON, Sir F. W., F.R.S.
GREGORY, Sir R. A.
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HARMER, Dr. S. F., F.R.S.
IM THURN, Sir E. F., K.C.M.G.
JEANS, Professor J. H., F.R.S.
KEITH, Professor A., F.R.S.
MORRIS, Sir D., K.C.M.G.
PERKIN, Professor W. H., F.R.S.
RUSSELL, Dr. E. J., O.B.E., F.R.S.
RUTHERFORD, Sir E., F.R.S.
SAUNDERS, Miss E. R.
SCOTT, Professor W. R.
STARLING, Professor E. H., F.R.S.
STRAHAN, Sir A., F.R.S.
WEISS, Professor F. E., F.R.S.
WHITAKER, W., F.R.S.
WOODWARD, Dr. A. SMITH, F.R.S.

EX-OFFICIO MEMBERS OF THE COUNCIL.

The Trustees, past Presidents of the Association, the President and Vice-Presidents for the year, the **President** and Vice-Presidents Elect, past and present General Treasurers and General Secretaries, past **Assistant** General Secretaries, and the Local Treasurers and Local Secretaries for the ensuing Annual Meeting

TRUSTEES (PERMANENT).

The Right Hon. Lord RAYLEIGH, O.M., M.A., D.C.L., LL.D., F.R.S., F.R.A.S.
Major P. A. MACMAHON, D.Sc., LL.D., F.R.S., F.R.A.S.

PAST PRESIDENTS OF THE ASSOCIATION.

Lord Rayleigh, O.M., F.R.S.
Sir A. Geikie, K.C.B., O.M., F.R.S.
Sir James Dewar, F.R.S.
Sir Norman Lockyer, K.C.B., F.R.S.
Arthur J. Balfour, O.M., F.R.S.
Sir E. Ray Lankester, K.C.B., F.R.S.
Sir Francis Darwin, F.R.S.
Sir J. J. Thomson, O.M., Pres.R.S.
Professor T. G. Bonney, F.R.S.
Sir E. Sharpey Schafer, F.R.S.
Sir Oliver Lodge, F.R.S.
Professor W. Bateson, F.R.S.
Professor A. Schuster, F.R.S.

PAST GENERAL OFFICERS OF THE ASSOCIATION.

Professor T. G. Bonney, F.R.S.
Dr. A. Vernon Harcourt, F.R.S.
Sir E. Sharpey Schafer, F.R.S.
Dr. D. H. Scott, F.R.S.
Dr. J. G. Garson.
Major P. A. MacMahon, F.R.S.

AUDITORS.

Sir Edward Brabrook, C.B.
Sir Everard im Thurn, C.B., K.C.M.G.

REPORT OF THE COUNCIL, 1917–18.

I. At their meeting in March the Council received the following resolution from the Local Executive Committee at Cardiff:—

> "That having fully considered the question of the visit of the British Association to Cardiff this year, the Committee is of opinion that under existing circumstances it is desirable to postpone the visit to the first opportunity after the war. The Committee is deeply disappointed that circumstances over which it has no control make this course advisable, but it is of opinion that the visit could not, during the war, be carried out in such a manner as the City and district would desire."

The Council adopted the following resolution:—

> "The Council of the British Association have considered the resolution of the Local Executive Committee at Cardiff, in which the opinion is expressed that it is desirable to postpone the visit of the Association to Cardiff. The Council sincerely regret the necessity for this decision, but under the circumstances fully concur in it, and it is, therefore, resolved that the Meeting at Cardiff be postponed."

The following resolution was subsequently passed by the Parliamentary Committee and confirmed by the City Council of Cardiff, and is referred to the General Committee:—

> "That in order to comply with the formalities of the Association, this Committee recommend the Council cordially to renew the invitation (formally presented on the 7th September, 1916, by an influential deputation) to the British Association to visit Cardiff in one of the following years, namely:—1919, 1920, or 1921, having regard to the unavoidable postponement of the visit this year, such renewed invitation to be made by letter in accordance with the suggestion received."

The Council desire to place on record their grateful appreciation of the cordial co-operation of the authorities at Cardiff in the discussions which have taken place.

II. The Council discussed the question of holding a Meeting of the Association or a General Conference in London during the present year, but proposals to such effect were withdrawn.

Having regard to the cancellation of the Annual Meeting, the Council have made arrangements similar to those which obtained last year for carrying on the necessary business of the Association.

III. The Council recommend that Sir Arthur Evans' term of office as President be extended until the beginning of the next Annual Meeting.

IV. The Association has received from the Royal Society a grant of 250*l*. for purposes of research and publication during the current year, and the Council returned to the Society a most cordial vote of thanks on behalf of the Association.

V. A grant of 6*l*. from the interest of the Caird Fund was made to the Committee appointed to arrange meetings, &c., on Geophysical subjects.

VI. The Council propose to the General Committee the following addition to the Rules :—

In Rule 1, Chap. X., following the words ". . . to cancel a ticket of admission already issued,"

"If it appears to the Council that it is not desirable that a person shall continue to be a Member or Associate of the Association, the Council shall direct the General Secretaries to ascertain whether that person is willing to resign his membership or associateship.

"If that person do not, within a time to be fixed by the Council, either resign or appeal in writing to the General Committee, the Council may declare him to be no longer a Member or Associate. Upon the appeal, the General Committee may make the like declaration by a majority of two-thirds of those present and voting.

"The Council shall also have power to refuse application for membership or associateship."

VII. The Council have received accounts from the General Treasurer during the past year, and these will be presented to the General Committee subject to audit.

VIII. The Council recommend to the General Committee that, in view of the diminution of business consequent upon the cancellation of the Annual Meeting, there be no change this year in the *personnel* of the Ordinary Members of Council, and that the operation of Rules 1 and 3, Chap. V., governing such change, be suspended.

In consequence of this recommendation, the Council do not notify the names of any of its members for retirement, and have made no nominations of new members.

IX. The General Officers have been nominated by the Council as follows :—

General Treasurer :	Prof. J. Perry.
General Secretaries :	Prof. W. A. Herdman. Prof. H. H. Turner.

X. CONFERENCE OF DELEGATES and CORRESPONDING SOCIETIES COMMITTEE :—

The following appointments have been made by the Council :—

Conference of Delegates.—Dr. F. A. Bather (*President*), Mr. Mark L. Sykes (*Vice-President*), Mr. W. Mark Webb (*Secretary*).

Corresponding Societies Committee.—Mr. W. Whitaker (*Chairman*), Mr. W. Mark Webb (*Secretary*), Dr. F. A. Bather, Rev. J. O. Bevan, Sir Edward Brabrook, Sir H. G. Fordham, Mr. J. Hopkinson, Mr. A. L. Lewis, Mr. T. Sheppard, Rev. T. R. R. Stebbing, Mr. Mark L. Sykes, and the President and General Officers of the Association.

The Council approved a proposal from the Committee that a Conference of Delegates should be held in London on or about July 4, and they therefore made the appointments above mentioned as a matter of urgency.

Dr.

THE GENERAL TREASURER IN ACCOUNT ADVANCEMENT OF SCIENCE,

RECEIPTS.

	£	s.	d.	£	s.	d.	£	s.	d.
To Balance brought forward :—									
Lloyds Bank, Birmingham				1,822	14	2			
Williams Deacon's Bank, Manchester				421	11	5			
Barclay & Co., Newcastle				281	0	4			
Bank of England—Western Branch :—									
On 'Caird Fund'	317	11	4						
Less General Account overdrawn	179	13	10						
				137	17	6			
				2,663	3	5			
Less Petty Cash overdrawn				2	15	11			
							2,660	7	6
Life Compositions (including Transfers)							67	0	0
Annual Subscriptions							532	0	0
New Annual Members' Subscriptions							4	0	0
Sale of Associates' Tickets							1	0	0
Sale of Publications							217	13	11
Grants from Royal Society:—									
In aid of Publication Expenses				150	0	0			
For purposes of Research				100	0	0			
							250	0	0
Donations							8	7	0
Interest on Deposits :—									
Barclay & Co., Newcastle				2	9	2			
Williams Deacon's Bank, Manchester				6	11	11			
Lloyds Bank, Birmingham				20	9	9			
„ „ 'Caird Fund'				34	3	0			
							63	13	10
Unexpended Balances of Grants returned							49	2	0
Dividends on Investments:—									
Consols 2½ per Cent.				87	4	4			
India 3 per Cent.				81	0	0			
Great Indian Peninsula Railway 'B' Annuity				24	6	9			
War Stock 5 per Cent.				43	3	0			
War Bonds 5 per Cent.				50	15	0			
							286	9	1
Dividends on 'Caird Fund' Investments :—									
India 3½ per Cent.				68	19	0			
Canada 3½ per Cent. (including extra ½ per Cent.)				75	0	0			
London and South-Western Railway Consolidated 4 per Cent. Preference Stock				75	0	0			
London and North-Western Railway Consolidated 4 per Cent. Preference Stock				63	0	0			
							281	19	0
							£4,421	12	4

Investments.

Nominal Amount. £	s.	d.	
4,651	10	5	Consolidated 2½ per Cent. Stock
3,600	0	0	India 3 per Cent. Stock
879	14	9	(Nominal) Great Indian Peninsula Railway £43 'B' Annuity
2,627	0	10	India 3½ per Cent. Stock, 'Caird Fund'
2,100	0	0	London and North-Western Railway Consolidated 4 per Cent. Preference Stock, 'Caird Fund'
2,500	0	0	Canada 3½ per Cent. (1930-50) Registered Stock, deposited with Treasury, 'Caird Fund'
2,500	0	0	London and South-Western Railway Consolidated 4 per Cent. Preference Stock, 'Caird Fund'
93	4	5	Sir Frederick Bramwell's Gift of 2½ per Cent. Self-Cumulating Consolidated Stock
863	2	10	War Loan 5 per Cent. Stock
1,400	0	0	War Bonds 5 per Cent., 1929-47
1,000	0	0	Lloyds Bank, Birmingham—Deposit Account included in Balance at Bank, Sir J. Caird's Gift for Radio-Activity Investigation
£22,214	13	3	

Value at 30th June, 1918, £15,335 4*s.* 10*d.* only.

WITH THE BRITISH ASSOCIATION FOR THE *Cr.*

July 1, 1917, to June 30, 1918.

PAYMENTS.

				£	*s.*	*d.*	£	*s.*	*d.*
By Rent and Office Expenses							85	7	8
Salaries, etc.							678	0	0
Printing, Binding, etc.							1,028	10	2
Grants to Research Committees:—				£	*s.*	*d.*			
Seismological Observations				100	0	0			
Colloid Chemistry and its Industrial Applications				10	0	0			
Old Red Sandstone Rocks of Kiltorcan				5	0	0			
Inheritance in Silkworms				3	0	0			
Women in Industry				10	0	0			
" " 1917				10	0	11			
Effects of the War on Credit, etc.				10	0	0			
" " 1917				10	0	0			
Archæological Investigations in Malta				10	0	0			
Distribution of Bronze Age Implements				0	18	6			
Artificial Islands in Highland Lochs				2	10	0			
Physiology of Heredity				15	0	0			
The 'Free Place' System				5	0	0			
Science Teaching in Secondary Schools				4	3	10			
Corresponding Societies Committee				25	0	0			
							220	13	3
Grants made from 'Caird Fund'							106	0	0
Balance at Lloyds Bank, Birmingham (with Interest accrued), including Sir James Caird's Gift, Radio-Activity Investigation, of £1,000 and Interest accrued thereon £139 1*s.* 8*d.*				1,877	6	11			
Balance at Bank of England—Western Branch:—									
On 'Caird Fund'	£493	10	4						
Less General Account overdrawn	68	4	10						
				425	5	6			
							2,302	12	5
Cash in hand				1	1	11			
Less Petty Cash overdrawn				0	13	1			
							0	8	10
							£4,421	12	4

JOHN PERRY, *General Treasurer.*

I have examined the above Account with the Books and Vouchers of the Association, and certify the same to be correct. I have also verified the Balances at the Bankers, and have ascertained that the Investments are registered in the names of the Trustees, or held by the Bank of England on account of the Association.

W. B. KEEN, *Chartered Accountant.*
October 8, 1918.

APPROVED—
EDWARD BRABROOK, } *Auditors.*
EVERARD IM THURN, }

LIST OF GRANTS, 1918.

RESEARCH COMMITTEES, ETC., APPOINTED BY THE GENERAL COMMITTEE, MEETING IN LONDON: JULY, 1918.

1. *Receiving Grants of Money.*

Subject for Investigation, or Purpose	Members of Committee	Grants		
SECTION A.—MATHEMATICS AND PHYSICS.		£	s.	d.
Seismological Investigations.	*Chairman.*—Professor H. H. Turner. *Secretary.*—Mr. J. J. Shaw. Mr. C. Vernon Boys, Dr. J. E. Crombie, Mr. Horace Darwin, Dr. C. Davison, Sir F. W. Dyson, Sir R. T. Glazebrook, Professors C. G. Knott and H. Lamb, Sir J. Larmor, Professors A. E. H. Love, H. M. Macdonald, J. Perry, and H. C. Plummer, Mr. W. E. Plummer, Professors R. A. Sampson and A. Schuster, Sir Napier Shaw, Dr. G. T. Walker, and Mr. G. W. Walker.	100	0	0
To arrange meetings in the ensuing year for the discussion of papers and reports on Geophysical subjects, and to co-operate with existing Committees in making recommendations for the promotion of the study of such subjects in the British Empire.	*Chairman.*—Sir F. W. Dyson. *Secretary.*—Dr. S. Chapman. Dr. C. Chree, Sir Charles F. Close, Mr. J. H. Jeans, Professor A. E. H. Love, Major H. G. Lyons, Professors H. F. Newall and A. Schuster, Sir Napier Shaw, Sir A. Strahan, Professor H. H. Turner, and Dr. G. W. Walker.	10	0	0
SECTION B.—CHEMISTRY.				
Colloid Chemistry and its Industrial Applications.	*Chairman.*—Professor F. G. Donnan. *Secretary.*—Professor W. C. McC. Lewis. Dr. E. F. Armstrong, Professor A. J. Brown, Dr. C. H. Desch, Mr. E. Hatschek, Professors H. R. Procter and W. Ramsden, Mr. A. S. Shorter, Dr. H. P. Stevens, and Mr. H. B. Stocks.	5	0	0
Research on Non-Aromatic Diazonium Salts.	*Chairman.*—Dr. F. D. Chattaway. *Secretary.*—Professor G. T. Morgan. Mr. P. G. W. Bayly and Dr. N. V. Sidgwick.	7	7	8
SECTION D.—ZOOLOGY.				
Experiments in Inheritance in Silkworms.	*Chairman.*—Professor W. Bateson. *Secretary.*—Mrs. Merritt Hawkes. Dr. F. A. Dixey and Dr. L. Doncaster.	17	0	0

1. *Receiving Grants of Money*—continued.

Subject for Investigation, or Purpose	Members of Committee	Grants		
SECTION F.—ECONOMIC SCIENCE AND STATISTICS.				
		£	s.	d.
Replacement of Men by Women in Industry.	*Chairman.*—Professor W. R. Scott. *Secretary.*—Miss Grier. Miss Ashley, Ven. Archdeacon Cunningham, Professor E. C. K. Gonner, Mr. J. E. Highton, and Professor A. W. Kirkaldy.	10	0	0
The Effects of the War on Credit, Currency, and Finance.	*Chairman.*—Professor W. R. Scott. *Secretary.*—Mr. J. E. Allen. Professor C. F. Bastable, Sir E. Brabrook, Professor Dicksee, Mr. B. Ellinger, Mr. A. H. Gibson, Professor E. C. K. Gonner, Mr. F. W. Hirst, Professor A. W. Kirkaldy, and Mr. E. Sykes.	10	0	0
SECTION H.—ANTHROPOLOGY.				
To excavate a Palæolithic Site in Jersey.	*Chairman.*—Dr. R. R. Marett. *Secretary.*—Mr. G. de Gruchy. Dr. C. W. Andrews, Mr. H. Balfour, Professor A. Keith, and Colonel Warton.	5	0	0
To conduct Archæological Investigations in Malta.	*Chairman.*—Professor J. L. Myres. *Secretary.*—Dr. T. Ashby. Mr. H. Balfour, Dr. A. C. Haddon, and Dr. R. R. Marett.	10	0	0
To report on the Distribution of Bronze Age Implements.	*Chairman.*—Professor J. L. Myres. *Secretary.*—Mr. H. Peake. Professor W. Ridgeway, Mr. H. Balfour, Sir C. H. Read, Professor W. Boyd Dawkins, Dr. R. R. Marett, and Mr. O. G. S. Crawford.	1	0	0
The Collection, Preservation, and Systematic Registration of Photographs of Anthropological Interest.	*Chairman.*—Sir C. H. Read. *Secretary.*—Dr. Harrison. Dr. G. A. Auden, Dr. H. O. Forbes, Mr. E. Heawood, and Professor J. L. Myres.	1	0	0
[To conduct Explorations with the object of ascertaining the Age of Stone Circles. (*Committee in suspense: grant for contingent liability.*)	*Chairman.*—Sir C. H. Read. *Secretary.*—Mr. H. Balfour. Dr. G. A. Auden, Professor W. Ridgeway, Dr. J. G. Garson, Sir Arthur Evans, Dr. R. Munro, Professors Boyd Dawkins and J. L. Myres, Mr. A. L. Lewis, and Mr. H. Peake.]	15	0	0

1. *Receiving Grants of Money*—continued.

Subject for Investigation, or Purpose	Members of Committee	Grants
	SECTION I.—PHYSIOLOGY.	
		£ *s. d.*
The Ductless Glands.	*Chairman.*—Sir E. S. Schafer. *Secretary.*—Professor Swale Vincent. Dr. A. T. Cameron and Professor A. B. Macallum.	9 0 0
	SECTION K.—BOTANY.	
Experimental Studies in the Physiology of Heredity.	*Chairman.*—Dr. F. F. Blackman. *Secretary.*—Mr. R. P. Gregory. Professors Bateson and Keeble and Miss E. R. Saunders.	15 0 0
To cut Sections of Australian Fossil Plants, with especial reference to a specimen of Zygopteris from Simpson's Station, Barraba, N.S.W.	*Chairman.*—Professor Lang. *Secretary.*—Professor T. G. B. Osborn. Professors T. W. Edgeworth David and A. C. Seward.	15 0 0
The Collection and Investigation of Material of Australian Cycadaceæ, especially Bowenia from Queensland and Macrozamia from West Australia.	*Chairman.*—Professor A. A. Lawson. *Secretary.*—Professor T. G. B. Osborn. Professor A. C. Seward.	7 17 0
	SECTION L.—EDUCATIONAL SCIENCE.	
The Effects of the 'Free-place' System upon Secondary Education.	*Chairman.*—Mr. C. A. Buckmaster. *Secretary.*—Mr. D. Berridge. Mr. C. H. Bothamley, Miss L. J. Clarke, Miss B. Foxley, Dr. W. Garnett, Professor R. A. Gregory, Mr. J. L. Paton, Professor H. Bompas Smith, Dr. H. Lloyd Snape, and Miss Walter.	5 0 0
	CORRESPONDING SOCIETIES.	
Corresponding Societies Committee for the preparation of their Report.	*Chairman.*—Mr. W. Whitaker. *Secretary.*—Mr. W. Mark Webb. Dr. F. A. Bather, Rev. J. O. Bevan, Sir Edward Brabrook, Sir H. G. Fordham, Mr. J. Hopkinson, Mr. A. L. Lewis, Mr. T. Sheppard, Rev. T. R. R. Stebbing, Mr. Mark L. Sykes, and the President and General Officers of the Association.	25 0 0

2. *Not receiving Grants of Money.**

Subject for Investigation, or Purpose	Members of Committee
SECTION A.—MATHEMATICS AND PHYSICS.	
Annual Tables of Constants and Numerical Data, chemical, physical, and technological.	*Chairman.*—Sir E. Rutherford. *Secretary.*—Dr. W. C. McC. Lewis.
Calculation of Mathematical Tables.	*Chairman.*—Professor M. J. M. Hill. *Secretary.*—Professor J. W. Nicholson. Dr. J. R. Airey, Mr. T. W. Chaundy, Professor L. N. G. Filon, Sir G. Greenhill, Professor E. W. Hobson, Mr. G. Kennedy, and Professors Alfred Lodge, A. E. H. Love, H. M. Macdonald, G. B. Mathews, G. N. Watson, and A. G. Webster.
Investigation of the Upper Atmosphere.	*Chairman.*—Sir Napier Shaw. *Secretary.*— Mr. C. J. P. Cave, Mr. W. H. Dines, Sir R. T. Glazebrook, Sir J. Larmor, Professors J. E. Petavel and A. Schuster, and Dr. W. Watson.
Radiotelegraphic Investigations.	*Chairman.*—Sir Oliver Lodge. *Secretary.*—Dr. W. H. Eccles. Mr. S. G. Brown, Dr. C. Chree, Sir F. W. Dyson, Professor A. S. Eddington, Dr. Erskine-Murray, Professors J. A. Fleming, G. W. O. Howe, H. M. Macdonald, and J. W. Nicholson, Sir H. Norman, Captain H. R. Sankey, Professor A. Schuster, Sir Napier Shaw, and Professor H. H. Turner.
Determination of Gravity at Sea.	*Chairman.*—Professor A. E. H. Love. *Secretary.*—Dr. W. G. Duffield. Mr. T. W. Chaundy and Professors A. S. Eddington, A. Schuster, and H. H. Turner.
To aid the work of Establishing a Solar Observatory in Australia.	*Chairman.*—Professor H. H. Turner. *Secretary.*—Dr. W. G. Duffield. Rev. A. L. Cortie, Dr. W. J. S. Lockyer, Mr. F. McClean, and Professor A. Schuster.
To discuss the present needs of Geodesy, including its relation to other branches of Geophysics, and to report to the next meeting of the British Association, with power to present an interim report to the Council if any question of urgency should arise.†	*Chairman.*—Colonel Sir C. F. Close. *Secretary.*—Colonel E. H. Hills. Sir S. G. Burrard, Dr. W. G. Duffield, Mr. Horace Darwin, Sir F. W. Dyson, Sir R. T. Glazebrook, Mr. A. R. Hinks, Sir T. H. Holdich, Professor Lamb, Sir Joseph Larmor, Professor A. E. H. Love, Colonel H. G. Lyons, Professor H. Macdonald, Mr. R. D. Oldham, Professor A. Schuster, Sir Napier Shaw, Professor H. H. Turner, and Dr. G. W. Walker.

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* Excepting the case of Committees receiving grants from the 'Caird Fund.'

† Joint Committee with Section E. Empowered to report to Council.

2. *Not receiving Grants of Money*—continued.

Subject or Investigation, or Purpose	Members of Committee
SECTION B.—CHEMISTRY.	
Fuel Economy; Utilisation of Coal; Smoke Prevention.	*Chairman.*—Mr. Robert Mond. *Secretary.*— The Rt. Hon. Lord Allerton, Mr. Robert Armitage, Professor J. O. Arnold, Mr. J. A. F. Aspinall, Mr. A. H. Barker, Professor P. P. Bedson, Sir G. T. Beilby, Sir Hugh Bell, Professor W. S. Boulton, Professor E. Bury, Dr. Charles Carpenter, Sir Dugald Clerk, Professor H. B. Dixon, Dr. J. T. Dunn, Mr. S. Z. de Ferranti, Dr. William Galloway, Professors W. W. Haldane Gee and Thos. Gray, Mr. T. Y. Greener, Sir Robert Hadfield, Dr. H. S. Hele-Shaw, Dr. D. H. Helps, Dr. G. Hickling, Mr. Grevil Jones, Mr. W. W. Lackie, Mr. Michael Longridge, Dr. J. W. Mellor, Mr. C. H. Merz, Mr. Bernard Moore, Hon. Sir Charles Parsons, Sir Richard Redmayne, Professors Ripper and L. T. O'Shea, Mr. R. P. Sloan, Dr. J. E. Stead, Dr. A. Strahan, Mr. C. E. Stromeyer, Mr. Benjamin Talbot, Professor R. Threlfall, Mr. G. Blake Walker, Dr. R. V. Wheeler, Mr. B. W. Winder, Mr. W. B. Woodhouse, Professor W. P. Wynne, and Mr. H. James Yates.
Absorption Spectra and Chemical Constitution of Organic Compounds.	*Chairman.*—Sir J. J. Dobbie. *Secretary.*—Professor E. E. C. Baly. Mr. A. W. Stewart.
SECTION C.—GEOLOGY.	
To investigate the Geology of Coal-Seams.	*Chairman.*—Professor W. S. Boulton. *Secretary.*—Dr. W. T. Gordon. Mr. G. Barrow, Professors Sir John Cadman, Grenville Cole, and W. G. Fearnsides, Dr. J. S. Flett, Dr. Walcot Gibson, Professors J. W. Gregory and P. F. Kendall, Dr. R. Kidston, Professor T. F. Sibly, Dr. A. Strahan, and Mr. J. R. R. Wilson.
The Old Red Sandstone Rocks of Kiltorcan, Ireland.	*Chairman.*—Professor Grenville Cole. *Secretary.*—Professor T. Johnson. Dr. J. W. Evans, Dr. R. Kidston, and Dr. A. Smith Woodward.
To investigate the Flora of Lower Carboniferous times as exemplified at a newly-discovered locality at Gullane, Haddingtonshire.	*Chairman.*—Dr. R. Kidston. *Secretary.*—Dr. W. T. Gordon. Dr. J. S. Flett, Professor E. J. Garwood, Dr. J. Horne, and Dr. B. N. Peach.

2. *Not receiving Grants of Money*—continued.

Subject for Investigation, or Purpose	Members of Committee
To excavate Critical Sections in the Palæozoic Rocks of England and Wales.	*Chairman.*—Professor W. W. Watts. *Secretary.*—Professor W. G. Fearnsides. Professor W. S. Boulton, Mr. E. S. Cobbold, Professor E. J. Garwood, Mr. V. C. Illing, Dr. Lapworth, and Professor J. E. Marr.
To excavate Critical Sections in Old Red Sandstone Rocks at Rhynie, Aberdeenshire.	*Chairman.*—Dr. J. Horne. *Secretary.*—Dr. W. Mackie. Drs. J. S. Flett, W. T. Gordon, G. Hickling, R. Kidston, B. N. Peach, and D. M. S. Watson.
To consider the Nomenclature of the Carboniferous, Permo-carboniferous, and Permian Rocks of the Southern Hemisphere.	*Chairman.*—Professor T. W. Edgeworth David. *Secretary.*—Professor E. W. Skeats. Mr. W. S. Dun, Professor J. W. Gregory, Sir T. H. Holland, Messrs. W. Howchin, A. E. Kitson, and G. W. Lamplugh, Dr. A. W. Rogers, Professor A. C. Seward, Mr. D. M. S. Watson, and Professor W. G. Woolnough.
To consider the preparation of a List of Characteristic Fossils.	*Chairman.*—Professor P. F. Kendall. *Secretary.*— Professor W. S. Boulton, Professor G. Cole, Dr. A. R. Dwerryhouse, Professors J. W. Gregory, Sir T. H. Holland, and S. H. Reynolds, Dr. Marie C. Stopes, Professors J. E. Marr and W. W. Watts, Mr. H. Woods, and Dr. A. Smith Woodward.
The Collection, Preservation, and Systematic Registration of Photographs of Geological Interest.	*Chairman.*—Professor E. J. Garwood. *Secretary.*—Professor S. H. Reynolds. Mr. G. Bingley, Dr. T. G. Bonney, Messrs. C. V. Crook, R. Kidston, and A. S. Reid, Sir J. J. H. Teall, Professor W. W. Watts, and Messrs. R. Welch and W. Whitaker.

SECTION D.—ZOOLOGY.

To nominate competent Naturalists to perform definite pieces of work at the Marine Laboratory, Plymouth.	*Chairman* and *Secretary.*—Professor A. Dendy. Sir E. Ray Lankester, Professor J. P. Hill, and Mr. E. S. Goodrich.
Zoological Bibliography and Publication.	*Chairman.*—Professor E. B. Poulton. *Secretary.*—Dr. F. A. Bather. Mr. E. Heron-Allen, Dr. W. E. Hoyle, and Dr. P. Chalmers Mitchell.

2. *Not receiving Grants of Money*—continued.

Subject for Investigation, or Purpose	Members of Committee
SECTION F.—ECONOMIC SCIENCE AND STATISTICS.	
Industrial Unrest.	*Chairman.*—Professor A. W. Kirkaldy. *Secretary.*— Sir H. Bell, Rt. Hon. C. W. Bowerman, Professors S. J. Chapman and E. C. K. Gonner, Mr. H. Gosling, Mr. G. Pickup Holden, Dr. G. B. Hunter, Sir C. W. Macara, and Professor W. R. Scott.
SECTION G.—ENGINEERING.	
To consider and report on the Standardisation of Impact Tests.	*Chairman.*—Professor W. H. Warren. *Secretary.*—Mr. J. Vicars. Professor Payne and Mr. E. H. Sainter.
SECTION K.—BOTANY.	
To consider and report upon the necessity for further provision for the Organisation of Research in Plant Pathology in the British Empire.	*Chairman.*—Professor M. C. Potter. *Secretary.*—Dr. E. N. Thomas. Professors Biffen and V. H. Blackman, Mr. Brierley, Mr. F. T. Brooks, Mr. Cotton, Professors Groom and T. Johnson, Dr F. Keeble, Mr. Pethybridge, Mr. J. Ramsbottom, Mr. Robinson, Dr. E. J. Russell, Mr. E. S. Salmon, Miss Lorrain Smith, Mr. H. W. T. Wager, and Miss Wakefield.
To consider the possibilities of investigation of the Ecology of Fungi, and assist Mr. J. Ramsbottom in his initial efforts in this direction.	*Chairman.*—Dr. H. W. T. Wager. *Secretaries.*—Mr. J. Ramsbottom and Miss A. Lorrain Smith. Mr. W. B. Brierley, Mr. F. T. Brooks, Mr. W. N. Cheesman, Professor T. Johnson, Dr. C. E. Moss, Professor M. C. Potter, Mr. L. Carleton Rea, and Mr. E. W. Swanton.
The Investigation of the Vegetation of Ditcham Park, Hampshire.	*Chairman.*—Mr. A. G. Tansley. *Secretary.*—Mr. R. S. Adamson. Dr. C. E. Moss and Professor R. H. Yapp.
The Structure of Fossil Plants.	*Chairman.*—Professor F. W. Oliver. *Secretary.*—Professor F. E Weiss. Professor A. C. Seward and Dr. D. H. Scott.
To consider and report upon the necessity for Further Provision for Training and Research in Horticulture.	Professor Bateson, Mr. F. T. Brooks, Dr. A. B. Rendle, Sir Albert Rollit, and Dr. E. N. Thomas.

2. *Not receiving Grants of Money*—continued.

Subject for Investigation, or Purpose	Members of Committee
SECTION L.—EDUCATIONAL SCIENCE.	
To consider the relations between the State and Education, and the means of giving effect to proposals for Educational Reform.	*Chairman.*—Sir Napier Shaw. *Secretary.*—Mr. D. Berridge.
The Influence of School Books upon Eyesight.	*Chairman.*—Dr. G. A. Auden. *Secretary.*—Mr. G. F. Daniell. Mr. C. H. Bothamley, Mr. W. D. Eggar, Professor R. A. Gregory, Dr. N. Bishop Harman, Mr. J. L. Holland, Dr. W. E. Sumpner, Mr. A. P. Trotter, and Mr. Trevor Walsh.
To consider and report upon the method and substance of Science Teaching in Secondary Schools, with particular reference to its essential place in general Education.	*Chairman.*—Professor R. A. Gregory. *Secretary.*—Dr. E. H. Tripp. Mr. W. Aldridge, Professor H. E. Armstrong, Mr. D. Berridge, Mr. C. A. Buckmaster, Miss L. J. Clarke, Mr. G. F. Daniell, Miss I. M. Drummond, Mr. G. D. Dunkerley, Miss A. E. Escott, Mr. Cary Gilson, Miss C. L. Laurie, Professor T. P. Nunn, and Mr. A. Vassall.
To inquire into the provision of Educational Charts and Pictures for display in schools.	*Chairman.*—Professor H. E. Armstrong. *Secretary.*—Professor R. A. Gregory. Mr. D. Berridge, Miss L. J. Clarke, Miss Drummond, Mr. O. J. R. Howarth, Sir Napier Shaw, and Professor H. H. Turner.
CORRESPONDING SOCIETIES COMMITTEE.	
To take steps to obtain Kent's Cavern for the Nation.	*Chairman.*—Mr. W. Whitaker. *Secretary.*—Mr. W. M. Webb. Mr. Mark L. Sykes.

RESEARCH COMMITTEES 'IN SUSPENSE.'

The work of the following Committees is in suspense until further notice. The *personnel* of these Committees will be found in the Report for 1917.

SECTION B.—CHEMISTRY.

To report on the Botanical and Chemical Characters of the Eucalypts and their Correlation.

Dynamic Isomerism.

Chemical Investigation of Natural Plant Products of Victoria.

SECTION D.—ZOOLOGY.

An investigation of the Biology of the Abrolhos Islands and the North-west Coast of Australia (north of Shark's Bay to Broome), with particular reference to the Marine Fauna.

Nomenclator Animalium Genera et Sub-genera.

To obtain, as nearly as possible, a Representative Collection of Marsupials for work upon (*a*) the Reproductive Apparatus and Development, (*b*) the Brain.

To aid competent Investigators selected by the Committee to carry on definite pieces of work at the Zoological Station at Naples.

To summon meetings in London or elsewhere for the consideration of matters affecting the interests of Zoology or Zoologists, and to obtain by correspondence the opinion of Zoologists on matters of a similar kind, with power to raise by subscription from each Zoologist a sum of money for defraying current expenses of the Organisation.

SECTION E.—GEOGRAPHY.

To aid in the preparation of a Bathymetrical Chart of the Southern Ocean between Australia and Antarctica.

SECTION G.—ENGINEERING.

To report on certain of the more complex Stress Distributions in Engineering Materials.

The Investigation of Gaseous Explosions, with special reference to Temperature.

SECTION H.—ANTHROPOLOGY.

To conduct Explorations with the object of ascertaining the Age of Stone Circles.

To investigate and ascertain the Distribution of Artificial Islands in the Lochs of the Highlands of Scotland.

To investigate the Physical Characters of the Ancient Egyptians.

To conduct Archæological and Ethnological Researches in Crete.

The Teaching of Anthropology.

To prepare and publish Miss Byrne's Gazetteer and Map of the Native Tribes of Australia.

To excavate Early Sites in Macedonia.

To conduct Anthropometric Investigations in the Island of Cyprus.

To investigate the Lake Villages in the neighbourhood of Glastonbury in connection with a Committee of the Somerset Archæological and Natural History Society.

To co-operate with Local Committees in Excavations on Roman Sites in Britain.

SECTION K.—BOTANY.

To carry out a Research on the influence of varying percentages of Oxygen and of various Atmospheric Pressures upon Geotropic and Heliotropic Irritability and Curvature.

The Renting of Cinchona Botanic Station in Jamaica.

SECTION L.—EDUCATION.

To inquire into and report upon the Methods and Results of Research into the Dental and Physical Factors involved in Education.

To examine, inquire into, and report on the Character, Work, and Maintenance of Museums, with a view to their Organisation and Development as Institutions for Education and Research; and especially to inquire into the Requirements of Schools.

Synopsis of Grants of Money appropriated for Scientific Purposes by the General Committee at the Meeting in London, July 5, 1918. The Names of Members entitled to call on the General Treasurer for Grants are prefixed to the respective Committees.

Section A.—Mathematical and Physical Science.

	£	*s.*	*d.*
*Turner, Professor H. H.—Seismological Investigations	100	0	0
*Dyson, Sir F. W.—Geophysical Discussions	10	0	0

Section B.—Chemistry.

*Donnan, Professor F. G.—Colloid Chemistry and its Industrial Applications	5	0	0
*Chattaway, Dr. F. D.—Non-Aromatic Diazonium Salts	7	7	8

Section D.—Zoology.

*Bateson, Professor W.—Inheritance in Silkworms	17	0	0

Section F.—Economic Science and Statistics.

*Scott, Professor W. R.—Women in Industry	10	0	0
*Scott, Professor W. R.—Effects of the War on Credit, &c.	10	0	0

Section H.—Anthropology.

*Marett, Dr. R. R.—Palæolithic Site in Jersey	5	0	0
*Myres, Professor J. L.—Archæological Investigations in Malta	10	0	0
*Myres, Professor J. L.—Distribution of Bronze Age Implements	1	0	0
* Read, Sir C. H.—Collection and Registration of Photographs of Anthropological Interest	1	0	0
* Read, Sir C. H.—Age of Stone Circles	15	0	0

Section I.—Physiology.

*Schafer, Sir E. S.—The Ductless Glands	9	0	0

Section K.—Botany.

*Blackman, Dr. F. F.—Physiology of Heredity	15	0	0
*Lang, Professor W. H.—Sections of Australian Fossil Plants	15	0	0
*Lawson, Professor A. A.—Australian Cycadaceæ	7	17	0
Carried forward	£238	4	8

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* Reappointed.

	£	s.	d.
Brought forward	238	4	8
Section L.—Educational Science.			
*Buckmaster, Mr. C. A.—The 'Free-place' System	5	0	0
Corresponding Societies Committee.			
*Whitaker, Mr. W.—For Preparation of Report.....	25	0	0
Total	£268	4	8

Caird Fund.

An unconditional gift of 10,000*l.* was made to the Association at the Dundee Meeting, 1912, by Mr. (afterwards Sir) J. K. Caird, LL.D., of Dundee.

The Council, in its report to the General Committee at the Birmingham Meeting, made certain recommendations as to the administration of this Fund. These recommendations were adopted, with the Report, by the General Committee at its meeting on September 10, 1913.

The following allocations have been made from the Fund by the Council to September 1918:—

Naples Zoological Station Committee (p. xix).—50*l.* (1912–13); 100*l.* (1913–14); 100*l.* annually in future, subject to the adoption of the Committee's report. (Reduced to 50*l.* during war.)

Seismology Committee (p. xii).—100*l.* (1913–14); 100*l.* annually in future, subject to the adoption of the Committee's report.

Radiotelegraphic Committee (p. xvi).—500*l.* (1913–14).

Magnetic Re-survey of the British Isles (in collaboration with the Royal Society).—250*l.*

Committee on the Determination of Gravity at Sea (p. xvi).—100*l.* (1914–15).

Mr. F. Sargent, Bristol University, in connection with his Astronomical Work.—10*l.* (1914).

Organising Committee of Section F (Economics), towards expenses of an Inquiry into Outlets for Labour after the War.—100*l.* (1915).

Rev. T. E. R. Phillips, for aid in transplanting his private observatory.—20*l.* (1915).

Oceanographical Laboratory, Edinburgh.—100*l.* (1916–17).

Committee on Fuel Economy.—25*l.* (1915–16).

To arrange Meetings and Discussions on Geophysical Subjects.—6*l.* (1917–18).

Sir J. K. Caird, on September 10, 1913, made a further gift of 1,000*l.* to the Association, to be devoted to the study of Radio-activity.

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* Reappointed.

REPORTS

ON THE

STATE OF SCIENCE, ETC.

REPORTS ON THE STATE OF SCIENCE, ETC.

Seismological Investigations.—Twenty-third Report of the Committee, consisting of Professor H. H. TURNER (*Chairman*), Mr. J. J. SHAW (*Secretary*), Mr. C. VERNON BOYS, Dr. J. E. CROMBIE, Mr. HORACE DARWIN, Dr. C. DAVISON, Sir F. W. DYSON, Sir R. T. GLAZEBROOK, Professors C. G. KNOTT *and* H. LAMB, Sir J. LARMOR, Professors A. E. H. LOVE, H. M. MACDONALD, J. PERRY, *and* H. C. PLUMMER, Mr. W. E. PLUMMER, Professors R. A. SAMPSON *and* A. SCHUSTER, Sir NAPIER SHAW, Dr. G. T. WALKER, *and* Dr. G. W. WALKER.

General.

OWING to the cancelling of the Cardiff meeting proposed for 1918 and to other reasons connected with the war, the present Report is made brief. It has been drawn up by the Chairman.

The Committee asks to be reappointed with a grant of 100*l.* (including printing), in addition to 100*l.* from the Caird Fund already voted. The grant was formerly 60*l.*, with 70*l.* for printing; 130*l.* in all; but during the war it has been reduced to 100*l.*, partly to meet the need for economy, partly because the printing has necessarily been less. The Government Grant Fund administered by the Royal Society has voted a subsidy of 200*l.* for 1918 as in recent years. With the above modification the budget remains practically the same as given in the Twentieth Report.

Owing to business reasons connected with the war, Mr. J. H. Burgess found it necessary to leave the Isle of Wight at the end of March, 1918. For half a dozen years he had devoted a considerable portion of his time (nominally one-half, but this was often exceeded in his enthusiasm for seismology) to the work at Shide. The Committee is greatly indebted to him for his prompt and valuable help when the sudden death of John Milne in 1913 left them in face of a threatened break in the work. Thanks to the special knowledge Mr. Burgess had acquired in working with Professor Milne, discontinuity was avoided, and whatever changes are found necessary in the future can be made with full consideration.

Mr. S. W. Pring remains at Shide for the present, though it is impossible to predict the length of his stay under present war conditions, which have already somewhat reduced the time he is able to devote (chiefly in the evenings) to seismology. His knowledge of Russian, which originally brought him into contact with Professor Milne, has been an important asset throughout, and has recently proved specially valuable in supplying translations of papers otherwise inaccessible.

The routine work generally is now in the hands of Miss Caws, who had been trained in it by Mr. Burgess. As a safeguard against her illness, and to enable her to take an occasional holiday, Miss E. F. Bellamy, of the Oxford University Observatory, has been instructed by Miss Caws in the work, and undertook the routine observations during the absence of Miss Caws from the middle of July to the middle of August. It is proposed to set up at least one Milne-Shaw seismograph at Oxford under Miss Bellamy's care. Mr. James Walker has kindly placed at the disposal of the Committee the basement of the Clarendon Laboratory in which Mr. C. V. Boys made his gravity determination. The suitability of Oxford as an observing site can thus be tested under good conditions, and the results of the tests in a basement of that character may have an even wider application when plans for the future come to be discussed.

Finally, since the departure of Mr. Burgess naturally reduces the working power of the staff, Miss Bellamy has been definitely transferred to the seismological service for the present. This transference was approved by the Board of Visitors of the Oxford University Observatory 'as a provisional and possibly temporary arrangement' which 'is not to prejudice the resumption of her position as Assistant [in the University Observatory] at the conclusion of the experiment, should that be her wish.' The nature of the experiment here mentioned has perhaps been sufficiently indicated, but a few words of explanation may be added for the sake of clearness.

It was mentioned in last year's Report that the question of the future of seismology had attracted the attention of more than one body. Besides our own Committee, the Geodetic Committee of Section A of our Association, in discussing plans for a Geodetic Institute, were led to consider the possible association, in such an institute, of other branches of Geophysics with Geodesy. It was further mentioned that the Geodetic Committee had thereupon been suitably enlarged for the purposes of this discussion; and it should perhaps have been added that they had been invited by the Conjoint Board of Scientific Societies to act as their Committee also, and to report to them as well as to the British Association—and had, with the approval of the Council of the British Association, accepted that invitation.

Their report was in favour of the association of the three branches Geodesy, Seismology, and Tides in one Geophysical Institute. It was generally approved by the Conjoint Board, who appointed a small Executive Committee to formulate definite plans.

The transference of some of the Shide work to Oxford during the next year or two is definitely not intended to prejudice, or to embarrass in any way, the discussion of these plans. But since we are in several respects somewhat in the dark (*e.g.*, as to the precise value of a basement as a site for instruments, of a University as a centre of organisation, &c.), the transference will provide experience which may possibly be of some assistance to the discussion. Meanwhile, it is also the simplest solution of the question of ways and means at the present rather difficult time.

Instrumental.

The wireless time-signals have been received at Shide regularly, with some interruptions owing to derangement of the apparatus. The transit lent by the Royal Astronomical Society has been in reserve, but not much used during the year.

Towards the end of 1917 the temporary use of a 'dug-out,' constructed for military purposes, was offered to Mr. Burgess, and the opportunity was taken to make some experiments. With Mr. Shaw's help the Milne-Burgess machine was dismounted from its pier at Shide, and remounted in the dug-out some few miles away. At some considerable personal trouble and inconvenience Mr. Burgess kept the machine running for a few weeks. [It was necessary to keep a pump going to avoid having the dug-out flooded.] No very satisfactory results were obtained, the wandering of the trace being just as serious as at Shide, and the experiments came to a natural end when the dug-out was reclaimed for military purposes. The main conclusion which emerged from the experiments was that rain had more to do with the wandering of the trace than had temperature. After rain the lines became much congested: when the rain ceased they were unusually expanded, returning to the normal separation when the weather had been fine for a few days. The inference seems to be that the wetting and drying of the ground caused slow movements in opposite directions—a conclusion in accord with previous experience at Shide. The dug-out was in a clay soil, which doubtless emphasised the effects.

Milne-Shaw Seismographs.

Several of these machines are nearing completion; that intended for Oxford is finished, and will be erected as soon as possible.

Suggested Corrections to Adopted Tables.

The work of disentangling the corrections to the adopted tables from other errors is attended with considerable difficulties, but nothing is more important, if the phases are to be rightly identified; and although progress is slow, the ground is being steadily cleared. One set of difficulties arises from ignorance of the clock errors, which may be expected especially at outlying stations. Recent experience aroused the suspicion that these are often considerable, so that accurate intervals S—P are attended by unexpectedly large errors in S and P separately. The experience here referred to is derived from the re-reduction of a number of the best observed earthquakes after applying the corrections to tables deduced in the last report, and carefully correcting the position of epicentre.

Hence attention was recalled specially to the investigation in the Introduction to 'The Large Earthquakes of 1913,' p. iii, which was confined to the use of intervals S—P, free from clock errors. This investigation gives no information about S and P separately which will enable us to correct the tables, and was naturally followed by a more comprehensive analysis where S and P were kept separate, the results of which were given in the Twenty-second Report, Table II. We may denote these two investigations by the symbols (1913) and (22) respectively.

Now for the smaller values of Δ (1913) differs essentially from (22), as is seen from Table I. below, and we must determine which is nearer the truth. For this the following method suggested itself.

Pairs of Stations on Opposite sides of the Epicentre.

Any pair of observing stations on directly opposite sides of the epicentre give a check on the values of S—P. Suppose for simplicity we had two stations, A and Z, at ends of a diameter of the earth, and the epicentre E lay midway between them, so that EA=EZ=90°, for which the tables give S−P=658 seconds. We are suggesting that this ought to be 658s.—17s.=641 seconds. If we are right, then 641 seconds will be observed at both A and Z. In proceeding to determine the epicentre we may use A alone (for in practice A may not be a single station but the whole body of European stations), and using our erroneous tables we should put the epicentre only 86°·8 from A, and therefore 93°·2 from Z; so that the observed 641 seconds at Z would be doubly in defect, since for 93°·2 the tables give 674 seconds. However we determine the epicentre (provided Δ_1 and Δ_2 are not too unequal), this double defect of 33s. or 34s. will be shared between A and Z. Two such antipodal stations are specially valuable because we cannot alter the sum of the two distances ($\Delta_A + \Delta_Z$) by changing the azimuth of the epicentre; and even when the antipodal condition is not quite fulfilled (as, say, for Pulkovo and Riverview, which are about 140° apart) a change of azimuth makes very little change in $\Delta_A + \Delta_Z$. For pairs of stations closer to the epicentre, the azimuth is often well determined by other stations; and unless they are very close to the epicentre the azimuth error only affects ($\Delta_1 + \Delta_2$) to the second order. Hence we have a good check on the values of S−P. The following satisfactory instances were collected from the published results of 1913, 1914, 1915. They are worth giving in detail to show the good accordance.

TABLE I.

Pairs of Stations on opposite sides of the Epicentre.

Δ_1	Δ_2	Mean	$(S-P)_1$	$(S-P)_2$	Mean
°	°	°	s.	s.	s.
6·0	6·9	6·4	+39	−10	+14
7·0	18·7	12·8	0	+ 7	+ 4
5·9	19·9	12·9	+22	+ 6	+14
5·9	20·4	13·2	+ 7	0	+ 4
7·8	20 0	13·9	+12	+26	+19
9·9	19·4	14·6	+30	− 2	+14
9·9	22·3	16·1	+ 4	+ 8	+ 6
18·6	23·1	20·8	+ 1	−21	−10
14·8	30·0	22·4	+14	−10	+ 2
22·8	36·2	29·5	− 3	− 5	− 4
26·3	36·8	31·6	− 1	− 4	− 2
20·8	53.1	37·0	+ 8	−21	− 6
25·9	49·0	37·4	− 7	+ 4	− 2
26·2	78·4	52·3	+ 2	− 9	− 4
40·2	69·5	54·8	−32	+15	− 8
47·8	86·3	67·0	− 9	−21	−15
47·2	87·0	67·1	−20	−10	−15
46·0	88·2	67·1	−20	−24	−22
58·6	79·1	68·8	−27	−10	−18
50·3	88·5	69·4	− 8	−12	−10
48·9	90·6	69·8	−13	− 3	− 8
65·6	75·1	70·3	−12	−15	−14
68·5	73·5	71·0	−12	−10	−11
43·6	90·9	72·6	− 8	−11	−10
63·9	81·4	72·6	− 1	−18	− 9
66·1	81·6	73·8	+ 3	−14	− 6

Forming groups of these we obtain the mean values of Table II. :—

TABLE II.

Suggested Corrections to Tabular S − P.

No. in Group	Mean Δ	Mean Correction	(1913)	(22)
	°	s.	s.	s.
1	6·4	+14	+ 4	− 4
4	13·2	+10	+ 8	− 8
4	18·5	+ 3	+ 3	− 8
4	33·9	− 4	−10	−13
2	53·6	− 6	− 7	− 6
6	68·2	−15	− 4	− 6
5	72·1	−10	+ 1	− 8

We infer that for the smaller values of Δ at any rate the investigation (1913), in which only S−P was used, is to be preferred to (22), in which S and P were treated separately.

Observations of PR_1 *and* SR_1.

But a knowledge of S−P will not suffice to correct the separate tables. We must find some other way of doing this, and recourse was had to the observations of PR_1 and SR_1.

We shall first assume that these represent reflections at the mid-point without loss of time. Thus PR_1 is a P wave reflected at the mid-point (M) between the epicentre (E) and the observing station (O) so that

$$EO=2EM=\Delta,$$

and the time for PR_1 is twice that for EM or $\Delta/2$.

In Table III. the first column gives Δ and the second gives the observed value of $\frac{1}{2}(S+P)-PR_1$, or as we may write it $\frac{1}{2}(S-P)+P-PR_1$, which is nearly constant. The observations were collected from the records of several observations, especially Pulkovo, in the years 1914 and 1915, and are fairly numerous for all but the small values of Δ. The actual

TABLE III.

Δ	Obsd.	Tables	$O-C_1$	$O-C_2$
	s.	s.	s.	s.
23	77	98	−21	−15
28	75	102	−27	−14
33	80	103	−23	− 9
38	83	100	−17	− 2
43	88	95	− 7	+ 5
48	91	88	+ 3	+10
53	95	85	+10	+10
58	98	83	+15	+10
63	102	82	+20	+ 8
68	106	83	+23	+11
73	109	87	+22	+11
78	109	92	+17	+ 9
83	106	92	+14	+ 9
88	105	96	+ 9	+ 7
93	102	101	+ 1	+ 4

figures given in the table were read from a smoothed curve. In the third column is given the corresponding quantity calculated from the adopted tables in use, followed in the fourth column by the differences $O-C_1$. In the next column $O-C_2$ is shown the effect of correcting these tables as in Table II. of the 22nd Report. It is seen at a glance that the tables are considerably in error, and that the suggested corrections reduce the errors. But before deciding to attempt any further reduction let us turn to the observations of SR_1, of which the following were collected :—

TABLE IV.

Observed Values of SR_1.

$S-P$	SR_1-S	Diff.	$S-P$	SR_1-S	Diff.
s.	s.	s.	s.	s.	s.
363	149	214	574	282	292
366	146	220	578	291	287
372	162	210	583	297	286
397	195	202			
(374)	(163)	(211)	(578)	(290)	(288)
525	234	291	606	332	274
530	249	281	634	341	293
541	266	275	647	382	265
542	263	279	673	357	316
550	257	293			
(538)	(254)	(284)	(640)	(353)	(287)

The records of SR_1 are often given to tenths of a minute only, suggesting some uncertainty; more observations are desirable, but those above quoted are consistent in showing that the difference $(S-P) - (SR_1-S)$ or $2S-P-SR_1$ is sensibly constant from (say) $S-P = 520$ seconds to 680 seconds, which may serve as a useful check.

Comparing the means (in brackets) with the adopted tables, we get the differences $O-C$, while the corrections of the 22nd Report give the column $O-C_2$.

TABLE V.

$2S-P-SR_1$.

$S-P$	Δ	Calc.	Obs.	$O-C_1$	$O-C_2$
s.	°.	s.	s.	s.	s.
374	40·3	212	211	− 1	+ 6
538	68·0	220	284	+64	+33
578	75·2	241	288	+47	+21
640	86·5	272	287	+15	+ 9

We again see at a glance that the adopted tables are sensibly in error, and that the corrections found in the 22nd Report, while they reduce these errors, do not annihilate them. We must proceed further in the same direction.

It is easily seen that the further alterations must be chiefly in SR_1, and not in S (or P). Thus let us fix attention on the worst case, where $S-P=538$s. For this value of $S-P$ the adopted tables give $\Delta=68°·0$; but when we correct the tables we get $\Delta=69°·2$. Note that $S-P$ is the observed quantity, and Δ is only inferred. But the consequent change in $(S-P)+(S-SR)$ is small and in the wrong direction; for though S is increased by 14 seconds, SR_1 is increased by 18 seconds. After altering Δ we have, however, still to apply the errors of S and of SR_1. The complete process may be represented thus, when the corrections used are those of the 22nd Report:—

	$S-P$	Δ	$\frac{1}{2}\Delta$	$+S$	$-SR_1$	$(S-P)+(S-SR_1)$
	s.	°	°	s.	s.	s.
Tables .	538	68·0	34·0	+1202	−1520	+220
Δ	—	+1·2	+0·6	+ 14	− 18	− 4
Errors .				− 3	+ 38	+ 35

We see at a glance that the efficient corrective is the error in SR_1 which is taken to be twice that of S at $\Delta/2$. The error of S at 34°·6 is found in the 22nd Report to be −19 seconds; if this were only larger numerically, say −34 seconds, we could completely destroy the + 64s. of Table V., column $O-C_1$.

The observations of SR_1 are not, however, so numerous as those of PR_1 to which we now return. Let us neglect the small change in Δ. Beginning at the bottom of the table, let us assume that we know that the error at $\Delta=93°$ is −7 seconds, from the 22nd Report. Then, since

$$P-PR_1=+1\text{s.}$$
$$PR_1=P-1\text{s.}=-7\text{s.}-1\text{s.}=-8\text{s.}$$

i.e. the error at $\Delta = 46°{\cdot}5 = -4$s., which so far accords quite well with that deduced independently in the same Table II. of the 22nd Report. But as we proceed upwards we shall not find the same good accordance. The errors for the smaller values of Δ deduced in this way from PR_1 are as in Table VI.:—

TABLE VI.

Errors of P *deduced from* PR_1.

Δ	From PR_1	From (22)	Old Tables δP_1	New	Possible δP_3	Corrn.
			s.	s.	s.	s. s.
11°·5	+10	+1	172	182	184	+12
			34	35	36	
14·0	+11	+1	206	217	220	+14
			33	29	31	
16·5	+ 7	+2	239	246	251	+12
			30	27	25	
19·0	+ 4	+2	269	273	276	+ 7
			30	26	18	
21·5	0	+1	299	299	294	− 5
			29	26	21	
24·0	− 3	0	328	325	315	−13
			25	24	25	
26·5	− 4	−1	353	349	340	−13
			25	23	26	
29·0	− 6	−3	378	372	366	−12
			24	22	25	
31·5	− 8	−4	402	394	391	−11
			23	21	24	
34·0	−10	−6	425	415	415	−10
			21	21	22	

TABLE VI.—*continued.*

Errors of P *deduced from* PR₁.

Δ	From PR₁	From (22)	Old Tables δP		New		Possible δP₃		Corrn.
36·5	−10	−6	446		436		437		− 9
				20		21		21	
39·0	− 9	−7	466		457		458		− 8
				21		22		21	
41·5	− 8	−7	487		479		479		− 8
				19		20		20	
44·0	− 7	−6	506		499		499		− 7
				18		21		20	
46·5	− 4	−4	524		520		519		− 5

We see that the investigation of the 22nd Report (shown in the third column of Table VI.) fails for the smaller values of Δ in much the same way as is manifested in Table II. above; viz. from $\Delta = 10°$ to $\Delta = 20°$ the errors are not sufficiently positive if we may accept the indications of PR₁, while near $\Delta = 35°$ they are not sufficiently negative. The column deduced from PR₁ starts with a hill and falls into a valley; in the investigation (22) the hill is cut down and the valley filled up; and it is reasonable to attribute these modifications to the effects of compromise due to the determination of the epicentre with the faulty tables.

In the fourth and succeeding columns of Table VI. the effects of applying the newly-suggested corrections are shown. First, under the heading 'Old Tables' are given the tabular values for P, followed by the differences δP_1. Under the heading 'New' are given the tables with corrections as from PR₁ and the differences δP_2. Now it is seen that these differences δP_2 are approximately constant from $\Delta = 29°{\cdot}0$ to $\Delta = 46°{\cdot}5$, whereas δP_1 drops steadily. We are reminded of the phenomenon shown by the Pulkovo angles of emergence. (See p. 54 of Dr. G. W. Walker's 'Modern Seismology'). In the last report Dr. Walker recalled attention to these observations, emphasising Galitzin's belief in them, and suggesting in explanation a focal depth of the order of 1,300 km. No support for this hypothesis has been otherwise forthcoming, and it seems possible that a simpler explanation may be found in errors of the tables; for a comparatively slight *further* modification would give angles of emergence in fair accord with the Pulkovo observations. Such a modification is shown in the column of Table VI. headed 'possible.' Its differences δP_3 show a fall to $\Delta = 20°$, then a rise to about $\Delta = 28°$, and then a fall again, which is all that is required. We proceed to show that this possibility is independently suggested by a study of the Y phenomenon or polychord.

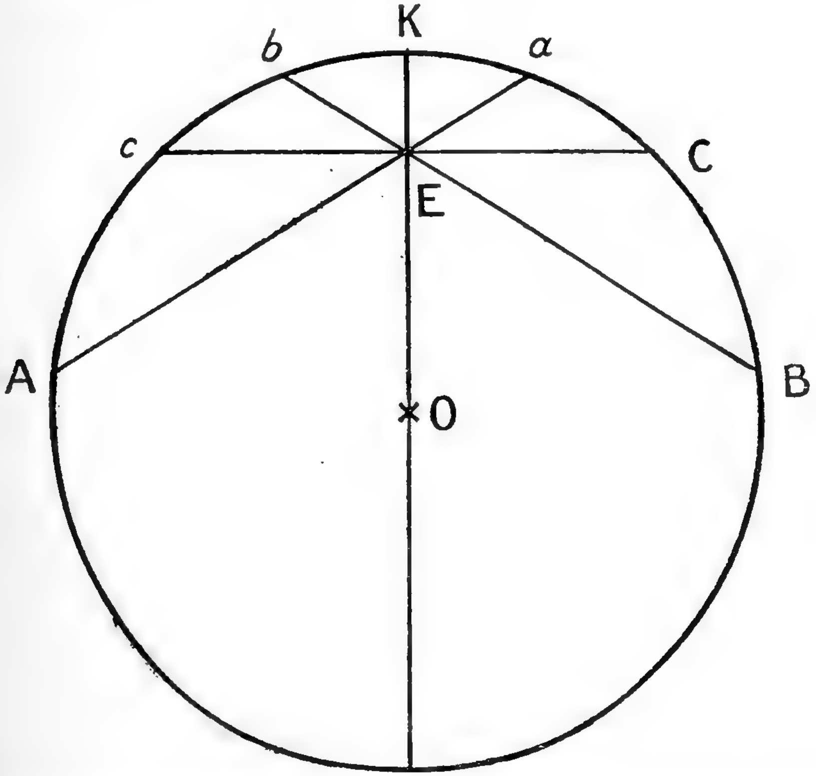
The Polychord or Y *Phenomenon.*

Is it simply PR₅ ?

In the 21st Report the following approximate times were deduced from the earthquake of 1913, March 14, for the Y phenomenon:—

Δ =	95°	100°	105°	110°
Time for Y =	1420s.	1470s.	1490s.	1520s.
Average vel.	14·9s.	14·7s.	14·2s.	13·8s.

The average velocity, added in the last line, falls off very definitely, and the hypothesis of a 'polychordal' P wave transmitted by numerous reflections with approximately uniform arcual velocity was therefore withdrawn. But in the course of the examination of Dr. G. W. Walker's hypothesis of deep-seated focus a modification of the hypothesis suggested itself which seems worth attention. Repeating the subjoined figure from the 20th Report,



we shall assume that cC is an arc of 17°·1 so that a P wave starting from a deep-seated focus E along EC will be reflected at C so as to strike the surface again at C_1 C_2 C_3 . . . where $CC_1 = C_1C_2 = C_2C_3 \ldots = 17°{\cdot}1$; and after five such reflections will reach a distance Δ from K (the epicentre) equal to $5{\cdot}5 \times 17°{\cdot}1 = 94°$. The whole time required would be, with adopted tables,

$$5{\cdot}5 \times 246\text{s.} = 1353\text{s.},$$

but if we adopt the corrections of Table VI. as in the column 'New' we should get

$$5{\cdot}5 \times 253\text{s.} = 1391\text{s.}$$

The value extrapolated from the above-quoted values for Y would be still greater, viz. 1410s., but we see at once that a comparatively slight increase to the tables would give this exact value: viz. the time for an arc of 17°·1 must be 256s., indicating a correction to tables of + 10s. near $\Delta = 17°$ instead of + 7s.

For paths slightly differing from EC, such as Ea or EB, the chords are greater, and five reflections will bring us beyond 94° in either case; in fact, there can be no PR_5 when Δ is much less than 94° (for the actual limit see below), which accords with the facts of the quake of 1913, March 14, from which the above figures were deduced in the 21st Report, if we exclude a doubtful Pulkovo observation. This limiting value for Δ gives us in fact the arc 17°·1, and consequently the depth of focus. If EC be a straight line we find EK = 0·011 of the radius; say 44 miles or 70 km. These figures apply only to this particular earthquake, and will also require modification if the path cC is curved; but they give the order of quantity suggested.

As we pass to greater values of Δ the wave must start along Ea or EB. If it starts along Ea, the total length of path will be less than 5·5aA, and cannot be so small as 5·0 aA. If it starts along EB the length will exceed 5.5bB or 5·5aA.

Thus Δ=110° may be reached in two ways: either by (let us say for illustration) 5 reflections or 6. The times of transmission would be (using column 'New' of Table VI.):—

$$5 \times \text{time for } 22^\circ = 5 \times 304\text{s.} = 1520 \text{ seconds,}$$
$$6 \times \text{time for } 18{\cdot}3^\circ = 6 \times 266 = 1596 \text{ seconds,}$$

and since we observe the *earliest* disturbance we fix attention on Ea and neglect EB.

Assuming the paths of the waves to be straight lines as in the figure, let cC subtend an angle 2C at the centre; and let aA, inclined to cC at an angle ϕ, subtend an angle 2A at the centre. Then

$$\cos A = \cos C \cos \phi = \cos 8^\circ{\cdot}55 \cos \phi$$
$$\text{arc } Ka = A - \phi.$$

In Table VII. are given, for various values of ϕ, first the arcs 2A and $A-\phi$, then the whole arcs $10A+(A-\phi)$; then the estimated times for Y from the figures quoted above from the 21st Report. From these we subtract the time for the arc $A-\phi$, which we can estimate only approximately by taking it as

$$\text{arc in degrees} \times 14{\cdot}9\text{s.}$$

The remainder, divided by 5, gives the time for the arc 2A, below which is subjoined the present tabular value and the necessary correction, followed by the correction deduced from PR_1 in Table VI.

Table VII.

		°	°	°	°	°
ϕ	=	0·0	3·0	5·0	6·0	7·0
2A	=	17·1	18·0	19·8	20·8	22·0
$A-\phi$ . .	=	8·6	6·0	4·9	4·4	4·0
Whole arc .	=	94·0	96·0	103·9	108·4	114·0
		s.	s.	s.	s.	s.
Whole time .	=	1410	1430	1485	1512	1548
Time of $(A-\phi)$	=	128	89	73	66	60
Time of 2A .	=	256	268	282	289	298
Tables . .	=	246	257	279	291	305
Correction .	=	+10	+11	+ 3	− 2	− 7
Table VI. . .	=	+ 6	+ 5	+ 3	+ 1	− 1

The last two lines are not *very* different, and we notice that the corrections now suggested are generally similar in form to those formerly found, but greater in amount. As has been remarked above, the existence of a hill and valley in the curve, which compromise has obliterated, is quite a fair possibility.

The question, however, whether the observations can be fitted to so considerable a hill and valley can only be answered after laborious re-reduction; such examination as has been made is not unpromising. but is embarrassed by the uncertainties of clock error already referred to. A glance at the records, for instance, of 1913, January 27, will show the doubtful nature of the records near the epicentre.

The explanation above suggested brings with it a number of questions. Firstly, why should PR_5 be specially prominent, compared, say, with PR_4 or PR_6? The answer is that PR_5 happens to fall in a place where it can be mistaken for S, while the others do not. But the suggestion of a sensible focal depth necessitates the re-investigation of other reflected waves, especially of PR_1. We notice two important points.

Firstly, the wave which starts along EC reaches the surface as PR_1 at $\Delta=8°\cdot6+17°\cdot1=25°\cdot7$; and it might at first sight appear that we cannot have any PR_1 for a value of Δ less than this, for the arcs 2A and 2B are both greater than 2C, as already remarked. But a wave starting along Ea reaches the surface after one reflection at

$$\Delta = 2A + A - \phi,$$

and from Table VII. we see that the sum of these quantities diminishes at first, though it ultimately increases. The minimum value is given by the condition

$$d\phi=3dA,$$

which leads to

$$(3^2-1)\sin^2\phi=\tan^2 C$$

$$\text{whence} \qquad \phi=3°,\ \Delta=24°.$$

Within $\Delta = 24°$, then, no PR_1 can be received.

Now, the evidence is distinctly in favour of the existence of some inferior limit for Δ of this kind. Within $\Delta = 24°$ the records are few and discordant, and the lowest value of $S - P_1$ hitherto found for which PR_1 has been recorded is 204 seconds, corresponding to $\Delta = 18°$, or a focal depth of, say, 25 miles. A more extended investigation of this point must, however, be deferred.

The second point is that at the point C (where $\Delta=25°\cdot7$) PR_1 arrives not by means of two equal arcs of 13°, but by unequal arcs of 8°·6 and 17°·1. Hence the tabular computation of Table VI. becomes unsuitable. Using the adopted tables we should get for $\Delta=26°$ by equal arcs of 13°, $\frac{1}{2}(S+P)-PR_1=99$ seconds, by arcs of 8°·7 and 17°·3 $\frac{1}{2}(S+P_1)$ $=105$ seconds. Hence the large negative values of O—C, at the head of Table III., should be still further increased; and, moreover, when we deduce from them corrections to P the dividing factor is 1·5 instead of 2·0, and the corrections apply to larger values of Δ, all of which changes emphasise the positive corrections to P for small values of Δ. As above remarked, however, EC does not give the minimum PR_1, which is for $\Delta=24°$, by arcs of 6° and of 18°, $\frac{1}{2}(S+P)-PR_1=107$ seconds, the computation by equal arcs giving 98 seconds.

For greater values of Δ PR$_1$ may come by either of two paths. It is easy to take from a diagram the alternatives as follows :—

		°	°	°	°	°	°	°
Δ . .	=	24	25	26	27	28	29	30
Arc $(A-\phi)$ . .		6·0	4·5	4·0	3·6	3·3	3·0	2·7
Long arc . .		18·0	20·5	22·0	23·4	24·7	26·0	27·3
		s.	s.	s.	s.	s.	s.	s.
$\frac{1}{2}(S+P)-PR_1$.		107	113	118	122	127	133	138
		°	°	°	°	°	°	°
Arc $(A+\phi)$ . .		6·0	8·0	8·9	9·7	10·5	11·3	12·0
Long arc . .		18·0	17·0	17·1	17·3	17·5	17·7	18 0
		s.	s.	s.	s.	s.	s.	s.
$\frac{1}{2}(S+P)-PR_1$,		107	104	104	105	106	107	150

Here it certainly looks as though the *observed* PR$_1$ starts with the longer arc $A+\phi$ instead of the short arc $A-\phi$ as we have assumed for PR$_5$; for only by this supposition can we obtain approximate constancy for the quantity $\frac{1}{2}(S+P)-PR_1$. There is nothing unreasonable in this difference between the two cases: for PR$_5$, if we are right in identifying it with Y, is usually read for S; we read the *first* big movement, and, as already remarked, the PR$_5$ by $A+\phi$ follows that by $A-\phi$. Hence the former is read. But in looking for PR$_1$ we should naturally take a movement which is not too near P. The PR$_1$ which starts with $A-\phi$ runs up closer and closer to P as ϕ increases.

We have, however, still to explain why $(S+P)/2-PR_1$ should be about 105s. instead of about 80s., as at the head of the 'observed' column in Table III. On the present hypothesis the tables are wrong to this extent. When $\Delta=28°$, for instance, if we take the *last* column of Table VI. the error of P is −12s. and that of S should be nearly double, say −20s., which gives for $(S+P)/2$ an error of −16s.: and PR$_1$ is in error by $2\times14=28$s.; making altogether 44s., which reduces the 106s. of the tables to 62s., as compared with 75s. observed. These corrections are apparently *too* large, and it may be readily admitted that the last column of Table VI. probably goes too far. If we use the first column we get, say, −8s. for $(S+P)/2$, and −22s. for PR$_1$, which is just the quantity required.

Somewhat similar considerations apply to PR$_2$. The whole arc is now

$$A-\phi+4A,$$

and becomes a minimum when

$$d\phi=5dA,$$

which leads to

$$(5^2-1)\sin^2\phi=\tan^2 C.$$

so that $\phi=1°{\cdot}7$, $A=8°{\cdot}75$; minimum $\Delta=42°$.

Generally, for PRn, the corresponding equation is

$$\{(2n+1)^2-1\}\sin^2\phi=\tan^2 C,$$

or $(2n+1)\phi=C$ approximately; so that when $n=5$, $\phi=0°{\cdot}77$, $A=8°\,58$; minimum arc being $93°{\cdot}6$, close to the value obtained by starting along EC.

Observations of PR_2 are fairly numerous beyond S—P=542 seconds (say $\Delta=69°$), but only three have been found for smaller values, viz.:

$$S - P = 487s., \quad 363s., \quad 360s.$$
$$\text{Say } \Delta = 59°, \quad 38°.5, \quad 38°.0,$$

according to adopted tables. Further scrutiny is of course desirable but the evidence is so far satisfactory.

Of PR_3 and PR_4 little more need be said at present than that they do not fall near enough to S to be confused with it, while PR_6 probably lies beyond S. The rough minima in Δ for their appearance are:

	PR_3	PR_4	PR_5	PR_6
Δ =	60°	77°	94°	111°
	s.	s.	s.	s.
Time =	896	1152	1408	1664
S (Tables) =	1103	1309	1496	1657
S (corrected) =	1102	1300	1474 ?	1637 ?

The above notes are obviously tentative and incomplete, but they represent the result of a good deal of work by the method of trial and error, and may serve to show possibilities. Especially is it hoped that they may show the importance of an identification of the phenomena through more accurate tables of P and S, on which the main computing strength of the Shide organisation is being concentrated for the present. It may be that there are too many variable elements to make great accuracy possible, but experience of working with the residuals suggests the contrary view, which is at any rate worth thorough testing, even if the ultimate result be disappointing.

Preliminary Report on Tides and Tidal Currents.

By H. LAMB *and* J. PROUDMAN.

It seemed most important in the first place to obtain a sort of conspectus of what has been done and what is in progress, in the way of observation and reduction, in various parts of the world. Owing to the circumstances of the time our attention has been mainly confined, so far, to work done in the British Empire and in the United States of America. As regards Great Britain, the more accessible literature has been consulted, whilst for India, Canada, Australia, New Zealand, and the United States valuable information has been furnished by various authorities, to whom special acknowledgment will, it is intended, be made in a more complete Report.

It is proposed in the future Report, or Reports, to give an account of the work done in the countries named, together with a critical examination of such points as appear to call for it.

In the course of the survey so far made, various suggestions have naturally presented themselves, some of which may indicate lines of research. The following may be mentioned:—

1. While the tide-tables as at present produced appear to be adequate for practical needs, the possibility of improvement should not be left out

of sight. There are many cases where the harmonic constants have not been determined with all the accuracy obtainable.

2. Harmonic analyses, and possibly more extended observations, relating to oceanic island stations appear to be wanting. These would probably give results of great theoretical value.

3. Continuous observations of tidal heights at off-shore stations are especially desirable, both as a test of hypotheses relating to the main tidal movements and as a foundation for more complete syntheses of tidal facts.

4. Further continuous observations of currents are also desirable. The only British observations of this kind which have been analysed appear to be those taken in and near the North Sea in connection with the "Conseil permanent international pour l'exploration de la mer."

5. Greater accuracy seems attainable in the harmonic analysis, more particularly, of the smaller semidiurnal and diurnal tides. When a year's record is treated by the methods in common use, only the numbers obtained for the larger tides can be assumed to be reasonably correct. Improvement may be sought by allowing for imperfect isolation of the different series. This is done by the U.S. Survey, but revised methods appear necessary except for the principal solar series.

6. Accurate determinations of the constants for the long-period tides of astronomical origin are much wanted, on account of the part which these tides play in various speculations. The numbers obtained by analysis of a single year's record are very uncertain, not through defect in the method of reduction, but in consequence of meteorological disturbances in the record itself. The analysis of observations extending over a long series of years might be expected to give more trustworthy results.

7. A comparative study should be instituted of the geographical distribution of well-attested harmonic constants for tides of different periods. This might lead to an improved dynamical conception of the great tidal movements.

8. A knowledge of the *free* periods of oscillation of the ocean, or of special regions of it, would be of the greatest interest, not only for its own sake, but as a basis for dynamical reasoning on the actual forced tides. It is not known whether any attempt has been made in this direction by an examination of the results obtained for different ports whose harmonic constants have been accurately determined when the predicted tide is subtracted from the observed. The residue might conceivably yield some indications as to the longer free periods. A further examination of the records attending such a disturbance as that of the Krakatoa explosion might also be fruitful.

Impact Tests.—Report of the Committee, consisting of Professor W. H. WARREN (*Chairman*), Mr. J. VICARS (*Secretary*), Professor PAYNE, *and* Mr. E. H. SANITER, *appointed to consider and report on the Standardisation of Impact Tests.*

Impact Tests of Materials.

IT is considered that ordinary static tests, such as the tension test on standard bars or the cold bending test, do not reveal the capacity of the material to resist shocks. In rails, axles, tyres and drawbars, armour plates, ordnance, moving parts in engines and machinery, the stresses are all more or less suddenly applied. It has long been recognised that the ordinary static tests in such cases should be supplemented by impact tests. Again, Mr. C. Fremont has recently shown that impact tests on wire and wire ropes reveal the weakness and want of homogeneity in the material in a much more satisfactory manner than static tests. Numerous examples could be quoted where normal static tests have failed to express or define in a satisfactory manner the resistance of material to suddenly applied loads. The ordinary tension test may give a reasonable strength per square inch, and a reasonable percentage of elongation; but the same material, when subject to impact, may break without much deformation and reveal a coarse fracture. Impact tests reveal the brittleness of the material or its tendency to fail by suddenly applied loads. Resilience is a function which is the reverse of brittleness, and expresses definitely the resistance to impact. It represents two factors, one of which is elongation, and the other the stresses producing them. A metal that shows a fair resilience will always give a fair elongation in a state of tension, but the converse is not true, as will be shown by the results of tension tests and impact tests of a certain steel used for the manufacture of high explosive shells.

The tensile strength per square inch of a steel bar tested in the ordinary way is not a true expression of the actual strength, or resistance to breaking expressed as 'tenacity,' because, at the moment of fracture, the area contracts locally, and it is this contracted area which breaks. Again, this contracted area does not vary with the strength exactly, but depends also upon other qualities of the material.

The hardness number, as determined by the penetration of a steel ball or a steel cone—represents more exactly the actual strength or tenacity of the material. The Brinell hardness number denoted by Δ is related to the ordinary tensile strength per square inch denoted by σ thus:—

$$\sigma = C\Delta,$$

where C is approximately constant for steels of the same kind; thus, for structural steel having a tensile strength of 26·7 tons per square inch,

$$\Delta = 143{\cdot}9 \text{ and } C = 0{\cdot}186.$$

The relation between impact and hardness tests has not been extensively studied, but it will be shown that there is an approximate ratio somewhat similar to that observed in impact and tension tests.

In regard to experiments made by impact machines on plain and nicked pieces, in every case the effect of nicking or notching a bar is to bring out more decidedly the properties which we have termed brittleness, or want of resilience, and it is this test we propose to more especially consider.

In order that impact tests on notched bars should be strictly comparable, it is necessary to consider the form and dimensions of the test-pieces, the apparatus used in testing them, and the method of record and measurement.

In regard to the form and dimensions of the test-pieces :—

In tension tests it is clear that the sizes of the test-pieces cannot be constant, but the proportions have been established on the law of similarity which ensures that the test-pieces of different dimensions should be geometrically similar in order that the results obtained may be strictly comparable.

Experience with impact on notched bars shows that the resilience referred to the area of the cross-section through the notch, when made on pieces 10 by 10 mm. and pieces 30 by 30 mm., are not strictly comparable, as the results obtained by the large piece are uniformly greater than those obtained with the smaller test-piece, and the difference is greater the greater the resilience of the materials. The reason for this difference appears to be due to the fact that in the rupture of a notched bar we have two distinct stages in the process : (1) the general deformation of the bar, which is proportional to the cube of the homologous dimensions ; and (2) the rupture of the piece through the notch, which is proportional to the square of the said dimensions.

The work of rupture should then be expressed by two terms—the work of deformation proportional to the cube, and the work of rupture without deformation proportional to the square or the area of the cross-section through the notch. Professor Schüle has recommended that the faces of the test-pieces on opposite sides at right angles to the length of the notch should be polished, and the volume of the piece strained in impact, shown by the dull surface, should be used in expressing the resilience.

The tests made by the authors show that in the brittle shell steel there was very little deformation, and the resilience is well expressed by the area of the cross-section through the notch, whereas in the case of the alloy steels the deformation was considerable, and was not confined to the area of the cross-section, but extended to some extent on each side of the notch. The method expresses with less accuracy the resilience of the more resilient material than that of the brittle or less resilient material when expressed in terms of the area through the notch, and relatively under-estimates the more resilient material. It should be noted that similarity in the form of the test-pieces should be also provided in the radius of the notch, and that of the supporting knife-edges.

Test-pieces.—For notched bar test-pieces, two standard forms have been recommended by the International Association for Testing Materials (*see* figs. 1 to 6).

A small test-piece, 60 mm. long by 10 by 10 mm. in cross-section, having a notch $2\frac{1}{2}$ mm. deep, rounded at the bottom to a radius of 1 mm.[1] This is easily prepared with a twist drill or a properly shaped milling cutter. A larger test-piece, 160 mm. long by 30 by 30 mm. in cross-section, having a circular notch 15 mm. deep, formed with a twist drill

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[1] The dimensions given are not exactly those recommended, but are those actually employed in the tests made by the Committee. The recommended depth of notch is 5 mm. and the bottom radius $\frac{2}{3}$ mm.

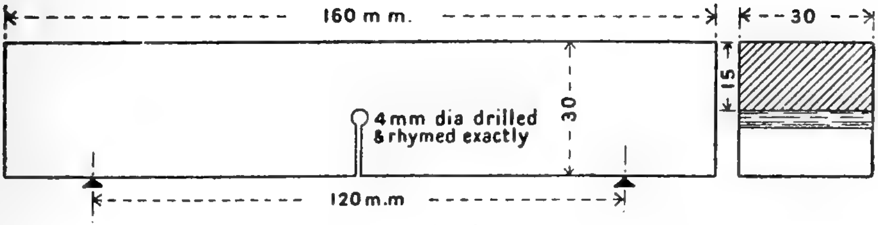


Fig. 1.

Scale Half Size

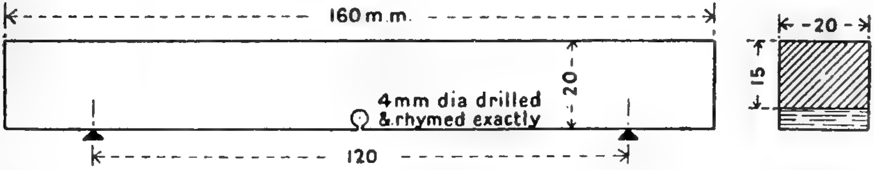


Fig. 2.

Half Size

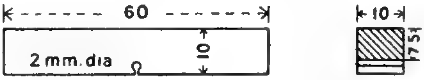


Fig 3.

Half Size

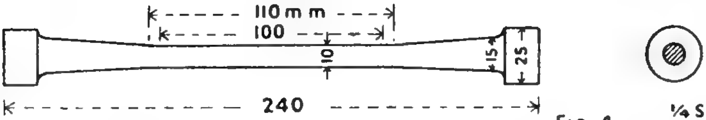
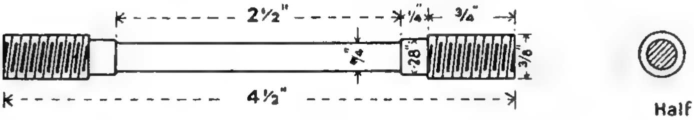


Fig. 4

¼ Size



Charpy Tension Piece

Fig 5

Half Size

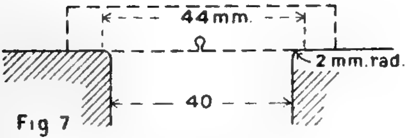


Fig 7

Detail of Anvil for Guillery Machine

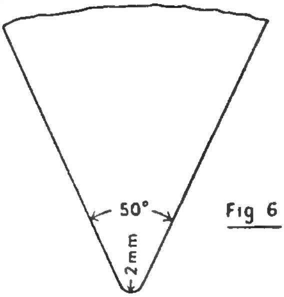


Fig 6

Detail of Tup for Drop-hammer

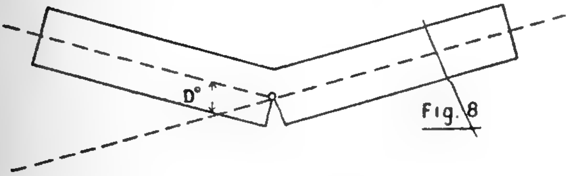


Fig. 8

and rhymer to a radius of 2 mm., the material between the hole and the bottom being cut away with a saw.

An intermediate size has been proposed and used extensively, and the authors have adopted it as well as the two former sizes; it is 160 mm. long by 20 by 20 mm. in cross-section, with a similar notch to the 30 by 30 mm. piece, but only 5 mm. deep.

In addition to notched bar tests the authors have made tension tests on specimens without notches.

(*a*) ¼ in. diameter and 2½ in. gauge length, broken with a single blow in a small Charpy machine.

(*b*) 10 mm. diameter and 100 mm. gauge length, broken with a series of blows in a Martens drop-hammer machine.

The advantage of the circular notch over the acute triangular notch is that it can be made and reproduced accurately in a regular manner, so that the conditions of the test in so far as the notch is concerned are kept as constant as possible.

The disadvantage is that more energy is consumed during the period when the bar undergoes deformation, before a crack is developed at the notch, than occurs with the acute triangular notch. The resilience expressed in regard to the area of the cross-section through the notch is greater with circular than with triangular notches, and increases with the radius of the circular notch. At the same time the relative results obtained in grading material with circular or triangular notches do not vary to any great extent. If, however, the work done during the two periods of deformation and fracture could be separated and accurately determined, the triangular notch would undoubtedly supersede the circular notch, as the results of the test referred to the area of the cross-section through the notch would more accurately express the resilience.

As to the advantages of the small test-pieces, 10 by 10 mm., over the larger, 30 by 30 mm.:—A larger number of pieces can be obtained from a given piece of material, and local defects more clearly exposed. Again, the selection of the test-pieces after a microscopic examination of a suitably prepared and etched surface revealing any heterogeneity is more completely accomplished with the smaller test-pieces. The larger test-pieces enclose more or less any local defects, and it is not so easy or convenient to obtain sufficient specimens.

The smaller test-piece can be broken in a smaller machine.

Impact-testing Machines.—All impact-testing machines should be designed in such a manner that the actual energy required to fracture the test-piece in one blow may be accurately determined. They should be calibrated from time to time, and the losses of energy due to friction and other causes should be accurately determined. The machines should be kept in good order and handled carefully. The machines used in the various tests made by the authors are sufficiently known, so that a detailed description is unnecessary, but it may be necessary to state the following particulars:—

A. *The Guillery Machine.*—This machine consists of a fly-wheel 21 in. diameter, carrying a knife with striking edge 2 mm. radius.

The knife-edges supporting the test-piece are spaced 40 mm. apart, and are rounded to 2 mm. radius. (*Vide* Fig. 7.)

The maximum velocity of impact is equivalent to a fall of 4·8 metres and the corresponding energy is 60 kilogrammetres. (K.G.M.)

The recording device consists of a centrifugal pump driven from the main axis and supplying a column of water in a glass tube, the height of which is proportional to the velocity of the wheel. A scale attached to the tube shows the number of revolutions and K.G.M. at any instant, and the drop in the water column after impact shows at a glance the K.G.M. absorbed by the fracture of the test-piece. The error is due to the energy lost by the release of the catch just before impact, and amounted to 0·8 K.G.M. The machine is only suitable for the 60 by 10 by 10 mm. notched bar test, and is more satisfactory for resilient than for non-resilient steel, as the former causes a greater depression of the water column. The machine is operated by hand through friction gearing.

B. *The Charpy Pendulum Hammer.*—These are made in three sizes, but the one used by the authors has a maximum capacity of 32 K.G.M. and a maximum fall of 1·42 metres; the striking edge of the pendulum is 2 mm. radius; the supports are spaced 40 mm. apart and are not rounded. This machine is arranged to test the 60 by 10 by 10 mm. notched bar, but it can also test a tension-piece with or without notches, and record the energy required to break it in a single blow. The usual size of the test-piece is ¼ in. in diameter, with screwed ends, and a gauge length of 2½ in. The arrangement for tension tests has been modified and considerably improved by one of the authors.

The Charpy Pendulum.

Method of determining Energy of Rupture.

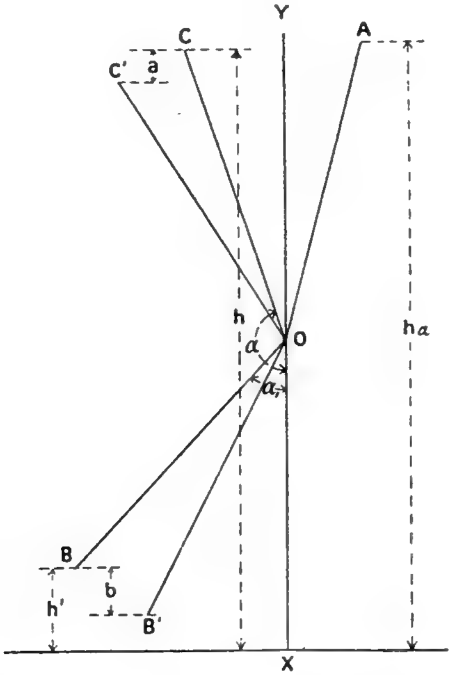


FIG. 8.

To obtain the energy absorbed in the rupture of the test-piece, multiply the difference of height of the centres of gravity of the pendulum at the beginning and end of the swing by the weight of the hammer. This result must be corrected for friction. (Fig. 8.)

Let OA = Initial position of pendulum.
OC = Position after free swing.
OC′ = ,, ,, second free swing.
OB = ,, ,, rupture of test-piece.
OB′ = ,, ,, first swing after rupture of test-piece.
K = Energy of rupture. W = weight of hammer.

Then—

$$\begin{aligned}\text{K} &= (\text{Energy just before impact}) - (\text{Energy just after impact}).\\ &= (\text{W}h_a - \text{friction loss over } \angle\ \text{AOX})\\ &\qquad - (\text{W}h' + \text{friction over } \angle\ \text{XOB})\end{aligned}$$

$$\begin{aligned}\text{But friction loss over } \angle\ \text{AOX} &= \tfrac{1}{2}\ \text{friction loss over } \angle\ \text{AOC}\\ &= \tfrac{1}{4}\ \text{W}a.\end{aligned}$$

Similarly friction loss over $\angle$ XOB $= \frac{1}{4}$ Wb.

$$\begin{aligned}\therefore \text{K} &= (\text{W}h_a - \tfrac{1}{4}\text{W}a) - (\text{W}h' + \tfrac{1}{4}\ \text{W}b).\\ &= (\text{W}h_a - \text{W}h') + (-\tfrac{1}{4}\text{W}a\ \tfrac{1}{4} - \text{W}b)\end{aligned}$$

but $h_a = h + \frac{1}{2}a$

$$\therefore \text{K} = \text{W}\ (h - h') + \tfrac{1}{4}\text{W}\ (a - b).$$

$$a = l\,(\cos \angle\text{COY} - \text{Cos} \angle\text{C}'\text{OY}) : b = l\,(\cos \angle\text{B}'\text{OX} - \text{Cos} \angle\text{BOX})$$

where l = length of pendulum from suspension to the centre of gravity.

By observing the decrement in the swing we may find values of a and b, and hence of $\frac{1}{4}$W $(a - b)$ for any value of α. Tabulate these values and plot $\angle$ BOX against the friction correction k'.

$$\begin{aligned}\text{K} &= \text{W}\ (h - h') + k'\\ &= \text{W}l \cos \alpha - \text{W}l \cos \alpha_1 + k'.\end{aligned}$$

The Direct Fall or Block Hammer.

The type used in these tests was designed by Martens, but a recording drum apparatus has been added, made by Messrs. Amsler. Various hammers can be used in this apparatus, but the authors, after much experimenting, decided to use a 36 K.G. for the more resilient steels, and a 12 K.G. hammer for the less resilient shell steel. The height of drop was 3 mètres in each case.

The hammer has a striking face with the sides inclined at 50°, and the ends rounded to a radius of 2 mm. The test-pieces are supported on specially designed steel castings, with edges rounded to a radius of 2 mm. and spaced 120 mm. apart in order to suit the 160 by 30 by 30 mm., and the 160 by 20 by 20 mm. test-pieces. The weights of the anvil are as follows :—

Steel castings	90 lb.
Cast-iron anvil to which the castings are bolted	2,300 ,,
Concrete foundations on shale rock	7,600 ,,
Total weight	9,990 lb.

Ratio of weight of hammers to anvil and foundations 1 : 277 and 1 : 832 respectively, so that, as far as rigidity of the anvil is concerned, the effect of the blows of the hammer would be as severe as possible under the circumstances, and the results would be much less than with an anvil on springs or timber.

The recording apparatus for determining the energy of rupture consists of a drum rotated at a constant speed by means of an electric motor. A style attached to the falling hammer describes a diagram on the drum showing the velocities of the tup just before and after impact. The apparatus can be attached to the frame of the machine and adjusted to suit the heights required for various tests.

In order to determine the losses of energy due to the friction of the hammer on the guides of the machine, and also that due to the deformation of the hammer and the frame, we may proceed in the following manner :—

First, calibrate a strong spring, such as a triple carriage-spring, in a static compression-machine by obtaining a diagram of the loads and corresponding deformations. The area of the diagram up to any given deformation gives the work done or energy corresponding with this deformation. Place the spring on the anvil of the impact machine and determine the deformations due to various heights of drop, and find the ratio of the height corresponding with the deformation of the spring to the actual height of the fall. If h = actual height, and h_1 = the height corresponding with the energy represented by the deformation of the spring, and n the ratio of h_1 to h, then—

$$n = \frac{h_1}{h}$$

and the energy = $n\,Wh$.

It should be noted, however, that we here assume that the work done in compressing a spring a definite amount is the same whether the load is applied steadily or by impact. This assumption is probably incorrect.

Copper crusher gauges may be used instead of or as a check on the spring.

Mr. P. Wélikhow, of Moscow, in order to show the relationship between the ordinary static tension tests and impact tension tests, used an impact machine precisely the same as that used by the authors, and, by means of a calibrated spring, determined the value of the energy due to a given fall, then placing a standard tension test-piece in the shackles of the machine resting upon a weaker calibrated spring, and noting the compression of this spring representing the kinetic energy remaining in the hammer after rupture of the test-piece. The energy required to break the test-piece was clearly the energy of the hammer found by the first test on the triple spring, less the work absorbed by the second spring.

All the conditions are practically identical in the two cases. The friction against the guides is exactly the same, the losses due to the deformation of the hammer, and the frame carrying the test-piece are the same in both cases, so that the fracture of the test-piece alone diminishes the work absorbed by the spring. Three kinds of steel were tested in tension by impact and by ordinary static tension, soft cast-steel, hard cast-steel, and extra hard cast-steel. The area of the stress-strain diagrams obtained in the static tension machine were determined. Thus, if P = the breaking load, T = the energy of rupture, Δl = the total elongation, and a the diagram factor, then :—

$$T = aP\Delta l \text{ and } P = \frac{T}{a\Delta l}.$$

The test-pieces had a length of 110 mm. and a diameter of 10 mm. The results are shown in the following Table I. :—

TABLE I.

—	—	Static tests	Impact tests
Soft Steel	Breaking load	3050	3040
	Elongation	31%	32%
	Contraction	63%	69%
Hard Steel	Breaking load	5240	4750
	Elongation	20%	20%
	Contraction	43%	48%
Extra Hard Steel . .	Breaking load	6630	6930
	Elongation	8%	11%
	Contraction	23%	24%

The results show that impact tension tests not only supplement the static tension tests by giving the kinetic strength of the material, but in certain cases can replace it as it gives all the characteristic values of the properties of the material, excepting the elastic limit. It should be noted, however, that the relatively massive frame forming the tension shackles in the Martens machine absorbs a large portion of the energy of the hammer at the moment of striking. Impact tests on steels in tension, in which a triangular or circular notch has been cut, give results similar to those obtained in static tension after local extension has commenced. Impact tension tests do not reveal the brittleness of the material like the notched bar tests. In regard to the determination of losses in the direct fall machine, we have adopted the following method :—

MARTENS' DROP HAMMER.

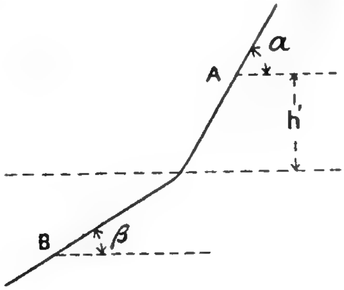
Method of determining the Energy of Rupture.

The energy of rupture is obtained by determining the energy of the tup just previous to and just after the impact, and taking the difference.

Thus if h_1 = equivalent height for veloc. before impact,
h_2 = ,, ,, ,, ,, after ,,
W = weight of tup,
K = energy absorbed in rupturing test-piece,
then $K = W\ (h_1 - h_2)$.

h_1 and h_2 are determined by taking an autographic diagram on a revolving drum, and simultaneously recording the velocity of the drum by means of a chronograph.

A small style attached to the tup describes a curve on the drum as shown below :—



The velocity of the tup before and after impact is $v_1 = \mathrm{V} \tan \alpha$ and $v_2 = \mathrm{V} \tan \beta$
where V is the velocity of the drum.

Connection is made to a chronograph, controlled from the testing laboratory, which indicates revolutions of the drum and ½ seconds, thus fixing V.

We can therefore either calibrate the apparatus for any given hammer and height of fall, by dropping the tup without the insertion of the test-piece and calculating the per cent. loss of energy, or we can determine the actual loss for every test. The former method would be used for ordinary commercial testing, as the latter involves the use of a chronograph for every test.

The former was used for R11 R19 R31 and 5960 steels, and the more accurate method for 3198 3184 2300 1324 and the gun steels.

When the chronograph is not employed, the method of calculation is as follows :—

$$\text{Veloc. at A is } v_1 = \mathrm{V} \tan \alpha \text{ and at B is } v_2 = \mathrm{V} \tan \beta$$

$$v_1^2 = 2gh_1 \quad v_2^2 = 2gh_2 \;\therefore\; h_1 - h_2 = \frac{1}{2}g \times (v_1^2 - v_2^2) = \frac{v_1^2}{2g}\left(1 - \frac{v_2^2}{v_1^2}\right) = h_1\left(1 - \frac{v_2^2}{v_1^2}\right).$$

$$\text{But } \frac{v_2^2}{v_1^2} = \frac{\tan^2 \beta}{\tan^2 \alpha} \;\therefore\; h_1 - h_2 = h_1\left(1 - \frac{\tan^2 \beta}{\tan^2 \alpha}\right).$$

$$\text{The energy of rupture is therefore } n\left[\mathrm{W}h\left(1 - \frac{\tan^2 \beta}{\tan^2 \alpha}\right) + \mathrm{W}h^1\right],$$

where h^1 is the height between the zero line and point A and n is a constant less than unity determined by calibration of the machine as above.

The height h_1 calculated in this manner is always less than the actual height h, and the difference $h - h_1$ due to frictional losses is greater as the weight of the hammer decreases. Let the weight of the hammer be 12 kilos. If sp = the speed of the drum in feet per sec. $= 11{\cdot}6 \frac{n.\pi.d}{12 \times 60}$ the velocity of the hammer at the moment of impact is :—

$$\text{sp.} \tan \beta = \frac{11.6 \; n.\pi.d}{12 \times 60} . \tan \beta = n.k_1 \tan \beta.$$

$$h_2 = \frac{n^2 k_1{}^2 \tan^2 \beta}{2g} = \cdot 0007377\ n^2 \tan^2 \beta \text{ feet.}$$

$$= \cdot 0002249\ n^2 \tan^2 \beta \text{ mètres.}$$

From a chronograph record, $n = 139 \cdot 5$ and from the diagram

$$\tan \beta = \frac{3 \cdot 43}{4 \cdot 29} \quad h_2 = \frac{\cdot 0002249 \times 139 \cdot 5^2 \times 3 \cdot 43^2}{4 \cdot 29^2} = 2 \cdot 797 \text{ mètres.}$$

The loss is represented by $h - h_2 = 3 - 2 \cdot 797 = 0 \cdot 203$ mètres.

In this case the loss due to friction is 6·8 per cent.

After impact measure from diagram $\tan \beta = \frac{5 \cdot 30}{7 \cdot 04}$, and then

$$\frac{\cdot 0002249 \times 139 \cdot 5^2 \times 5 \cdot 30^2}{7 \cdot 04^2} = 2 \cdot 480 \text{ mètres}$$

Therefore the loss due to rupture of test-piece is

$$2 \cdot 797 - 2 \cdot 480 = 0 \cdot 317 \text{ mètres.}$$

If W=12 kilos the total energy absorbed in rupture=

$$12 \times 0 \cdot 317 = 3 \cdot 804 \text{ K.G.M.}$$

The frictional losses with the 36 kilo hammer were 1·8 per cent.

Remarks on Impact-Testing Machines.

The Charpy pendulum hammer is a very suitable machine for testing brittle materials, as the swing of the pendulum after impact is greater than with less brittle materials. The Guillery machine is a very suitable machine for testing tough materials, as the water column descends to a greater extent than with less tough materials.

In both machines the energy of the moving masses at the moment of impact is expended in causing the rupture of the test-piece, and in producing deformations of the frame of the machine and the anvil, the remaining energy in the moving masses is shown by the angle moved through by the pendulum, and the fall of the water column in the Charpy and Guillery machines respectively. The errors due to the deformations of the frame and anvil cannot be easily calculated. If we have a pendulum anvil as well as a pendulum hammer, we can find the actual energy absorbed by the test-piece, after determining the losses due to friction. If the masses representing the pendulum anvil are about twenty times the mass of the pendulum hammer, such a machine would give results of comparative value which could be used in expressing definitely the resilience of the material. Dr. Stanton found that with a pendulum anvil the energy of rupture was 5 per cent. lower than in a similar machine with a fixed anvil.

In the direct fall machine such as the one used by the authors, provided with the apparatus for the determination of the energy of the hammer at the moment of and immediately after impact, the difference between these energies is not entirely expended in the rupture of the test-piece, but the losses due to deformations of the hammer and anvil are relatively small, and, when carefully used, this machine will give satisfactory results. If the anvil is supported on springs the results would compare more or less with the double pendulum, but the compression of the springs could not be determined as accurately as the movement of the pendulum anvil.

To standardise the impact test, it would be desirable to agree as to the magnitude of the moving masses and the type of machine, as the blow would be much sharper in the direct fall machine in consequence of its more massive anvil, and in specifying the resilience it is necessary to assume that all the conditions affecting the results should be maintained practically constant.

In connection with the notched bar tests made by the authors, the angle of rupture was measured after fracture (fig. 8). It is only possible to do this accurately when there is contact over the whole surface. In the tougher materials there is considerable sliding of the surfaces, one may be convex and the other concave. Again, in some of the larger pieces, both parts were convex. If the angles are plotted against energy of rupture, it will be found that a relationship exists :—

$$\frac{\text{Energy of rupture per sq. cm.}}{\text{Angle of rupture}} = \frac{K}{D}.$$

In the various tables of results it will be seen that this ratio is more or less constant, and any difference is largely due to the difficulty in correctly measuring the angle of rupture.

Mesnager found that for the smaller test-pieces $K=0{\cdot}375\ D$, and for the larger test-pieces $K=1+0{\cdot}58\ D$.

He also found that if R denoted the tensile strength of the material in kilogrammes per sq. cm., then :—

For the small pieces :—$R+2{\cdot}66\ D=95$,
" " larger " $R+1{\cdot}72\ D=87$.

A similar relationship could be established between the angle of rupture and hardness by plotting a sufficient number of tests, but all such equations would be more or less approximate, and in the case of brittle steels the angle is too small to measure and the method fails entirely.

The steels tested by the authors have the following composition :—

TABLE II.

Chemical Analysis.

Mark	C	Si	S	P	Mn	Cr	V	Ni %
R11	·29	·083	·027	·024	·48	·56	—	2·88
R19	·25	·108	·038	·031	·71	—	—	3·27
R31	·30	·121	·027	·028	·65	—	—	—
5960	·22	·140	·032	·028	·50	·81	·17	—
3198	·44	·12	·014	Trace	·87	—	—	—
1324	·43	·13	·023	·008	·83	—	—	—
2300	·50	·13	·024	·015	·68	—	—	—
3184	·45	·074	·019	·012	·72	—	—	—

Conclusions on Results.

The results of the small notched-bar tests on the Charpy and Guillery machines are given in Tables VII. to VIII., and those obtained with Martens' direct-fall machine are given in Tables IX. to XII.

The shell steels are much less homogeneous in quality than the other steels and have a very low resilience. Again, the angle of rupture was too small to be measured accurately.

With the small test-pieces the energy required to produce rupture was approximately the same in both the Guillery and the Charpy machines, but the former was more severe upon the steels denoted by **R11**, **R19**, and the gun steel than the latter.

In the direct-fall machine on the larger test-pieces, the energy required to produce rupture was less for the brittle shell steels, and greater for the steels denoted by R11, R19, and the gun steel. The brittle shell steels tested would naturally give low results owing to the severity of the blow on the more rigid anvil, but this did not affect to the same extent the three other steels, and the higher results are due to the larger test-pieces, and correspond more or less with similar results obtained by Mesnager and others on large and small test-pieces.

The results are shown more clearly in the Summary 1, Table III., but for the carbon steel R31 and the vanadium chrome steel, 5960, the results are irregular, the latter being highest in the Guillery machine, K.G.M. =13.11, and only about one-third of this in the direct-fall machine. In regard to the ratio of the energy of rupture per sq. cm. to the angle of rupture, Summary 2, Table IV., it appears that the values given for various steels are so variable that the method cannot be considered as anything more than a rough approximation, and the equations derived by Mesnager can only apply to the particular steels included in his experiments.

The hardness numbers obtained by the Amsler cone given in Summary 3, Table V., show that the material in the small and large test-pieces was not exactly the same, and these differences would affect the results of the notched-bar tests to a corresponding extent, if the differences were due entirely to hardness, but the spread under the punch in the smaller test-piece may account to some extent for the smaller hardness number obtained. It is clear, however, from the nature of these tests, and the difficulty of keeping all the conditions affecting them constant, that impact tests on notched bars cannot be expected to give results comparable in regularity with those obtained in the ordinary static tension tests; at the same time they reveal in a striking manner the brittleness of the material. The results obtained by static tension and impact tension on the small test-pieces used in the Charpy machine corroborate those obtained by Mr. P. Wélikhow in so far as they show that impact tension tests give results comparable with static tension tests, but Tables XIII. and XIV. show that the energy of rupture is greater in the impact tests than in the static tests, also that the elongations and contractions of area of fracture do not differ to any considerable extent. The closer agreement obtained by Wélikhow is due to the larger amount of energy absorbed in the tension shackle of the direct-fall machine used by him, and the closer approximation to the conditions of the ordinary static test. The brittle shell steels gave excellent results in both the static and the impact tests, and there was nothing to suggest brittleness excepting the coarse crystalline fractures which occurred in two of the heats. Again, in the case of the other steels, there was nothing to suggest their resilience and toughness excepting their larger contractions of area of rupture, and their fine silky fractures. In regard to the impact tension tests in the direct-fall machine on standard test-pieces with a series of blows from hammer of 12, 18, and 36 kg., and falls of 2 and 3m., it should be remembered that, although the anvil was very rigid, the tension shackle would, in consequence of its large mass relative to that of the test-piece, reduce considerably the severity of the impact, and the number of blows in each case necessary to produce rupture would be a measure of the endurance of the material. The elongation per blow decreases at first, then remains constant even after the test-piece has begun to neck slightly, and then increases near the last blow to about its initial value. The material is modified by the first blow and a hardening effect produced. Tables XV. to XVII. and Summary 4, Table VI., give the results of these tests, from which it will be seen that the relative values of the results vary with the weight of the hammer and the drop.

We consider that satisfactory impact tests can be made by means of the Charpy or the Guillery machines and that the smaller test-piece 60 by 10 by 10 mm. is preferable to the larger 160 by 30 by 30 mm., as the former is better adapted for revealing local defects, and can be broken with a smaller machine. Test-pieces may be cut out of the portions of the material where local defects appear to exist, and these are suggested by the appearance of the polished surface after etching.

It does not appear to be necessary to substitute a pendulum anvil for the ordinary fixed anvil.

There does not appear to be any definite relationship between different kinds of materials connecting the impact test properties with the static tension test properties. The effect on the material being different in the two tests seems to indicate that a standard impact test should be laid down by the British Standards Committee as well as the standard tensile test.

The extended use of steel for utility purposes seems to point to the suggestion being an urgent one.

TABLE III.

SUMMARY 1.

Energy of Rupture.

K.G.M. per sq. cm. at notch.

Mark	Guillery	Charpy	Martens' Drop Hammer		Remarks
	10×10	10×10	20×20	30×30	
3198	1·49	1·11	·68	·87	Carbon Steel
2300	2·49	1·22	·87	1·09	,, ,,
1324	2·02	1·85	1·04	·96	,, ,,
*1324	1·68	1·18	·86	·85	,, ,,
3184	2·17	1·49	1·08	1·19	,, ,,
Gun Steel	9·80	10·85	15·09	11·33	
R31	10·71	10·58	11·43	2·45	Carbon Steel
5960	13·11	10·66	4·24	3·51	Vanadium Chrome
R11	8·54	14·24	20·16	17·68	Nickel Chrome
R19	5·91	12·84	20·11	16·10	Nickel Steel

* These figures are a mean of 1324 A1 A7 A14, *i.e.*, neglecting A20 which gave exceptionally high results throughout.

TABLE IV.

SUMMARY 2.

$$\text{Ratio, } \frac{\text{Energy of rupture per sq. cm.}}{\text{Angle of rupture}} = \frac{K}{D}.$$

Mark	Guillery	Charpy	Drop Hammer		Remarks
	10×10	10×10	20×20	30×30	
3198	∞	∞	∞	∞	Carbon Steel
2300	∞	∞	∞	∞	,, ,,
1324	∞	∞	∞	∞	,, ,,
3184	∞	∞	∞	∞	,, ,,
Gun Steel	·592	·639	·851	·734	
R31	·466	·474	·564	·990	Carbon Steel
5960	·509	·525	·756	·781	Vanadium Chrome
R11	·217	·369	·865	·907	Nickel Chrome
R19	·326	·547	·696	·841	Nickel Steel

TABLE V.

SUMMARY 3.

Hardness by the Amsler Cone

Mark	Guillery	Charpy	Drop Hammer		Remarks
	10×10	10×10	20×20	30×30	
3198	172	168	178	200	Carbon Steel
2300	194·5	191	201	201	,, ,,
1324	198	187	196	209·5	,, ,,
3184	173	178	187	195	,, ,,
Gun Steel	289	282	246	231	
R31	125	121	154	153	Carbon Steel
5960	221	220	218	239	Vanadium Chrome
R11	148	146	225	200	Nickel Chrome
R19	226	213	245	206	Nickel Steel

TABLE VI.

SUMMARY 4.

Impact Tension. Martens' Drop Hammer.
Number of Blows required for Rupture.

Mark	18 kg. 2 mts.	18 kg. 3 mts.	36 kg. 2 mts.	Remarks
Gun Steel	13·5	8·5	—	?
R31	11	9·5	5	Carbon Steel
5960	11	5	3	Vanadium Chrome
R11	16	9	3	Nickel Chrome
R19	11	7	3	Nickel Steel

TABLE VII.

Guillery Apparatus.

Test-piece 10 × 10 × 60. Area at notch ·75 sq. cm.

Mark	Energy of rupture		Angle of rupture	$\frac{K}{D}$	Hardness	Remarks
	K.G.M.	$\frac{\text{K.G.M.}}{\text{sq. cm.}}$				
		K.	D°			
3198 B1	·7	·93	0	∞	173	Fracture : Coarse crystalline, traces of fine crystals at compression edge.
3198 B9	1·2	1·59	0	∞	169	
3198 B17	1·5	1·99	0	∞	166	
3198 B24	1·1	1·46	0	∞	181	
2300 B1	1·6	2·13	0	∞	199	
2300 B7	1·9	2·53	0	∞	195	
2300 B14	2·1	2·80	2	1·400	194	
2300 B21	—	—	—	∞	190	
1324 A1	1·2	1·59	0	∞	193	
1324 A7	1·2	1·59	0	∞	199	
1324 A14	1·4	1·86	0	∞	194	
1324 A20	2·3	3·05	0	∞	205	Very rough and jagged fract.
3184 B2	1·6	2·13	0	∞	175	
3184 B9	1·6	2·14	3	·713	178	
3184 B15	2·2	2·93	5	·586	167	
3184 B26	1·1	1·47	0	∞	171	
Gun Steel 2	8·9	11·66	15	·777	289	Minutely fine crystals.
,, ,, 4	9·2	9·11	15	·607	291	
,, ,, 6	6·6	8·64	22	·393	286	
R31 4	8·1	10·8	23	·470	125	Fine crystals, minutely fine at edges.
R31 5	7·9	10·53	23	·458	125	
R31 6	8·1	10·8	23	·470	—	
5960 4	8·1	10·8	20	·540	221	
5960 5	8·2	10·93	20	·546	221	
5960 6	13·2	17·6	40	·442	248	Minutely fine crystalline.
R11 2	6·4	8·54	37	·231	148	Fine crystals, minutely fine at edges.
R11 3	6·3	8·40	37	·227	148	
R11 8	6·5	8·67	45·1	·193	—	
R19 1	4·5	6·00	27·5	·218	221	Minutely fine crystalline.
R19 4	4·4	5·87	13·5	·435	222	
R19 5	4·4	5·87	—	—	236	

TABLE VIII.

Charpy Apparatus.

Test-piece 10 × 10 × 60. Area at notch ·75 sq. cm.

Mark	Energy of rupture		Angle of rupture	$\frac{K}{D}$	Hardness	Remarks
	K.G.M.	$\frac{\text{K.G.M.}}{\text{sq. cm.}}$				
		K	D°			
3198 B1	·85	1·13	0	∞	173	Coarse crystalline fracture, fine crystals at extreme compression edge.
3198 B9	·86	1·14	0	∞	161	
3198 B17	·80	1·06	0	∞	163	
3198 B24	·83	1·10	0	∞	174	
2300 B1	·78	1·04	0	∞	184	
2300 B7	1·03	1·37	0	∞	190	
2300 B14	·96	1·28	0	∞	191	
2300 B21	·90	1·19	0	∞	199	
1324 A1	1·05	1·40	5	·280	197	
1324 A7	·85	1·13	0	∞	182	
1324 A14	·75	1·00	0	∞	190	
1324 A20	2·92	3·88	8	·485	180	1324 A20 Finer crystals.
3184 B2	1·25	1·66	0	∞	178	
3184 B9	1·23	1·63	2	·815	175	
3184 B15	1·05	1·40	1	1·40	194	
3184 B26	·96	1·28	3	·427	165	
Gun Steel 1	8.38	10·94	18	·607	284	Minutely fine cryst. Silky at edges.
,, ,, 3	8·25	10·80	16	·674	284	
,, ,, 5	8·17	10·82	17	·637	277	
R31 1	8·12	10·83	23	·473	120	Fine cryst., minutely fine at edges.
R31 2	7·84	10·45	22	·475	120	
R31 3	7·84	10·45	22	·475	123	
5960 1	8·12	10·83	21	·517	220	Fine cryst., minutely fine at edges.
5960 2	8·02	10·69	20	·535	218	
5960 3	7·84	10·45	20	·523	222	
R11 7	10·57	14·10	38·6	·365	151	Fine crystal, minutely fine at edges.
R11 10	11·00	14·67	37·5	·391	142	
R11 11	10·45	13·95	37·7	·352	145	
R19 6	12·17	16·24	27·0	·610	206	Minutely fine crystalline.
R19 9	9·06	12·08	27·5	·441	214	
R19 12	7·68	10·21	17·3	·590	218	

TABLE IX.—*Martens' Drop Hammer.*

Weight of tup 36 kg. Height of fall 3 mts.
Test-piece 20 × 20 × 160. Area at notch 3 sq. cms. approx.

Mark	Energy of rupture		Angle of rupture	K/D	Hardness	Remarks
	K.G.M.	K.G.M./sq. cm.				
		K	D°			
Gun Steel 7	47·02	15·58	18	·866	248	Fine crystalline, minutely fine at the edges.
,, ,, 8	44·47	14·82	17	·872	244	
,, ,, 9	46·02	15·31	19	·805	259	
,, ,, 10	44·43	14·64	17	·861	232	
R31 1	37·68	12·56	19	·661	151	Fine crystalline.
R31 2	—	—	20	—	151	
R31 3	28·56	9·52	20	·476	152	
R31 4	36·60	12·20	22	·555	157	
5960 1	13·80	4·60	7	·657	217	
5960 2	17·28	5·76	7	·823	218	
5960 3	7·08	2·36	3	·787	220	
R11 1	63·12	21·04	24	·877	231	Minutely fine crystalline with deep cracks. R19 "Horn type" fracture.
R11 3	63·72	21·24	25	·850	227	
R11 4	54·60	18·20	21	·867	216	
R19 1	60·84	20·28	28	·724	240	
R19 2	62·52	20·84	38	·548	261	
R19 3	57·60	19·20	23	·817	230	

TABLE X.—*Martens' Drop Hammer.*

Weight of tup 36 kg. Height of fall 3 mts.
Test-piece 30×30×160. Area at notch 4.5 sq. cms. approx.

Mark	Energy of rupture		Angle of rupture	K/D	Hardness	Remarks
	K.G.M.	K.G.M./sq. cm.				
		K	D°			
Gun Steel 11	46·59	10·34	16	·646	230	Fine crystalline, minutely fine at edges.
,, ,, 12	52·74	11·61	17	·683	230	
,, ,, 13	59·64	13·16	15	·877	240	
,, ,, 14	46·05	10·19	14	·728	224	
R31 5	13·68	3·04	3	1·013	170	Fine crystalline.
R31 6	—	—	2·5	—	152	
R31 7	9·18	2·04	2·5	·816	142	
R31 8	10·26	2·28	2	1·14	149	
5960 5	24·84	5·52	5	1·104	243	
5960 6	9·72	2·16	9·5	·227	240	
5960 7	15·30	3·40	3	1·133	235	
5960 8	13·32	2·96	4·5	·658	237	
R11 1	79·56	17·68	20	·884	201	Minutely fine crystalline with deep cracks. R 19·1 Fine crystalline with minutely fine crystals at edge.
R11 2	85·14	18·92	22	·860	194	
R11 3	76·86	17·08	18	·949	197	
R11 4	75·78	16·84	18	·936	210	
R19 1	53·64	11·92	17	·701	158	
R19 2	77·76	17·28	16	1·080	207	
R19 3	78·30	17·40	20	·870	207	
R19 4	80·10	17·80	25	·712	205	

TABLE XI.—*Martens' Drop Hammer.*

Weight of tup 12 kg. Height of fall 3 mts.
Test piece 20 × 20 × 160. Area at notch ·3 sq. cms. approx.

Mark	Energy of rupture		Angle of rupture	$\frac{K}{D}$	Hardness	Remarks
	K.G.M.	K.C.M. / sq. cm.				
		K	D°			
3198 B1	2·36	·79	0	∞	169	Tup 36 kg.
3198 B9	1·15	·39	0	∞	180	
3198 B17	1·90	·63	0	∞	180	Fracture : Coarse crystalline. 3184/B26 finer than others.
3198 B24	2·66	·89	0	∞	183	
2300 B1	2·29	·76	0	∞	202	
2300 B7	3·73	1·25	0	∞	194	
2300 B14	1·88	·63	0	∞	201	
2300 B21	2·53	·84	0	∞	208	
1324 A1	2·33	·78	0	∞	194	
1324 A7	3·17	1·06	0	∞	194	
1324 A14	2·22	·74	0	∞	194	
1324 A20	4·75	1·56	0	∞	202	
3184 B2	3·13	1·08	0	∞	187	
3184 B9	4·52	1·53	2	·765	193	
3184 B15	2·54	·86	0	∞	182	
3184 B26	2·53	·84	0	∞	187	

TABLE XII.—*Martens' Drop Hammer.*

Weight of tup 12 kg. Height of fall 3 mts.
Test-piece 30 × 30 × 160. Area at notch 4·5 sq. cms. approx.

Mark	Energy of rupture		Angle of rupture	$\frac{K}{D}$	Hardness	Remarks
	K.G.M.	K.G.M. / sq. cm.				
		K	D°			
3198 B1	—	—	0	∞	180	Fracture : Coarse crystalline.
3198 B9	3·85	·85	0	∞	203	
3198 B17	3·91	·87	0	∞	206	
3198 B24	3·98	·88	0	∞	210	
2300 B1	4·85	1·08	0	∞	201	
2300 B7	3·80	·85	0	∞	198	
2300 B14	5·05	1·12	0	∞	198	
2300 B21	5·84	1·29	0	∞	207	
1324 A1	3·82	·85	0	∞	201	
1324 A7	3·83	·84	0	∞	215	
1324 A14	3·82	·85	0	∞	213	
1324 A20	6·04	1·31	0	∞	209	
3184 B2	6·37	1·41	0	∞	198	
3184 B9	5·18	1·15	0	∞	196	
3184 B15	4·38	·97	0	∞	198	
3184 B26	5·54	1·23	2	·615	187	

TABLE XIII.—*Comparison of*

STATIC. Impact by

Mark	Ultimate Strength $\frac{\text{Tons}}{\text{in.}^2}$	Elongation			Contraction of Area	Fracture	Energy of rupture $\frac{\text{K.G.M.}}{\text{cb. cm.}}$
		General	Local	Total on 2″			
		%	Inch	%	%		
Gun Steel 1	51·06	7·5	·21	18·0	62·6	Minutely fine crystals, cup-shaped.	12·86
,, ,, 2	48·88	8·0	·28	22·0	60·0	—	15·05
,, ,, 3	—	—	—	—	—	—	—
,, ,, 4	—	—	—	—	—	—	—
R11 1 .	50·83	4	·21	14·5	62·64	Minutely fine crystals, silky at edges, cup-shaped.	10·33
2 .	—	—	—	—	—	—	—
3 .	—	—	—	—	—	—	—
R19 1 .	50·55	5·5	·25	18	61·30	Ditto	12·74
2 .	—	—	—	—	—	—	—
3 .	—	—	—	—	—	—	—
R31 1 .	33·97	—	—	—	59·40	Ditto	—
3 .	33·44	—	—	—	59·40	Ditto	—
5960 2 .	52·0	—	—	—	59·40	Ditto	—

TABLE XIV.—*Comparison of*

STATIC. Impact by

Mark	Ultimate Strength $\frac{\text{Tons}}{\text{in.}^2}$	Elongation			Contraction of Area	Fracture	Work of rupture $\frac{\text{K.G.M.}}{\text{cb. cm.}}$
		General	Local	Total on 2″			
		%	Inch	%	%		
3184 B2	43·97	15	·15	22·5	31	20% cryst. 80% V.F.C.	13·85
3184 B9	43·43	18	·09	22·5	31	V.F. cryst.	13·65
3184 B15	42·89	15	·15	22·5	31	,,	13·50
3184 B26	42·36	16	·18	25	36	,,	14·82
3198 B1	43·26	12	·24	24	36	,,	14·51
3198 B9	43·80	15	·17	23·5	36	,,	14·40
3198 B17	43·71	14	·17	22·5	39	,,	13·80
3198 B24	42·82	13	·18	22	36	,,	13·19
2300 B1	45·57	13	·17	21·5	34	5% cryst. 95% V.F.C.	13·70
2300 B7	44·24	13	·12	19	28	70% cryst. 30 V.F.C.	11·75
2300 B14	46·47	12	·13	18·5	28	20% cryst. 80% V.F.C.	11·76
2300 B21	46·65	15	·11	20·5	31	10% cryst. 90% V.F.C.	13·37
1324 A1	46·29	13	·09	17·5	24	50% cryst. 50% V.F.C.	11·32
1324 A7	46·30	14	·08	18	22	70% cryst. 30% V.F.C.	11·69
1324 A14	44·58	15	·10	20	28	50% cryst. 50% V.F.C.	12·48
1324 A20	45·48	14	·09	18·5	24	70% cryst. 30% V.F.C.	11·75

Static and Impact Tension.

Charpy Apparatus IMPACT.

Energy of rupture		Elongation			Contraction of Area	Fracture
K.G.M.	K.G.M./cb. cm.	General	Local	Total on 2″		
		%	Inch	%	%	
28·73	14·36	11	·13	17·5	58·5	Minutely fine crystalline. Silky at edges.
24·12	12·06	9	·14	16	58	Cup-shaped.
27·30	13·65	13	·12	19	59	Ditto
31·31	15·65	14	·14	21	62·5	Ditto
27·86	13·93	3	·18	15	58·1	Ditto
32·43	16·21	—	—	—	—	Ditto
26·16	13·08	5	·11	15·5	59·1	Ditto
26·76	13·38	9	·18	18	57·7	Ditto
28·72	14·36	10	·15	17·5	58·4	Ditto
30·78	15·39	13	·12	19	58·4	Ditto
—	—	—	—	—	—	—
—	—	—	—	—	—	—
—	—	—	—	—	—	—

Static and Impact Tension.

Charpy Apparatus. IMPACT.

Energy of rupture		Elongation			Contraction of Area	Fracture
K.G.M.	K.G.M./cb. cm.	General	Local	Total on 2″		
		%	Inch	%	%	
35·73	17·86	17	·11	22·5	38	V.F.C. traces cryst.
43·02	21·51	19	·12	25	41·5	Very fine cryst.
45·98	22·99	23	·12	29	42	,, ,,
42·94	21·47	23	·12	29	48·5	,, ,,
28·12	14·06	15	·05	17·5	41	,, ,,
45·06	22·53	23	·12	29	43·5	,, ,,
35·83	17·91	16	·14	23	41·5	,, ,,
39·85	19·92	20	·10	25	41·5	,, ,,
32·0	16·0	15	·09	19·5	33	V.F.C. traces cryst.
37·11	18·55	16	·13	22·5	37	,, ,,
39·18	19·59	15	·13	21·5	41	Very fine cryst.
30·0	15·0	14	·09	18·5	40·5	,, ,,
39·15	19·57	18	·12	24	42	,, ,,
38·21	19·10	20	·10	25	40·5	,, ,,
32·92	16·46	14	·14	21	38	,, ,,
43·49	21·74	22	·08	26	44	,, ,,

TABLE XV.—*Impact Tension.*

Martens' Drop Hammer.

Test-piece 10 mm. dia. Area 78·54 sq. mm.
Weight of tup 36 kg. Height of fall 2 mts.

No. of Blow.	Elongation in cm.			
	R31 6	5960 5	R11 1	R 19 1
	on 4·25″		on 2·5″	
1	1·2	·60	·38	·36
2	·8	6	·33	33
3	1·0	broke at change of section	broke	broke
4 (necked)	·9	—	—	—
5	broke	—	—	—
	on 4·25″		on 100 mm.	
Total elongation	3·9	1·2 cm.	1·17	1·70 cm.
Per cent. elongation	32%	10%	11·7	17%
Local elongation	—	—	·66	·68 cm.
General elongation	—	—	5%	10%
Contraction of area	60%	60%	60%	60%

TABLE XVI.—*Impact Tension.*

Martens' Drop Hammer.

Test-piece 10 mm. dia. Area 78·54 sq. mm.
Weight of tup 18 kg. Height of fall 3 mts.

No. of Blow	Elongation in cm.						
	R11 3	R19 3	R31 2	R31 5	5960 3	Gun Steel 7	Gun Steel 8
	on 2″		on 4·25″		on 100 mm.		
1	·19	·15	·20	·40	·20	·28	·23 cm.
2	·13	·13	·80	·50	·60	·18	·20
3	·14	·13	·40	·50	·20	·23	·18
4	·18	·10	·50	·40	·30	·20	·18
5	·13	·08	·40	·50	broke	·20	·18
6	·15	·05	·30	·20	—	·20	·18
7	·18	broke	·40	·40	—	·23	·30
8	·30	—	·40	·40	—	·25	broke
9	broke	—	·50	broke	—	broke	—
10	—	—	broke	—	—	—	—
	on 100 mm.		on 4·25″		on 100 mm.		
Total elong.	2·13	1·65 cm.	3·9	3·3	1·3 cm.	1·875	1·45 cm.
% elong.	21·3%	16·5%	36·0%	31·0%	12·0%	18·75%	14·5%
Local elong.		·68 cm.	—	—	—	·73	·56 cm.
General ,,	13·0%	9·5%	—	—	—	11·5%	9·0%
Contr. of area	66·0%	60·0%	58·0%	57·0%	60·0%	59·8%	63·1%

Table XVII.—*Impact Tension.*

Martens' Drop Hammer.

Test-piece 10 mm. dia. Area 78·54 sq. mm.
Weight of tup 18 kg. Height of fall 2 mts.

No. of Blow	Elongation in cm.					
	R11 2	R19 2	R31 4	5960 4	Gun Steel 5	Gun Steel 6
	on 2″		on 4·25″		on 100 mm.	
1	·13	·13	·30	·20	·18	·18
2	·08	·06	·40	·20	·15	·13
3	·08	·11	·30	·20	·13	·10
4	·06	·02	·30	·10	·13	·10
5	·10	·10	·40	·20	·13	·10
6	·06	·08	·30	·10	·13	·10
7	·06	.09	·20	·10	·13	·10
8	·06	·11	·20	·20	·13	·10
9	·10	·12	·30	·20	·13	·10
10	·05	·15	·30	·10	·13	·10
11	·10	broke	broke	broke	·18	·10
12	·10	—	—	—	broke	·10
13	·10	—	—	—	—	·13
14	·14	—	—	—	—	·18
15	·18	—	—	—	—	broke
16	broke	—	—	—	—	—
	on 100 mm.		on 4·25″		on 100 mm.	
Total elong.	2·15	1·50 cm.	3·00	1·16 cm.	1·55	1·625 cm.
% elong.	21·5%	15·0%	27·3%	10·6%	15·5%	16·25%
Local elong.	·53	·61 cm.	—	—	·76	·58 cm.
General elong.	16%	9%	—	—	8%	10·5%
Contr. of area	63%	63%	60%	60%	58·5%	60·0%

Test on Munition and Alloy Steels in Static Tension.

Test Number	Young's Modulus	Original Dimensions		Stress in lbs.		Stress in tons per sq. in.	Limit of Elasticity from Martens' mirrors	Ratio of Limit to Break
		Diam.	Area	Total	Per sq. in.			
		Inch	sq. in.					
1324 A 20	29·12 × 10^6 lbs. per sq. in.	·3949	·1224	12,840	104,900	46·84	18·3	·39
2300 B 7	29·32 × 10^6 lbs. per sq. in.	·3938	·1218	12,030	98,700	44·06	16·5	·37
3198 B 24	29·04 × 10^6 lbs. per sq. in.	·3935	·1216	11,800	97,000	43·30	14·7	·34
3184 B 26	28·85 × 10^6 lbs. per sq. in.	·3935	·1216	11,340	93,300	41·70	14·7	·35
Gun Steel 9	28·80 × 10^6 lbs. per sq. in.	·3932	·1214	13,880	114,400	51·06	31·65 (from diagram)	·62
Gun steel 10	Martens' mirrors not used	·3940	·1219	13,340	109,500	48·88	38·1	·78

Tests on Alloy Steels in Tension.

Test Number	Young's Modulus	Original Dimensions		Stress in lbs.		Stress in tons per sq. in.	Apparent Limit of Elasticity from Auto-diagrams	Ratio of Limit to Break
		Diam.	Area	Total	Per sq. in.			
		Inch	sq. in.					
R11 1	—	·386	·1170	14,110	120,590	53·83	50·2	·93
R11 2	28·22 × 10^6 lbs. per sq. in.	·3937	·1217	14,160	116,320	51·93	—	—
R19 1	—	·3937	·1217	13,780	113,230	50·55	42·6	·84
R19 2	28·22 × 10^6 lbs. per sq. in.	·3937	·1217	13,640	112,100	50·04	—	—
R31 1	29·50 × 10^6 lbs. per sq. in.	·3937	·1217	8,900	73,150	32·70	22·2	·68
R31 3	29·30 × 10^6 lbs. per sq. in.	·3937	·1217	8,760	72,000	32·20	21·1	·66
5960 2	29.00 × 10^6 lbs. per sq. in.	·3937	·1217	13,650	112,300	50·15	39·0	·79

For Impact Report.

Contracted Dimensions		Contraction of Area per cent.	Elongations measured after fracture		Local Elongation	General Elongation per cent.	Total Elongation per cent. on 4 ins.	Yield Point by Mirrors	Remarks
Diam.	Area		on 4 ins.	on 2 ins.					Fracture
Inch	sq. in.		Inch	Inch	Inch				
·35	·096	21·3	·62	·37	·12	12·5	15·5	19·2	85% crystalline. 15% very fine cryst.
·34	·091	24·8	·60	·37	·14	11·5	15·0	16·5	50% crystalline. 50% very fine cryst.
·33	·086	29·3	·68	·44	·20	12·0	17·0	16·5	20% crystalline. 80% very fine cryst.
·32	·080	34·2	·73	·46	·19	13·5	18·25	18·4	Very fine crystalline.
·24	·045	62·6	·51	·36	·21	7·5	12·75	38·20	Minutely fine cryst., cup-shaped.
·25	·049	60·0	·60	·44	·28	8·0	15·0	—	,, ,,

For Impact Report.

Contracted Dimensions		Contraction of Area per cent.	Elongations measured after fracture		Local Elongation	General Elongation per cent.	Total Elongation per cent. on 4 ins.	Remarks
Diam.	Area		on 4 ins.	on 2 ins.				Type of Steel
Inch	sq. in.		Inch	Inch	Inch			
·236	·0437	62·6	·37	·29	·21	4·0	9·25	Ni. cr. steel.
—	—	—	—	—	—	—	—	,, ,,
·245	·0471	61·30	·47	·36	·25	5·5	11·75	Ni. steel.
—	—	—	—	—	—	—	—	,,
·246	·0475	59·40	—	—	—	—	—	C. steel.
·246	·0475	59·4	—	—	—	—	—	,,
·246	·0475	59·4	—	—	—	—	—	V. cr. steel.

Archæological Investigations in Malta.—Report of the Committee, consisting of Professor J. L. MYRES (*Chairman*), Dr. T. ASHBY (*Secretary*), Mr. H. BALFOUR, Dr. A. C. HADDON, *and* Dr. R. R. MARETT.

Excavations in the Ghar Dalam Cave, Malta, in July and August 1917.

The excavations of the present year were conducted once more under the supervision of Mr. G. Despott, Curator of the Natural History Museum at the University of Malta.

Two trenches were dug, one at 50 feet, the other at 110 feet from the mouth of the cave; each of them was about 26 feet long, 4 to 5 feet wide, and 12 feet deep—the latter being a depth not hitherto reached. A large amount of material, some 70 boxes (five cartloads) in all, has to be gone through systematically; the results cannot therefore be immediately available.

Mr. Despott calls particular attention to the discovery of some very fine pottery, several implements, a fairly good quantity of human remains (no doubt in the upper strata), and the remains of three species of elephants—*Elephas mnaidrensis*, *Elephas melitensis*, and *Elephas falconeri* (the last two being found in much lower strata than the first). The results are described as most satisfactory, and a great deal more important than those of last year.

Exploration of the Palæolithic Site known as La Cotte de St. Brelade, Jersey.—Report of the Committee, consisting of Dr. R. R. MARETT (*Chairman*), Mr. G. F. B. DE GRUCHY (*Secretary*), Dr. C. ANDREWS, Professor A. KEITH, Mr. H. BALFOUR, *and* Colonel R. GARDNER WARTON.

THANKS to a generous grant by the Société Jersiaise, in augmentation of the sum available from the funds of the British Association, work will be carried on during the summer as circumstances permit. Several workers have promised to come over from Oxford if allowed to travel. Labour will probably be available as soon as the potato crop has been gathered.

Excavation is possible in three directions:—(1) The rearward portion of the cave-filling needs to be removed, so as to open up the narrow outlet to the north at floor level. The amount of rock-rubbish to be attacked is not great, but some very large and awkwardly placed blocks will have to be broken up. (2) As soon as the floor has been completely cleared of the dump in process of demolition, a shaft can be sunk near the entrance, so as to explore the lower depths in which organic remains are known to occur. (3) A continuation of the rodent bed has recently been discovered in the opposite corner of the ravine near the spot where Mousterian implements have been found. Unfortunately the talus is very loose and dangerous here, but means may be found to cope with the difficulties.

The 'Free-Place' System.—Report of the Committee, consisting of Mr. C. A. BUCKMASTER *(Chairman)*, Mr. DOUGLAS BERRIDGE *(Secretary)*, Mr. C. H. BOTHAMLEY, Dr. LILIAN J. CLARKE, Professor BARBARA FOXLEY, Dr. W. GARNETT, Sir R. A. GREGORY, Professor H. BOMPAS SMITH, Dr. H. LLOYD SNAPE, *and* Miss C. M. WATERS, *appointed to inquire into and report upon the Effects of the 'Free-Place' System upon Secondary Education.*

I. INTRODUCTION.

THE Free-place system is a name given to an arrangement by which, in return for certain State grants administered by the Board of Education, secondary schools, working in connection with the Board, offer a certain number of places in the school, free of all tuition fees, to pupils who have had at least two years' previous education in public elementary schools.

At the present time a school complying with the Board's regulations as to the provision of free places receives approximately 2*l*. 10*s*. more for each scholar over 11 years of age than a non-complying school. This latter class of school represents a surviving 'vested interest,' and no additions are made to grants on behalf of those already in it.

The Board retain power to modify, waive, and interpret their regulations dealing with these schools and free places and do so with a fair amount of freedom.

Thus certain secondary schools, in receipt of grants from the Board, are not required to provide the full 25 per cent. of free places, and some schools which before the introduction of the system were in receipt of grants are entirely exempted from this condition, receiving less grant in consequence.

The ostensible object of this grant was to offer facilities for secondary education to boys and girls whose parents could not afford to pay secondary school fees. It was to assist the poor to secure higher education for their children. But the determination of the question as to who should and who should not be thus helped on the ground of poverty was obviously beset with the most serious difficulties, and the Gordian knot was cut by assuming that all parents who sent their children to the public elementary schools of the country might legitimately be considered to be in need of assistance in meeting the expense of secondary education for their children. A precedent for this conclusion already existed; for many years previously the Science and Art Department, with the sanction of the Treasury, had extended to all children attending elementary schools the classification of 'industrial,' and had interpreted 'industrial' as equivalent to an income not exceeding 150*l*. a year. The two tests are not, however, identical.

Just as in practice the requirement of the State that all children must be educated means that only persons living in houses below a certain rateable value are ever called upon by the educational authority to send their children to an efficient school, so the mere fact of attending a public elementary school is in its turn taken as evidence of straitened means. As a compromise it is perhaps satisfactory: as a real solution of the difficulty it seems illogical and haphazard.

The condition that a certain proportion of free places was to be reserved for pupils from public elementary schools came into force in 1907 when Mr. Reginald McKenna was President of the Board of Education. In the estimates for that year an additional sum of 75,000*l.* was taken for secondary schools and an additional 120,000*l.* in the following year. Mr. McKenna, in explaining these estimates to the House of Commons, said: 'These free places must not be confused with scholarships. They would be for public elementary school children who would not be asked to compete with children outside. They would only be asked to pass a qualifying examination. The general rule would be that any school receiving the additional grant (provided for in these estimates) should offer at least 25 per cent. of its places for public elementary school children who should enter free. There were cases where, however, 25 per cent. of the places would not be used in any case in this way, and in these cases it is proposed to give the Board of Education power to waive the requirement. . . . . The increase in grant was in the ratio of 3 to 5. . . . The policy of the Board was to democratise the secondary schools by raising the general level of education and securing for the humblest in the land the opportunity of education for their children in really good schools.'

Objection was raised during the debate that even 25 per cent. of free places was not enough and that all restriction on the number of such places should be removed. To this objection Mr. McKenna replied that 'while a school might be with or without fees, whatever the scale of fees was it must be approved by the Board of Education. The schools might have as many more free places (than 25 per cent.) as they liked, and he personally trusted that where the school was provided by the local education authority the places would all be free.' (*Times* Report.)

He further pointed out that his proposals would divide secondary schools into two groups, viz.: those that elected to go on as before with the previous scale of grants and those that decided to comply with the 25 per cent. rule and receive grants on the new and higher scale.

In the course of this debate Mr. McKenna also stated that at that time there were 600 secondary schools recognised by the Board of Education, and that these schools had a total of 104,938 scholars of whom over 56,000 came from public elementary schools, and of these 29,000 paid no fees at all.

In the previous year a departmental committee of the Board of Education had reported on the question of admission to secondary schools of children unable to pay the full school fee, and this report, which has not been made public, may be assumed as the basis on which Mr. McKenna's system was built.

In the report of the Board of Education for the year 1906-7 reference is made to the free-place question as follows:—'The opportunity which an increase of grant has offered has been used to secure that all secondary schools aided by grants shall be accessible to all scholars who are qualified to profit by the instruction given therein. The fees charged . . . have in many cases constituted a barrier to the admission of children of working men who are desirous to obtain and able to profit by secondary education. . . . It is not unreasonable to require that, in return for additional financial aid, the authorities responsible for the schools should admit free a certain number of children from public elementary schools. It is accordingly laid down that in all schools where a fee is charged a proportion of places, which will ordinarily be not less than one quarter, shall be open without payment of fee to scholars from public elementary schools applying for admission provided that the applicants are able to show by a qualifying examination their fitness to profit by the education given in the school.' (*Times* Summary, December 31, 1907.)

It is of interest to note that in the Training College regulations for the same year emphasis is laid on the condition that students may only be excluded on 'reasonable grounds,' and that exclusion on the grounds of religion or of social status is not 'reasonable,' thus corresponding to the policy of the Board in regard to admission to secondary schools in relation to social position.

It would appear that in actual practice a school can comply with this 25 per cent. rule if one quarter of its scholars come from public elementary schools and are not paying fees either as holders of school scholarships, county scholarships, local or other scholarships, or for other reasons. As such scholarships are generally awarded by a more or less rigid competitive examination, it is theoretically possible that a school might still comply with the 25 per cent. free-place rule and yet not have offered any free places not attached to specific scholarships. This is, however, not a very likely result, and the general position is fairly summed up in the words of a recent report to the Kent Education Committee while referring to the free-place system:—

> 'No special preparation is necessary for free-place scholars at secondary schools. The school record and the oral test are of decisive importance and any written examination is only preliminary. The object of the examination is to select, not so much the children who are superior to their fellows in present attainment, as those who give evidence of superior aptitude and intelligence, and in making the award adequate attention is given to character and physical health.'

This may, we think, be taken as an admirable exposition of the award of free places at its best.

The free-place system is in fact a compromise, and grew out of a struggle, none the less real because veiled, between the more radical local authorities of the North of England and the Board of Education as successor to the defunct Science and Art Department.

Under the latter body School Boards had established science schools supported partly by grants for science, art, and manual instruction, and attended by children of both sexes who had passed through the ordinary elementary school curriculum and wanted some further education. When, as a condition of the grants, these schools were urged to provide efficient literary instruction in English and at least one modern language they became secondary schools in all but name, and flourished for a time exceedingly. But the decision in the Brighton case, followed by the famous Cockerton judgment, that a School Board could not legally spend the rates on schools of this type, which were, as a rule, without fee or with fees not exceeding a shilling a week, led ultimately to the abolition of the School Board system and the creation of the local education authorities, with definite powers for secondary education, in its place. Several of these new local authorities followed the policy of their School Board predecessors and kept the fees of the reconstructed organised science schools at an almost nominal sum since the Board of Education's regulations required a fee of some amount to be charged.

The Board strove for some years to raise the school fee—not, it must be admitted, from a desire to exclude the poorer children from the schools, but from a wish to increase the school's resources, to emphasise the importance of secondary education, and to squeeze out all children who were not determined to take their secondary school training seriously and stay at school sufficiently long to profit by the school instruction. The opposition, represented by certain local authorities, concentrated its efforts in making secondary education as accessible as possible to any child that desired it, and as a result of these contrary forces in truly English fashion the free-place expedient was devised. Like many other illogical devices it has shown during its ten years' existence that it is workable and that it possesses a remarkable amount of vitality. Whether in the immediate future it will be superseded by some more comprehensive system it is impossible to foresee.

II. Summary of Information derived from the Heads of Schools.

Copies of a questionnaire were sent to the 910 schools which receive grants from the Board of Education; 384 replies (42 per cent.) have been received.

A very large number of schools say they are quite satisfied with the present working of the system; others, whilst not objecting to the principle of the system, point out difficulties they have found in its working, or make suggestions for improving it. In this analysis more attention is naturally given to suggested alterations than to expressions of perfect agreement; but it must be remembered that as far as the evidence goes the system is working very well in the large majority of those schools whose pupils are drawn from the elementary schools to the extent of more than 50 per cent., including free-place holders.

Mode of Admission.

In the majority of cases this is by means of a written competitive examination, but a considerable number of schools add an oral test which is often conducted by the head of the secondary school and sometimes in presence of a representative of the elementary schools and (or) an education officer. When this oral test is made, the object is generally to determine the general intelligence of the child as contrasted with its mere knowledge (see under 'Ability'), but sometimes it is used as a means of finding out whether the parent on the one hand can afford the necessary books, &c. (see under 'Finance'), or, on the other, if he requires the financial help of a free place, and also whether the parent will keep the child at school for a sufficient time to enable it to benefit by beginning a secondary education. In a few cases the parent is obliged to sign an undertaking to keep the pupil at school until he or she has reached the age of 16. (See under 'Finance.')

In cases where the admission is by means of a competitive examination, the actual competition is of the most varied kind; in large schools of high reputation situated in important towns, there are often ten candidates for each vacant place; in the country schools, however, complaint is frequently made that 'there is no real competition'; 'less than half marks qualify'; 'almost anyone can gain a free place.' In considering the replies as to the ability of the pupils it is necessary to bear these facts in mind.

Proportion reaching Matriculation.

A very large number of schools have made returns purporting to be the percentage of free-placers who reach matriculation standard; since, however, these returns are very difficult to understand they are not included in the present analysis—*e.g.*, a large school in the Midlands, which is represented on the Headmasters' Conference and has obtained a large number of University scholarships, states that 13 per cent. of the free-placers reach matriculation standard, whilst a small mixed school in the North of England gives the percentage as 80; this is only one of the many examples, and it would seem that either educational results vary inversely as the standing of the school, or that different headmasters have different ideas as to what is meant by 'matriculation standard.' It is probable that the explanation is to be found in the following, which is typical of a large number received:—'A satisfactory proportion reach the standard of the Junior Oxford and Cambridge Local Examinations; a few reach matriculation standard, but the majority leave at too early an age to do so.'

Speaking generally, it seems that those free-placers who are capable of benefiting by a secondary education at all, reach the average standard of the school; whilst in schools where the large majority of the pupils have been in elementary schools the standard reached by free-place holders may be higher than that reached by others.

Physique.

Only two schools report that the physique of the boys is insufficient to stand the strain of a secondary education; in the case of girls, however, it is sometimes mentioned that home duties after school hours, or long journeys home (either by train or bicycle), impose a strain which prevents them from obtaining the full advantage of a secondary school life.

Games and Corporate Life.

In schools with a large proportion of ex-elementary pupils there is, of course, no difficulty; some of the other schools report that the free-placers keep themselves too much to themselves—it is never mentioned that the fee-paying pupils keep themselves apart from the others, but this possibility must not be lost sight of. Speaking generally, free-placers seem to join in the games and corporate life of the school as far as their journey home and financial considerations allow.—(See under 'Finance.')

Ability.

Opinions as to the ability of free-placers vary much; in schools where the percentage of ex-elementary pupils is high they are generally said to be above the average. In schools with a smaller percentage of ex-elementary pupils the opinion is less complimentary, and the following complaints have been received:—

(1) The average ability is satisfactory, but they reach the limit of their capacity for advanced work sooner than do the others.

(2) A considerable number are quite unfit to benefit from a secondary education.

(3) The competitive examination that is held fails to discover the best candidates; this is partly due to the essential difference between the curricula of the elementary and secondary schools; the mere fact that the children can write neatly and sum correctly is no proof that they can benefit from the study of languages and mathematics.

Industry.

A very few complaints have been received under this head; and those few will be considered under the paragraph 'Tenure and Finance.'

Character.

A number of complaints have been received respecting the moral attitude of free-place holders, especially in regard to their ideas of school honour. Some schools report a considerable improvement in this respect during their secondary education. Other and less frequent complaints are:—

(1) Lack of *esprit de corps*;
(2) Want of ambition;
(3) Want of personal cleanliness.
(4) Bad manners;
(5) Lack of modesty (from a girls' school).

It is probable, however, that hardly any of these complaints can be urged against the free-place holders *per se*.

Curriculum.

The incorporation of free-place holders with the class organisation of schools is often attended with difficulty, especially in schools where the percentage of ex-elementary pupils is small; the difficulty mentioned is that the children have not begun Latin, French, science, or mathematics; it is also added by a few schools that the high standard obtained by the free-placers in arithmetic causes trouble.

Although many schools mention the difficulty, it does not seem to be acute if the free-placer enters at or under the age of 12; for in this case an extra lesson in the afternoon during one term, or an arrangement for teaching the lower forms in sets, enables the more able pupils to catch up the others. In the case of those who enter above the age of 13 it is, however, frequently mentioned that the whole curriculum of the school is upset, the fee-payers are retarded in their progress and the free pupils fail to benefit from their lessons; it is generally agreed that no free place should be given to such children, and, since no school is required by the Board of Education to admit free-placers over 13 years of age, the difficulty, such as it is, must be considered to be created by the schools or the authorities themselves.

Dinners.

Although one large school wrote asking how it was possible for there to be any difficulty in the matter of school dinners, a very considerable number state that they are a constant problem. The schools situated in large towns and drawing their pupils from their own immediate district seldom make provision for dinner, but in those attended by pupils from a distance it is very common for a meal to be provided at a cost of from 4*d*. to 9*d*. per day; the usual charge is 6*d*., but one school states that they provide a non-meat meal at 3*d*.; in very many cases the free-placers cannot afford even this, and the resulting problem is met in various ways. The London County Council, the Kent Educational Authorities, and possibly some others seem to make special maintenance grants to cover the cost. In some cases where pupils, whether free-placers or others, bring sandwiches a separate room or a separate table is provided; one girls' school mentions that every effort is made to make this table as attractive as possible by placing flowers, &c., upon it. At one large school for boys some of the free-placers earn their dinners by waiting upon the others first and taking their own when the ordinary meal is over. In many cases, however, the matter seems to be left to private charity, often that of the head of the school or Governors.

Amongst the schools which find a difficulty in the matter of dinners, there is a general agreement that the children require a good meal in the middle of the day.

Social Status.

Several schools state that since they received free-placers the 'better-class' parents have withdrawn their children and it has been necessary to reduce the boarding fees; a few state that this may be 'snobbishness,' but it is a fact they must take into consideration. It seems, however, certain that this class exclusiveness is becoming less strongly marked, and need not be considered a serious obstacle to the development of the system.

Tenure of Free-Placers and Financial Considerations.

These two subjects are so frequently reported upon in the same connection that it is convenient to consider them together here. The chief complaints are:—

(1) Free-placers are under no obligation to give notice, they can 'just stay away' at will; a fee-paying parent can be sued for a term's fees if a pupil is withdrawn without notice, but this is not possible in the case of a free-placer, unless a definite undertaking has been given by the parent.

(2) Free-placers are very frequently withdrawn from schools after about two years—*i.e.* before they have been really able to benefit from a secondary education; this is sometimes caused by the parents being unable to keep their children at school longer without a maintenance grant; sometimes because the child is only 'sent to a secondary school in order to obtain testimonials'; and sometimes because the child does not wish 'to be bothered' by having to prepare for examinations.

(3) Some schools report that they only accept free-placers whose parents sign an undertaking to keep them at school until the end of the school year in which they become 16; and cases are on record where damages have been recovered when such an undertaking has been broken.

(4) The very poor can seldom, if ever, allow their children to accept free places without some form of maintenance grant.

(5) In many schools where there is a games subscription some of the free-placers can only pay this if there is a maintenance grant; failing this, they are cut off from much of the corporate life of the school.

(6) It is impossible for children to travel long distances to school and to stand the mental and physical strain of life in the secondary school unless they have a good meal in the middle of the day; many of the free-placers cannot afford this without a maintenance grant, and they consequently fail to derive much benefit from their post-elementary education.

(7) Many free places are given to children whose parents can well afford to pay the fees: it is reported by many schools that most of their fee-paying pupils are those who have tried for but failed to obtain a free place; others report that quite well-to-do people send their children to elementary schools and then pay for extra coaching to enable them to gain free places; while one boarding school was asked to receive as a boarder a child who was in the school as a free-placer.

In connection with this point, one school suggests that it is unfair to prevent those parents who have made an effort to send their children to secondary schools from receiving the benefit of a free place, the more so since such children would as a rule afford better material to build upon.

(8) The rule that no one can be deprived of a free place for an offence which would not cause the expulsion of a fee-payer has the effect of keeping in school pupils who, because of unsatisfactory character or lack of industry or ability, ought not to be educated directly or indirectly at public expense.

The following are the chief alterations suggested by the teachers:

(1) Free places should at first be awarded for one year only, with power of renewal.

(2) Power should be given to the Governors to withdraw free places from those whose reports are frequently bad.

(3) Free places should only be given to those in need of financial assistance.

(4) The money now wasted upon pupils who are unlikely to benefit from a secondary education should be devoted to providing maintenance grants to the more deserving.

(5) When school dinners are provided, the free place should be combined with a maintenance grant, paid direct to the school, to cover the cost of this.

(6) Maintenance grants should, when necessary, be made to keep former holders of free places at one of the Universities.

(7) A grant should in all cases be made to cover all games subscriptions and railway tickets to school matches, &c.

III. SUMMARY OF INFORMATION DERIVED FROM THE OFFICIALS OF COUNTY AND BOROUGH AUTHORITIES FOR HIGHER EDUCATION.

Requests for an expression of opinion on the free-place system were sent out to the 50 Counties and 75 County Boroughs in England that are responsible for the local control of higher education.

Replies were received from 36 Counties and 45 County Boroughs—*i.e.* from 65 per cent. of the whole number. Quite a number did more than answer the five main questions, and supplied full descriptions of their schemes and opinions as to their working. These fuller answers were most helpful in arriving at a fair judgment of the trend of administrative thought.

1. The chief fact that emerges clearly from the returns is that *County Scholarship Schemes and Free Places tend to merge into one system.* It will perhaps be well to put clearly here what is historically the difference between the two classes, for in many areas the difference is purely historic and no longer exists. Before the rule was established that grant-earning schools must normally offer each year free places to the number of 25 per cent. of the total entrants to the school of the previous year, many local education authorities gave scholarships to secondary schools to boys and girls at about the age of 12. These scholarships sometimes carried more than free education, providing travelling expenses, books, and maintenance allowances of varying amounts. They were usually for a period of three or four years, rarely longer, and only a few holders, with the help of intermediate scholarships, stayed the full life of a secondary school up to 18 years of age. The Board's free-place scheme cut across these arrangements. The distribution of free places depended on the situation and numbers of the secondary school, not on the juvenile population of the district, and the period of tenure was 'up to the school-leaving age.' Authorities therefore had two paths to choose from; they could either turn their county scholars into 'free-placers' by extending the period of tenure up to the age of 18, adding or subtracting where necessary to make

up the 25 per cent., or they could keep their scheme for county scholars intact and add another for free-placers to meet the Board's demands. The returns show that, in the area of at least two-thirds of those making returns, whether Counties or County Boroughs, the former scheme has been adopted. Free-place holders and county scholars are indistinguishable. Only in a few instances do the returns show whether this has meant the combination of the advantages of both schemes. The lengthened tenure is obligatory, but it may be balanced by dropping the allowance previously given to county scholars for travelling, &c., the Board's scheme demanding merely freedom from tuition and entrance fees. Some indication of what has happened may be gained from the name retained; where all are called county scholarships the incidental advantages often remain; where all are called free places they carry as a rule nothing but the minimum requirements of the Board. The existence of two schemes side by side is certainly confusing and must add to the trouble of administration.

2. *Travelling expenses* are paid to holders of free places in 26 Counties out of 36; in the County Boroughs they are apparently considered unnecessary.

Maintenance allowances of some kind are paid in 61 per cent. of the areas, but they are very small indeed, usually confined to 'necessitous' cases, and sometimes to those over 14 years of age. County Councils seem slightly more generous than County Boroughs, but this is probably due to the factor of distance, which makes some contribution to the cost of dinner at school imperative. Few allowances rise to a figure beyond that needed to cover this single expense. In areas where there is a double scheme of county scholarships and free places the allowances for travelling and maintenance are frequently confined to the former, who represent the pick of the candidates in the examination. As the capacity to do well in an examination bears some relation to the relative poverty and consequent ill-feeding of the child, this results in the poorer children obtaining the least help; where travelling expenses are not covered the free places are not really open to the country labourer's child.

3. The returns as to *ability* of holders of free places compared with other pupils are rather indefinite. Of those who replied to the question about 40 per cent. of the County Boroughs and about 30 per cent. of the Counties consider the free-place holder above the ordinary fee-paying pupil in ability.

4. Very few of those who sent returns have any belief in *Higher Elementary Schools*, 8 among the Counties and 5 among the County Boroughs alone holding that some of the children might do better there than in secondary schools. There is, however, a considerable body of opinion that *Junior Technical Schools* would be useful in this way. This is especially the case among the Counties.

The chief trouble is the shortness of the school life of the secondary scholar, and this makes some of the officials think that three years in a technical school would be a better investment. Where a full four or five years' course is taken most of the returns are that the results are satisfactory.

5. The tendency of teachers in elementary schools to *keep back their pupils* from competing for scholarships is reported as decreasing and now only occasional. In this matter the teachers in the County Boroughs seem in advance of those in the Counties, but it must be remembered that in country districts the facilities for making use afterwards of a secondary education are much less than in the town, and teachers may well hesitate to urge any but the cleverest to make the necessary sacrifices. These, too, are greater for the country than for the town parent from the nature of the case.

IV. NUMERICAL ANALYSIS OF OPINIONS RECEIVED FROM THE SCHOOLS AFFECTED.

Percentage of the schools not satisfied with the system:—

Schools with more than 40 per cent. of free-place holders	30 per cent.
,, ,, between 20 and 40 per cent. ,, ,,	45 per cent.
,, ,, less than 20 per cent. ,, ,,	54 per cent.
*Schools with more than 40 per cent. of ex-elementary pupils	42 per cent.
,, ,, between 20 and 40 per cent. ,, ,,	66 per cent.
,, ,, less than 20 per cent. ,, ,, ,,	58 per cent.

More are satisfied in large towns where competition is keener and the standard consequently higher.

Masters seem more easily satisfied than mistresses—*e.g.*:

	Satisfied.	Not Satisfied.
Girls	48	60
Boys	66	51
Mixed	40	19

Complaints about character came from 32 per cent. of Girls' and 11 per cent. Boys'.
Complaints about late entry came from 6 per cent. of Girls' and 3 per cent. Boys'.
Complaints about strain came from 4 per cent. of Girls' and 2 per cent. Boys'.

On questions *re* Social Status, Dinner Difficulties, Ability and Curriculum, the complaints are about equally divided between the Boys' and Girls' Schools.

V. THE PERCENTAGE OF FREE-PLACE CHILDREN ACTUALLY IN THE SCHOOLS.

The following numbers are obtained from 'Statistics of Public Education,' 1913 and 1914:—

	Boys.	Girls.
Fee-paying Pupils:		
Ex-public Elementary Schools	33.8	27.2
Other Schools	31.1	35.3
	64.9	62.5
Free Pupils:		
Ex-public Elementary Schools	33.3	35.4
Other Schools	1.8	2.1
	35.1	37.5

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* It must be remembered that the number of ex-elementary pupils in any school is almost always in excess of the number of free-place holders, and that consequently these two sets of results are based upon different data.

The percentage of free pupils admitted during the year is given:—

	Boys.	Girls.
Fee-paying Pupils	70.2	69.1
Free Pupils	29.8	30.9

These numbers point to the duration of school life being greater amongst the free pupils than amongst those who pay fees.

The Age at which Free Pupils are Admitted.

'Statistics of Public Education' give figures from which the following are calculated:—

	Fee Paying.		Free Pupils.	
	Boys.	Girls.	Boys.	Girls.
Under 9 years of age	8.3	8.9	0.0	0.0
9 and under 10	5.9	4.3	.2	.1
10 ,, ,, 11	7.7	6.3	2.2	1.5
11 ,, ,, 12	9.9	8.9	9.4	8.8
12 ,, ,, 13	15.3	14.1	13.0	12.8
13 ,, ,, 14	13.5	13.2	3.9	4.7
Over 14	9.6	12.2	1.1	3.0
	70.2	68.9	29.8	30.9

In order to compare the age at entry of the two classes it is convenient to obtain a percentage of each separate class. This gives:—

	Fee Paying.		Free Pupils.	
	Boys.	Girls.	Boys.	Girls.
Under 9	11.8	13.0	0.0	0.0
9 and under 10	8.4	6.2	.7	.3
10 ,, ,, 11	11.0	9.1	7.3	4.9
11 ,, ,, 12	14.1	13.0	31.5	28.5
12 ,, ,, 13	21.8	20.5	43.6	41.4
13 ,, ,, 14	19.3	19.1	13.0	15.2
Over 14	13.6	19.1	3.9	9.7
	100.0	100.0	100.0	100.0

CONCLUSIONS AND RECOMMENDATIONS.

N.B.—Dr. Snape was prevented by impaired health from attending the meetings of the Committee and preferred, as he had not had the opportunity of participating in the discussions, not to sign this report. Mr. Bothamley is not in agreement with the terms of Recommendation 8, which is therefore put forward in the name of the remaining members of the Committee.

1. The replies received to the questions asked from the various authorities prove that the system is, as a whole, acting well in schools in which more than 50 per cent. of the pupils are drawn from the elementary schools; the difficulties met are almost entirely confined to schools with a smaller percentage of ex-elementary school children. There is, however, but little doubt that some of the children now holding free places would derive greater educational benefit from a course at a higher elementary, junior technical, or trade school.

2. Free places should not be awarded to children entering the

secondary schools over 12 years of age; otherwise the work of such schools suffers.

3. A good mid-day meal is essential for those who have to attend school at some distance from their homes; but the average charge for this is more than the parents of many free-place holders can afford to pay. It should be the duty of the school or the local authority to see that no scholar's education is impaired from this cause.

4. To make the free-place system fully efficient it is necessary that in many cases maintenance grants should be given for the years of school life above the age of compulsory attendance at a full-time day school. This grant should be of about the value of the average wage of the children of the same age in the district; and should be made by the local education authority, acting on the advice of the school authorities; and this advice should be given only after careful inquiry into the needs of each individual case. If such grants are made it is believed that the present temptation to parents to remove promising pupils from secondary schools before they have been able to derive full benefit from them will be removed.

5. The strength and efficiency of the free-place system is dependent for its success on the provision of greater facilities for the support of secondary school children of exceptional ability at the Universities and higher technical schools; this can be met only by the provision of a larger number of scholarships from secondary schools, and these of greater value than is at present the case.

Unless supplemented by large school scholarships it is, for example, nothing but a mockery to offer a scholarship of 40*l.* or 50*l.* a year tenable at Oxford or Cambridge to a candidate whose home circumstances do not permit of a very substantial addition thereto being made.

6. It should be possible to remove from the free-place list the names of pupils who are reported for habitual laziness; such removal to be made by the governing body of the school acting upon the report of the head-master.

7. The award of a free place should not be based exclusively upon the results of a written examination, but in conjunction with an oral examination conducted by the head of the secondary school with the aid of one or more persons appointed by the local education authority from the contributory schools.

8. The free-place system should be available for all classes of the community; those parents who have made an effort to forward their children's education by paying fees for them whilst young should not be prevented, as at present, from gaining the benefit of a free secondary education; the difficulty may probably be best met by ruling that all candidates must have been educated for two years in a school inspected by the Board of Education and classed by that Board as 'efficient.'

Plant Pathology.—Report of the Committee, consisting of Professor M. C. POTTER (*Chairman*), Dr. E. N. THOMAS (*Secretary*), Professors B. T. P. BARKER, BIFFEN, *and* V. H. BLACKMAN, Mr. BRIERLEY, Mr. F. T. BROOKS, Mr. COTTON, Professor T. JOHNSON, Drs. F. W. KEEBLE *and* G. H. PETHYBRIDGE, Messrs. J. RAMSBOTTOM *and* W. ROBINSON, Dr. E. J. RUSSELL, Mr. E. S. SALMON, Miss A. LORRAIN SMITH, Dr. W. G. SMITH, Mr. H. W. T. WAGER, *and* Miss E. M. WAKEFIELD, *upon the necessity for further provision for the Organisation of Research in Plant Pathology in the British Empire.*

THE Committee appointed last July have met on several occasions and very carefully considered the position with regard to the necessity for the provision of further facilities for the organisation of research in plant pathology in the British Empire.

They confine their remarks in the present report to the consideration of conditions in Great Britain.

They conclude that the present opportunities for training, research, and correlation in plant pathology are quite inadequate.

They are of opinion that there is grave necessity (see Appendix A) for the provision of further facilities for the organisation of research in plant pathology, and that the following developments must be secured:—

1. The establishment of a central institute devoted to the study of plant disease, and the establishment of a laboratory for the supply of pure cultures.[1]

N.B.—It is realised that it may not be possible, or at any rate convenient, for such an Institute to attempt to cover the whole field of agricultural, horticultural, and arboreal plant disease.

2. The encouragement of local Stations for the study of such aspects as local conditions of produce, climate, &c., make particularly possible or desirable (as, for instance, in fruit-growing areas, &c.).
3. The encouragement at the Universities of instruction in the phenomena and underlying scientific principles of plant disease.
4. The insistence, as far as possible, upon the study of chemistry, physics, and bacteriology as a necessary preliminary to training in plant pathology, which should be approached preferably by way of a degree in botany, followed by research work at an institution of experimental phyto-pathology.
5. The production of a new publication for the inclusion of abstracts and research in plant pathology.

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[1] The Committee is informed that there is every reason to suppose that a central institute is about to be established.

APPENDIX A.

FRUIT.

APPLE.	LOSSES.
Scab. *Fusicladium dendriticum*	General over England, causing falling of young fruit and largely responsible for supplies of small, poor fruit, which does not keep well. Could be controlled by spraying.
Brown Rot. *Monilia fructigena*	Probably large.
Blossom Wilt. *Monilia cinerea*	A serious disease, specially in the S.E. counties.
Canker. *Nectria ditissima*	Severely cripples the trees, especially on wet, heavy land, and responsible for heavy losses.
Mildew. *Podosphaera leucotricha*	Seriously injures certain varieties in various localities.
Bitter Pit	Fruit badly damaged in some localities.
Silver Leaf. *Stereum purpureum*	At present not believed to be serious in apples.
PEAR.	
Scab. *Fusicladium pirinum*	Often very bad, and causing serious losses. Could be controlled by spraying.
Brown Rot. *Monilia fructigena*	?
PLUM.	
Silver Leaf. *Stereum purpureum*	Very serious in Victoria and Czar plums. Threatens their extinction in some localities.
Brown Rot. *Monilia cinerea*	Causes much loss of young wood and fruit in some localities.
Rust. *Puccinia pruni*	Causes early defoliation in certain seasons.
BLACK CURRANT.	
Rust. *Cronartium ribicola*	Very bad in many counties in 1917, causing early defoliation.
—	
Spot. *Gloeosporium ribis*	?
GOOSEBERRY.	
American Mildew. *Sphaerotheca mors-uvae*	Formerly very serious in many parts. Much less in 1917.
Die-back. *Botrytis cinerea*	Serious in many localities.

CEREALS.

WHEAT.	
Puccinia glumarum	Sometimes serious. 10 per cent. = 800,000 quarters per annum.
Ophiobolus	*Locally serious.*
Puccinia graminis	Sporadic.
Titletia tritici	In aggregate quite material.
BARLEY.	
Ustilago hordei	Often serious.
Helminthosporium	Often serious.
Ophiobolus	?
OATS.	LOSSES.
Rust. *Puccinia spp.*	?
Ustilago avenae	Often serious.
Ophiobolus	?

FODDER.

CLOVER.	
Sclerotinia trifoliorum	Very common locally, and probably largely responsible for clover sickness.

ROOTS.

CARROT.	LOSSES.
Sclerotinia sclerotiorum	At times destructive in store.
TURNIP AND SWEDE.	
Phoma napobrassicae	Very destructive locally in the North.
Bacterial Diseases	Very bad at times.
Finger and Toe	Widespread, and very destructive in certain localities.
MANGELS.	
Rhizoctonia violacea	At times destructive.
Phoma betae	Locally destructive.

POTATOES.

Blight. *Phytophthora infestans*	Average loss in British Isles one ton or more per acre. Administrative action taken. (Spraying.)
Wart Diseases. *Synchytrium endobioticum*	Very serious indeed. Administrative action taken. (Immune varieties.)
Black-leg. *Bacillus phytophthorpus*	At times very considerable and apparently increasing. Inspection of growing seed crop necessary.
Corky Scab. *Spongospora subterranea*	Difficult to control. Locally bad.
Sclerotinia sclerotiorum	Bad in West of Ireland.
Leaf Curl. (*Probably physiological*)	Bad, especially in gardens and allotments.
Bacillus solanacearum	? Good seed essential.
Sprain	?
Dry Rot. *Fusarium caeruleum*	Causes serious losses in store, especially amongst early varieties.
Verticillium	? Apparently increasing; responsible for local failure of crop.

VEGETABLES.

BEAN.	
Pod Canker. *Colletotrichum lindemuthianum*	Causes considerable damage in certain seasons.
Rust. *Uromyces fabae*	?
PEAS.	
Streak. Bacterial ?	?
Mildew. *Erysiphe polygoni*	?
BRASSICA.	
Finger and Toe. *Plasmodiophora brassicae*	Very considerable.
Bacteriosis. *Pseudomonas campestris*	?
CELERY.	
Leaf Spot. *Septoria apii*	Considerable.
ONIONS.	
Mildew. *Peronospora schleideni*	Considerable in certain seasons.
Sclerotinia sp.	Locally responsible for serious damage.
TOMATO.	
Rust. *Cladosporium fulvum*	Annually responsible for serious losses under glass.
Potato Disease. *Phytophthora infestans*	Responsible for decay of much fruit in the open.
Canker. *Mycosphaerella citrullina*	Very serious at a few centres in the past. At present almost absent.
Stripe. Cause obscure	Causes very serious losses in many parts under glass.

Corresponding Societies Committee.—Report of the Committee, consisting of Mr. W. WHITAKER (*Chairman*), Mr. WILFRED MARK WEBB (*Secretary*), Dr. F. A. BATHER, *the* Rev. J. O. BEVAN, Sir EDWARD BRABROOK, Sir H. G. FORDHAM, Sir THOMAS HOLLAND, Mr. T. V. HOLMES, Mr. J. HOPKINSON, Mr. A. L. LEWIS, Mr. THOMAS SHEPPARD, *the* Rev. T. R. R. STEBBING, *and the* PRESIDENT *and* GENERAL OFFICERS. (*Drawn up by the Secretary.*)

THE Committee held a special meeting on January 8, 1918, to consider the proposal to commandeer the British Museum and passed the following resolution, which was sent to Mr. Lloyd George, Sir Alfred Mond, Lord Rothermere, and Lord Sudeley:

> 'The Corresponding Societies Committee of the British Association which represents provincial societies in the Kingdom with an aggregate membership of 46,000 protests against the use of the British Museum including the Natural History Museum as Departmental Offices.
>
> 'Apart from the damage to irreplaceable specimens which would result and the confusion which would be introduced into the whole collection, such a step would stop scientific work of great importance to the nation and essential to the successful prosecution of the War.'

The Conference of Delegates will be held in the apartments of the Geological Society, Burlington House, London (by kind permission of the Council), on Thursday, July 4.

Dr. F. A. Bather will be President; Mr. Mark Sykes, Vice-President.

At the first meeting the President will deliver his Address, entitled, 'The Contribution of Local Societies to Adult Education.' Upon this a discussion will be invited.

Mr. B. B. Woodward, F.L.S., F.G.S., will exhibit a Typomap of the British Isles, on which naturalists may record the distribution of species.

The question of 'Grants for Regional Museums' will be introduced by Mr. Percival Westall and discussed.

At the afternoon meeting Mr. Martin C. Duchesne, F.S.I., will open a discussion with a paper on 'Afforestation.'

The Committee asks to be reappointed and for a grant of 25*l*.

Conference of Delegates of Corresponding Societies.

The meetings of the Conference took place on Thursday, July 4, 1918, at Burlington House, London, by kind permission of the Geological Society. At ten o'clock the President (Dr. F. A. Bather, F.R.S.) delivered the following address, entitled:—

The Contribution of Local Societies to Adult Education.

It is one thing to achieve greatness, another to have greatness thrust upon one. While I thoroughly appreciate the honour of being selected to preside over the deliberations of a Conference, which, let me mention, I first attended in 1881, yet I could have wished that the dignity had been thrust upon me at less short notice. With adequate time for the preparation of an address such as custom requires, I could have pleased myself, if not my hearers, by unloading the burden of certain ponderings during these many years on the subjects prescribed by the Council of the Association as suitable for our discussion. But in these days every man's time is filled, and you will readily pardon me if instead I ask your advice and help towards a Report which I have been asked to draw up for another committee.

The subject of the desired Report is 'The Extent and Scope of the Work of Naturalists' and similar Societies up and down the country' in special reference to 'non-vocational adult education,' or, as I have phrased it for our purposes, 'The Contribution of Local Societies to Adult Education.'

The reference admits of some latitude in the interpretation of the term Local Societies. As regards restriction of place, a rigid interpretation of the word 'local' would exclude not only such bodies as the Royal, the Linnean, and the Geological Societies, but also the Selborne Society and the Museums Association. This would be a mistake. Again, a society must not be excluded because its headquarters are in London, or even because it has a Royal Charter. The Geologists' Association is confessedly an educational body for amateurs. The most obvious activity of the Zoological Society is the education of the populace. Some meetings of the Royal Geographical Society and the lectures of the Royal Institution appeal intentionally to those who are not professed students of science.

As regards restriction of subject, the bodies to be discussed are in the main societies for the promotion of natural history studies, but include a considerable number which devote their attention in large part to other branches of physical science, to archæology and history, and even to philosophy and polite literature. The line between naturalists' societies and the others is vague and fluctuating, and the name is often an unsafe guide to classification. A society with the words 'natural history' in its title may drift into archæology and stay there, perhaps half-a-century, till some prophet of nature arises in the neighbourhood with force enough to re-introduce the old studies.

Probably every district has the societies which it needs, and if people prefer one subject rather than another they are only to be commended for cultivating it. The educational effect depends less on the subject than on the way in which it is approached. Our ultimate classification will therefore be based on method rather than on matter.

In compiling my own list I have excluded societies for the propagation of the Arts and Crafts, Photographic Societies except when they conduct regional surveys, and purely literary societies such as the hundreds of Shakespeare Societies. Some societies that do not, at least in their titles, claim connection with natural history or with science of any kind have been included because the papers read before them occasionally deal with the facts or theories of Natural Science.

To appreciate the educational influence of these societies we have first to consider their number, distribution, and strength.

For nearly forty years the British Association for the Advancement of Science has attempted to draw to its bosom some if not all of those societies scattered throughout our islands which promote any branch of knowledge that comes within the purview of the Association itself. These Corresponding Societies are divided into two classes: (1) Those which 'undertake local scientific investigation and publish the results.' These are Affiliated Societies. (2) Those which 'encourage the study of Science,' as opposed presumably to investigation, and (it is implied) do not publish results because they have none to publish. These are Associated Societies.

For our present purpose the distinction drawn by the British Association between Affiliated and Associated Societies does not greatly trouble us. Indeed a society that 'encourages a study,' even though it refrain from publication, may be doing more educational service than a small body of professional investigators publishing technical papers and making no appeal to the public.

In 1883 the number of publishing societies regarded as worthy of admission was 175 for the whole of the British Isles. This number included the Cumberland Association, the Midland Union, and the Yorkshire Naturalists' Union, which three bodies represented 70 societies. Twenty of those societies were also in the general list, so that the number of presumably non-publishing societies comprised in the Unions for about half of England alone was 50. Considering the difficulty, then as now, of obtaining information, we may say that for the British Isles at that date a total estimate of 200 publishing and 200 non-publishing active societies would probably have been within the mark. The number of 39 actually placed on the roll of Corresponding Societies in 1885 therefore represented about one-tenth the total number and one-fifth the admissible number. This was good enough for a beginning, but, as expounded in Sir George Fordham's Address to the Conference of Delegates in 1914, the number did not increase materially till the widening of the entrance qualifications in 1905, when he records a total of 72. High-water mark, according to Sir George, was reached in 1912 with a total of 114.

Last year, 1917, the numbers were: Affiliated, 88; Associated, 32; total, 120. But of the Affiliated Societies two were outside the British Isles.

This, however, gives a most imperfect idea of the total number of eligible societies in these islands. It is not easy to estimate what that number may be, but I have made an attempt. Taking all the lists available, such as Griffin's 'Year-book of Scientific and Learned Societies,' the Catalogue of the Natural History Museum Library, the lists of the Unions, and the 'Museums Directory,' I have compiled a card index. It contains 392 names. But even this is certainly incomplete, as will appear from various considerations. For instance, I was able to supplement the aforesaid published lists from my own personal knowledge, and no doubt other people could in the same way supply names of other societies which ought to be in these lists.

Another line of argument is derived from the geographical distribution of the societies listed. This is shown on a map exhibited here. Two facts are manifest on this map. One, the extensive areas without any indication. Some of these are due to paucity of population, but others must be assigned as much to our own ignorance as to any lack of interest on the part of the inhabitants. That I have been able to credit certain districts with a goodly number is due to the existence of Unions, such as the Yorkshire Naturalists' and the South-Eastern, which have swept a large proportion of the societies into their lists. It is only such lists that have told me of the continued existence of societies which for years had given to the outer world no sign of life. Where Unions have lapsed, as in the case of the Midland Union, or have never existed, as in S.W. England and East Anglia, our information is undoubtedly deficient, probably by at least one-half. The second fact that emerges is the congregation of the recorded societies in or near the great cities. Greater London finds room for about 50, Manchester 13, Liverpool 11, Glasgow 7, Edinburgh and Dublin 8 each, Leeds 9. The region round Bradford, Halifax, and Huddersfield, 14 or 15. It was here that the Yorkshire Naturalists' Union came into being, with its constituent societies each within a walk of the others. Newcastle, Carlisle, and Worcester have 6 each; Hull 5; York, Birmingham, Bath, Norwich, and Southampton are each credited with 4. This makes 158 out of our 392. Partly this concentration is due to density of population but not entirely. Something is due to fashion: Bath, for instance, has a reputation to keep up. But a good deal is due to the publicity attending such efforts in these places. One society joins a Union and the rest follow. There are certainly societies in many a town that is not so marked on the map, but they live a life apart, and we hear nothing of them. Instances of this are Lancaster, Wolverhampton, Coventry, Lichfield, Colchester, and Salisbury—each of them 'no mean city,' and probably boasting more than one scientific society.

Taking all these facts into consideration, I am convinced that our list might be increased to 500 or 550 without losing its character.

But this is not all: widely though the net may be cast there are a number of societies carrying on educational work of considerable value, yet too small or obscure to be caught in its meshes. Any estimate of their number must be quite vague, and yet it is worth attempting if one wants a true picture of the state of the country. Take the Borough of Wimbledon with its population of nearly 60,000. In the list as compiled there are only two societies entered, of which one is associated to this Conference. There are, however, six others known to me as doing good educational work. It is quite likely that the same proportion obtains in many other towns. The inclusion of such societies in our list would raise the number to at least 1,000.

We may pause here to consider whether it would not be advantageous for us to bring more of these societies within our fold. In the early days of this Conference the conditions of admission included local scientific investigation and the publication of results. Since the delegate became *ex-officio* a member of the General Committee a reasonably high standard was certainly desirable. Now that the rule of 1905 admits non-publishing societies as associates, without representation on the general committee, we should make more strenuous efforts to obtain their co-operation. Even on the ground of investigation, the publication of a report is no criterion of the value of the society. The contents of the report may lack originality, and, on the other hand, the members may do excellent work but prefer to publish in some other form than a special organ of their own. This is recognised by the S.E. Union, which compiles and publishes a list of such papers produced by its members. The multiplication of trivial Reports and Proceedings is not an unmixed blessing to anyone except the printer, and I long regretted that the British Association should have felt obliged to make this a test for admission.

Our object is to encourage and co-ordinate the work of local societies, and we cannot do this effectively so long as we remain out of direct touch with 88 per cent. of them. Perhaps the conditions of membership might be eased by making it possible for a society to become a member of the Association by compounding for a term of years, on the principle of the life member. Especially in present circumstances we can hardly expect individuals or societies to pay a pound apiece for the privilege of some five hours' attendance at this Conference. But if a society could secure representation for 30 or 40 years by a single payment of 10*l.*, this would be an inducement to it to send a delegate, and to continue its activities sufficiently to conform to our standard. On the other hand, the attendance of a delegate at the Association meetings and at this Conference would, let us hope, react favourably on the Society.

Hitherto I have considered only the number of societies. It may be worth while to estimate, however roughly, the number of individual members. Taking our own list for 1916 and excluding the associates of the large Unions and the members of the oversea societies, we find 88 Affiliated Societies with a total membership of 22,535, or an average of 256; and 31 Associated Societies with a membership of 7,079, or an average of 228. The total average is about 248. This number is, however, liable to correction, because in most of the larger societies a considerable proportion of the members are also members of other societies in the list. Also it is hardly fair to reckon as characteristic the Institution of Mining Engineers with its 3,600 members. Probably it would be fair to take 200 as the average number of members in a society of the kind we are considering. Certainly if we include all our supposed thousand societies, this would not be an underestimate. That gives a grand total of 200,000 individual members for the British Isles. From one point of view, a respectable number; but in reference to the whole population of forty-five millions, only 0·4 per cent.

Fortunately the educational influence of our societies is not confined to their actual members. Often it reaches a large proportion of the surrounding population. Let us now turn to this aspect of our subject and see how the societies work. In a sense all their activities have an educational bearing, but some act more directly than others. The chief of these are Lectures, Excursions, and Museums.

At our Newcastle Conference (1916) the subject of Lectures was dealt with in so admirable a manner by Mr. Percival Ashton in his paper and by Professor R. A. Gregory in the Interim Report of the Committee on Popular Science Lectures[1] that it is impossible for me to add anything. Only for the sake of reminder I would emphasise this point. A distinction must be drawn between lectures *to* the society and lectures *by* the society. The society presumably consists of persons who, if not already learned, at least are prepared to learn. They lend a ready ear, and need no argument to convince them of the interest or utility of the studies which they have themselves combined to promote. Before such an audience the lecturer starts, without apology, in the middle of his subject. Lectures arranged by the society for an outside public stand on a different footing. They must be attractive and attractively advertised. The lecturer has to make good, to persuade, to convince. The former class of lectures may profitably convey definite instruction; the latter class should be rather in the nature of propaganda. They may afford a glimpse of the marvels of science or the fascination of the natural world, but their most useful service at the present day will be, in the words of the above-mentioned Report, 'to show as many people as possible that they are personally concerned as citizens with the position of science in the State, in industry, and in education.' The Report spoke of the hostility or unreceptiveness of the general public towards science. This attitude, and the equally distasteful one of a jesting tolerance, have been greatly modified by the war. Now is our great opportunity. The scientific principles at the base of food, of agriculture, of munitions, and the like urgent problems are no longer despised. The treatment of the wounded, protection against vermin and insect-borne disease, and the care of children afford many openings. The historical background of the war, the ethnology of Central Europe and the Balkans, the influence of language, the nature of frontiers: these are questions that have a less insistent appeal for the multitude, but they will find their audiences all the same. There is scarcely a branch of human knowledge and mental activity that has not been stirred into new life by the present struggle. Our societies must be ready to take advantage of this ferment, so that on the advent of peace the public mind shall not revert to its old stagnation.

The second educational method is by Excursions. Under this head are included visits to natural objects, to antiquarian remains, to zoological and botanical gardens, and to museums of science or of art. These are as a rule but lectures in another form; at any rate they are demonstrations. They are confined to the members, as a rule, but they usually prove more attractive than the indoor meetings, and so swell the ranks by introducing folk who come first for amusement but may remain for instruction.

Of a more serious character are those field excursions on which some actual work is done. Either specimens are collected and records noted, as on the popular Fungus Forays, or a systematic survey is conducted. As typical of a body undertaking such work, one may instance the Yorkshire Naturalists' Union. In a Presidential Address to that body in 1904, Mr. W. Denison Roebuck[2] said: 'Our true function is not an educational one, but one of original research at first-hand, and the publication of results. The only educational aspect of our work is that in which the observer teaches himself by his observations, and in which original workers influence each other. We leave the task of training the recruits from whom future observers will arise to the schools, colleges, universities, who are better equipped for such a task. It is our business to observe facts . . . and to place them on record . . .

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[1] Rep. Brit. Assoc. 1916, pp. 326-351.

[2] 1904, Trans. Yorksh. Naturalists' Union, Part 35, p. 14.

and particularly it is our function to preserve the field-naturalist observing the inter-relationships of natural phenomena in the open, rather than the technical operator working in the laboratory.' I do not think that Mr. Roebuck need have been at such pains to disclaim the educational value of this work. There is no better training for a naturalist than observation in the field, and presumably even the members of the Yorkshire Naturalists' Union are not all ready-made experts. Even if they have to pass an examination before being given a member's card, still nature transcends any teaching and the more one's circle of knowledge spreads the wider are the limits to the unknown. No education is more solid and permanent than one founded on a first-hand acquaintance with hard facts, in the field no less than in the laboratory. If our societies wish to increase their educational force, let them follow the example of their Yorkshire colleagues.

The third and last of the methods by which our societies work is the establishment and care of Museums. Some societies exist for this purpose alone, as the Norwich Museum Association and the Horsham Museum Society. Others have always regarded it as a primary function; such are the Ludlow Natural History Society and the Whitby Literary and Philosophical Society. Others again have begun with the collections accumulated by members, have gradually formed these into a private museum, then have thrown this open to the public under gradually diminishing restrictions, and finally have transferred the whole to the town, either with the retention of a share in its government or completely. Such was the history of the Thurso Public Museum, founded by the Thurso Natural Science Association, and of the Dudley Geological Museum formed by the Dudley and Midland Geological Society. Whether as cause or consequence of relinquishing their museums, these two societies are now dead. In my list there are no less than 52 societies—more than a quarter—now actively responsible for museums, and in some cases museums of great reputation. Still more societies have their headquarters at museums, and often help in the museum work. While it is well that museums should be placed on such a sound financial footing as a municipal rate can best supply, still it is desirable that an intimate connection should be maintained between the public museum or museums of a town and the various local societies. As an educational instrument the museum, if properly managed, is unsurpassed. Like the field and the laboratory it teaches by concrete objects, which make a more vivid impression than the words of a book or lecture. The lecture is only for one brief hour, the excursion demands an occasional holiday, but the museum teaches all the time. The museum forms a centre for the members of the society, serves to attract fresh members, and by its varied exhibits and special exhibitions should be making an ever fresh appeal to one or another class of the neighbouring population. But to this audience I need not emphasise the educational value of a properly conducted museum. All you have to do, if your society maintains a museum, is to see that it does conduct it properly. If you do not know what that means, come on to the Conference of the Museums Association and we will tell you.

I have purposely given a mere sketch of these educational activities, for it is waste of breath to preach to the converted, and on this occasion it is I who wish to get advice from you. I may fittingly conclude with an extract from the Report of the South-Eastern Union for 1917 :[3] 'We believe that one result of the war will be a stirring up of educational enthusiasm and activity, both nationally and locally. The S.E. Union of Scientific Societies and its individual affiliated societies are educational institutions. Each society can do much within its own area to quicken local interest in the geography and geology, the fauna and flora, the history and antiquities, and in the immediate and future civic problems and possibilities of the district.'

Yes—we can all do this, if we will only recognise our powers. And in these days, when one has powers of this kind it is a duty to exercise them.

Sir Edward Brabrook (Balham and District Antiquarian and Natural History Society, and Lewisham Antiquarian Society), in proposing a vote of thanks to the President, said that he spoke both as founder and first

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[3] *S.E. Naturalist*, p. xxiii.

President of the two Associations which he represented, and he claimed that they had done what was in their power to form an educational centre in their district of London, and in one direction they had so successfully educated their members that quite a number of them had sought and obtained fellowship of the Society of Antiquaries.

The phase of education to which the President had particularly directed their attention was that of the education of the general public. The only point in which they had perhaps failed in their original intention, to his mind, was, that they began with the idea of combining Archæology or Antiquarianism and Natural History, and that their contributions to Natural History had been very slight, and practically they had abandoned that branch. He was sorry that it was so, but it could not be helped; a different people were interested perhaps in Archæology from those who were interested in Natural History.

He thought that in striking an average of 200 as the membership of local societies the President had erred in excess.

Mr. W. **Whitaker** (Essex Field Club), who seconded the vote, urged that in estimating the value of societies they must not be led astray by numbers; they should consider the proportion of working members. On the question of lectures, those 'to' the Society were supposed to instruct, not only the societies, but the inhabitants generally, and very often these lectures were more or less open—even free, or for some slight payment. The primary object of local societies was to deal with more local science; their next duty was to spread abroad that knowledge. That was where the educational part came in. They could not, however, do that until they had started the first. Then another way in which local societies might do good in their neighbourhood in an unpretentious way was by helping the schools. Schools would be glad of assistance as to the fauna and flora of their districts. He was speaking now of pupils being taught something of their surroundings. It was a teaching that appealed to those who were taught. He had the pleasure of doing something of the sort himself. For instance, he had fifteen or sixteen girls from a school as an audience over Hampstead Heath. They really appreciated seeing things and having them explained, and he was told by one of their teachers that they had investigated for themselves and they wanted to see what there was under the soil. If you could get a spirit of that sort in the schools it would grow. It gave an appetite that would increase, a healthy, wholesome appetite. There was, further, the effect of this work on the teacher. Some teachers were apt to forget that those they taught had not the knowledge they had themselves. Taking the children out brought them into more intimate contact with those they had to teach; they got a better idea of what to teach and how it was to be put.

In museums it was very important that local societies should get into touch with the local authorities. His idea was, that in large places there should be some meeting-place belonging to the local authority, where not only their natural history societies but other public societies and public bodies should have some sort of resting-place or meeting-place.

However humble their societies might be, they might and should exercise a considerable influence on the educational work of our country.

Mr. **Robert Cockburn Miller** (Edinburgh Geological Society, and Edinburgh Field Naturalists' and Microscopical Society), who gave a list of the societies of Edinburgh, said that one of the difficulties that they had —and he could speak as a contributor to several of the societies for many years—was that of funds. The subscriptions were small, and in these days the publication of 'Transactions' cost a good deal. It was a curious thing that, while there were charities of all kinds, there had been wonderfully little contributed to these societies, although they had done an immense amount of very valuable work.

With regard to the subject of the President's paper, he said that a field naturalists' society which was in the fiftieth year of its existence had a very large number of members who were engaged in teaching, and it was very encouraging to see the enthusiasm of these teachers in finding some new kind of plant or animal, and in ascertaining from the others, or else from the books which they carried with them, all that could be known about it. Constantly, also, one heard them mention that they encouraged their scholars to bring them specimens of things that they themselves could not find.

Several parts of Scotland had excellent museums; he would not mention names, because they were so numerous. In regard to illustrations of birds and bird life, Mr. Miller intimated that pupils brought specimens, but that they had been distinctly told that there must be no destruction or cruelty in providing them; that where this condition was fulfilled the museums were glad of the specimens.

Mr. Miller went on to say that corporations and other local authorities did take an interest in local societies, and in Edinburgh their Geological Society was now housed in the Corporation buildings. Again, corporations could mark interesting features. They had several examples in Edinburgh; for instance, at a place where Agassiz had stayed.

On the popular educational side, Mr. Miller mentioned the work of one scientific man who took an interest in the education of adults. They had in Edinburgh for many years, John George Goodchild, who was a member of most of the societies, and he used to gather round him as many of the people as he could get and demonstrate at the museum, or take them into the country and show them different things. He remembered many instances which pointed very strongly to the value of these excursions as enunciated by Mr. Whitaker.

The Rev. J. O. **Bevan** (Woolhope Naturalists' Field Club) maintained that it would be a most desirable thing if those associated with their local societies would pay more attention to the schools, and get the interest of the head and assistant teachers enlisted in their subjects. No doubt one great difficulty in securing systematic instruction would be the provision of suitable teachers, and local societies should take pains to ascertain the local conditions, and do what they could to further the provision of proper teaching and facilities.

Mr. J. **Hopkinson** (Hertfordshire Natural History Society) agreed with the President in drawing a distinction between publishing and non-publishing societies, and that the authorities of the Association were quite right in giving a higher status to the former. In Hertfordshire they had far more good papers than they could afford to publish : they had to cut them down, and decline some. They had not for some years printed a single paper which had not been the result of local investigation, or did not instruct others how to make local investigations.

It was only in our large towns that a society could afford a museum. Their museum at St. Albans had a grant from the County Council of 150*l*. a year; the rest of the funds being contributed by subscriptions. He knew the museum was doing good educational work, especially among children, and it was visited by people not only from distant parts of this country but also from abroad.

Mr. J. **Wilson** (Quekett Microscopical Club) said they published 'Transactions' which were largely quoted. They had various collections of microscopical specimens, and the Club, with its discussions, was largely taken advantage of by local members. During the last four years members of the Club to the number of a hundred had gone from eight to ten in the evening almost every day of the week, to give lectures to soldiers and sailors at various headquarters, and these lectures had been appreciated.

Mr. T. **Sheppard** (Hull Scientific Society) said he had developed from one of the most optimistic into the most pessimistic of men because he was afraid that the interest in scientific work was decreasing, and something would have to be done to increase it. In what they had done in his own county, or the eastern part of it, it looked as if they were going to natural-historyise the whole population. But the extraordinary result was, they had less people taking an interest. In the old days when they had classes they had twice or three times the membership in their societies that they had now. Another thing he was a little pessimistic about was the way in which their British Association for the Advancement of Science—the one institution which existed for that purpose—should have set them the example of not having an annual meeting. There was absolutely no excuse for not having a meeting in that or some other room in London.

Mr. W. **Whitaker** supplemented his remarks by saying that local societies might help in the formation of libraries. Their societies could help in filling up lists of scientific works in their localities. There must be many men who had numbers of books that they did not specially want. It would be very much better to do distributing work in their lives than to leave it to their executors to deal with, and it would be a good thing if they handed some of their well-collected scientific literature to some public museum or library in their neighbourhood. Libraries were one of the chief means of furthering education.

Miss **Margaret C. Crosfield** (Holmesdale Natural History Club) spoke of a revival of interest in her neighbourhood, where the school teachers were entering into the work and spreading it among the children. They had admitted teachers into their society on special terms—a special subscription of half-a-crown.

Mr. **Whitaker** interpolated that the same was done at Croydon: teachers were admitted at half-subscription.

The President thanked the speakers for the many suggestions made, some of which probably would find a place in his Report. The influence of their societies in teaching teachers of course was a very important one. In regard to this there was the difficulty teachers had in getting away to excursions. It was just conceivable that if one could emphasise the value of the work of these societies, acting through the teachers, to the children, some influence might be brought to bear on the educational authorities to facilitate the attendance of teachers at excursions in school hours, in the same way as in some places visits to museums were reckoned as part of the educational course.

What Mr. Miller had told them about Edinburgh reminded him of the public labels he had been pleased to observe at St. Albans. Local societies should bring influence to bear on their municipalities to allow them to put up tablets on historic buildings, and so on, in a conspicuous and artistic manner, which would be of great advantage to the public and to themselves, but they must not rely too much upon these corporate bodies. The old signboards put up all over the country by the Cyclists' Touring Club were most valuable, but when this work was placed in the hands of County Councils, for some years one found these old boards of the C.T.C. gradually falling into decay and nothing to replace them. Anybody who cycled about the country found great diversity in the counties. These were matters in which such societies as theirs could bring a certain amount of influence to bear on those public bodies.

He thought perhaps on the general question the most important remarks were those contributed by Mr. Sheppard. His were another example of the fact that people valued most what they had to take most trouble to get and what they had to pay for. Another cause of the lamentable results to which Mr. Sheppard referred might perhaps be that the interest excited by museum visits had nothing continuous about it: they were perpetually interesting people, but they were not leading them on. To get permanent results, the museum curator should give the children facilities for continuing the study of any subject in which he found that their interest was aroused. One must not, however, demand too much from the museums; it does not in the least follow that a boy who takes an interest in history, is going to be an historian; it does not follow that because a boy has taken interest in geological specimens he is going to become a geologist; only, if you want him to follow up a special subject, he must not be taught in a scrappy way.

The Report of the Corresponding Societies Committee was read by the Secretary and it was agreed that the Council of the Association be requested to appoint Mr. Mark Sykes a member of the Committee.

Kent's Cavern.

The question of Kent's Cavern was raised by Mr. Bevan, and after some discussion he proposed a resolution to the effect that the Council be asked to appoint a Committee consisting of Mr. William Whitaker, Mr. Mark Sykes and Mr. Wilfred Mark Webb to deal with the matter. This was seconded by Mr. T. Sheppard and carried.

The second meeting was held at 2 P.M., and MR. MARTIN C. DUCHESNE started a discussion with the following paper upon:—

Afforestation: Its Practice and Science.

Introduction.

Afforestation—a life-long interest to a few—until recently was little more than a word to the average politician and the public. The war, however, has opened many eyes to the grave and pressing importance of an assured national timber supply. My object is to emphasise this importance and to bring out the need also for closer association of science with practice in building up our future timber reserves.

The case for afforestation was strong before the war, but actual war experience has made it overwhelming. Our imports of timber, amounting to 3½ cubic feet per head of population in 1851, had steadily increased to 10½ cubic feet per head in 1911. Meanwhile the home supplies had deteriorated. The United Kingdom, caught without sufficient home reserves, had to continue importing timber on a large scale at *any* expense. The costs were enormous, involving (1) an additional expense of nearly 40,000,000*l*. above the pre-war prices for necessary supplies of timber during only the *first two* years of war; (2) absorption of tonnage urgently needed for other purposes; (3) loss of cargoes sunk by the enemy; (4) depreciated exchange. In our extravagant reliance on imported timber we ran risks, as the recent Forestry Report reminds us, 'against which every other considerable country has long taken care to protect itself.'

National Timber Demands.

Up to comparatively recent times the national importance attached to timber was confined almost to the provision of oak for the Navy and wood for fuel. These demands have been supplanted by others, and the problem of oak for the Navy is replaced by that of props for the mines and timber for national industries and uses. Building, constructional, and transport trades demand timber in vast quantities. As a munition—for aeroplanes, army wagons, artillery spokes, sleepers, huts, ammunition boxes, shipping, railway and transport purposes, trenches, fuel, and in many other directions—timber has never been so indispensable as in this war. For national reconstruction purposes—not only here, but also with our allies, especially in the devastated areas—the demand for timber will be very great.

The Coast Erosion Commission, in 1909, recommended afforestation of 9,000,000 acres to make the country independent of foreign supplies. The Government reply was the creation of the Development Fund, which we were promised would do much for forestry, but which has been a severe disappointment to all parties. With our 3,000,000 acres of woodlands, we are still, with the exception of Portugal, the worst afforested nation in Europe.

The need—great in any event—for a comprehensive scheme of real encouragement to forestry the war has now shown to have very vital relation to the safety of the realm.

The Forestry Report.

In the Final Report of the Forestry Sub-Committee of the Reconstruction Committee the proposals now under Government consideration are developed. These proposals represent a basis for State afforestation combined with encouragement to private enterprise.

To account for the poor condition of our woods, the Forestry Report refers to the fall in value of small hardwood timber and oak bark, the increased demand for coniferous timber, old and unsuitable methods of management, game preservation, and love of the picturesque. In my opinion the most serious causes have been omitted, namely :

1. The agricultural depression of the past generation, which denuded the countryside and chilled the spirit of enterprise.

2. The glutting of the home timber markets with the produce of the world's virgin forests at prices that very often represented little beyond the cost of felling, transport, and marketing, in addition to importers' or agents' profits.

3. The unfair handicaps from which forestry suffered, and to which I refer later, and the neglect of the State, shown by the absence of *any* endeavour to remove those handicaps.

4. An absolute indifference to forestry and lack of encouragement of native timber by the consumers of timber, by industrial concerns, by the Government departments, and by all sections of the community.

Absence of well-managed State or Crown forests in the past is rightly noted as a drawback to the private owner, who had nothing to guide his efforts at timber production by the system of High Forest, comparatively new to this country. He had to pick up knowledge as best he could, buy his experience as to trees to plant and incur sad losses.

The proposals of the Forestry Report include planting 1,770,000 acres in addition to replanting and improving existing woods, with the object of making the United Kingdom independent of imported timber, in emergency, for three years. This moderate requirement, however, is subject entirely to satisfactory arrangements being made with Canada, which 'contains the only large reserves within the Empire.' Failing such arrangements, the Report admits that a much larger scheme will be necessary for the United Kingdom, owing to the precarious nature of foreign supplies, combined with their steady rise in price.

I would submit that a larger scheme—based on a five years', in place of three years', emergency reserve of timber—is now necessary for the following amongst other reasons :

1. The Forestry Sub-Committee was appointed in July, 1916, and since their Report was prepared there have been large and unforeseen developments, including :

(*a*) The 'break-up' of Russia and the existing uncertain position in that country and the Baltic, on which sources we have relied in the past for over 70 per cent. of our timber supply.

(*b*) Further vast quantities of our native timber have been felled, as compared with the quantity mentioned at the date of the Report.

2. The war goes on indefinitely, with demands accumulating, and if this war lasts nearer five years than three, surely a five years' reserve for the future should be assured.

3. The developments in the air and under the sea even in the near future are impossible to estimate; our reliance on shipping is more fully appreciated and its resources must not be taxed by timber transport in an emergency.

In view of the national importance of the creation of reserves of timber to meet *any* future emergency, I hope that an extended scheme will be instituted.

The general case for afforestation in the Report is based on these three propositions :

1. That dependence on imported timber is a grave source of weakness in war.

2. That our supplies of timber, even in time of peace, are precarious and lie too much outside the Empire.

3. That afforestation would increase the productiveness and population of large areas of the British Isles which are now little better than waste.

Preliminary to afforestation schemes is the creation of a Forest Authority, to whom details as to afforestation must be left for decision.

As to afforestable land the Forestry Report estimates that the United Kingdom contains between four and five million acres of rough and waste land from which to select the area required for afforestation.

The association of small holdings with forestry is advocated by the Forestry Report because forestry combines so well with agriculture.

The encouragement suggested for private planters includes a possible reduction of assessments for rates and taxes, and the abolition of extraordinary traffic is recommended. It is proposed that the Forest Authority should be empowered to confer with the railway companies to obtain a reduction of railway rates. Suggestions are made for the organisation of the home timber industry and the development of woodland industries. Financial proposals include *optional* forms of assistance which might be offered to landowners, including either: (1) State sharing expenses and proceeds, or (2) State making grants or conceding loans at low interest, or possibly (3) Landowner to be relieved from rates and taxes on the afforested land for an agreed number of years It is suggested that an owner who wished to regain control of his woods might do so by repaying the amount of the State contribution, plus compound interest.

As to forestry organisation, references are made to: (1) pressing on forestry surveys and taking stock of existing woods; (2) provision of seedlings; (3) training of forest officers and men; (4) research and experiment; (5) advice on forest management; (6) forest pests.

The only forest pests referred to are the pine weevil and pine beetle. The Forestry Report suggests that the Forest Authority might 'issue and enforce orders calling on owners of woodlands to take definite steps for dealing effectively with such pests.' You will note that there is no suggestion for the State to do anything but compel others to incur expense for the benefit of the community.

I would respectfully submit that the State and others have obligations as well as the landowner. It is for the State to give a lead in proof of a sincere desire *at last* to encourage forestry. Before calling upon others to deal effectively with insect pests, it is surely for the State to make proper grants for education and research in these directions, and *first of all* to point out a *practical and economical* method of dealing with such pests.

Constantly we are reminded of the obligations and responsibilities of the landed interests.

Has the State no Obligation to fulfil?

Has the consumer of timber in any industrial undertaking no obligation or responsibility to encourage native production of the raw material he uses?

Has the pulp manufacturer and newspaper proprietor no responsibility or obligation to encourage the demand for and creation of reserves of spruce and other pulp-wood in this country?

Have the railway authorities no obligations with reference to reasonable rates for the transport of timber, or the highway authorities for proper facilities for carting timber over their roads?

Are the innumerable users or artisans who rely on timber either for their trades or their homes under no responsibility or obligation to encourage native forestry?

Have not the general public, who not only enjoy the woodland scenery of the countryside but also have an interest in timber as an important raw material for the safety of the realm, an obligation to support and encourage forestry?

It would have been possible for them to encourage private enterprise without making large demands on public funds, but their past indifference has been complete.

Since real progress in forestry is impossible until the handicaps are removed, I may be pardoned for referring in detail to them.

By their removal real encouragement will be given to private enterprise and estate forestry.

Private enterprise and voluntary effort are as British as dependence upon the State is German.

Let us now consider for a moment

The National Importance of Estate Forestry.

State operations must be limited principally to large areas and to waste and hill land. Better soils and smaller areas must be left to private enterprise.

Estate forestry enjoys the following principal advantages :

(1) It can ensure the necessary reserves of timber at least cost to the country.

(2) It can plant the smaller areas.

(3) It can plant the better soils and areas near urban and industrial centres.

(4) It can grow ash and other valuable hardwoods on the better soils, whereas the waste areas and hill lands will be limited principally to conifers.

(5) It can combine various branches of agriculture with forestry to great advantage and provide winter work for those engaged in agriculture at other seasons.

(6) It can grow willows and other trees on short rotations and so encourage rural industries.

In the past estate forestry has received no assistance of any kind from the State. It is due to the patriotism of private owners—who planted and kept up their woods in spite of all the difficulties and handicaps—that reserves of native timber have been available which have been of great value to us in this war. I trust that this fact will be recognised to the extent of removing the following handicaps :

1. *Transport.*—High and often prohibitive railway rates are a grievance of old standing in British forestry and if not corrected will prejudice the whole future of afforestation. In few districts in Great Britain has the timber been able to reach its proper and best markets, owing to the high railway rates.
2. '*Extraordinary*' *Traffic.*—Timber pays towards the upkeep of the highways throughout the period of its growth. Yet it is liable to pay a further large sum when it is felled for damage to the roads incurred in its removal.
3. *Rates and Taxes.*—The Agricultural Rates Act does not apply to woodlands, therefore when an owner plants agricultural land he is immediately penalised. Death duties have had a detrimental effect, and both rating and taxing authorities have done much to discourage forestry.
4. *Markets.*—The consumer of timber offers no encouragement of any sort to native timber production. On the contrary, by a cheapening policy he helps to depress it.
5. *Losses* in planting from frost, drought, insects, fungi, and other causes.
6. *Confidence.*—Low prices and lack of demand have shaken confidence in home timber production as an investment. To ensure planting by estates it is essential that this confidence should be restored.

There are many other handicaps due to the general neglect and want of interest in forestry.

Organisation.

In developing or reconstructing an industry everything is dependent on organisation.

We must have organisation of existing timber supplies, and organisation of future timber production. We must have also organisation of knowledge to prevent losses and ensure proper application of Practice with Science.

II. *Practice with Science.*

'Practice with Science' has been always the motto of the Royal Agricultural Society. Forestry touches science at many points, and in the large developments of the near future science must play a leading part. I hope it will always be the policy also of the Royal English Arboricultural Society.

In the past a great gulf has existed between science and practice, but by organisation this gulf should be bridged.

The scientific man has worked at his problem in his own world, and his researches and experiments were often unknown outside it. The practical man has gone on groping in the dark, observing things that happen, but reasoning badly as to cause and effect. What we wish to see is the removal of barriers and the advance of science and practice hand in hand, and the two branches brought closer together.

The Journal of Forestry offers a good medium for the interchange of knowledge and for the co-operation of scientific and practical men with regard to forestry.

Let us consider the directions in which they can work to mutual advantage, and particularly in solving the urgent problems likely to arise in the immediate future.

In view of the large areas to be planted and the great quantities of seedlings which will be required, the first important problem in which science can assist forestry will relate to tree seeds and the raising and protection of the seedlings.

Tree Seeds.

The large planting developments pending will be carried out not only in this country but also on the Continent to replace forests and woods felled or destroyed in the war. In the past we have relied too much on Continental seed. Although in some directions it may be advantageous to use seed collected from the country of origin, we must organise now a proper collection of native seed. The felling of so large a proportion of seed-bearing trees in this country makes the matter urgent.

State grants are required to institute *seed-testing stations* and proper facilities in other necessary directions.

Since the *quality* of the seed is a prime factor for successful planting, with each variety of tree we must decide on the best *type, age,* character, and situation of the parent-tree from which the seed is collected. Geographical position and altitude are of less importance with native than with imported seed.

Foresters differ as to the best *age* of the parent-tree, although the completion of height-growth is assumed generally to be the best age.

Take Scots Pine as an illustration.

The late Mr. Grant Thompson, who had a long experience, estimated the best age of the parent-tree to be sixty to seventy years. Seed from old trees is unsatisfactory and the cones are then very small. If, however, the size of cone and vigour of seedlings are the principal guides, considerably younger parent-trees are apparently practicable. Isolated trees growing on commons frequently bear very large cones at fifteen to twenty years of age, and fully developed seed which produces vigorous seedlings. One hesitates to suggest collecting seed from Scots Pine trees quite so young, but there is no doubt in my mind that the parents had better be too young than too old.

With Larch—and in this case we may have to rely more on native seed in the future—it is generally considered that seeds from the cones of larch of pitwood size will be unsatisfactory. Yet some practical foresters say they have obtained good results from such cones.

Take also the *different types* of the same forest tree, which types, in some cases, for good or ill, may be transmitted to the offspring. The oak is an example in which very careful selection of the seed appears necessary, and we have all noticed the extreme differences of type in the Corsican Pine. One type of Corsican in a parcel will have the characters of the coarser Austrian type, whereas another may be of a fine and erect description.

In some directions it may be quite sound to select seed from what appear at the first glance to be unsatisfactory or coarse trees. Seed from hedgerow ash may possibly be more satisfactory than that from fine ash trees growing in high forest. The seed of the former has better means of ripening and other advantages, and in this case the rough tree is not due to unsatisfactory seed but to incorrect methods of production. The same argument may apply to Scots Pine grown on open commons.

The average *yields* of conifer seed per bushel of cones is a point on which little information exists, and tests should be made and results compared and tabulated.

The *storing* and *extraction* of the seed and other points which I cannot now touch upon afford also matter for discussion.

Nursery Work.

Successful *germination* of the seed after sowing is of the first importance.

The most important factor is moisture and, of course, warmth. It is usual to soak the seed to encourage early germination in the seed-beds. I think far greater attention should be given to this point, particularly with the seed of Douglas Fir and others that give uncertain results. The germination is left often too much to chance and to the risks of the weather, and I am convinced that far more even and certain germination can be obtained as a result of experiment and mutual discussion.

Broadcast v. Drill Sowing.

Both broadcast and drill sowing have their advocates, and it depends to a certain extent on the conditions which should be adopted.

The advantages of broadcast sowing comprise chiefly :

(1) Less land is required for the seed-beds.

(2) Less labour is required for sowing and a given quantity of seed is sown more quickly.

(3) Once a vigorous crop of seedlings has sprung up, the weeds are suppressed naturally and in the later stages less attention is required.

(4) Less expense is involved in shading and other operations.

One of the disadvantages of broadcast sowing is suppressing the weeds in the early stages.

The advantages claimed for drill sowing are that the seeds can be hoed between the lines and that the seedlings are properly mulched and less crowded.

Broadcast sowing is far more general now than drill sowing, both here and in America.

Thickness of Sowing.

The number of square feet covered per pound of seed is a point to which attention should be given. Many experienced men prescribe eighty to a hundred square feet to the pound of seed for the broadcast sowing of most conifers. All agree, however, that Sitka Spruce requires double or treble the area per pound of seed.

The area should be based, of course, on the number of seeds to the pound and the percentage of germination. There are also special characteristics attaching to each variety of tree, and I think that a revised table on this point is required.

Shading, &c.

Protection from sun and frosts is an important question in the early stages of seedling production. Various devices are used for protective purposes, including wire netting, rods of bamboo, boughs, &c. Birch boughs are an inexpensive resource for this purpose, and all agree as to the wisdom of *not* using the boughs of conifers.

Shading the seed-beds with cheese-cloths or coarse canvas is common in America and might be adopted in this country with certain varieties such as Sitka Spruce.

The important point is to prevent 'damping off' or the encroachments of fungi, while allowing proper light and air to get to the seedlings and protecting them in their early stages from extremes of temperature.

The *fungi and other pests* attacking the seedlings, and also the trees after planting, and steps to combat them, also the question of *manures* and their application to forestry operations, afford many points in which we need and hope for the assistance of science.

Woman Labour.

Attention might be called to the great possibilities offered to female labour in the work of seedling production. Women have great aptitude for gardening, and there are probably few directions where they can be more usefully employed in the near future than in supervising the various operations connected with nursery work. I hope that full facilities for training them will be instituted and proper opportunities afforded them for extending their usefulness in this direction.

Afforestation.

It is seldom appreciated how gravely forestry and planting have been depressed during the past generation by losses and mishaps in establishing the crop.

Great opportunities lie open to science for assisting forestry to prevent or minimise losses from frost, drought, insects, fire, gales, and particularly fungi. I would remind you that in this country the extension of forestry as an industry is in its infancy, and in many directions offers almost a virgin field for scientific investigation. The problem is urgent for replanting the felled areas at the earliest moment, before the vigorous growth of grass and undergrowth entail far greater expense in establishing the crop. Science already has pointed to a possible method of keeping down bracken by spraying with a weak solution of sulphuric acid. The burning over of the areas to produce potash for the benefit of the young trees is worthy of extended investigation, as can be judged by observation of results secured where burning has been done effectively.

Transplanting.

When planting out, the proportion of losses varies greatly with each description of tree. Corsican Pine is admittedly one of the most difficult, although intelligent and careful nursery treatment reduces the losses materially. Transplanting every year from the one-year seedling is a good method to adopt, but usually somewhat expensive.

A treatment I have found successful with Corsican Pine consists in taking the one-year seedlings from the seed-beds (but not separating them) late in April and transplanting them thickly but upright in lines. The following season the seedlings can be transplanted into lines, say fifteen to the yard. In addition to being transplanted yearly, they should be 'slacked' also at least once during the summer. Slacking consists in lifting them with a fork, and treading them in again without taking them out of the ground. Slacking is important also to check the growth of Douglas Fir, but damp weather should be chosen for the operation.

I fear practical foresters often confuse cause and effect, and I will give an illustration. Yew and holly are probably two of the most uncertain trees to transplant. The foliage in both cases usually dies back after transplanting. Many gardeners and foresters will tell you as a guide to results that if the leaves fall off the tree will live, but if the withered foliage is retained the tree will die. Professor J. B. Farmer, however, informs me that the retention of the withered or dead leaves is probably the *cause* of death, and that if these are removed few of the trees will die.

I have always advocated as a result of observation that it is best to cut *Thuya plicata* down to ground level after transplanting from the seed-bed.

I mention these facts also to indicate the advisability under certain circumstances of removing the lower branches of Douglas Fir when planting out. From comparing results I am sure this reduces losses, and it also prevents the seedlings from being blown over by gales. I would remind you that the Douglas Fir is the safest of all trees to prune.

Time will not allow of detailed reference to losses from frost, drought, fire, and gales, but I hope these matters will have full attention from scientists in the future.

Real and effective help may be given to forestry by this means.

Conclusion.

Forestry is entitled to every encouragement. Enough has been said as to State encouragement, which should be at least threefold :

1st. The removal of handicaps.
2nd. The prevention of losses.
3rd. The ensuring of a proper return from planting.

Of equal importance is the encouragement of forestry by the individual, including the townsman and even the school children of the rising generation. There is always one effective method of encouraging any industry or pursuit, and that is creating interest and disseminating knowledge.

A national Arbor Day is suggested—a movement very popular and effective in America. Anything that will encourage forestry should be assisted, but whatever steps are taken should be on sound and properly organised lines. It must not lead to haphazard planting and bad results. The most important branch of forestry in the future must be *sylviculture*, and this should be borne in mind in encouraging Arbor Day, or planting of trees in general. Arboriculture and town planting on garden city lines deserves every encouragement, but this must not prejudice proper methods of sylviculture, or the cutting down of timber on proper rotation in State forests.

I mention this only as a timely warning, but I hope that an Arbor Day may be instituted and even war memorials take the shape of planting trees. I think that I can vouch for the co-operation of the Forestry Societies in establishing Arbor Day and secure the assistance of experienced foresters to supervise the actual planting.

What is necessary to put all these forestry matters on a proper footing? *Proper support* of the Forestry Societies, *real encouragement* by the State and by those in authority, and *effective interest* by industrial concerns, urban voters, and the British public.

Mr. J. Hopkinson (Hertfordshire Natural History Society) reminded the Conference that last year, after his address as President, he suggested that an Arbor Day should be instituted. He considered Afforestation to be one of the most important questions that could be brought before them. We were rapidly exhausting our forests; for several years we had been cutting down our trees at an enormous rate. His object in suggesting that this subject should be brought before them again was, that they should pass a resolution in the Conference fixing a day, and pledging themselves, and the members of their societies, as far as they possibly could, each to plant at least one tree on that day. He hoped they would communicate this to their societies, and get them to pass a resolution to the same effect. He suggested the month of October as about the best to plant trees, and we had in that month a very memorable day : the 21st of October (Trafalgar Day). He was of opinion that for the whole of the United Kingdom, Great Britain and Ireland, we could not have a better one. He would go further, and suggest that each of them in their respective locality should communicate with their Parliamentary representative, urging not only that the State should accept it, but that it should be made a National Holiday.

He believed it could be done by very strong pressure. Possibly they might not keep to October 21; but they should keep as close to it as possible. He would move 'That the members of this Conference pledge themselves to the best of their ability to plant one tree at least on an established day and to endeavour to get as many other members of their Society as they can to do the same.'

Sir Charles Bathurst (now Lord Bledisloe) was very glad to second the resolution, which he was sure ought to commend itself to every patriot who realised the position in which we had found ourselves in relation to timber during the war, and the extreme difficulty of repairing within a reasonable time the wastage which the war has occasioned. He hoped that the resolution would not be taken only to refer to those who had large properties or who were carrying on scientific operations—he ventured to hope that it would be made to apply to everyone who owned land of an agricultural character throughout the country, so that this patriotic obligation would rest upon and, he hoped, affect the conscience of, everyone interested in agricultural land. We owed great thanks to Mr. Duchesne for the way in which he had for years past pushed the claims of Forestry. The nation was under a real debt to him for the work which he had so patriotically undertaken. All his prophecies before the war—and he (Sir Charles) had listened to a good many of them—with regard to the subject had been more than fulfilled. But an apathetic public disregarded his warning. Perhaps Mr. Duchesne and he had that much in common, because he had uttered similar jeremiads to deaf ears as to the effect on the country of shortsighted neglect in the matter of the home production of essential foods. As far as anyone could at present foresee, after the war shipping tonnage would be scarce for several years. Unfortunately home-grown timber would be scarcer than ever, although we should be all the more dependent upon home-grown supplies. The gentleman who had just spoken had very properly said that we must increase them. He said that landowners would not plant trees. No; a certain sort would not, and he for his part, as one of them, did not blame them. It was very difficult to induce them to provide any commodities out of which there was not a fair chance of making a reasonable profit. He did not regard timber as having been in the past such a commodity. We must alter all that, or the country would not get timber any more than it could get food without reasonable encouragement and inducement. We must look to the Government, not only to show us how to do it by carrying on timber production commercially on a large scale itself, but also to help those who were prepared to co-operate with it in this national task. He lived on the border of the Forest of Dean; and the past experience there of commercial timber production on the part of the Government was not such as to carry great conviction to the individual landowner who was prepared to do his part in his own generation. In the further course of his remarks, Sir Charles said that there was a great scarcity of timber seed, and asked what was the Government doing to provide this timber seed, to enable landowners to carry out the task that they were asked by the Government to carry out for the next ten or twenty years? They were cutting down in the summer trees which in the autumn might yield some of these seeds. Sir Charles concluded with the observation that he always listened to Mr. Duchesne with increasing interest and increasing conviction, and he looked forward to the time when all landowners, and perhaps the general public also, would realise the enormous importance of the gospel which Mr. Duchesne so effectively preached.

Mr. A. W. Oke (Brighton and Hove Natural History and Philosophical Society) suggested that the names of John Evelyn and William Cobbett should be associated with the subject, and after remarking that everything was going to be done after the war, asked what was going to happen in the case of the insect pests, with the fungi and the other things that were spoiling the trees as they existed now. He did hope that something would be done at once.

Mr. William Dale (Hampshire Field Club and Archæological Society) asked Mr. Duchesne why he had got his knife into the bracken. It made an excellent and exceedingly warm litter; he had also heard that the tops made excellent food; but he had not had the courage to try them.

The President remarked that he had. They were not nice, but they were good.

Mr. **Whitaker** thought it a capital thing that they should have heard an expert on his own particular subject. For himself, he was met with certain difficulties. It seemed to him that some folk wanted to make our country a purely agricultural one. They must allow us other industries. We had got to recollect one thing. England is a very small land and it became a question whether such an insignificant bit could supply all its own needs. If timber is wanted—and it is now—he very much doubted whether we could produce all we wanted. We ought to increase our products; but in the case of some of our timber supplies we cannot, because they do not grow in this country. He agreed with the speaker heartily that care should be taken to treat our trees properly. With reference to an Arbor Day, if he had to plant a tree it must be in his garden. He did not want a tree in his garden; he should cut one down if it were there, unless it were an apple-tree or something of that sort. He thought we should increase our supply of fruit in this country. This Arbor Day seemed to him a little bit of a festival as much as anything else, and he did not see why we should have any more Bank Holidays. Undoubtedly Government should in many instances give a lead, but that Government should take over everything, or heavily subsidise everything, seemed a mistake. He hoped people would be a little more careful about how they called upon us to take up one particular thing and about calling in the Government to help.

The **President** sympathised with Mr. Whitaker's remarks very strongly. Had planting a tree anything to do with the good of the country except sentimentally? The difficulty really came in our suburbs and towns. We had got a large population in our suburbs. Where were we to plant? That was the big difficulty he had been trying to solve for a long time. What we wanted to do was far more to bring pressure to bear upon people to do something practical in the way of High Forest cultivation. Alluding to the devastation of which Mr. Hopkinson had spoken, and to there being no provision as far as he could see for replanting, the President said that, if there was not good reason for it in such cases as this, they might bring such influence as their Societies had to bear, they could get all their members to write to their members of Parliament and make themselves generally unpleasant on the matter. He took it that in Mr. Duchesne's opinion the preservation and collection of seeds was a task on which they might be engaged. If he could give them some practical instructions or suggestions that they might bring before the members of their societies, he would be glad. Insect pests and fungi had been mentioned. Perhaps if some of their members turned more detailed attention to those practical points, they would be doing a service.

Mr. **Bevan** observed that Arbor Day was a practical thing in the United States, and pointed out that it enabled teachers to get the children to help in it and to be receiving instruction by means of it. He thought Mr. Duchesne would have added to the value of his paper if he had included the subject of wood-pulp. As to Government assistance, one should differentiate. He thought this particular matter was a subject on which the Government must come in. If one did not get a reasonable return for forty or fifty years, it was absolutely necessary. There could be no reasonable objection to the Government making a reasonable bargain by lending a certain amount of money on reasonable interest. On the subject of wood-pulp he said that Canada not only exports to the Mother Country a considerable amount of timber and wood-pulp, but to the United States. He was told that the timber from one acre of ground every day was made into wood-pulp for the use of one of the New York papers. There was no question about it that this was one of the most important subjects, and that the Government had been criminally negligent up to the present time.

The **Secretary** (the Selborne Society) supported Mr. Hopkinson. Because there were one or two difficulties mentioned by Mr. Whitaker, he did not see that that was any reason why we should not have an Arbor Day in this country. It would be a very complimentary thing to the United States on Independence Day to do their best to start an Arbor Day. It would give them an opportunity also to send a message of a practical character. If Mr. Whitaker wanted an apple-tree, let him plant an apple-tree on Arbor Day. The resolution only pledged them to the best of their ability. Perhaps the best thing would be to do it collectively, and ask a landowner in the neighbourhood to plant an acre. That would be increasing sylviculture, and it would be a sort of advertisement of High Forestry. He should like to support the motion even if it were to be modified in the carrying out.

The President, before Sir Charles Bathurst left, expressed the thanks of the Conference to him for leaving his 'sweet' duties in order to give them an address.

Sir Charles Bathurst said that it was a real pleasure to him and a real recreation from his 'sweetmeats.'

Mr. Mark Sykes (Manchester Microscopical Society), speaking on Arbor Day, said he did not think it was practical as proposed. Where were they going to get the land, and from whom were they going to get the permission to plant a tree? He did not see how that Conference could pledge its societies or the societies their members. What was wanted was, that the subject should be taken up by the landowners and by the Government; by all the people who had large tracts of land. There should be a systematic laying out of large plots, and a proper system of planting trees suitable to the ground in which they were planted: trees both of commercial and food value. This should be done chiefly by the landed proprietors. They came into properties; it cost nothing to plant trees; the seeds were there in thousands and millions. Land which has borne a forest is land best suited to bear another. There was nothing better than leaves from the trees for the ground; and the ground was already prepared for a future forest.

Mr. Hopkinson thought one objection was already met by his reservation 'to the best of their ability.'

Mr. Duchesne, who felt very much flattered by the length and interest of the discussion, could not agree with Mr. Sykes that there was no cost in planting trees; they found it very costly. From his experience of the forests of Canada, also, he could assure them that it was not correct that new forests sprang up from the old forests. He had been all over the Continent, and in every country their first aim was to get natural production from the seeds. Unfortunately grass and weeds grew up so fast that they smothered the seedlings. Therefore they had to raise trees in the nursery and plant them out.

He was particularly interested in wood-pulp, but there were so many points to deal with, and he had dealt with wood-pulp in a paper read in the early part of the year. Spruce (white deal) could be grown for wood-pulp.

Replying to Mr. Whitaker, who had protested against being urged to do one thing from one quarter and another from another, and as if each thing should be our sole business in life, Mr. Duchesne said that their suggestions as to afforestation did not conflict with any of those for food production, whether it were cereals or fruit. What they suggested was not that the whole of our supply should be grown: it was quite impossible. Obviously, we could not grow mahogany, though there is no other country in the world that can produce so many varieties successfully. But we must create reserves, so that in an emergency we could draw on them as an insurance. The Prime Minister had spoken of the immense quantity of tonnage taken up in the transport of timber to this country.

As to Arbor Day, he was in favour of anything that would encourage interest and educate the people in the country—the children particularly. He supported Arbor Day because he thought it would do a great deal to encourage forestry.

His great wish was that those men sent from the lumber camps in Canada to fell the timber in this country and France, should go back to their own country and take an interest in forestry as well as in lumber.

As to agriculture, he had been connected with it all his life, and was as keen as anyone on it, and he quite agreed with Mr. Whitaker as to the extension of fruit industries in this country, particularly in the growing of apples and such fruit with discretion.

One speaker had referred to John Evelyn and William Cobbett. He had for a text in his last paper an extract from John Evelyn's book, which was of course a classic of Forest Literature—an extract from Evelyn's 'Sylva,' written in 1664 :

'It will appear that we had better be without gold than without timber.'

He wanted bracken destroyed on the areas to be planted, because it came up so thickly that it suppressed their little trees after they had planted them—larch trees, for instance.

Mr. Duchesne dwelt upon the urgent importance of the collection of seeds. He hoped in the coming season to make a larger appeal for the collection of tree seeds, and he would communicate with Mr. Webb and the President, and if the societies in every direction would help them in collecting, full instructions and every assistance would be given in that collection.

The PRESIDENT said, if they could have a supply of the instructions sent, they would be delighted to send them to their societies.

The following resolution was now carried *nem. con.*

> 'That the Delegates present at this Conference pledge themselves to the best of their ability to plant a tree on Arbor Day and to induce all the members of their societies to do the same; and that the suggested day be October 21.'

The SECRETARY then read a note on an exhibit of a Typomap made by Mr. B. B. Woodward, F.L.S., F.G.S.

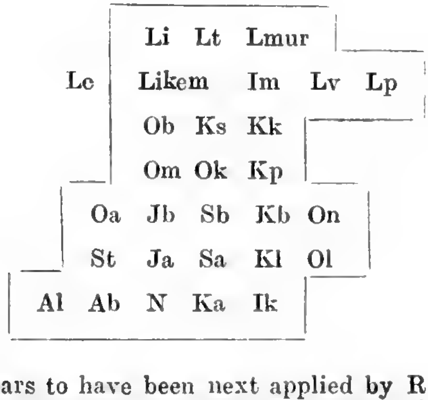
The accompanying Typomap was prepared in connection with the Committee of the British Association appointed 'to formulate a definite system on which collectors should record their captures.' This committee appears to have lapsed without completing its mission.

The object of the map is to enable observers to record occurrences with sufficient approximate geographical accuracy without incurring the expense of specially engraved maps.

When working out the distribution of a given species the observer can take one of these maps and mark those areas in which it occurs in any way that may best suit him. If used in illustrating a printed paper, occurrences can be shown by using heavier type, or printing the area in question in *red* as done in the 'Catalogue of the British Species of *Pisidium*,' published by the Trustees of the British Museum.

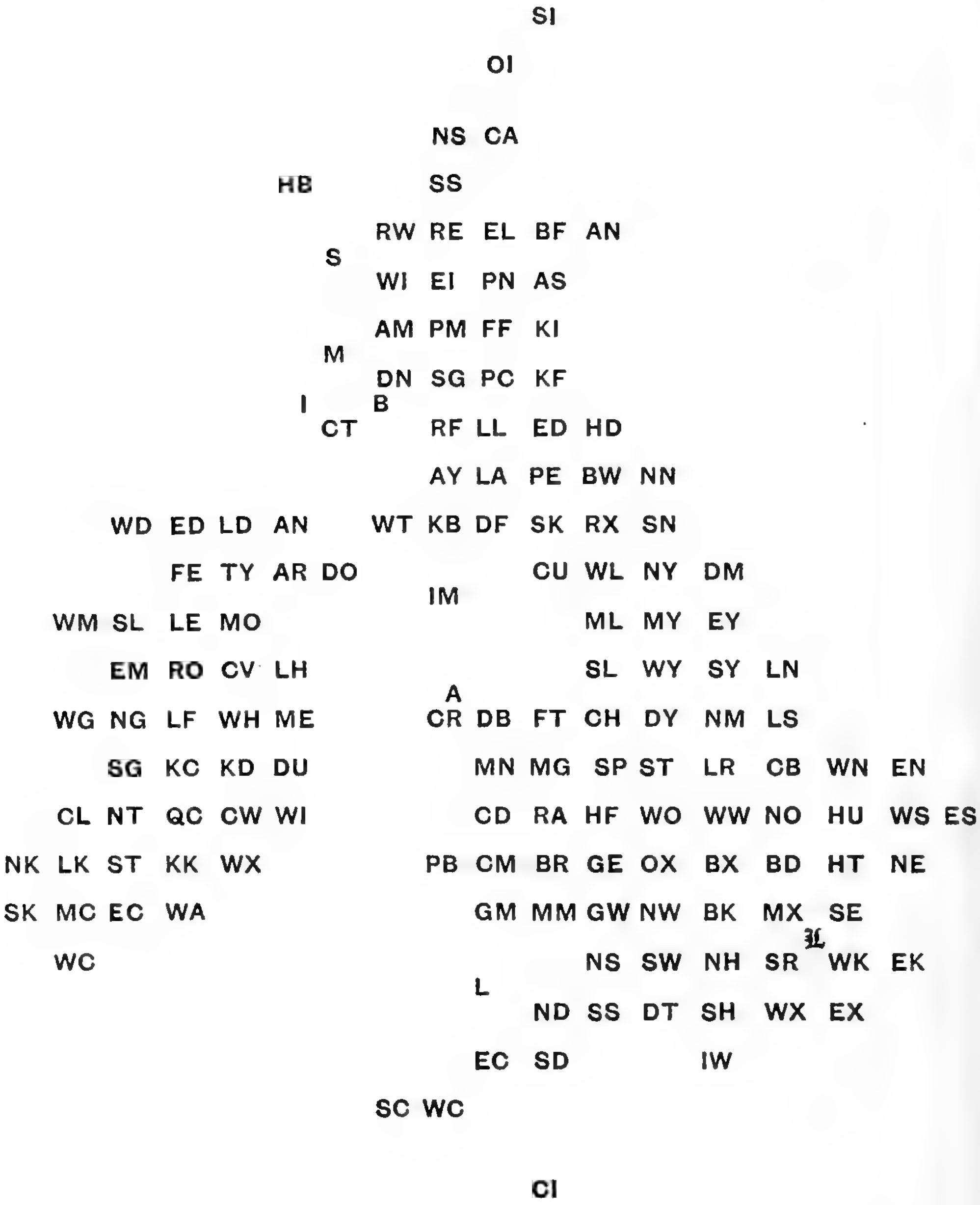
It may be of interest to point out that the first typomap designed was that for Finland utilised in the 'Herbarium Musei Fennici . . . editio secunda. I. Plantæ Vasculares,' 8vo., Helsingfors, 1889, published by the 'Societas pro Fauna et Flora Fennica.'

Being the first of its kind it seems of sufficient interest to be reproduced here.



The principle appears to have been next applied by R. Lloyd Praeger to the case of Ireland (*Irish Naturalist*, xv. 1906, pp. 88-94) with great success. His further attempt in the same article to extend the treatment to the whole of the British Islands was, however, not quite so successful, and the present version was undertaken by myself with the view of obtaining a better total result, the arrangement for Ireland being left undisturbed.

TYPOMAP OF THE BRITISH ISLES.



KEY TO THE SYMBOLS FORMING THE MAP.

A = Anglesey.
AM = Argyll, Main.
AN (Scot.) = Aberdeen, North.
AN (Ire.) = Antrim.
AR = Armagh.
AS = Aberdeen, South.
AY = Ayr.

B = Bute, Arran and Clyde Is.
BD = Beds.
BF = Banff.
BK = Berks.
BR = Brecon.
BW = Berwick.
BX = Bucks.

CA = Caithness.
CB = Cambridge.
CD = Cardigan.
CH = Cheshire.
CI = Channel Is.
CL = Clare.
CM = Carmarthen.
CR = Carnarvon.
CT = Cantire.
CU = Cumberland.
CV = Cavan.
CW = Carlow.

DB = Denbigh.
DF = Dumfries.
DM = Durham.
DN = Dumbarton.
DO = Down.
DT = Dorset.
DU = Dublin.
DY = Derby.

EC (Eng.) = East Cornwall.
EC (Ire.) = East Cork.
ED (Scot.) = Edinburgh.
ED (Ire.) = East Donegal.
EI = East Inverness.
EL = Elgin.
EK = East Kent.
EM = East Mayo.
EN = East Norfolk.
ES = East Suffolk.
EX = East Sussex.
EY = North-east Yorks.

FE = Fermanagh.
FF = Forfar.
FT = Flint.

GE = Gloucester, East.
GM = Glamorgan.
GW = Gloucester, West.

HB = Hebrides.
HD = Haddington.
HF = Hereford.
HT = Herts.
HU = Hunts.

I = Islay, etc. (Ebudes S.).
IM = I. of Man.
IW = I. of Wight.

KB = Kirkcudbright.
KC = King's County.
KD = Kildare.
KF = Kinross+Fife
KI = Kincardine.
KK = Kilkenny.

L = London (Postal District).
L = Lundy I.
LA = Lanark.
LD = Londonderry.
LE = Leitrim.
LF = Longford.
LH = Louth.
LK = Limerick.
LL = Linlithgow.
LN = Lincoln, North.
LR = Leicester+Rutland.
LS = Lincoln, South.

M = Mull, etc. (Ebudes, Mid.).
MC = Mid Cork.
ME = Meath.
MG = Montgomery.
ML = Mid. (or West) Lancs.
MM = Monmouth.
MN = Merioneth.
MO = Monaghan.
MX = Middlesex.
MY = Mid. West Yorks.

ND = North Devon.
NE = North Essex.
NG = North Galway.
NH = North Hants.
NK = North Kerry.
NM = Notts.
NN = North Northumberland.
NO = Northants.
NS (Eng.) = North Somerset.
NS (Scot.) = North (or East) Sutherland.
NT = North Tipperary.
NW = North Wilts.
NY = North-west Yorks.

OI = Orkneys.
OX = Oxford.

PB = Pembroke.
PC = Perth, South (or West) + Clackmannan.
PE = Peebles.
PM = Perth, Mid.
PN = „ North (or East).

QC = Queen's County.

RA = Radnor.
RE = Ross, East.
RF = Renfrew.
RO = Roscommon.
RW = Ross, West.
RX = Roxburgh.

S = I. of Skye, etc. (Ebudes North).
SC = Scilly Is.
SD = South Devon.
SE = South Essex.
SG (Scot.) = Stirling.
SG (Ire.) = South Galway.
SH = South Hants.
SI = Shetlands.
SK (Scot.) = Selkirk.
SK (Ire.) = South Kerry.
SL (Eng.) = South Lancs.
SL (Ire.) = Sligo.
SN = South Northumberland.
SP = Salop.
SR = Surrey.
SS (Eng.) = South Somerset.
SS (Scot.) = South (or West) Sutherland.
ST (Eng.) = Stafford.
ST (Ire.) = South Tipperary.
SW = South Wilts.
SY = South-east Yorks.

TY = Tyrone.

WA = Waterford.
WC (Eng.) = West Cornwall.
WC (Ire.) = West Cork.
WD = West Donegal.
WG = West Galway.
WH = Westmeath.
WI (Scot.) = West Inverness.
WI (Ire.) = Wicklow.
WK = West Kent.
WL = Westmorland.
WM = West Mayo.
WN = West Norfolk.
WO = Worcester.
WS = West Suffolk.
WT = Wigton.
WW = Warwick.
WX (Eng.) = West Sussex.
WX (Ire.) = Wexford.
WY = South-west Yorks.

LIST OF COUNTIES, WITH THEIR SYMBOLS.

ENGLAND.

Beds	BD
Berks	BK
Bucks	BX
Cambridge	CB
Cheshire	CH
Cornwall, East	EC
„ West	WC
Cumberland	CU
Derby	DY
Devon, North	ND
„ South	SD
Dorset	DT
Durham	DM
Essex, North	NE
„ South	SE
Gloucester, East	GE
„ West	GW
Hants, North	NH
„ South	SH
Hereford	HF
Herts	HT
Hunts	HU
Kent, East	EK
„ West	WK
Lancashire, Mid. (or W.)	ML
„ South	SL
Leicester with Rutland	LR
Lincoln, North	LN
„ South	LS
London (Postal District)	𝔏
Middlesex	MX
Monmouth	MM
Norfolk, West	WN
„ East	EN
Northants	NO
Northumberland, North	NN
„ South	SN
Nottingham	NM
Oxford	OX
Rutland. See Leicester.	
Salop	SP
Somerset, North	NS
„ South	SS
Stafford	ST
Suffolk, West	WS
„ East	ES
Surrey	SR
Sussex, East	EX
„ West	WX
Warwick	WW
Westmorland + Lancs., N.	WL
Wilts, North	NW
„ South	SW
Worcester	WO
Yorks, North-west	NY
„ Mid-west	MY
„ North-east	EY
Yorks, South-west	WY
„ South-east	SY

Channel Is.	CI
I. of Man	IM
I. of Wight	IW
Lundy I.	L

WALES.

Anglesey	A
Brecon	BR
Cardigan	CD
Carmarthen	CM
Carnarvon	CR
Denbigh	DB
Flint	FT
Glamorgan	GM
Merioneth	MN
Montgomery	MG
Pembroke	PB
Radnor	RA

SCOTLAND.

Aberdeen, North	AN
„ South	AS
Argyle, Main	AM
Ayr	AY
Banff	BF
Berwick	BW
Caithness	CA
Cantire	CT
Clackmannan. See Perth, South.	
Cromarty. See Ross.	
Dumbarton	DN
Dumfries	DF
Edinburgh	ED
Elgin	EL
Fife. See Kinross.	
Forfar	FF
Haddington	HD
Inverness, E.	EI
„ W.	WI
Kincardine	KI
Kinross + Fife	KF
Kircudbright	KB
Lanark	LA
Linlithgow	LL
Nairn. See East Inverness.	
Orkneys	OI
Peebles	PE
Perth, North (or East)	PN
„ Mid.	PM
„ South (or West), with Clackmannan	PC
Renfrew	RF
Ross with Cromarty, East	RE
„ „ „ West	RW
Roxburgh	RX
Selkirk	SK
Shetlands	SI
Stirling	SG
Sutherland, North (or E.)	NS
„ South (or W.)	SS
Wigton	WT

Hebrides	HB
Skye, &c. (Ebudes, N.)	S
Mull, &c. (Ebudes, Mid.)	M
Islay, &c. (Ebudes, S.)	I
Bute and Clyde Is.	B

IRELAND.

Antrim	AN
Armagh	AR
Carlow	CW
Cavan	CV
Clare	CL
Cork, East	EC
„ Mid.	MC
„ West	WC
Donegal, East	ED
„ West	WD
Down	DO
Dublin	DU
Fermanagh	FE
Galway, West	WG
„ North	NG
„ South	SG
Kerry, North	NK
„ South	SK
Kildare	KD
Kilkenny	KK
King's Co.	KC
Leitrim	LE
Limerick	LK
Londonderry	LD
Longford	LF
Louth	LH
Mayo, East	EM
„ West	WM
Meath	ME
Monaghan	MO
Queen's Co.	QC
Roscommon	RO
Sligo	SL
Tipperary, North	NT
„ South	ST
Tyrone	TY
Waterford	WA
Westmeath	WH
Wexford	WX
Wicklow	WI

SUBDIVISIONS OF COUNTIES.

ENGLAND.

CORNWALL, *East and West:* are separated by the high-road from Truro, through St. Columb to the inland extremity of Padstow Creek.

DEVON, *North and South:* are divided by a line beginning at the Tamar, about midway between Tavistock and Launceston, passing over the ridge of Dartmoor, and joining the western canal at Tiverton.

ESSEX, *North and South:* are divided by the high-road from Waltham and Epping to Chelmsford, and thence by the Rivers Chelmer and Blackwater to the coast.

GLOUCESTER, *East and West:* are separated by the Thames and Severn Canal and the River Severn to Tewkesbury.

HANTS, *North and South:* are separated by the high-roads from Winchester westward to Stockbridge, eastward to Petersfield, and continued thence to the borders of Wilts and Sussex.

KENT, *East and West:* are separated by the River Medway nearly up to Staplehurst, and thence by the high-road through Cranbrooke to the border of Sussex.

LANCASHIRE, *Mid.* (*West* of Watson) *and South:* are divided by the River Ribble. Lancashire to the north-west of Morecambe Bay is united with Westmorland.

LINCOLN, *North and South:* are separated by the River Witham from Boston to Lincoln, thence by the Foss Dyke to the border of Nottinghamshire.

NORFOLK, *East and West:* are divided by the line 1° E. long.

NORTHUMBERLAND, *North and South:* are divided by the River Coquet and a line from the Linn Bridge to Carter Fell.

SOMERSET, *North and South:* are separated by the River Parret, from Bridgewater to Ilchester, and thence round to the northern extremity of Dorset.

SUFFOLK, *East and West:* are divided by the line 1° E. long.

SUSSEX, *East and West:* are divided by a line along the high-road from Brighton to Cuckfield, thence by Crawley to the borders of Surrey.

WILTS, *North and South:* are divided by the Kennet and Avon Canal.

YORK, first divided into East and West Humber, by the Rivers Humber, Ouse, Swale, and Wiske.

S.E. and N.E. Yorks are then separated by the East Riding boundary.

S.W. and Mid.-W. Yorks by the Leeds and Liverpool Canal, and the River Aire below Leeds; and

Mid.-W. and N.W. Yorks by the boundary between the N. and W. Ridings.

SCOTLAND.

ABERDEEN, *North and South:* are separated by the watersheds eastward and westward of Inverury.

ARGYLE, *Main, and Cantire*; are divided by the Crinan Canal.

INVERNESS, *East and West:* are separated by the watershed between east and west Scotland, continued along L. Erricht to the borders of Perthshire. Nairn is included in E. Inverness.

PERTH, *North* (*East* of Watson) *and Mid.:* are divided by the Rivers Garry and Tay.

Mid. and South (*West* of Watson)*:* by the watershed between the Rivers Tay and Forth.

ROSS, *East and West:* are divided by the watershed between the east and west coasts.

SUTHERLAND, *North* (*East* of Watson) *and South* (*West* of Watson)*:* are separated by the watershed.

IRELAND.

CORK, *East and Mid.:* are divided by the railway line from Charleville to Cork, and west shore of Cork Harbour.

Mid. and West: by the Killarney Railway from the Kerry border to Millstreet, thence in straight lines to Macroom and Bandon and the Bandon River.

DONEGAL, *East and West:* are divided by a line separating the baronies of Bannagh, Boylagh, and Kilmacrennan from those of Tirhugh, Raphoe, and Innishowen.

GALWAY, *North and West:* are divided by L. Corrib.

North and South: by the railway from Oranmore to Ballinasloe.

KERRY, *North and South:* are divided by the line separating the baronies of Magunihy and Trughanacmy from those of Glanarought, Dunkerron, Iveragh, and Corkaguiny.

MAYO, *East and West:* are divided by the railway from Ballina to the head of L. Mask.

TIPPERARY, *North and South:* are divided by the line of the watershed.

The SECRETARY next gave a summary in the author's absence of a paper by Mr. Percival Westell on 'Grants to Regional Museums.'

The PRESIDENT did not think they could do more than express their thanks for the paper, and to say that they did not see their way to do anything further in the matter. If anyone should take up the case it should be the Museums Association.

It was agreed to send a copy of the Arbor Day resolution, signed by the President and Secretary, to the United States Minister of Agriculture.

In conclusion the Conference expressed its thanks to its President, and to the Geological Society for its kindness in lending the meeting room.

THE CORRESPONDING SOCIETIES OF THE BRITISH ASSOCIATION FOR 1918–1919.

Affiliated Societies.

Full Title and Date of Foundation	Headquarters or Name and Address of Secretary	No. of Members	Entrance Fee	Annual Subscription	Title and Frequency of Issue of Publications
Andersonian Naturalists' Society, 1885	Royal Technical College, Glasgow. Harry G. Cumming	200	2s. 6d.	2s. 6d.	Annals, occasionally.
Ashmolean Natural History Society of Oxfordshire, 1828	Miss A. L. Stone, 2 St. Margaret's Road, Oxford	260	None	5s.	Proceedings and Report, annually.
Belfast Natural History and Philosophical Society, 1821	Museum, College Square. J. M. Finnigan	200	None	1l. 1s.	'Irish Naturalist,' monthly; Report, annually.
Belfast Naturalists' Field Club, 1863	Museum, College Square	330	5s.	5s.	'Irish Naturalist,' monthly; Report, annually.
Berwickshire Naturalists' Club, 1831	Rev. J. J. M. L. Aiken, B.D., Manse of Ayton, Berwickshire	300	10s.	5s.	History of the Berwickshire Naturalists' Club, annually.
Birmingham and Midland Institute Scientific Society, 1859	H. H. Whitfield, Birmingham and Midland Institute, Paradise Street, Birmingham	108	None	10s. 6d. and 5s.	Records of Meteorological Observations, annually.
Birmingham Natural History and Philosophical Society, 1858	Avebury House, Newhall Street, Birmingham. W. H. Foxall, F.R.G.S.	207	None	1l. 1s.	Proceedings, annually.
Bournemouth Natural Science Society, 1903	R. A. de Paiva, 13 Carysfort Road, Bournemouth	456	None	10s.	Proceedings, annually.
Brighton and Hove Natural History and Philosophical Society, 1854	Henry Cane, 9 Marlborough Place, Brighton	130	None	10s.	Report, annually.
Bristol Naturalists' Society, 1862	Miss Ida M. Roper, F.L.S., 20 Berkeley Square, Bristol	150	5s.	10s. and 5s.	Proceedings, annually.
British Mycological Society, 1896	Carleton Rea, 34 Foregate Street, Worcester	140	None	10s.	Transactions, annually.
Buchan Club, 1887	J. F. Tocher, D.Sc., Crown Mansions, Union Street, Aberdeen	180	5s.	5s.	Transactions, annually.
Burton-on-Trent Natural History and Archæological Society, 1876	A. Slator, D.Sc., 174 Ashby Road, Burton-on-Trent	120	None	6s.	Transactions, occasionally.
Canada, Royal Astronomical Society of, 1884	Royal Canadian Institute, Toronto. W. E. W. Jackson, M.A	550	None	2 dollars	Journal, monthly; Handbook, annually.
Caradoc and Severn Valley Field Club, 1893	H. E. Forrest, 37 Castle Street, Shrewsbury	164	5s.	5s.	Transactions and Record of Bare Facts, annually.
Cardiff Naturalists' Society, 1867	G. D. Shepherd, Gresham Chambers, Kingsway, Cardiff	520	None	12s. 6d.	Transactions, annually.
Chester Society of Natural Science, Literature, and Art, 1871	Grosvenor Museum, Chester. G. P. Miln	850	None	5s. and 2s. 6d.	Report and Proceedings, annually.
Cornwall, Royal Geological Society of, 1814	The Museum, Public Buildings, Penzance. W. H. Pellew.	80	None	1l. 1s.	Transactions, annually.
Cornwall, Royal Institution of, 1818	Henry Jenner, F.S.A., County Museum, Truro	191	None	1l. 1s.	Journal, annually.
Cornwall, Royal Polytechnic Society, 1833	E. W. Newton, Pendarves Road, Camborne, Cornwall	300	None	10s.	Report, annually.
Cotteswold Naturalists' Field Club, 1846	Roland Austin, Public Library, Gloucester	107	1l.	15s.	Proceedings, annually.
Croydon Natural History and Scientific Society, 1870	Public Hall, Croydon. G. W. Moore	109	None	10s., 5s., and 2s. 6d.	Proceedings and Transactions, annually.
Dorset Natural History and Antiquarian Field Club, 1875	Rev. Herbert Pentin, M.A., St. Peter's Vicarage, Portland	400	10s.	10s.	Proceedings, annually.

Affiliated Societies —continued.

Full Title and Date of Foundation	Headquarters or Name and Address of Secretary	No. of Members	Entrance Fee	Annual Subscription	Title and Frequency of Issue of Publications
Dublin Naturalists' Field Club, 1885	Mrs. Long, 4 Palmerston Villas, Upper Rathmines, Dublin	64	5s.	5s	'Irish Naturalist,' monthly; Report, annually.
Dumfriesshire and Galloway Natural History and Antiquarian Society, 1862	James Flett, Ewart Public Library, Dumfries	350	None	5s.	Transactions and Proceedings, annually.
Durham, University of Philosophical Society, 1896	J. A. Smythe and J. W. Bullerwell, Armstrong College, Newcastle-on-Tyne	200	None	10s. and 5s.	Proceedings, half-yearly.
East Anglia, Prehistoric Society of, 1908	W. G. Clarke, 12 St. Philip's Road, Norwich	265	None	5s.	Proceedings, annually.
East Kent Scientific and Natural History Society, 1857	A. Lander, J.P., 17 High Street, Canterbury	60	None	10s. and 5s.	Transactions, annually.
Eastbourne Natural History, Photographic, and Literary Society, 1867	Miss Jay, Technical Institute, Eastbourne	220	2s. 6d.	5s.	Transactions and Journal, quarterly.
Edinburgh Field Naturalists' and Microscopical Society, 1869	Allan A. Pinkerton, 20 George Street, Edinburgh	208	None	5s.	Transactions, annually.
Edinburgh Geological Society, 1834	Synod Hall Buildings, Castle Terrace, Edinburgh. J. J. McBeath	170	10s. 6d.	12s. 6d.	Transactions, annually.
Elgin and Morayshire Literary and Scientific Association, 1836	H. B. Mackintosh, The Museum, Elgin	110	None	5s.	Transactions, occasionally.
Essex Field Club, 1880	Essex Museum of Natural History, Romford Road, Stratford. Percy Thompson, F.L.S.	300	None	15s.	'Essex Naturalist,' half-yearly. Special Memoirs, occasionally.
Glasgow, Geological Society of, 1858	Peter Macnair, F.R.S.E., and H. R. J. Conacher, 207 Bath Street, Glasgow	197	None	10s.	Transactions and Proceedings, annually.
Glasgow, Natural History Society of, 1851	Alex. Ross, 409 Great Western Road, Glasgow	250	None	7s. 6d.	'Glasgow Naturalist,' quarterly.
Glasgow, Royal Philosophical Society of, 1802	Prof. Peter Bennett, 207 Bath Street, Glasgow	1,000	1l. 1s.	1l. 1s.	Proceedings, annually.
Hampshire Field Club and Archæological Society, 1885	W. Dale, F.S.A., F.G.S., The Lawn, Archer's Road, Southampton	250	5s.	10s. 6d.	Proceedings, annually.
Hampstead Scientific Society, 1899	C. O. Bartrum, B.Sc., and R. W. Wylie, M.A., 32 Willoughby Road, Hampstead, N.W.	289	None	Minimum 5s.	Report and Proceedings, annually.
Hertfordshire Natural History Society and Field Club, 1875	John Hopkinson (Librarian), Weetwood, Watford	168	None	10s.	Transactions, one or two parts annually.
Holmesdale Natural History Club, 1857	Mrs. Perrin, Owlpen, Redhill	80	None	10s., 5s., and 3s.	Proceedings, occasionally.
Hull Geological Society, 1889	J. W. Stather, F.G.S., Newland Park, Hull	55	None	5s.	Transactions, occasionally.
Hull Scientific and Field Naturalists' Club, 1886	T. Stainforth, B.A., The Museum, Hull	140	None	5s.	Transactions, annually.
Ipswich and District Field Club, 1903	Miss M. Fletcher, Sproughton, Ipswich	132	None	2s. 6d.	Journal, occasionally.
Ireland, Statistical and Social Inquiry Society of, 1847	W. Lawson, Dr. N. M. Falkiner, and Herbert Wood, 93 Stephen's Green, Dublin	80	None	1l.	Journal, annually.
Leeds Geological Association, 1873	E. Hawkesworth, Cross Gates, Leeds	106	None	5s.	Transactions, occasionally.
Leicester Literary and Philosophical Society, 1835	Corporation Museum. F. B. Lott, 7 Stoneygate Avenue, Leicester	254 Membs. & Associates	None	Members 1l. 1s.; Associates 10s. 6d.	Transactions, annually.
Lincolnshire Naturalists' Union, 1893	Arthur Smith, F.L.S., City and County Museum, Lincoln	110	None	5s.	Transactions, annually.

Liverpool Biological Society, 1886	Prof. Herdman, F.R.S., Zoology Department, The University, Liverpool	80	None	1l. 1s.	Proceedings and Transactions, annually.
Liverpool Botanical Society, 1906	E. Horton, Common Hall, Hackens Hey, Liverpool	123	None	5s.	'Lancashire and Cheshire Naturalist,' usually monthly.
Liverpool Engineering Society, 1875	T. L. Miller (Acting), 325 Royal Liver Buildings, Liverpool	582	None	1l. 1s., 10s. 6d., and 5s.	Transactions and Report, annually.
Liverpool Geographical Society, 1891	A. Ellis Cookson, 5 Hargreave's Buildings, Liverpool	560	None	Members 1l. 1s.; Associates 10s.6d.	Transactions and Report, annually.
Liverpool Geological Society, 1859	T. A. Jones, 27 Rockfield Road, Anfield, Liverpool	85	None	10s. 6d.	Proceedings, annually.
London: Quekett Microscopical Club, 1865	Jas. Burton, 8 Somali Rd., West Hampstead, N.W. 2	450	None	10s.	Journal, half-yearly.
London: Selborne Society, 1885	Avenue Chambers, Bloomsbury Square, W.C. 1. W. M. Webb, F.L.S.	2,000	None	5s.	'Selborne Magazine,' monthly.
Man, Isle of, Natural History and Antiquarian Society, 1879	Miss Margaret Cannell, 118 Buck's Road, Douglas, Isle of Man	296	2s. 6d.	7s. 6d. and 5s.	Proceedings and Transactions, annually.
Manchester Geographical Society, 1884	E. Steinthal and H. Sowerbutts, 16 St. Mary's Parsonage, Manchester	634	None	Members 1l. 1s.; Associates 10s.6d.	Journal, quarterly.
Manchester Geological and Mining Society, 1838	5 John Dalton Street, Manchester. Noah T. Williams	402	None	2l. 2s., 1l. 5s., and 1l.	Transactions of Inst. of Mining Engineers, monthly.
Manchester Microscopical Society, 1880	William Dixon, Broadwater, 43 Pine Road, Didsbury, Manchester	166	5s.	6s.	Transactions and Report, annually.
Manchester Statistical Society, 1833	F. Vernon Hansford, 3 York Street, Manchester	149	10s. 6d.	10s. 6d.	Transactions, annually.
Marlborough College Natural History Society, 1864	J. C. Aisop, M.A., Marlborough College	150	1s. 6d.	3s.	Report, annually.
Midland Counties Institution of Engineers, 1871	G. Alfred Lewis, M.A., Midland Road, Derby	330	1l. 1s.	2l. 2s. and 1l.	Transactions of Institution of Mining Engineers, monthly.
Museum Association, 1889	E. E. Lowe, B.Sc., Museum and Art Gallery, Leicester	Members (Insts.) 117 Associates (Persons) 115	None None	1l. 1s. 10s. 6d.	Museums Journal, monthly. Museums Directory, occasionally.
Norfolk and Norwich Naturalists' Society, 1869	S. H. Long, M.D., 31 Surrey Street, Norwich	283	None	7s. 6d.	Transactions, annually.
North of England Institute of Mining and Mechanical Engineers, 1852	Neville Hall, Newcastle-upon-Tyne. Allan Cordner	1,203	None	2l. 2s. and 1l. 5s.	Transactions of Inst. of Mining Engineers, monthly.
North Staffordshire Field Club, 1865	H V. Thompson, Central Technical School, Stoke-on-Trent	595	5s.	5s.	Transactions and Report, annually.
Northamptonshire Natural History Society and Field Club, 1876	H. N. Dixon, M.A., 17 St. Matthew's Parade, Northampton	210	None	10s.	Journal, quarterly.
Northumberland, Durham, and Newcastle-upon-Tyne, Natural History Society of, 1829	Hancock Museum, Newcastle-on-Tyne. C. E. Robson and J. A. Richardson	389	None	21s.	Transactions, annually.
Nottingham Naturalists' Society, 1852	Prof. J. W. Carr, M.A., University College, Nottingham	100	2s. 6d.	5s.	Report and Transactions, annually.
Paisley Philosophical Institution, 1808	J. Gardner, 3 County Place, Paisley	535	5s.	7s. 6d.	Report and Meteorological Observations, annually.
Perthshire Society of Natural Science, 1867	Tay Street, Perth. S. T. Ellison	310	None	5s. 6d.	Transactions and Proceedings, annually.
Rochdale Literary and Scientific Society, 1878	J. Reginald Ashworth, D.Sc., 55 King Street, South, Rochdale	225	None	6s.	Transactions, biennially.

Affiliated Societies—continued.

Full Title and Date of Foundation	Headquarters or Name and Address of Secretary	No. of Members	Entrance Fee	Annual Subscription	Title and Frequency of Issue of Publications
Rochester Naturalists' Club, 1878	Edmund Page, 42 Balmoral Road, Gillingham, Kent	110	None	5*s.*	'Rochester Naturalist,' quarterly.
Sheffield : Sorby Scientific Society, 1918 (formerly Sheffield Nat. Club)	C. H. Wells, 80 Brookhouse Hill, Sheffield	156	None	5*s.*	Report, bi-annually; Proceedings, occasionally.
Somersetshire Archæological and Natural History Society, 1849	The Castle, Taunton. Rev. F. W. Weaver, C. Tite, and H. St. George Gray	905	10*s.* 6*d.*	Minimum 10*s.* 6*d.*	Proceedings, annually.
South Africa, Royal Society of, 1906	G. M. Clark, South African Museum, Cape Town	207	None	2*l.*	Transactions, occasionally.
South-Eastern Union of Scientific Societies, 1896	H. Norman Gray, 334 Commercial Road, E. 1	about 13,000	None	Minimum 5*s.*	'South-Eastern Naturalist,' annually.
Southport Literary and Philosophical Society, 1880	W. Allanach, B.Sc., Victoria Science and Art Schools, Southport	186	None	7*s.* 6*d.*	Proceedings, occasionally.
South Staffordshire and Warwickshire Institute of Mining Engineers, 1867	G. D. Smith, 3 Newhall Street, Birmingham	150	1*l.* 1*s.* and 10*s.* 6*d.*	2*l.* 2*s.* and 1*l.* 1*s.*	Transactions of Inst. of Mining Engineers, monthly.
Torquay Natural History Society, 1844	Harford J. Lowe, F.G.S., The Museum, Torquay	151	10*s.* 6*d.*	1*l.* 1*s.*	Journal, annually.
Tyneside Geographical Society, 1887	Geographical Institute, St. Mary's Place, Newcastle-on-Tyne. Herbert Shaw, B.A.	1,000	None	1*l.* 1*s.* and 10*s.*	Journal, quarterly.
Vale of Derwent Naturalists' Field Club, 1887	J. E. Patterson, 2 East Avenue, Benton, Newcastle-on-Tyne	150	None	2*s.* 6*d.*	Transactions, occasionally.
Warrington Literary and Philosophical Society, 1870	J. S. Manson, M.D., 14 Bold Street, Warrington	140	None	5*s.*	Proceedings, biennially.
Warwickshire Naturalists' and Archæologists' Field Club, 1854	Museum, Warwick. C. West, Cross Cheaping, Coventry	70	None	5*s.*	Proceedings, annually.
Woolhope Naturalists' Field Club, 1852	W. E. H. Clarke, Cathedral Chambers, King Street, Hereford	200	10*s.*	10*s.*	Transactions, occasionally.
Worcestershire Naturalists' Club, 1847	Education Offices, Worcester. F. T. Spackman, F.G.S.	180	10*s.*	5*s.*	Transactions, annually.
Yorkshire Geological Society, 1837	Albert Gilligan, B.Sc., The University, Leeds	184	None	13*s.*	Proceedings, occasionally.
Yorkshire Naturalists' Union, 1861	The Museum, Hull. T. Sheppard, M.Sc., F.G.S.	380 and 3,050 Associates	None	10*s.* 6*d.*	Transactions, annually; 'The Naturalist,' monthly.
Yorkshire Philosophical Society, 1821	Museum, York. C. E. Elmhirst.	400	None	2*l.*	Report, annually.

Associated Societies.

Balham and District Antiquarian Society, 1897	Miss M. Gardiner, 14A St. James' Road, Wandsworth Common, S.W. 17	65	None	5*s.*	Report, annually; Papers, occasionally.
Barrow Naturalists' Field Club and Literary and Scientific Association, 1876	W. L. Page, 5 Cavendish Street, Barrow	150	None	5*s.* and 2*s.* 6*d.*	Report and Proceedings, annually.
Battersea Field Club, 1894	Public Library, Lavender Hill, Battersea, S.W. 11. Miss L. B. Morris	48	2*s.* 6*d.*	3*s.* 6*d.*	—

Bradford Natural History and Microscopical Society, 1875	Fred. Jowett, Hummondale, Eldwick, Bingley	75	1*s.*	4*s.*	—
Bradford Scientific Association, 1875	W. Newbould, 34 Burnett Avenue, Bradford	120	None	5*s.* and 2*s.* 6*d.*	—
Catford and District Natural History Society, 1897	Thomas Coote, 25 Hawstead Road, Catford, S.E. 6	52	None	5*s.*	—
Dunfermline Naturalists' Society, 1902	Robert Somerville, B.Sc., 31 Cameron Street, Dunfermline	160	None	5*s.*	—
Ealing Scientific and Microscopical Society, 1877	F. McNeil Rushforth, Coley Lodge, 21 Florence Road, Ealing, W. 5	106	None	10*s.* and 2*s.* 6*d.*	Report and Transactions, annually.
Grimsby and District Antiquarian and Naturalists' Society, 1896	The Museum, Grimsby. A. Bullock (Acting Sec.)	60	None	2*s.* 6*d.*	—
Halifax Scientific Society, 1874	J. H. Lumb, 32 Undercliffe Terrace, Halifax	170	None	2*s.* 6*d.*	—
Hastings and St. Leonards Natural History Society, 1893	W. de Muller, B.A., 14 St. Matthew's Gardens, St. Leonards-on-Sea	380	1*s.*	3*s.* 6*d.*	Report, annually. 'Hastings and East Sussex Naturalist,' occasionally.
Hawick Archæological Society, 1856	J. J. Vernon, 81 High Street, Hawick	300	None	2*s.* 6*d.*	Transactions, annually.
Inverness Scientific Society and Field Club, 1875	Thomas Wallace, Ellerslie, Inverness	160	None	5*s.*	Transactions, occasionally.
Lancashire and Cheshire Entomological Society, 1877	Royal Institution, Liverpool. William Mansbridge	90	None	5*s.*	Report and Proceedings, annually.
Leeds Naturalists' Club and Scientific Association, 1868	Edward J. T. Ingle, 18 Strattan Street, Leeds	100	None	5*s.* and 3*s.* 6*d.*	Proceedings, occasionally.
Letchworth and District Naturalists' Society, 1908	W. Percival Westell, F.L.S., The Museum, Town Square, Letchworth	260	None	2*s.* 6*d.*	—
Lewisham Antiquarian Society, 1885	J. W. Brookes, Pembroke Lodge, Slaithwaite Road, Lewisham, S.E.	73	None	5*s.*	Transactions, occasionally.
Liverpool Microscopical Society, 1868	Royal Institution, Liverpool. R. Croston	63	None	10*s.* 6*d.*	Report, annually.
Llandudno and District Field Club, 1906	L. S. Underwood, Brinkburn, Llandudno	107	None	5*s.*	Proceedings, annually.
London: London Natural History Society, 1913	J. Ross, 18 Queen's Grove Road, Chingford, E. 4.	200 Members and Assoc.	2*s.* 6*d.*	7*s.* 6*d.* and 5*s.*	Transactions, annually.
London: South London Entomological and Natural History Society, 1872	Stanley Edwards, F.L.S., 15 St. German's Place, Blackheath, S.E. 3	180	2*s.* 6*d.*	10*s.*	Proceedings, annually.
Maidstone and Mid-Kent Natural History and Philosophical Society, 1868	Maidstone Museum. A. Barton and J. W. Bridge	61	None	10*s.*	Report, occasionally.
Newcastle-upon-Tyne, Literary and Philosophical Society of, 1793	Newcastle-upon-Tyne. Alfred Holmes	2,961	None	1*l.* 1*s.*	Report, annually; Lectures occasionally.
Preston Scientific Society, 1893	Lecture Hall, 119A Fishergate, Preston. F. Chadderton	400	None	5*s.*	Papers, occasionally.
Scarborough Philosophical and Archæological Society, 1828	A. J. Burnley, 43 Moorland Road, Scarborough	80	None	1*l.* and 10*s.*	Report, annually.
School Nature Study Union, 1903	H. E. Turner, 1 Grosvenor Park, Camberwell, S.E.	1,350	None	2*s.* 6*d.*	'School Nature Study,' quarterly.
Southport Society of Natural Science, 1890	P. H. Christian, 9 Russell Road, Southport	168	None	5*s.*	Report, biennially.
Teign Naturalists' Field Club, 1858	John S. Amery, Druid, Ashburton, Devon	120	None	2*s.* 6*d.*	Report, annually.
Tunbridge Wells Natural History and Philosophical Society, 1884	Dr. D. Davies, 8 Lonsdale Gardens, Tunbridge Wells	95	None	10*s.* 6*d.* and 5*s.*	Report, annually.
Warrington Society, 1898	The Old Academy, Bridge Foot, Warrington. James Richardson	103	10*s.* 6*d.*	1*l.* 11*s.* 6*d.*	Report, annually.
Watford Camera Club and Photographic Society, 1902	A. Dain, 100 High Street, Watford	50	None	—	—
Wimbledon Natural History Society, 1911	Charles H. Tame, 12 Kenwyn Road, S.W. 19	120	None	1*s.*	—

Catalogue of the more important Papers, especially those referring to Local Scientific Investigations, published by the Corresponding Societies during the year ending May 31, 1918.

⁂ This Catalogue contains only the titles of papers published in the volumes or parts of the publications of the Corresponding Societies sent to the Secretary of the Committee in accordance with Rule 2.

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Colloid Chemistry and its General and Industrial Applications.— Second Report of the Committee, consisting of Professor F. G. DONNAN (*Chairman*), Professor W. C. MCC. LEWIS (*Secretary*), Dr. E. F. ARMSTRONG, Professor ADRIAN J. BROWN, Dr. C. H. DESCH, Mr. E. HATSCHEK, Professors H. R. PROCTER and W. RAMSDEN, Mr. A. S. SHORTER, Dr. H. P. STEVENS, *and* Mr. H. B. STOCKS.

INTRODUCTION.

THE plan already adopted of arranging the subject-matter under two heads, viz. (1), classification according to scientific subject, and (2), classification according to industrial process and general application of colloid chemistry to other sciences, has been employed in the preparation of the Second Report.

The subjects dealt with under the first head in the accompanying Report are :—

1. Peptisation and Precipitation.
2. Emulsions.
3. The Liesegang Phenomenon.
4. Electrical Endosmose, Part I.

The subjects dealt with under the second head are :—

1. Electrical Endosmose, Part II.
2. Colloid Chemistry in the Textile Industries.
3. Colloids in Agriculture.
4. Sewage Purification.
5. Dairy Chemistry.
6. Colloid Chemistry in Physiology.
7. Administration of Colloids in Disease.

The Committee has again to express its deep sense of obligation to the gentlemen who under somewhat difficult circumstances have compiled the various sections which make up the present Report.

It is hoped that the very valuable material which has now been collected in the First and Second Reports will serve the purpose of emphasising the fundamental importance of colloid chemistry for operations and processes which, at first sight, appear to be wholly distinct, and at the same time will serve to co-ordinate such information and to render it available for the benefit of all who are engaged in operations in which colloid chemistry plays a part.

A number of subjects have not as yet been considered. It is hoped that these will be discussed in the Third Report. In this connection the Secretary (*Muspratt Laboratory, University, Liverpool*) would be glad of suggestions from those engaged in chemical industry regarding subjects or problems met with in technical work which could be considered as coming within the scope of the Committee's activities. It is felt that such co-operation, which at the present time would be particularly valuable, is not impossible.

(20895.) Wt. 36589—540. 2750. 1/19. D & S. G. 2.

REPORT ON PEPTISATION AND PRECIPITATION.

By Professor WILDER D. BANCROFT, *Cornell University.*

Sufficiently small particles will be kept in suspension in a liquid by the Brownian movements. Any method which will form small particles and will keep them from coalescing will give rise to colloidal solutions. Tentative theories of peptisation have been discussed by Lottermoser,[1] Jordis,[2] Mecklenburg,[3] and von Weimarn.[4] If we adopt Freundlich's view[5] that adsorption always lowers the surface tension, a theory of peptisation follows at once,[6] because an adsorbed film with a low surface tension on the solvent side and a high one on the other side will tend to disintegrate or peptise the other substance as internal phase.

When a liquid is adsorbed by a solid, it will tend to peptise it and in some cases will do so. Water peptises tannin readily and amyl acetate peptises pyroxylin. At higher temperatures the peptising action increases. Gelatine is peptised by warm and not by cold water. Glass is peptised by hot water[7] and vulcanised rubber by various heated organic liquids,[8] while fused baths peptise metals.[9]

There are a number of cases where mixed solvents will peptise a solid much better than either one alone—celluloid nitrate in ether and alcohol, caseine in pyridine and water,[10] and probably cinchonine in chloroform and alcohol,[11] as well as phloretine in ether and water.[12] The theory of this has not been worked out. Cellulose nitrate swells in alcohol and not in ether;[13] but it is not known whether this is universal or whether alcohol peptises cellulose nitrate at higher temperatures. Zein is also peptised in mixed solvents.[14]

Relatively little work has been done on direct peptisation by means of a dissolved non-electrolyte, but a good deal of stress has been laid on the cases where a non-electrolyte prevents the formation of a visible precipitate. A concentrated solution of sugar in water will prevent the precipitation of calcium silicate,[15] silver chromate, and silver chloride;[16] also of lime and of the hydrous oxides of copper,[17] uranium, and iron.[18] Invert sugar is about seven times as effective as cane sugar in holding up hydrous ferric oxide.

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[1] Lottermoser, *Jour. prakt. Chem.* (2) **68**, 341 (1903); **72**, 39 (1905); **73**, 374 (1906); *Zeit. phys. Chem.* **62**, 371 (1908).

[2] Jordis, *Van Bemmelen Gedenkboek*, 215.

[3] *Zeit. anorg. Chem.* **74**, 260 (1912).

[4] *Lehre von den Zuständen der Materie*, **1**, 60 (1914).

[5] *Kapillarchemie*, **52**, 154 (1909); Patrick, *Zeit. phys. Chem.* **86**, 545 (1914).

[6] Bancroft, *Jour. phys. Chem.* **70**, 85 (1916).

[7] Barus, *Am. Jour. Sci.* (3) **41**, 110 (1891); (4) **6**, 270 (1898); **7**, 1 (1899); *Phil Mag.* (5) **47**, 104, 461 (1899).

[8] Barus, *Am. Jour. Sci.* (3) **42**, 359 (1891).

[9] Lorenz, *Van Bemmelen Gedenkboek.* 395.

[10] Levites, *Zeit. Kolloidchemie*, **8**, 4 (1911).

[11] Oudemanns, *Jour. Chem. Soc.* **26**, 533 (1873).

[12] Schiff, *Zeit. phys. Chem.* **23**, 355 (1897).

[13] Private Communication from Professor Chamot.

[14] Galeotto and Giampalmo, *Zeit. Kolloidchemie*, **3**, 118 (1908).

[15] Weisberg, *Bull. Soc. Chem.* Paris (3), **15**, 1097 (1896).

[16] Lobry de Bruyn, *Ber. deutsch. Chem. Ges.* **35**, 3079 (1902).

[17] Graham, *Jour. Chem. Soc.* **15**, 253 (1862).

[18] Riffard, *Comptes rendus*, **77**, 1103 (1873).

Grimaux[19] showed that glycerine prevents the precipitation of hydrous ferric oxide by caustic potash.

If one ion of an electrolyte is adsorbed more than the other ion, it will tend to peptise the adsorbing material and to give rise to a colloidal solution containing positively or negatively charged particles according to the nature of the adsorbed ion. Univalent ions are not all adsorbed alike ; nor are bivalent or trivalent ions. The order of adsorption is specific with each substance. Certain univalent ions are adsorbed by certain substances more than certain bivalent or trivalent ions.[20] In many cases there is, however, a marked tendency to increased adsorption with increasing valence, as formulated in Schulze's so-called law.[21] It seems to be a general rule that insoluble electrolytes adsorb their own ions markedly. Consequently, a soluble salt having an ion in common with a sparingly soluble electrolyte will tend to peptise the latter.

Freshly precipitated silver halides are peptised by dilute silver nitrate or the corresponding potassium halide,[22] the silver and the halide ions being adsorbed strongly. Many oxides are peptised by their chlorides or nitrates, forming so-called basic salts.[23] Sulphides are peptised by hydrogen sulphide.[24] Gelatine is liquefied or peptised by a potassiun iodide solution. The peptisation of hydrous oxides by caustic alkali can be considered as a case of common ion or as the preferential adsorption of hydroxyl ion.[25] Hydrous chromic oxide gives an apparently clear green solution when treated with an excess of caustic potash ; but the green oxide can be filtered out completely by means of a collodion filter, a colourless solution passing through.[26] Hantzsch[27] considers that hydrous beryllium oxide is peptised by caustic alkali, copper oxide is peptised by concentrated alkali,[28] and so is cobalt oxide.[29] In ammoniacal copper solutions part of the copper oxide is apparently colloidal and part is dissolved.[30] Freshly precipitated zinc hydroxide is peptised by alkali ; but the solution is very instable, the zinc hydroxide often coagulating inside of half an hour.

The relatively small amount of zinc remaining in solution is present chiefly or entirely as sodium zincate.[31] The bulk of the

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[19] *Comptes rendus*, **98**, 1485, 1540 (1884).

[20] Bancroft, *Jour. Phys. Chem.* **19**, 363 (1915).

[21] Schulze, *Jour. prakt. Chem.* (2), **25**, 431 (1882) ; **27**, 320 (1884).

[22] Lottermoser, *Jour. prakt. Chem.* (2) **60**, 341 (1903) ; **72**, 39 (1905) ; **73**, 374 (1906) *Zeit. phys. Chem.* **62**, 371 (1908).

[23] Müller, *Ber. deutsch. chem. Ges.* **39**, 2856 (1906) ; *Zeit. anorg. Chem.* **52**, 316 (1907). Szilard, *Jour. Chim. phys.* **5**, 488, 636 (1907). Graham, *Jour. Chem. Soc.* **15**, 254 (1862).

[24] Spring, *Ber. deutsch. chem. Ges.* **16**, 1142 (1883). Prost, *Jour. Chem. Soc.* **54**, 653 (1888). Winssinger, *Bull. Soc. chim.* Paris (3) **49**, 452 (1888). Linder and Picton, *Jour. Chem. Soc.* **61**, 116 (1892). Meunier, *Comptes rendus*, **124**, 1151 (1897). Young, *Jour. Phys. Chem.* **21**, 1, 14 (1917).

[25] Bancroft, *Jour. Phys. Chem.* **20**, 99 (1916).

[26] Fischer and Herz, *Zeit. anorg. Chem.* **31**, 352 (1902). Fischer, *Zeit. anorg. Chem.* **40**, 39 (1904). Nagel, *Jour. Phys. Chem.* **19**, 331, 569 (1915).

[27] *Zeit. anorg. Chem.* **30**, 289 (1902).

[28] Loew, *Zeit. anal. Chem.* **8**, 463 (1870). Fischer, *Zeit. anorg. Chem.* **40**, 39 (1904).

[29] Tubandt, *Zeit. anorg. Chem.* **45**, 368 (1905).

[30] Peligot, *Ann. Chim. Phys.* (3) **63**, 343 (1861). Guignet, *Comptes rendus*, **55**, 741 (1862). Grimaux, *Comptes rendus*, **98**, 1434 (1884).

[31] Hantzsch, *Zeit. anorg. Chem.* **30**, 289 (1902) ; **75**, 371 (1912) ; Fischer and Herz, *Zeit. anorg. Chem.* **31**, 352 (1902) ; Klein, *Zeit. anorg. Chem.* **74**, 157 (1912).

evidence seems to be that alumina is not peptised appreciably by alkali and that it goes into solution as sodium aluminate,[32] though the other view has been supported.[33] Adsorption of hydroxyl ion accounts for the peptisation of silicic acid[34] and caseine by alkalies. Caseine can also be peptised by acids. A. Müller[35] has prepared colloidal solutions of aluminum, iron, cobalt, thorium, and yttrium oxides by peptisation with dilute hydrochloric acid, and Bentley and Rose[36] have peptised freshly precipitated alumina with 8 per cent. acetic acid. It is possible, but not probable, that the peptisation is done by a trace of metallic salt formed by the acid and not by the hydrogen ion.

There are no cases where it has been shown conclusively that peptisation is due chiefly to adsorption of undissociated salt, but undoubtedly such instances will be found. Water-peptisable colloids like gelatin,[37] gum arabic,[38] dextrine,[39] soap,[40] or saponine,[41] will peptise many precipitates, and they are often called protecting colloids, because they prevent the agglomeration and consequent settling of finely divided precipitates. Caseine is not peptised by water. but acts a protecting colloid when peptised by acids or alkalies; Hydrous chromic oxide when peptised by caustic potash can then prevent the precipitation of hydrous ferric oxide &c. If too much ferric oxide is present, all the chromic oxide is carried down by it.[42]

Solutions of copper oxide in ammonia will peptise chromic oxide. [43]Molybdic acid is not precipitated from its salts by uranyl salts, but tungstic acid is. In presence of tungstic acid, practically all the molybdic acid is precipitated. This is obviously a case of adsorption and the converse is undoubtedly true that no tungstic acid would be precipitated in presence of a sufficient excess of a molybdate.[44] Aniline dyes, which are insoluble in benzene, can be peptised by a benzene-soluble colloid such as the so-called zinc or magnesium resinate.[45]

Since a colloidal solution is one in which a finely divided phase is kept from coalescing in some way, it is clear that there may be any number of colloidal aluminas, for instance, varying from anhydrous

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[32] Herz, *Zeit. anorg. Chem.* **25**, 155 (1900). Hantzsch, *Zeit. anorg. Chem.* **30**, 289 (1902). Rubenbauer, *Zeit. anorg. Chem.* **30**, 331 (1902). Fischer and Herz, *Zeit. anorg. Chem.* **31**, 355 (1902). Slade, *Jour. Chem. Soc.* **93**, 421 (1908); *Zeit. anorg. Chem.* **77**, 457 (1912); *Trans. Faraday Soc.*, **10**, 150 (1914). Blum, *Jour. Am. Chem. Soc.* **35**, 1499 (1913).

[33] Mahin, Ingraham and Stewart, *Jour. Am. Chem. Soc.* **35**, 30 (1913).

[34] Graham, *Jour. Chem. Soc.* **17**, 324 (1864).

[35] Svedberg, *Die Methoden zur Herstellung kolloider Lösungen anorganischer Stoffe*, 400 (1909).

[36] *Jour. Am. Chem. Soc.* **35**, 1490 (1913).

[37] Eder's *Handbuch der Photographie*, 5th Ed. **3**, I, 28 (1902). Lüppo-Cramer. *Phot. Correspondenz*, **44**, 578 (1907).

[38] Lefort and Thibault, *Jour. Chem. Soc.* **42**, 1322 (1882).

[39] Lachaud, *Bull. Soc. Chim. Paris* (3) **15**, 1105 (1896).

[40] Spring, *Zeit. Kolloidchemie* **4**, 161 (1909); **6**, 11, 109, 164 (1910).

[41] Schiaparelli, *Jour. Chem. Soc.* **46**, 333 (1884).

[42] Northcote and Church, *Jour. Chem. Soc.* **6**, 54 (1854); Nagel, *Jour. Phys. Chem.* **19**, 331 (1915).

[43] Prud'homme, *Jour. Chem. Soc.* **25**, 672 (1872).

[44] Miss Hitchcock, *Jour. Am. Chem. Soc.* **17**, 483, 520 (1895); Wöhler. *Zeit. Elektrochemie*, **16**, 693 (1910).

[45] Soxhlet, *Art of Dyeing and Staining Marble, &c.* 76 (1902).

alumina (Al_2O_3) up to the most highly hydrous form that can be obtained. As a matter of fact, people have generally been satisfied with distinguishing only two sets of colloidal solutions, which they have called solutions of alumina and metalumina, stannic and metastannic acids, &c.[46] While adsorption will cause peptisation under suitable conditions, the disintegrating power of the adsorbed substance is relatively small and often is not sufficient to break up solid masses. A protecting colloid, for instance, will prevent the formation of a precipitate when it may not be able to disintegrate a massive precipitate.

The preparation of colloidal solutions by peptisation is usually classed under the general head of dispersion methods. Five different types may be distinguished :—

1. *Removal of Agglomerating Agent.*—If a precipitate has settled from a colloidal solution owing to the addition of too much of an agglomerating agent, the precipitate may go back into apparent solution if the excess of agglomerating agent is washed out. No colloidal solution will be obtained if it is impossible to wash out the coagulating agent or if the agglomeration has gone too far.[47] If a silver halide precipitate is washed on a filter at once, the silver salt is apt to run through the filter when the excess of potassium salt has been removed and there is present only the amount which would have kept the silver halide in suspension originally. When the rare earth nitrates are precipitated by ammonia and then washed, they are liable to stay suspended in the liquid when the ammonium nitrate is nearly all removed. In alloy work stannic oxide should be washed with dilute nitric acid and not with water. Zinc sulphide is apt to form a colloidal solution when the ammonium salt is washed out,[48] and copper ferrocyanide does the same thing if all the copper sulphate is removed by washing.[49] In fact, Chautard[50] claims that the quickest way to wash a gelatinous precipitate is to evaporate the solution to dryness and heat before trying to wash. Merely evaporating on a water-bath is not always sufficient.[51]

2. *Addition of Peptising Agent.*—Instead of washing out a precipitating agent, a peptising agent may be added. Ammonia is very effective in suspending clay,[52] silicic acid is peptised readily by caustic soda,[53] and Prussian blue is peptised by oxalic acid or by potassium oxalate. In some cases the concentration of the peptising agent has to be high, as when oxides are peptised by alkali, and people usually assume the formation of compounds.

The action of soap on rouge or carbon black[54] looks like a disintegration ; but it is not. If a suspension of carbon black in water

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[46] Hantzsch, *Zeit. anorg. Chem.* **30**, 338 (1902) ; Bancroft, *Jour. Phys. Chem.* **19**, 232 (1915).

[47] Cf. Abegg and Schroeder, *Zeit. Kolloidchemie*, **2**, 85 (1907).

[48] Donnini, *Jour. Chem. Soc.* **66** II. 318 (1894).

[49] Berkeley and Hartley, *Phil. Trans.* **206** A, 486 (1906).

[50] *Jour. Chem. Soc.* **26**, 527 (1873).

[51] Wright, *Ibid.* **43**, 156 (1883) ; Kratz : *Jour. Phys. Chem.* **16**, 121 (1912).

[52] Skey, *Chem. News*, **17**, 164 (1868) ; **22**, 236 (1870) ; **34**, 142 (1876) ; see also Doelter, *Handbuch der Mineralchemie*, **2**, 122 (1912).

[53] Graham, *Jour. Chem. Soc.* **17**, 324 (1864).

[54] Spring, *Zeit. Kolloidchemie*, **4**, 161 (1909) ; **6**, 11, 109, 164 (1909). Bancroft, *Jour Phys. Chem.* **20**, 107 (1916).

be filtered several times through filter-paper, the water will finally run through clear, and the carbon black will be held back by the filter-paper. If a soap solution be poured on the filter, a black filtrate is obtained and the filter-paper is no longer black. All the carbon black has passed through the filter paper. The same thing can be done with rouge, except that a red filtrate is obtained instead of a black one. At first sight it seems that though the soap must have broken up the carbon or the rouge into finer particles, which then passed through the filter, but this is probably not so. The filter-paper is porous enough at first to let through the particles of carbon or rouge, as is shown by the fact that some of the suspended matter does pass through the filter at first. The cellulose adsorbs the carbon black or the rouge, and this clogs the filter to such an extent that the pores are not large enough to let the remaining particles through. The soap removes the rouge or the carbon black from the paper because it adsorbs these substances more strongly, and everything, therefore, goes through the paper. That this is the true explanation can be shown in two ways. In the first place, the experiment does not succeed if the rouge or the carbon is two coarse. In the second place, Spring showed that we are dealing with an adsorption of carbon black by filter-paper. If the black filter-paper be reversed and washed with water, the water removes only the black which is not in immediate contact with the paper.

3. *Mechanical Disintegration.*—If a solid be ground sufficiently fine, it will necessarily form a colloidal solution for a time. This has been done experimentally by Wegelin[55] in the case of a number of metals. The addition of gelatin makes it easier to disintegrate ductile metals. Since a finely divided solid is more soluble, it is possible that it may go into solution and then precipitate in another form. This seems to happen with quartz. When reduced to an impalpable powder by long grinding, quartz can be converted into colloidal hydrous silicic acid merely by boiling with water.[56]

4. *Electrical Disintegration.*—When a direct current arc is formed under water between two wires, the metal is disintegrated and colloidal solutions of platinum, iridium, palladium, gold, silver, and cadmium may be obtained in this way.[57] Satisfactory conditions are obtained with 30 to 40 volts and 5 to 10 amperes. A trace of alkali in the water causes formation of finer particles, presumably owing to the stabilising effect of the hydroxyl ion. The disintegration is chiefly at the cathode.

The method is not satisfactory with organic liquids, because two much decomposition of the liquids takes place. Svedberg found empirically that this decomposition could be decreased very much if the current density were made as small as possible.[58] He therefore used an oscillatory discharge from an induction coil with a condenser in parallel or in series. The best results are obtained with large capacity, small self-induction, low resistance, and short

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[55] *Zeit. Kolloidchemie*, **14**, 65 (1914).
[56] Desch, *The Chemistry and Testing of Cement*, 58 (1911).
[57] Bredig, *Zeit. Elektrochemie*, **4**, 514 (1898) ; *Zeit. Phys. Chem.* **31**, 258 (1899).
[58] Svedberg, 424.

arc. By this improved method Svedberg succeeded in preparing colloidal solutions of all the metals, including the alkali metals. Liquid methane, ether and isobutyl alcohol at low temperature were especially satisfactory with the metals of the alkalies and the alkaline earths. The order of disintegration of some of the metals under similar conditions was found to be Fe, Cu, Ag, Al, Ca, Pt, Au, Zn, Sn, Cd, Sb, Tl, Bi, Pb, the iron being the least rapidly disintegrated and the lead the most rapidly disintegrated. There is no apparent relation either with the order of the boiling-points or with the order of disintegration by cathode rays or canal rays.

5. *Electrochemical Disintegration.*—With a lead cathode in caustic soda solution, the lead disintegrates when the current density exceeds a critical value, and the solution is coloured black like ink, with fine particles of metallic lead.[59] This is due to the temporary formation of a sodium-lead alloy, which then disintegrates in contact with water. Similar results can be obtained with cathodes of tin, bismuth, thallium, arsenic, antimony, and mercury. E. Müller[60] obtained colloidal solutions of tellurium with a tellurium cathode. This seems to be due to the formation of polytellurides, which break down and set free tellurium. In the presence of oxygen there may also be an oxidation of a telluride. Fischer[61] has obtained metallic copper in the solution by using a high current density with a copper anode in sulphuric acid. Cuprous sulphate is formed, which breaks down to metallic copper and cupric sulphate. This experiment has not yet been made to give colloidal copper ; but this could probably be done if one were to add a suitable protecting colloid. The disintegration of all electrodes by an alternating current when the current density is high is undoubtedly due to the temporary formation and subsequent breaking down of a hydrogen or metallic alloy.

Three classes of colloidal solutions have been distinguished, in which the stabilisation is due : to adsorbed liquid ; to adsorbed non-electrolyte, which may be in true solution or may be itself in colloidal solution ; and to an adsorbed ion. The last case is the easiest one to treat theoretically and is therefore taken up first. So long as the particles are all charged positively or all charged negatively, they will repel each other and will not coalesce. If the charge is neutralised or counter-balanced in any way, the particles will agglomerate[62] unless some other factor comes in. If a suspension is stabilised by the preferential adsorption of hydrogen ion from hydrochloric acid solution, the solution contains free hydrogen ions, free chlorine ions, and the adsorbed hydrogen ions which make the suspension behave like a cation though with a different migration velocity from that of hydrogen. If the suspension is made to adsorb an anion in an amount equivalent to the hydrogen ion adsorbed, the

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[59] Reed, *Jour. Franklin Inst.* **139**, 283 (1895).
Bredig and Haber, *Ber. deutsche. Chem. Ges.* **31**, 2741 (1898).
Haber and Sack, *Zeit. Elektrochemie* **8**, 245 (1902) ; *Zeit. Anorg. Chem.* **34**, 286 (1903).

[60] *Zeit. Elektrochemie* **11**, 521, 701 (1905).
Haber, *Ibid.* **11**, 660, 827 (1905).

[61] *Ibid.* **9**, 507 (1903).

[62] Hardy, *Zeit. Phys. Chem.*, **33**, 385 (1900). Burton, *Phil. Mag.* (6), **12**, 472 (1906) ; **17**, 583 (1909).

suspended particles will be electrically neutral. This can be done by adding an electrolyte with a readily adsorbed anion. Since this is a matter of selective adsorption, the concentration of the added anion necessary to cause an adsorption equivalent to the hydrogen adsorption will vary with each anion. To put the matter more generally, the amount of an electrolyte necessary to precipitate a colloidal solution will vary with the nature of the cation, the anion, and the dispersed phase. While it is generally true that an ion of higher valance will be adsorbed more strongly than one of lower valence, this so-called law of Schulze[63] is only a first approximation and should be considered only as a guide.

That some univalent ions are absorbed more strongly by some substances than some bivalent or trivalent ions is shown clearly in data by Odén on colloidal sulphur[64], given in Table I. In the second column are the liminal concentrations necessary to coagulate the sulphur, given in gram atoms per litre of the cations; in the third column are given the reciprocals of those values, the so-called atomic precipitating powers.

TABLE I.

Coagulation of Sulphur at 18°–20°.

Salt.	Liminal value gram-atoms Cations per litre.	Atomic precipitating power of cation.
HCl	6	0·16
LiCl	0·913	1·1
NH_4Cl	0·435	2·3
$(NH_4)_2SO_4$	0·600	1·7
NH_4NO_3	0·506	2·0
NaCl	0·153	6·1
Na_2SO_4	0·176	5·7
$NaNO_3$	0·163	6·1
KCl	0·021	47·5
K_2SO_4	0·025	39·7
KNO_3	0·022	45·5
RbCl	0·016	63
CsCl	0·009	108
$MgSO_4$	0·0093	107·5
$Mg\ NO_3)_2$	0·0080	125
$CaCl_2$	0·0041	245
$Ca(NO_3)_2$	0·0040	247
$Sr(NO_3)_2$	0·0025	385
$BaCl_2$	0·0021	475
$Ba(NO_3)_2$	0·0022	461
$ZnSO_4$	0·0756	13·2
$Cd(NO_3)_2$	0·0493	20·3
$AlCl_3$	0·0044	227
$CuSO_4$	0·0098	102
$Mn(NO_3)_2$	0·0096	105
$Ni(NO_3)_2$	0·0446	22·4
$UO_2(NO_3)_2$	0·0137	73

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[63] *Jour. Prakt. Chem.* (2), **25**, 431 (1882); **27**, 320 (1884). Bancroft, *Jour. Phys. Chem.*, **19**, 364 (1915).

[64] *Der Kolloide Schwefel*, 156 (1912).

Under the conditions of Odén's experiments, sulphur is a negative colloid, and the precipitation is therefore due to an adsorption of cations. The first thing to be noticed is that hydrogen ion is not adsorbed strongly by sulphur, the precipitating power of hydrochloric acid being much less than that of lithium, ammonium, sodium, potassium, rubidium, or cæsium chloride. Instead of these univalent cations precipitating at the same concentration, the required concentration of lithium chloride is, in round numbers, one hundred times that of cæsium chloride. The liminal values for barium and strontium are nearly equal, but calcium chloride requires a distinctly higher concentration. If we take the different bivalent ions the values range from 0·0756 for zinc to 0·0022 for barium, a ratio of over thirty to one. The univalent cæsium ion has a greater precipitating power than the bivalent zinc, cadmium, nickel, and uranyl ions; and about the same precipitating power as the bivalent copper, manganese, and magnesium ions. The trivalent aluminum ion has about the same precipitating power as the bivalent calcium ion, and distinctly less precipitating power than bivalent strontium and barium ions. The specific nature of the adsorption comes out extraordinarily clearly with sulphur, about the only orthodox thing being that nitrate, chloride, and sulphate behave practically alike, though even here Odén considers that sulphate has a slight protecting action. This specific nature appears more clearly, perhaps, if we arrange the cations in order, the one with the greatest precipitating power coming first: Ba, Sr > Ca, Al > Mg, Cs, Mn, Cu > UO_2 > Rb > K > Ni, Cd, Zn > Na > NH_4 > Li > H.

Sulphur is admittedly an extreme case, but Freundlich[65] gives data for colloidal platinum from which I deduce the order: Al, Pb > Ba, UO_2 > Ag > K, Na. Bivalent lead has practically the same precipitating power as trivalent aluminum. Univalent silver is nearer to bivalent uranyl and barium than to univalent potassium and sodium. If more cations had been studied we should very likely have got more distinct evidence of specific action. As it is, it takes 130 millimols NaOH per litre to coagulate the platinum, and only 2·5 millimols NaCl. The change from chloride to hydroxide has a more marked effect than the change from sodium to barium. It seems very probable that barium hydroxide would have no greater precipitating power than sodium chloride. From Pappadà's experiments with colloidal silver[66] I deduce the following order of adsorption: Al > Ba, Sr, Ca > H > Cs > Rb > K > Na > Li. From these data Pappadà concludes that the migration velocity is the determining factor with the univalent cations; but this cannot be true. The difference between aluminum and hydrogen is not very great, one drop of M/10 HCl producing a coagulation and one drop M/20 $AlCl_3$. In tenth-normal solutions potassium iodide, nitrate, and sulphate produce no coagulation. The reason given by the author is that these anions react with the colloidal silver,

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[65] *Kapillarchemie*, 352 (1909).

In normal solutions the iodides, nitrates and sulphates are said to precipitate at the same concentrations as the corresponding chlorides and bromides. The effect of concentration is a little obscure in other respects since 5 or 6 drops of normal KCl precipitate 2 cc. 0·06 per cent. Ag, whereas it takes only 30 drops N/10 KCl to produce precipitation. The essential thing, from my point of view, is that the different univalent cations have different liminal values; the difference between hydrogen and lithium is greater than that between hydrogen and aluminum.

From experiments on mastic[67] we get the data given in Table II.

TABLE II.

Coagulation of Mastic.

Salt.	Liminal value, gram atoms.	Atomic precipitating power of cation.
NaCl	1·0	1
$AgNO_3$	0·125	8
$HgNO_3$	0·00125	800
HCl	0·010	100
$CaCl_2$	0·025	40
$BaCl_2$	0·025	40
$ZnSO_4$	0·050	20
$Al_2(SO_3)_2$	0·0004	2,500
$Al_2(NO_3)_2$	0·0004	2.500
$FeCl_3$	0·0003	3,300

If we consider the mercury in mercurous nitrate as a univalent ion, it is very much out of place, precipitating at much lower concentrations than the barium, calcium, and zinc salts. Of course, the formula should be written $Hg_2(NO_3)_2$ with Hg_2 as a bivalent ion.[68] In this case the precipitating power becomes 1,600 instead of 800, which puts it up much nearer the trivalent cations than the bivalent ones. The order of cations is: Fe, Al > Hg_2 > H > Ba, Ca > Zn > Ag Na. Only three anions are given in the table, so it is impossible to tell what effect the anions have. A good many experiments have been made on mastic with different acids, but the degree of electrolytic dissociation varies so as to make these results inconclusive. With Prussian blue Pappadà[69] found the order of the cations to be: Fe, Al, Cr > Ba, Cd > Sr, Ca > H > Cs > Rb > K > Na > Li. Sulphates, nitrates, chlorides, bromides, and iodides all behaved alike. Practically the same order of the cations was obtained for copper ferrocyanide.[70] In the cases studied by Pappadà the specific adsorption appears to play a very small part. The data for arsenic

[66] Pappadà, *Gazz. chim. ital.* **42**, I, 263 (1912).
[67] Freundlich, *Kapillarchemie*, 367 (1909).
[68] Ogg, *Zeit. phys. Chem.* **27**, 285 (1898).
[69] *Zeit. Kolloidchemie*, **6**, 83 (1911).
[70] Pappadà, *Zeit. Kolloidchemie*, **9**, 136 (1911)

sulphide,[71] however, give variety enough. The order of cations is Ce, In, benzidine, Al > new fuchsine, crystal violet > quinine > morphine, UO_2 Sr, Ca > Be, Zn, Ba > Ng > p-chloraniline. toluidine > aniline > strychnine > guanidine > H > K > Na > Li. The organic cations come in where they please and play havoc with any rule as to valency. The chlorides and nitrates give practically the same values, and the sulphates are not far out of line, though it seems probable that the restraining power of sulphate is rather greater than that of chloride or nitrate. The liminal values in gram atoms of the cation per litre are 0·0056, 0·0066, 0·0086, 0·110, and > 0·250 for potassium nitrate, sulphate. formate, acetate, and citrate, from which one can deduce that the order of adsorption of anion is: citrate > acetate > formate > sulphate > nitrate, chloride. It is a great pity that Freundlich did not try other combinations, such as barium acetate, for instance.

From the experiments on hydrous ferric oxide,[72] the order of adsorption of the precipitating anions appears to be Cr_2O_7 > SO_4 > OH > salicylate benzoate > formate > Cl > NO_3 > Br > I, while the order for the cations is: H > Ba > Mg > Tl, Na, K. The univalent ions do not all behave alike, and neither do the bivalent ones; but the upholders of Schulze's law can comfort themselves with the fact that the two sets do not overlap except in the case of hydrogen. There is no such comfort in the case of albumin. I have shown[73] that the probable order of adsorption of anions, so far as known, is: sulphocyanate, iodide > chlorate > nitrate > chloride > acetate > phosphate > sulphate $\geq$ tartrate, the sulphocyanate ion being adsorbed the most and the tartrate ion the least. Here there is nothing even to suggest Schultze's law, and the firm belief which most people have in Schultze's law is probably one reason for the marked failure to account satisfactorily for the phenomena with albumin. With the cations albumin appears to be fairly orthodox, for the order of adsorption appears to be Th, UO_2 > Cu, Zn > Ca > Mg > Li > K, Na > NH though even here the lithium stands higher in the series than it has been found with other substances.

While there is unquestionably a tendency for ions of a higher valence to be adsorbed more strongly than ions of a lower valence, the experiments which have been cited show that there are many exceptions, and that the fundamental rule is that the adsorption is specific both as regards the adsorbing substance and the ion adsorbed.

Albumin is a specially interesting case because it is peptised readily by cations or anions. When it is negatively charged, as in a slightly alkaline solution, a strongly adsorbed anion will make it more negative and more stable. Consequently, precipitation by a sodium salt will be more effective the less readily the anion is adsorbed. On the other hand, in acid solutions the

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[71] Freundlich, *Kapillarchemie*, 351 (1909). Freundlich and Schucht, *Zeit. phys. Chem.* 80, 564 (1912).

[72] Freundlich, *Kapillarchemie*, 352, 358, (1909) Zsigmondy, *Kolloidchemie*, 18 (1912). Pappadà, *Zeit. Kolloidchemie*, 9, 233 (1911).

[73] Bancroft, *Jour. Phys. Chem.* 19, 352 (1915).

sodium salt with the most strongly adsorbed anion will be the most effective in causing precipitation. Negatively charged albumin is precipitated readily by sodium chloride, and not at all by sodium iodide, while positively charged albumin is precipitated by sodium iodide much more readily than by sodium chloride.

If one over-runs the point of electrical neutrality, the suspension may become stable again because it is stabilised by preferential adsorption of an ion having the opposite sign. If one adds a little less than the equivalent amount of a dilute potassium bromide solution to a dilute silver nitrate solution, one gets a positively-charged colloidal solution of silver bromide because the silver bromide is stabilised by adsorbed silver ions. If one adds slightly more than the equivalent amount of the potassium bromide solution, there is obtained a negatively-charged colloidal solution of silver bromide, stabilised by adsorbed bromine ions. If more bromide solution is added, the silver bromide will coagulate because there will come a point at which the slight adsorption of the potassium ion counterbalances the adsorption of the bromine ion. In other words, silver bromide precipitates, when there is a distinct excess of silver nitrate, stays in suspension as a positively charged colloid when there is only a slight excess of silver nitrate, precipitates, when the suspension becomes electrically neutral, stays in suspension as a negatively charged colloid when there is a slight excess of potassium bromide, and precipitates when there is a distinct excess of potassium bromide. At the two ends of this series there is also the possibility of true solution of silver bromide in silver nitrate or potassium bromide.

An interesting case of the precipitation of a colloid by an electrolyte is to be found in the action of sea-water on muddy river water. Skey[74] pointed out that suspended mud is precipitated by electrolytes, and Waldie[75] has discussed the clearing of the water of the Hooghly. When a river flows into the ocean, the current becomes less, and some of the suspended mud is dropped on this account; but that is relatively unimportant in many cases. Schloesing[76] called attention to the fact that the formation of deltas is due primarily to the coagulation of the suspension by the electrolytes in the salt water. Another interesting case of the neutralisation of an electrical charge is the precipitation of positively charged colloids by β rays.[77]

Since the important thing in the neutralisation of an adsorbed ion is the adsorption of an ion of the opposite charge, we may get neutralisation when we have a colloid with the opposite charge. In other words, we may neutralise an adsorbed ion with another adsorbed ion instead of by a free ion. The usual statement is that sols having the same charge do not affect each other perceptibly, while sols having opposite charges precipitate

[74] *Chem. News*, **17**, 160 (1868).

[75] *Chem. News*, **30**, 37 (1874).

[76] *Jour. Chem. Soc.*, **24**, 750 (1871).

[77] Hardy, *Jour. Physiology*, **29**, 29 (1903). Höber, *Physikalische Chemie der Zelle und Zewebe*, 332 (1911); Burton, *The Physical Properties of Colloidal Solutions*, 172 (1916).

each other.[78] Neither of these statements is as accurate as it should be. I shall take up first the case of sols having opposite charges. Positive and negative colloids will precipitate each other when in proper proportions and provided adsorption takes place.[79] I see no theoretical reason why we should not have a positively charged and a negatively charged sol, neither of which adsorbed the other to any appreciable extent. In that case these two sols would not precipitate each other. Since complete neutralisation takes place only when one sol has adsorbed the amount of the sol carrying an equivalent amount of the ion having the opposite charge, it follows that the amount of one sol necessary to precipitate a given amount of another sol will vary with the degree of adsorption; it will therefore be a specific property and not an additive one. This can be tested experimentally on data by Biltz given in Table III.[80]

TABLE III.

1·4 mg. gold completely precipitated by

CeO_2	Fe_2O_3	ThO_2	ZrO_2	Cr_2O_3	Al_2O_3
4	3	2·5	1·6	0·3	0·1 –0·2 mg.

28 mg. Sb_2O_3 completely precipitated by

Fe_2O_3	ThO_3	CeO_2	ZrO_2	CrO_3	Al_2O_3
32	20	11	6·5	3·0	2·0 mg.

24 mg. Ag_2S_3 completely precipitated by

Fe_2O_3	ThO_2	CeO_2	ZrO_2	Al_2O_3	Cr_2O_3
13	6	4	2	2	0·5 mg.

Alumina is more effective than chromic oxide in precipitating antimony sulphide, and much less effective in precipitating arsenic sulphide. The alumina must therefore be adsorbed more by antimony sulphide than chromic oxide, while the reverse must be true for arsenic sulphide. Cerium oxide is less effective than ferric oxide and thorium oxide in precipitating gold, but is more effective than either of these in precipitating the sulphides of antimony and arsenic. The phenomenon is thus specific, varying with the nature of the two colloids. This seems not to have been realised before. In fact, Freundlich says definitely[81] that 'one seems to find approximately the same order regardless of what sol is to be precipitated.' This statement is true, but it missed the important thing in the experiments, which was that the order was not always the same.

We can now take up the case of sols having the same charge. The statement that neither has any perceptible effect on the other is based solely on the fact that no precipitation occurs. We know, however, that cases of adsorption are not limited to colloids or electrolytes having opposite signs. Charcoal adsorbs both bases and acids. Silver bromide adsorbs silver ions or bromine

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[78] Freundlich, *Kapillarchemie*, 444 (1909). Zsigmondy, *Kolloidchemie*, 56 (1912). Höber, *Physikalische Chemie der Zelle und Zewebe*, 294 (1914).

[79] Bancroft, *Jour. Phys. Chem.*, **18**, 555 (1914).

[80] Freundlich, *Kapillarchemie*, 445 (1909).

[81] Freundlich, *Kapillarchemie*, 445 (1909).

ions, as the case may be. There is, therefore, no theoretical reason why precipitated hydrous ferric oxide might not adsorb chromic oxide, and *vice versa.* If the precipitated substance will do this, there is no reason why the peptised substance should not. Nagel[82] has shown recently that this does occur, and that it accounts for the behaviour of mixtures of chromic and ferric salts with excess of alkali. Hydrous chromic oxide is peptised by caustic potash, while hydrous ferric oxide is not. If the chromium salt is present in large amount relatively to the iron salt, the ferric oxide will adsorb the peptised chromic oxide and be peptised by it, going apparently into solution. If the ferric salt is present in excess, it will adsorb the peptised chromic oxide, carrying it out of the liquid phase. It is to be noticed that the chromic oxide, when in excess, acts as a so-called protecting colloid to the iron oxide. Everybody is familiar with the fact that gelatine is adsorbed by colloidal gold, for instance; but that is usually treated under the heading of protective colloids rather than under the heading of mutual action of two colloids. The case of chromic and ferric oxides is merely another illustration of the fact that the distinction between a suspension colloid and an emulsion colloid is now arbitrary and unsatisfactory.[83]

Coming back for a moment to the behaviour of two oppositely charged colloids, there is a special hypothetical case which is perhaps worth mentioning. Suppose we have two sets of finely divided particles, neither of which adsorbs the other appreciably, and let us also suppose that one set of particles adsorbs a given cation very strongly, while the other set of particles adsorbs a given anion very strongly. If we take a mixture of these two sets of particles and add a small amount of the salt of the given base and the given anion, we shall have a colloidal solution which will conduct electricity very well, but which will contain no free ions to speak of because, by definition, the cations have been practically completely adsorbed by one set of particles and the anions by the other set of particles. This particular case has not been realised, but an intermediate one seems to have been found by McBain and Martin[84] in sodium palmitate solutions.

'Most authors since Kahlenberg and Schreiner[85] have, as a matter of course, ascribed the conductivity exhibited by soap solutions largely to free alkali hydroxide. In previous papers from this laboratory the same tentative suggestion was made, but it was each time clearly stated that it was only a working hypothesis until these experimental data should be ascertained. Now it is certain that the conductivity of soap solutions is, only to a very minor extent, due to hydroxyl ions. Further, on account of the fact that the rise of boiling point in certain soap solutions is practically all required to account for the sodium ions alone,[86] the conductivity cannot be wholly ascribed to simple

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[82] *Jour. Phys. Chem.* **19**, 331 (1915).

[83] Bancroft, *Jour. Phys. Chem.* **18**, 556 (1914).

[84] *Jour. Chem. Soc.* **105**, 965 (1914).

[85] *Zeit. Phys. Chem.* **27**, 552 (1898).

[86] McBain, *Trans. Faraday Soc.* **9**, 99; *Zeit. Kolloidchemie*, **12**, 256 (1913)

palmitate ions. The suggestion we made is that we have here a new type of aggregate or micelle, the mobility of which, owing to the reasons given in the paper cited, is comparable with that of a true anion. Of course, further investigations are proceeding in this laboratory in order to bring this to the test of direct experiment. Incidentally, the above shows, further, that undissociated soap is present chiefly or entirely in colloidal form.'

As I see the matter, the sodium palmitate is hydrolysed and the hydroxyl ions are adsorbed to a great extent by the undissociated palmitate, and possibly by the insoluble palmitate acid also, though this seems less probable. The adsorbing substance thus becomes the anion, owing to the adsorbed hydroxyl. Because of electrometric measurements, McBain[87] considers that there is practically no hydrolysis. Electrometric measurements only show the concentration of hydroxyl ions in solution. I do not believe for a moment that an adsorbed hydrogen ion or hydroxyl ion behaves electrometrically like a free hydrogen or hydroxyl ion. An adsorbed chlorine ion, for instance, would not give a test with silver nitrate. Under these circumstances the electrometric measurements are satisfactory for showing the concentration of hydroxyl ions in the solution, but they are utterly worthless for showing the degree of hydrolysis of sodium palmitate. For the same reason I am very sceptical as to any conclusion in regard to albumin solutions which is based on electrometric measurements.[88]

So-called irregular series [89] have been observed when a suspension of a positively-charged colloid is added to a suspension of a negatively-charged colloid. When increasing concentrations of aluminium sulphate were added to a negatively-charged solution of mastic there was at first no precipitation, and the suspension was charged positively because the mastic was present in excess. At higher concentrations of aluminum sulphate, the suspension became electrically neutral, and complete precipitation took place. At still higher concentrations the mastic was held in suspension by the hydrolysed alumina, and the suspension was charged positively. At still higher concentrations of aluminum sulphate complete precipitation occurred. This apparently abnormal result is due to the fact that the experiment is not exactly what it purports to be—the addition of one colloidal solution to another. Instead of adding a colloidal solution of alumina, there was added a so-called solution of aluminum sulphate, which hydrolysed to colloidal alumina and sulphuric acid, with possibly some aluminum sulphate left unchanged especially in the higher concentrations. The amount of free sulphuric acid is always equivalent to the amount of alumina, and the two concentrations increase proportionally. The so-called abnormal precipitation at the higher concentrations is merely a precipitation by sulphate ions, and is absolutely normal.

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[87] McBain and Martin, *Jour. Chem. Soc.* **105**, 957 (1914).

[88] Bancroft, *Jour. Phys. Chem.* **19**, 349 (1915).

[89] Neisser and Friedmann, *Zeit. angew. Chem.* **1906**, 1953; Bechhold, *Zeit. Phys. Chem.* **48**, 285 (1904); Buxton and Teague, *Zeit Phys. Chem* **57**, 47, 64 (1907); Freundlich, *Kapillarchemie*, 402 (1909).

Since the precipitation of one colloid by another may take place within a relatively narrow range of concentrations, it is not surprising that people have postulated the existence of definite chemical compounds in order to account for the precipitates. The literature on the subject is in a worse state even than that on the so-called basic salts. For instance, ferric arsenate, aluminum silicate, stannic phosphate, and cupric eosinate are not formed under ordinary conditions by precipitation from solutions. The precipitation is due to the mutual coagulation of two colloids, though the resulting precipitate may simulate a compound to the extent that it may be peptised without change under certain conditions.

While the theory of peptisation and precipitation, as outlined, accounts satisfactorily for most of the facts, there are certain points which are not covered by it at present. A mixture of the two water-peptisable colloids, gelatine and gum arabic, is said to behave exactly like casein.[90] Under certain conditions gelatine and tannin form an insoluble or non-peptisable mixture;[91] but we do not know why. The case of chrome tanning is not difficult because the chromic oxide would not normally be peptised under the conditions of the experiment, and it has been shown that there is no necessary change in the gelatine.[92] We also cannot account at present for the stability or instability of metal sols in different organic liquids; in this case as well as in the other two, the trouble is in our ignorance of the facts and not in any shortcomings of the theory.

EMULSIONS.

By E. HATSCHEK, *Sir John Cass Technical Institute, London.*

The term Emulsion is used in the following to denote a disperse system both phases of which, *considered in bulk and at ordinary temperature*, are liquid. The qualifying clause, although not generally stated in such explicit terms, seems desirable as, on one hand, the distinction between liquid and solid becomes somewhat vague with particles approaching ultra-microscopic dimensions, while, on the other, the same system, *e.g.* rosin in water, may be a suspension at lower and an emulsion at higher temperature.

One characteristic of emulsions, which distinguishes them sharply from systems with solid disperse phase, follows immediately from the definition : there is no upper limit to the ratio : Volume of disperse phase/Volume of continuous phase. With solid or, better, undeformable particles of disperse phase there is such a limit (apart from the ideal case of space-filling polyhedra of equal size) which, for spherical particles of uniform radius, is approximately 74/26.

It is obvious that, with a liquid or deformable disperse phase, spherical particles in closest contact do not constitute a limiting case,

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[90] Tiebackx, *Zeit. Kolloidchemie*, **8**, 198, 238 (1911).

[91] Wood, *Jour. Soc. Chem. Ind.*, **27**, 384 (1908).
Von Schroeder, *Zur Kenntniss des Gerbeprozesses.*
Levites. *Zeit. Kolloidchemie*, **8**, 4 (1911).

[92] Lumière and Seyewetz, *Bull. Soc. Chim.*, Paris (3) **29**, 1077 (1903).

as—at least theoretically—a further increase in the relative volume of disperse phase can lead to flattening at the points of contact of contiguous spheres and eventually to a polyhedral structure of the system. A limit is only reached when the thin films of continuous phase which separate the polyhedra of disperse phase are no longer capable of cohering. The practical possibility of such systems is demonstrated by some of S. U. Pickering's emulsions with up to 99 per cent. of disperse phase. The complete conditions for the stability of such films will be discussed further on, but it can be said at once that a low inter-facial tension is, if possibly not sufficient, certainly necessary.

Conversely, emulsions with a very low content of disperse phase, in which the particles are small and separated by layers of continuous phase of some thickness compared with the extent of interface, are possible and moderately stable even when the interfacial tension is high, viz. of the order of 30 to 40 dyne/cm. Such emulsions may be produced by agitation, by distilling the two phases together, or by 'precipitating' an alcohol or acetone solution of the disperse phase with a large excess of water. The properties of such emulsions with a disperse phase consisting of mineral oils, aniline, nitrobenzene, oleic acid or castor oil, amounting to one part in a thousand, or less, of the total volume, are throughout those of fine suspensions or of suspensoids. The (negative) electric charge is of the same order as on suspensoid particles (Lewis); is similarly affected by hydrogen and hydroxyl ions (Ellis); the maximum concentrations at which the emulsions are stable are of the same order as for suspensoid sols (Lewis), and the phases may be separated by filtration through suitable septa under considerable pressure (Hatschek). The effect of interfacial tension is altogether subordinate to that of the electric factors.

Emulsions containing larger percentages of disperse phase than those mentioned, in particles of microscopic or approaching microscopic size, are stable, or in fact anything more than transient, only when the interfacial tension between the phases is low, as has already been mentioned. In the emulsions occurring in nature, such as milk or latex, this is generally brought about by the protein content of the continuous phase, while in the emulsions prepared artificially the agent which lowers the interfacial tension is very generally a soap. The stability of such emulsions is, however, again dependent on the phase ratio and is generally not complete unless this approaches the figure corresponding to closest packing. Thus, if oil and a dilute soap solution are shaken until the whole of the oil is dispersed, the resulting emulsion separates into a layer of soap solution containing only a very small fraction of oil and a 'cream' containing 75 per cent., or more, of oil; the latter is stable, provided the walls of the containing vessel are wetted only by the continuous phase and no oil in bulk is in contact with the cream. The rate of separation depends naturally on the difference in density of the phases, the viscosity of the continuous phase and the degree of dispersion: it is obvious, although the case has chiefly a theoretical interest, that a system stable in all ratios is conceivable if both phases have the same density, *e.g.* castor oil in water with a little alcohol.

The connection between low interfacial tension and emulsification was first insisted on by Quincke, but the principal quantitative investigations are due to Donnan. They comprise experiments carried out with the drop pipette on the emulsification of glycerides in alkali solution, which show, in agreement with Quincke, that free fatty acid, *i.e.* the possibility of soap formation at the interface, is a necessary condition if emulsification is to take place; determinations of the drop numbers for hydrocarbon oils discharged into solutions of salt of the fatty acids, and experiments in which the hydrocarbon oil was dispersed in these solutions by shaking under strictly defined conditions. The two last series give concordant results and show that the first salt of the fatty acid series to exert an appreciable emulsifying action is the one which shows the first marked reduction of surface tension, viz. that of lauric acid. Donnan also finds that there is an optimum concentration of soap, and explains it as due to the balance between the reduction of interfacial tension, which promotes, and the electrolyte effect, which counteracts, dispersion.

A similar result, viz. that increase of soap concentration beyond a certain limit was detrimental to emulsification, had been obtained by S. U. Pickering. According to him the optimum concentration depends both on the phase ratio and on the absolute volumes of the phases, so that no simple explanation appears to offer itself. The same author also gives a number of experiments in which the emulsifying agent is not in solution—either true or colloidal—but a precipitate such as 'basic iron, copper or nickel sulphate,' *i.e.* the precipitates formed by adding lime water to the respective sulphates. If water containing one of these substances is agitated with oil—more particularly mineral hydrocarbons of 250° to 359° boiling-point and about 0·85 sp. gr.—the oil is completely emulsified. After an examination of various finely divided solids which show only a transient effect or none at all, Pickering comes to the conclusion that the chief factor in the formation of stable emulsions of oil as disperse phase in water is the existence of a layer of small solid, non-crystalline particles which *are more easily wetted by water than by oil* (the italics are mine, E. H.) at the interface.

While Pickering thus concludes that a low interfacial tension is not the principal, or in fact a necessary, condition of emulsification, the discrepancy between the two views is probably only apparent, at any rate if the 'solid' state of the particles in the interfacial layer is not insisted upon. If low tension is not the direct agent it is nevertheless active indirectly in bringing about—in such solutions as alone come into question—the formation of absorption films having some of the properties postulated. On the other hand, the substances used by Pickering would obviously not accumulate at the interface (more strictly on the water side of it) unless this arrangement led to a lowering of the interfacial tension.

That a film or membrane covering the whole of the interface is a necessary condition of stability in emulsions is the conclusion pronounced by W. D. Bancroft after a most exhaustive review of the available material. The relative solubility of this film in the two phases, or the difference in interfacial tensions between them and the film, determines the nature of the emulsion, *i.e.* which of the two phases, in given conditions, will be the disperse and which the continuous phase.

These views derive strong confirmation from a series of experiments by G. H. A. Clowes. He prepares an emulsion with oil as disperse phase by shaking olive oil with a dilute solution of NaOH in water. If a quantity of $CaCl_2$ slightly in excess of the equivalent of the NaOH is added to this emulsion, it transforms itself spontaneously into one having water as disperse and oil as continuous phase. This can be re-converted into the original emulsion by adding NaOH until the original OH' concentration is restored. Magnesium, iron, and aluminium have an effect similar to that of calcium. Since the oleates of these metals are much more soluble in oil than in water, their formation would cause a considerable reduction in the interfacial tension between the film and the oil phase, so that the film would tend to become convex towards the oil and concave towards the aqueous phase, *i.e.* oil would become the continuous phase and water the disperse. The whole process is an actual reversal and is therefore sharply distinguished from such phenomena as the separation of emulsions into two (no longer disperse) phase by the addition of electrolytes or of substances which decompose the material of the interfacial film.

Evidence similar, and complementary, to that afforded by Clowes's experiments is provided by an investigation by A. U. M. Schlaepfer, the object of which was to produce emulsions of water dispersed in oil by using a finely divided substance more completely wetted by oil than by water : soot accomplished the desired result.

Earlier experiments by Walter Ostwald, made with the intention of determining the type of emulsion which would result from the agitation of oil with water only, showed that either type was possible and that the result depended largely upon secondary factors, such as the state of the containing vessel and its previous wetting by one or the other phase. Conclusions drawn by this author regarding the limiting phase ratio have been proved incorrect both theoretically and experimentally. Donnan also found that the state of the vessel introduced considerable experimental complications. Although the method used by these and other authors—viz. agitation of the total volumes of both phases—is perhaps as good as any other arbitrary method, it neither corresponds to the probable process of formation of natural emulsions nor to the technical methods adopted for the production of stable emulsions, in which the gradual addition of the disperse phase during, and *pari passu* with, the process of dispersion is generally considered an essential condition of success.

The theoretical interest of emulsions is considerable and is likely to become even greater. Viewed as disperse systems of two liquid phases they are the only ones in which the phase ratio is accurately known and therefore specially adapted for studying the physical properties, *e.g.* the viscosity of such systems. They have also acquired very great importance in biology in view of some modern hypotheses on the constitution of protoplasm, the possible existence of lipoid films and cognate phenomena, such as the action of 'antagonistic' ions and of anæsthetics. While at present the conclusions respecting such complicated problems drawn from the study of comparatively simple and coarse systems may perhaps constitute a theoretical edifice somewhat disproportionately large for its slight experimental foundation, there can be no doubt that the trend of research is in the right direction.

Technically also emulsions are of considerable importance. They are employed—speaking, of course, very generally—where it is necessary to administer or exhibit a liquid in a varying degree of dilution, while the ordinary solvents for it are inadmissible on economical, technical, or physiological grounds. In such cases, or in a great number of them, the active liquid may be used as disperse phase of an emulsion, the continuous phase of which is so selected as to be indifferent; in addition it must wet, or be absorbed by, the surfaces to which the emulsion is eventually applied. Examples are: the medicinal emulsions of such liquids as cod-liver oil or petroleum (in which further desirable ingredients like malt extract, hypophosphites, &c., may be in solution in the aqueous phase); emulsions of cresols and other substances for use as antiseptic and anti-parasitic preparations; fat solvents such as carbon tetrachloride emulsified with 'monopol' soap (obtained by saponifying sulphonated castor oil); emulsions of fats in a great variety of menstrua and used as leather 'foods' and dressings, &c. The preparation of such emulsions is of course generally a trade secret; as regards the emulsifying agent, this is, however, very generally a soap in all technically used emulsions.

Emulsions occur in industrial processes as undesirable by-products, such as very persistent emulsions of mineral oils or of wool-fat in the course of refining; the condense water from reciprocating engines, which contains the oil used in the lubrication of slide valves and cylinders and is a very perfect type of the stable oil-water emulsion, &c. In all these cases the means of preventing the formation of an emulsion, or of separating it when formed, can be deduced from the theoretical considerations set forth above, although unfortunately their practical application is in many cases somewhat difficult.

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This paper, like the preceding one, describes experiments with emulsions obtained by dispersing olive oil in dilute NaOH solution. By adding $CaCl_2$ in excess of the alkali they are spontaneously transformed into emulsions having water as disperse phase, which can be re-transformed into the first type by adding NaOH in excess.

M. H. FISCHER and M. O. HOOKER, On the formation and decay of emulsions, 'Koll.-Zeitschr.'; **18**, 129, 1916.

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The author, following Pickering, concludes that a finely divided solid more easily wetted by oil than by water should be capable of producing emulsions with water as disperse phase and proves his conclusion experimentally by using soot as emulsifying agent.

THE LIESEGANG PHENOMENON.

By E. HATSCHEK, *Sir John Cass Technical Institute, London.*

This phenomenon was observed by its discoverer, after whom it is called, when carrying out the following experiment in the course of some researches on Golgi's method of staining animal tissues with silver chromate:

A glass plate is coated with 5 per cent. gelatin gel containing a small amount of potassium bichromate. A drop of strong silver nitrate solution is then placed on the gel and immediately begins to diffuse into the latter. The silver nitrate of course reacts with the bichromate in the gel, the products of reaction being silver bichromate and potassium nitrate. Although there is thus a contınous supply of both components, the insoluble silver salt is, however, not deposited in a continuous zone round the periphery of the original drop, *but in a series of concentric rings, separated by apparently clear zones*, the width of which increases with the distance from the centre.

The importance of the phenomenon was immediately perceived by R. E. Liesegang, who made it the subject of a very large number of experiments of great ingenuity, and who first suggested that it supplied the simplest explanation of the formation of a natural product, viz., of banded agates. It may be as well to anticipate somewhat and to indicate at once the reasons for attaching importance to what at first sight may appear only a curious laboratory experiment. A large number of stratified structures occur both in organic and inorganic nature, the explanation of which has so far generally involved one or more of the following assumptions: a periodic supply of either or both components of a reaction; a periodic supply of a catalyst, activating or inhibiting agent; or, finally, a periodic external agency, such as, *e.g.*, variations of mean temperature. The Liesegang phenomenon, on the other hand, is proof that periodic structures may appear where all factors which can possibly exert any influence are constant. Where it is applicable as the basis of explanation it therefore leads to that economy of assumptions which is the desideratum of every hypothesis.

The conditions of the experiment have been varied by Liesegang and subsequent observers. The gel containing one component may be allowed to set in a test tube and the solution of the other poured on top. Or the gel may fill the bend of a U-tube and two solutions may diffuse into it in opposite directions from the limbs. Finally, bodies of gel containing one component may be submerged in solutions of the other. The results are substantially the same in all cases, although a given reaction may not produce them in an equally marked manner with every arrangement.

The phenomenon has also been studied in gels other than gelatin such as agar and silicic acid, and even in porous media of very much coarser structure than gels. The nature of the gel, and to a much slighter degree its concentration, are now fully proved to have a marked specific influence on the result with any given reaction. Thus, the reaction between silver nitrate and potassium bichromate leads to stratifications in gelatin, but not in agar, while on the other hand the reaction between lead nitrate and potassium chromate produces them in agar, but not in gelatin, while neither of the two leads to a stratified deposit if it takes place in silicic acid gel. A great number of reactions have also been investigated, some in all three gels and over wide ranges of concentrations, and well marked stratifications have been obtained particularly with the following precipitates; lead iodide and lead chromate in agar, lead carbonate in agar and in silicic acid, phosphates of the heavy metals in various gels, sulphides in various gels and in sand, &c.

Certain reactions, within wide limits of concentration, do not produce stratifications in certain gels. It has, however, been shown by Liesegang and by Hatschek—and the point is again of importance for the explanation of natural structures—that they can nevertheless be obtained as pseudo-morphoses after an intermediate product of reaction. Thus Liesegang places a drop of silver nitrate solution on a gelatin film containing sodium chloride; the resulting silver chloride forms only a continuous band. If a small fragment of potassium bichromate is placed some distance from the edge of the drop of silver nitrate, the usual silver chromate strata are formed round it when the silver salt has diffused so far, but are promptly transformed into silver chloride. The final result is stratifications of silver chloride round the site of the bichromate, although such cannot be produced directly. By a slightly different procedure Hatschek obtains strata of lead chromate in gelatin, also as pseudomorphoses after silver chromate, although the reaction between lead nitrate and potassium chromate in gelatin leads only to a continuous band of lead chromate in the ordinary way.

Microscopic observation of the stratifications, both while in course of formation and after completion of the reactions, have been made by Liesegang himself and by later investigators. Only in a few reactions—of which the original silver chromate one is the best example—are the 'clear' spaces between the rings practically free from the insoluble compound: in most cases the rings contain a large number of small, and the clear spaces a small number of large, crystals or crystalline aggregates. A striking macroscopic illustration is afforded by cadmium sulphide in silicic acid gel, which exhibits no clear spaces at all, but a continuous succession of alternately yellow and pink bands. As is well known, the two shades are due to the difference in the size of the particles and both may be obtained by precipitating aqueous solutions of different concentrations. It is an open question whether, in many cases, the actual amount of reaction product in equal volumes of ring and clear space is not approximately the same.

As regards the theory of the phenomenon, the first explanation of the origin of periodic deposits was given by Wilhelm Ostwald. It is based on the assumption of 'metastable' supersaturation, and is, in fact, the principal experimental evidence adduced by him for the existence of solutions in that condition. According to him, silver chromate is formed as the silver nitrate diffuses into the bichromate-gelatin, but at first remains in supersaturated solution until the limit of metastability is reached. When this happens, the silver chromate is precipitated and 'on the precipitate thus formed the silver chromate, *in respect of which the vicinity of the ring is supersaturated* (the italics are mine, E. H.) is deposited and reinforces it; this continues until the soluble chromate removed from the vicinity has gone into the precipitate.'

H. Bechhold, while generally accepting this theory, has shown that it is at least incomplete by demonstrating conclusively that the phenomenon is profoundly affected by factors which it fails to take into account, such as the solubility of the precipitate in the second reaction product, *e.g.*, the solubility of silver chromate in ammonium nitrate, ammonium bichromate having been employed in his experiments.

R. E. Liesegang also realised that the *experimentum crucis* would be the failure to produce a second ring system in a layer of gelatin already containing one, since the crystals forming the latter should obviously prevent supersaturation anywhere in their vicinity. He nevertheless succeeded in obtaining such a secondary system, but found that it was formed at a level below that of the primary stratifications. This result satisfied him that the experiment did not refute the supersaturation theory, a conclusion which it is difficult to accept. There is no obvious reason why a deposit of silver chromate which *ex hypothesi* (see the italicised passage in the quotation from Ostwald) prevents supersaturation radially over some distance amounting to millimetres, should not do so equally at right angles to that direction, viz., into the depth of the layer of gelatin.

E. Hatschek carried out experiments of a more direct character in the test tube. Crystalline lead iodide was suspended in agar containing also potassium iodide. When lead nitrate solution was allowed, to diffuse into this gel, the usual, very perfect stratifications of lead iodide were formed, although crystalline nuclei were disseminated through the gel and should have made supersaturation impossible.

R. E. Liesegang does not consider that this result is incompatible with the supersaturation theory and suggests that the 'radius of action' of the nuclei is too small to prevent the formation of strata which, with the particular reaction, occur at very small distances from each other. Without going into any speculations regarding the mechanism of this action, it can be said *a priori* that Liesegang's objection, if valid, would be equally fatal to Ostwald's theory itself.

The reason suggested by Liesegang to prove his own experiment inconclusive is, finally, eliminated in a somewhat similar experiment by L. J. de Whalley (published by E. Hatschek). He obtained a second system of stratifications of lead chromate in agar, which already contained a very fine system of strata of the same compound, *in a test tube.* As the reacting solutions in this arrangement must inevitably pass through, and meet in the vicinity of, existing strata, the case is different from that of the flat layer used by Liesegang, and appears to leave no escape from the conclusion that supersaturation was prevented throughout the formation of the second system of strata.

An alternative theory of periodic precipitation has been advanced by S. C. Bradford and supported by some experimental evidence, the most striking of which consists of photographs of preparations in strongly coloured solutions, such as the alkali chromates. According to him, one of the reacting solutes is adsorbed by the layer of precipitate, the result being a zone practically free from it, so that the clear space between the strata is at once accounted for. Considering the uncertain and conflicting results of adsorption experiments with solutions of electrolytes, it would be desirable to support what is undoubtedly an attractive suggestion by direct evidence—which Bradford so far has not obtained—that the solutes in question are actually adsorbed by the appropriate precipitates, *e.g.*, that potassium chromate is really adsorbed by lead chromate, or potassium sulphides by lead sulphide.

Apart from the difficulties already set forth, any theory must be pronounced inadequate which leaves—as do both Ostwald's and Bradford's—the gel out of account altogether. There is an abundance of material to show that the same reaction, if carried out in different gels, leads to entirely different results, in other words, that the gel has a specific effect and does not merely act as an indifferent medium which prevents mixing or currents. In this connection a suggestion made by H. Freundlich incidentally in a paper on another subject is of interest: that the formation of periodic strata may be an instance of the coagulation by electrolytes of a suspensoid sol. While at first sight the distinction between a sol of, say, silver chromate and a 'metastable supersaturated solution' of the same substance may (apart from the fact that we know hardly anything definite about the latter type of systems) seem rather subtle, further consideration shows that the former assumption immediately explains the specific effect of the gel. If electrolyte coagulation is the deciding factor, the protective effect of the gel must play an important part in promoting or inhibiting the formation of strata, and some such effect is easily traced in the comparative material collected principally by E. Hatschek. The consistent differences in the results obtained in gelatin, agar, and silicic acid gels point in this direction, as the protective effects of the three substances are widely different: taking Zsigmondy's 'gold figures' as measuring this property, the protective effect of gelatin and agar is respectively 100 and 2, while that of silicic acid is negligible. These facts, of course, form merely the starting-point for a theory of the Liesegang phenomenon, and a very large amount of work would still be required to show its general validity.

The lack of a general theory of the formation of the Liesegang stratifications does not, of course, preclude suggesting a similar origin of stratified structures in nature or attempts to reproduce such experimentally. Liesegang led the way by explaining the bands in agate in this fashion, *i.e.*, by diffusion of iron salts into the gelatinous silica from which the stone probably originates, in preference to the earlier assumption of alternate deposition. Many similar suggestions in regard to both geological and histological examples are thrown out in his book entitled 'Geological Diffusions' and in his numerous papers. The importance of the phenomenon for botanical anatomy and histology has been insisted on chiefly by E. Kuester. Its possible bearing on the transformation of cartilage into bone has been pointed out by H. Bechhold, and experimental work on this subject should be very fruitful. E. Hatschek and A. Simon have shown that a whole series of apparently disconnected peculiarities of gold deposits in quartz can be explained by assuming the latter to have originally been gelatinous silicic acid, in which the reduction of the solutions of gold salts was brought about by one of many possible agents.

In all these directions little more than a beginning has been made, and the experimental reproduction and elucidation of natural periodic structures should for a long time to come be one of the most fruitful fields for applied colloidal chemistry. It seems probable that investigation will have to be extended to gels made anisotropic by stress, since it is evident that most of the gel-like constituents of organisms are in such a condition, at least during long periods.

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ELECTRICAL ENDOSMOSE. I.

By T. R. Briggs, *Cornell University.*

1. *Electrical Endosmose, Cataphoresis and Allied Phenomena.*

On passing an electric current through a porous diaphragm immersed in a liquid, one often observes a flowing of the liquid through the diaphragm; this flow is commonly from the anode to cathode, but may take place in the opposite direction. This curious phenomenon was described first by Reuss,[1] working at Moscow, in 1808, and to it has been given the name *electrical endosmose.* Reuss, who employed clay diaphragms in water, noticed that, as the current forced water through the clay toward the negative pole (cathode), there also occurred migration of suspended clay particles in the direction of the positive pole (the anode). This migration of particles in suspension has come in time to be called *cataphoresis*, and the term should be limited to this meaning. There has arisen, however, a great deal of confusion regarding the use of the two expressions, *electrical endosmose* being employed to include

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[1] Wiedemann, *Elektricität*, **1**, 1007 (1893).

cataphoresis,[2] and *cataphoresis*, on other occasions, being made in turn to do double service.[3]

Electrokinetic phenomena in two-phase systems of liquid, and solid may be analysed into four distinct processes, of which electrical endosmose and cataphoresis are the ones commonly met with. So far as the electric current is concerned, it is possible to distinguish two cases, as follows :—

(1) *A difference of potential sending a current through the system may produce a relative displacement of the phases.*

(*a*) If the solid is fixed in the form of a porous diaphragm the liquid may be forced through the diaphragm. Electrical endosmose.

(*b*) If the solid is in the form of a suspension and is free to move, the solid may migrate through the liquid. Cataphoresis.

(2) *A relative displacement of the phases may produce a difference of potential and consequently an electric current may flow through the system.*

(*a*) If the solid is fixed in the form of a porous diaphragm through which liquid is forced, a difference of potential and an electric current may be established between the extremes of the diaphragm. Quincke's 'diaphragm current.'

(*b*) If the finely divided solid is dropped through the liquid, a difference of potential and a current may be set up between the upper and lower liquid strata. Billitzer's experiments.[4] This case resembles closely the drop electrode.

Wiedemann[5] is to be credited with the first quantitative study of electrical endosmose, and he was able, as a result, to deduce three empirical generalizations :

(1) The mass of liquid transported in unit time through a porous diaphragm, is directly proportional to the strength of the electric current ; and, for a given diaphragm material and given current strength, it is independent of the length and sectional area of the diaphragm.

(2) The difference in hydrostatic pressure maintained by electrical endosmose between the two sides of a porous diaphragm, varies directly as the current strength, and for a given diaphragm material and a given current, is proportional directly to the length and inversely to the sectional area of the diaphragm ; it is also proportional to the specific resistance of the liquid in the case of an aqueous solution.

(3) For a given diaphragm material, the difference in hydrostatic pressure maintained between the two sides of a porous diaphragm is proportional to the applied potential and is independent of the dimensions of the diaphragm.

Quincke[6] forced liquid through an apparatus containing a porous diaphragm and found that differences of potential were produced. He measured these differences and the "diaphragm currents" which

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[2] Cf. Patents of Botho Schwerin (Gesellschaft für Elektroosmose).

[3] Cf. Cruse, *Phys. Zeit.*, 6, 201 (1905) ; Hittorf ; *Zeit. phys. Chem.*, **39**, 613 (1902); **43**, 239 (1903) ; Morton ; *Cataphoresis* (1898).

[4] Drude's *Ann.* **11**, 937 (1903). Cf. Freundlich, *Kapillarchemie*, 230 (1909).

[5] *Pogg-Ann*, **87**, 321 (1852) ; **99**, 177 (1856).

[6] *Pogg.-Ann.*, **107**, 1 (1859) ; **110**, 38 (1860).

resulted and arrived at the following generalization, which may be regarded as the converse of Wiedemann's third law :

"When water is forced at a certain rate through a porous diaphragm, the difference of potential produced is independent of the dimensions of the diaphragm but is proportional directly to the hydrostatic pressure."

The problem was subsequently taken up by Helmholtz,[7] who developed quantitatively and mathematically an hypothesis which Quincke has previously put forward in a qualitative way. It was suggested that, under most circumstances, solids and liquids become electrically charged when brought into contact. The distribution of charges is such that the surface of the solid is charged oppositely to the more or less mobile layer of liquid next it and with which it is in contact. This orientation of charges gives rise to a so-called electrical double layer. A potential gradient applied externally tends to produce a displacement of the electrically charged layer of liquid (in case the solid is fixed in the form of a capillary tube or diaphragm) and if the liquid is not a perfect insulator, the displacement results in a continuous flow[8] of liquid along the surface of the solid.

Freundlich,[9] following a treatment used by Perrin[10] has developed the following expression for the amount of liquid (V_e) transported in unit time through a porous diaphragm :

$$V_e = \frac{q\epsilon ED}{4\pi\ \eta l} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

In this equation E is the total fall in potential through the diaphragm, D and η are respectively the dielectric constant and the viscosity coefficient of the liquid and ϵ is the potential of the Quincke-Helmholtz double layer at the solid-liquid interface. Since $E = RI$ and $R = 1/\gamma q$ where R is the total resistance, I is the current strength, l and q refer respectively to the length and cross section of the diaphragm, while γ is the specific resistance of the liquid, equation (1) may be written

$$V_e = R_o \frac{\epsilon\ ID}{4\pi\ \eta\gamma} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

Since for a given liquid and diaphragm at constant temperature, ϵ, η, D and γ are constant, V_e is proportional only to the current, which flows through the diaphragm and the equation stands in agreement with the first of Wiedemann's empirical laws. If one calculates the difference of hydrostatic pressure P_e produced by electrical endosmose equation (3) is the result :

$$P_e = \beta\, 2\, \epsilon\ ED \quad . \quad . \quad . \quad . \quad . \quad . \quad (3).$$

where β is inversely proportional to the size of the pores in the diaphragm. D, ϵ, and β being constant for a given diaphragm and liquid at constant temperature, equation (3) is a mathematical statement of Wiedemann's third law.[11]

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[7] Wied. *Ann.*, 7, 337 (1879) et. seq.

[8] Cf. Lamb, *Phil. Mag.*, (5) 25, 52 (1888).

[9] *Kapillarchemie*, 225 (1909) ; Cf. Briggs : *Jour. Phys. Chem.* 21 (1917).

[10] *Jour. Chim. Phys.*, 1904.

[11] Cf. Quincke, *Pogg Ann.*, 113, 513 (1861).

2. *Electrical Endosmose with Pure Liquids, Coehn's Rule.*

The early experiments on electrical endosmose taken in conjunction with those on the migration of suspended particles (cataphoresis) made it appear that solids were charged negatively in contact with water. When turpentine was used instead of water, however, Quincke found that conditions were reversed and that such solids as quartz, shellac, silk, clay, asbestos, porcelain, ivory shavings, animal membranes, &c., were electropositive, with the single exception of sulphur. Sulphur weakly electronegative against turpentine, against water was the most strongly electronegative of all the solids which Quincke studied.

Coehn[12] has considered the question raised by these differences, and has proposed the following empirical rule :

When two non-miscible substances, one of which is a pure liquid, are in contact, the substance with the higher dielectric constant is positive against the substance with the lower.

Quincke's data appear intelligible in the light of Coehn's rule. Water and turpentine have dielectric constants of 81 and 5, respectively. Furthermore, the constant in the case of water is one of the largest known and we should expect nearly every substance to be electronegative against water. In contact with turpentine, however, many substances ought to be electropositive, exactly as Quincke found was the case experimentally. Coehn's rule appears to hold fairly well for pure liquids (although there are some weak points in his own evidence)[13], but when applied to aqueous solutions, especially those containing dissolved electrolytes, the rule fails utterly.

3. *Electrical Endosmose with Solutions. Effect of Acids, Bases and Salts.*

In all the early experiments, as we have seen in the preceding sections, water flowed to the cathode. Not only pure water showed this unidirectional tendency, but aqueous solutions appeared to do so as well, the only difference being that the rate of flow was less for solutions than for the pure solvent.[14] Consequently, after the acceptance of the physical theory of the electrical double layer, the belief became general that all solids were charged negatively by contact either with water or with aqueous solutions.

Nevertheless, instances[15] had been recorded where aqueous solutions flowed to the anode rather than towards the cathode. Hittorf[16] found, for instance, that cadmium chloride solutions flowed to the anode through animal membrane but went to the cathode through earthenware, and although Perrin is usually credited with the first definite statement that "reversals" to the anode were possible and could be produced at will by suitable choice of electrolyte in

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[12] *Wied. Ann.*, **64**, 227 (1898), *Zeit. Elektrochemie*, **16**, 586 (1910).

[13] Cf. Briggs, *Jour Phys. Chem.*, **21**, 204 (1917).

[14] Porrett, *Thomson's Annals of Philosophy*, **8**, 74 (1816) : Daniell, *Phil Trans.*, **129**, 97 (1839) ; Gernez, *Comptes rendus*, **89**, 303, 318 (1879).

[15] Wiedemann. *Elektricitat*, **2**, 153 (1883) ; Gore, *Proc. Roy. Soc.* **31**, 253 (1880)

[16] *Zeit. Phys. Chem.* **39**, 613 (1902) ; **43**, 239 (1903).

solution, the point was really established with remarkable clearness by Parker.[17]

Perrin's contribution[18] to what was still an obscure phenomenon, did, however, constitute a great step forward. He devised an apparatus which enabled him to employ many different powdered substances in the form of pervious diaphragms. Turning his attention to the effect of dissolved substances and using extremely dilute solutions (never more concentrated than N/50 and usually about N/500), he concluded first that *electrolytes* alone among solutes influenced the course of electrical endosmose and that the ions had a specific effect. Hydrogen and hydroxyl ions proved particularly active. With a diaphragm of insoluble chromic chloride, for example, dilute alkalies flowed to the cathode whilst dilute acids flowed to the anode—a clear cut reversal. Similar acid alkali reversals were found with alumina, carborundum, sulphur, gelatine, graphite, naphthalene, etc., although none was observed with cotton wool, glass and iodoform. Whenever reversal did occur, there was a certain hydrogen ion concentration at which no flow at all occurred, this point corresponding approximately to an isoelectric condition of the diaphragm.[19]

Since flow to the cathode indicated an electronegative diaphragm, whilst flow to the anode pointed to an electropositive one, Perrin concluded as follows:—

> 'The electric potential of any surface whatever in aqueous solution is invariably increased [made more positive or less negative] by the addition of a monobasic acid and is invariably lowered [made more negative or less positive] by the addition of a non-acid base.'

Perrin considered next a large number of other ions. He found that, excepting hydrogen and hydroxyl, none of the common univalent ions was of much influence on electrical endosmose. Polyvalent ions were more active. Briefly, the results may be summarized in the following statement, sometimes referred to as Perrin's valence rule, which one should compare with the Schulze-Hardy rule of flocculation:

Every diaphragm tends to become charged positively in an acid solution and negatively in an alkaline one. Every ion of unlike sign tends to neutralize the charge on the diaphragm and this tendency increases rapidly with the valence.

Perrin's rule has been extended to alcoholic solutions by Baudouin[20], incompletely to liquid ammonia by Ascoli[21] and by Guillaume[22] to the so-called Bose-Guillaume phenomenon.

Morse and Horn[23] have made use of electrical endosmose to remove air from the pores of porous cups, before impregnating the

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[17] *Johns Hopkins Dissertations*, **31**, 23 (1901); Cf. Briggs, *Jour. Phys. Chem.* **21**, 235 (1917).

[18] *Jour. Chim. Phys.* **2**, 601 (1904).

[19] Cf., however, Bethe and Toropoff, *Zeit. Phys. Chem.* **89**, 597 (1915).

[20] *Comptes rendus*, **138**, 898 (1904).

[21] *Comptes rendus*, **137**, 1253 (1903).

[22] *Ibid.* **147**, 53 (1908); Cf. Briggs: Jour. Phys. Chem. **21**, 215 (1917).

[23] *Amer. Chem. Jour.*, **26**, 801 (1901).

latter with copper ferrocyanide. This led Frazer and Holmes[24] to carry out experiments with an elaborate electro-osmometer, in which they noticed the usual acid-alkali reversals and concluded that the effect of the ions bore some relation to their migration velocities. Coehn[25] has also carried out some interesting electro osmotic measurements with a Pukall filter and solutions of H_2SO_4, $CuSO_4$, HNO_3, acetic acid, alkali metal sulphates, alkali and heavy metal nitrates.

Barratt and Harris[26] in some excellent work with diaphragms of gelatine, agar and parchment, have confirmed in the main the valence rule of Perrin. Their data suggest the problem of finding out what effect the salts of Hofmeister's series would have on endosmose through gelatine and other albumenoids. Recently this question has been investigated by Bethe and Toropoff[27] and although the data are incomplete, there is reason to believe that the lyotrope series really does play an important part.

An elaborate study of electric endosmose in neutral solutions has been completed by Elissafoff[28] in Freundlich's laboratory. The procedure was based on Lemström's[29] method of measuring endosmetic movements in a single capillary without the direct application of electrodes. Elissafoff's data show that Perrin's valence rule holds only to a limited extent. So far as the alkali metal and alkaline earth metal cations are concerned the valency rule holds satisfactorily,[30] but fails in the case of heavy metal and organic cations. For example, certain univalent organic cations appeared quite as effective in neutralizing the charge (see the second part of Perrin's rule) on negative glass or quartz as did the divalent light metal cations. Silver as ion belonged to the divalent metals; mercuric chloride was as effective as aluminum sulphate and far more so than chlorides of the divalent alkaline earths. That the anion is also active was demonstrated by experiments with potassium benzoate and sodium picrate, these anions restraining the tendency of the potassium or sodium to neutralize the negative charge on the walls of the capillary.

No reversal by acids was observed, but the strength of the solutions employed was never greater than one ten-thousandth normal. With certain salts, however, reversals were obtained. Against solutions of thorium nitrate of sufficiently high concentration the glass or quartz became electropositive and a similar reversal occurred with solutions of methyl violet, a basic dye. One should compare this with what Larguier des Bancels[31] found with wool and basis dyes, where the latter showed a striking tendency to make the wool positive.

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[24] *Amer. Chem. Jour.*, **40**, 319 (1908); H. N. Holmes, *Dissertation* (*Johns Hopkins*, 1907).

[25] *Zeit. Elektrochemie*, **16**, 586 (1910).

[26] *Zeit. Elektrochemie*, **18**, 221 (1912); *Biochemical Jour.*, **6**, 315 (1912).

[27] *Loc. cit.*

[28] *Zeit. Phys. Chem.*, **79**, 385 (1912).

[29] *Drude's Ann.*, **5**, 729 (1901).

[30] Freundlich and Elissafoff have employed electro-osmosis to estimate the valency of radium. The results agree with the assumption that radium is a divalent metal belonging to the alkaline earth group. *Phys. Zeit.*, **14**, 1052 (1913).

[31] *Comptes rendus*, **149**, 316 (1909).

4. *Theories of Electrical Endosmose. Contact Electrification and Adsorption.*

Wiedemann believed that the electric current exerted a tractive action upon the liquid in a capillary tube and that the liquid was carried thus from anode to cathode, regardless of the substance composing the walls. In opposition to this view, Graham,[32] Quintus Icilius and Breda and Logemann,[33] showed conclusively that no transport of liquid occurred unless a diaphragm or its equivalent were present. As I observed in the earlier pages of this paper, we owe to Quincke and to Helmholtz the electrical double layer theory of contact electrification. The Coehn rule is an interesting development of this theory. But both Quincke and Helmholtz contributed little to further our understanding of why and how an electrical double layer or its equivalent may be formed when solid and liquid are placed in contact.

For the special case of a metal in contact with its own ions in solution the Nernst theory holds. It is only natural that there should have been proposed an analogous explanation of the contact potentials of non-metallic solids. Every solid dissolves in water to a certain extent and the electrical double layer might be supposed to be produced by differences in the rates of ion diffusion—if the cation diffused faster, a separation of charges would tend to occur and the solid (or liquid immediately in contact with the solid) would become negative. Bredig[34] has given vague expression to this idea by observing that the Coehn rule points to some relation between the solubility of ions in different media and the dielectric constant.

As a matter of fact, the explanation outlined above cannot be the correct one for the case of a solid immersed in a pure liquid, unless one postulates that the liquid remains unsaturated with respect to the solid or that fresh liquid is being supplied constantly. The electrical charge does not disappear when the liquid is saturated with the particular solid, although its sign and intensity may change, while the potential difference at the liquid interface in a concentration cell exists only so long as a difference in concentration is maintained. No *permanent* potential difference can possibly be produced as the result of unequal ion mobilities. Perrin has offered an explanation of his acid-alkali rule by postulating that, since hydrogen and hydroxyl ions are abnormally mobile, they are correspondingly small, and are able thereby to crowd to the surface of a solid more closely than the other ions. This might account for the solid being positive in acid and negative in alkaline solutions. Perrin was unable, nevertheless, to reconcile his theory with all the facts, for he observed that lithium bromide failed to charge a chromic chloride diaphragm negatively although bromine ions are twice as mobile as lithium ions.

Haber[35] has suggested for the particular case of glass against water that the solid is essentially a hydrogen electrode, and that the

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[32] (2) *Phil. Mag.* (4) 8, 151 (1854).
[33] (3) *Pogg. Ann.*, 100, 149 (1857).
[34] *Zeit. Elektrochemie*, 9, 738 (1903).
[35] *Haber and Klemensiewicz, Zeit. Phys. Chem.*, 67, 413 (1909).

magnitude of the potential difference depends upon the concentration of hydrogen ions in solution. Guided by Haber's theory, Cameron and Oettinger[36] performed some rather inconclusive experiments on the potential produced by acid and alkaline solutions forced through a capillary of glass. Haber's theory, as Freundlich points out, is open to the serious objection that electrical endosmose does not depend entirely upon hydrolysis of the dissolved solute, as it should do if the concentration of hydrogen ions is the only factor. Acidity and alkalinity, while of very great influence, are not the only factor determining electro-osmotic effects.

Freundlich[37] was the first to point out clearly the intimate relations existing between adsorption and electrical endosmose. This development may be said to be the result of his own work on adsorption and the speculation of Perrin[38] regarding the analogies between the behaviour of suspensions and the peculiarities of electrical endosmose. Freundlich went still further than Perrin. He had already shown the relation between adsorption and the stability of suspensions and had pointed out the validity of the Schulze valence rule for adsorbed light-metal cations and the ordinary anions. He had discovered, too, that many organic ions as well as the heavy metal cations were exceptions to the Schulze rule. He was able, as a result, to emphasize the similarity between the Schulze rule and the valence rule of Perrin, and, from Elissafoff's data, he showed that exceptions to Schulze's rule were exceptions likewise to Perrin's. From this it was only a step forward to apply to electro-osmotic phenomena a definite theory based upon adsorption, or more specifically, upon the selective or preferential adsorption of ions.

Freundlich called the difference of potential between solid and solution, the "adsorption potential." If a cation is adsorbed to a greater extent than the accompanying anion, the solid becomes positively charged, and if it is employed as a diaphragm, the electrical endosmose will occur from cathode to anode. For the case of a solid against pure water it is only necessary to postulate selective adsorption, either of the ions already present in water or produced by the solid dissolving. When preferential ion adsorption occurs, the number of ions actually adsorbed is very small, because the charge on a single ion is relatively large and the electrical double layer that is established opposes any further spatial separation of positive and negative ions.

Freundlich[39] has recently modified his original theory of the the adsorption potential, without improving matters appreciably and not without adding several complicating hypotheses. He suggests that the contact potential of the diaphragm depends upon the nature of the material of which it is composed (upon differences in solution tension of the ions thrown out) and that it is affected only indirectly by adsorption. In my opinion contact potential does undoubtedly depend upon the nature of the solid itself, but the important thing

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[36] *Phil. Mag.* (6), **18**, 586 (1909).

[37] *Kapillarchemie*, 245 (1909); *Zeit. Phys. Chem.* **79**, 407 (1912).

[38] *Jour. Chim. Phys.*, **3**, 85, (1905).

[39] Freundlich and Elissafoff, *Zeit. Phys. Chem.*, **79**, 407 (1912).

is the power of the solid to adsorb selectively the ions present in the liquid from the beginning, or produced by the solid dissolving.[40]

Frazer and Holmes[41], following a suggestion rejected by Whetham,[42] have advanced a distinctly different hypothesis based upon the solvate theory. If the hydration of the cation is greater than that of the anion, for example, liquid should be carried from anode to cathode; and this is what the authors found to be the case with neutral salts of the alkalies against earthenware. Since the mobility of an ion might be regarded as an inverse measure of its hydration, one could expect a strong flow to the cathode in an alkaline solution and a strong flow to the anode in an acid solution. This deduction agreed with the facts as far as they were determined by Frazer and Holmes. Barratt and Harris, who favoured a similar theory, were rather overwhelmed by its consequences, for they calculated that anywhere between 18 and 370 molecules of water were transported through agar diaphragms for every molecule of solute decomposed electrolytically.[43]

The solvate theory of Frazer and Holmes cannot be correct, for one would have to conclude, in consequence, that there is a fundamental difference between electrical endosmose and Quincke's diaphragm currents. Moreover the theory assigns to the diaphragm a subordinate and purely mechanical rôle. Neither does it explain why mere traces of lanthanum salts, for instance, reduce the flow of an alkaline solution, or why an acid solution *flows to the cathode* through powdered glass. If there is any relation between endosmose and ion mobility, it is better to consider it an indirect one, produced by a possible relation between ion mobility and ion adsorption, as I pointed out when discussing Perrin's speculations.

After careful consideration of the facts in the case, it would appear that the most satisfactory working hypothesis to account for contact electrification of this type (and hence to serve as basis to an understanding of electrical endosmose and cataphoresis) is the one proposed originally by Freundlich and emphasized recently by Bancroft.[44]

By virtue of their surface properties solids are able to adsorb substances from a liquid with which they are in contact. They may adsorb a particular ion preferentially, in which case we have selective ion adsorption and either a positive or negative charge on the solid. The adsorbing substance tends to be peptized by the adsorbed ion.

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[40] The modified Freundlich theory of the ionization of colloid aggregates, according to which particles of a basic nature, such as ferric hydroxide, are believed to give off OH ions to the liquid and become positively charged, while particles of acid nature, such as silica, give up H ions to the liquid and become electro-negative. The suggestion has received the support of Zsigmondy and many others. While it is easy thus to account for the charge borne by substances such as silica and ferric hydroxide, it is by no means so simple to do so with substances such as sulphur, carborundum, and diamond, all of which are charged electrically when placed in contact with water or suitable aqueous solutions. Compare Burton, *The Physical Properties of Colloid Solutions* (1916).

[41] *Am. Chem. Jour.*, **40**, 319 (1908).

[42] *Theory of Solution*, 292 (1902).

[43] In connection with Frazer and Holmes' theory, see Bethe and Toropoff, *Zeit. Phys. Chem.*, **89**, 597 (1915).

[44] *Jour. Phys. Chem.*, **16**, 312 (1912); *Trans. Am. Electrochem. Soc.*, **21**, 233 (1913).

Or solid may adsorb the solvent itself and be peptized, while the other possibilities, all of which tend to produce peptization, are adsorption of a non-electrolyte, an indissociated salt, or a second colloid.[45] Since electrical endosmose has to do with electrically charged surfaces, we are concerned chiefly with preferential adsorption of ions.

It is necessary to postulate that every solid has a specific adsorbing power for a given ion, depending upon the specific surface[46] of the solid, upon the temperature, upon the concentration of the particular ion in the solution and upon the other ions present, or adsorbed previously by the solid. When the ion content of a liquid is vanishingly small, we shall have but little ion adsorption and little electrical endosmose. On the other hand 'pure' water shows marked endosmose through many diaphragms. This is a case of preferential ion adsorption where the irons are produced both from the ionization of water itself and the solution of the solid, which is a very important matter in some cases (notably glass).[47] Since the majority of solids are charged negatively against water, hydroxyl ions are probably adsorbed in preference to hydrogen ions. In discussing the potential of a solid against water *originally pure*, we must accordingly take two factors into account.[48]

(1) The specific adsorption capacity of the solid for hydrogen and hydroxyl ions produced by the dissociation of water.

(2) The dissolution of the solid, which, though extremely slight in many cases, may produce ions that are strongly adsorbed.

Hydrogen ions are often adsorbed preferentially from solutions containing them, especially from acids, though we have seen that the rule is by no means a general one. Experiments by the author have shown that aluminum, which is positive in dilute hydrochloric acid, is weakly negative in citrate acid where the equivalent selective adsorption of the citrate ion must be greater than that of the hydrogen ion. Moreover, we know that metal sulphides are peptized by hydrogen sulphide, an acid, yet the adsorbed ion is sulphur and not hydrogen; for the particles in suspension are electro-negative.[49]

In general the same statement applies to the adsorption of hydroxyl ions. Solids seem to have a somewhat greater adsorption affinity for hydroxyl ions than for hydrogen ions, though there are notable exceptions to this generalization. The general theory covering the electrical endosmose of all liquids and solutions may be formulated as follows:—

(1) Electrical endosmose depends upon the preferential or selective adsorption of ions and is influenced only by those ions which are adsorbed by the diaphragm.

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[45] Cf. Bancroft, *Jour. Phys. Chem.*, 20, 85 (1916).

[46] Wo. Ostwald, *Grundriss der Kolloidchemie*, 29 (1912).|

[47] Cf. Briggs, Bennett, and Pierson, *Jour. Phys. Chem.*, 22, 256 (1918); *Trans. Am. Electrochem. Soc.*, 31, 257 (1917).

[48] In this connection, compare the statement of Schwerin, Brit. Pat. 10793 (1909) wherein he emphasises the importance of taking into account the dissolving of the diaphragm.

[49] Winssinger, *Bull. Soc. chem.*, Paris (3), 49, 452 (1888); Linder and Picton, *Jour. Chem. Soc.*, 61, 116 (1892).

In this connection compare the beautiful experiments of Lottermoser, *Jour. prakt. Chem.* (2), 72, 53 (1905).

(2) Any circumstance or condition which changes the adsorption produces an effect upon electrical endosmose. Electrical endosmose varies, therefore, with the condition of the surface (for a given solid), with the relative and absolute ion concentrations, with the temperature and so forth.

(3) The *direction* of endosmose indicates the sign of the diaphragm; the *rate* of endosmose is proportional to the intensity of the charge on the diaphragm in case the potential gradient through the diaphragm is constant. When the liquid flows to the cathode, the diaphragm is negative; when it flows to the anode the diaphragm is positive. No flow at all probably indicates an iso-electric condition.[50]

(4) A diaphragm tends to become positive by the selective adsorption of cations, and negative by the adsorption of anions.

(5) The positive charge produced by an adsorbed cation is neutralized more or less by the addition of an adsorbed anion, the effect increasing with the concentration of the anion. Similarly, the negative charge produced by an anion is neutralized by an adsorbed cation.

(6) Electrical endosmose measures the tendency of a solid to form an electrical suspension in a given liquid, but it does not measure the tendency of the solid to form a non-electrical suspension, such as is produced by adsorbed solvent, solute or neutral colloid.[51]

5. *Adsorption Potential, Temperature and other Factors.*

Returning to equation 1 it is hardly necessary to point out that ϵ, representing the potential of the Quincke-Helmholtz double layer, stands also for the 'adsorption potential' of the solid-liquid interface. Quincke and also Von Tereschin have calculated values[52] of ϵ for a glass-water interface, using data obtained by electro-osmotic experiments with capillary tubes. The values lie close to 50 millivolts and are of the same order of magnitude as those[53] calculated from the migration velocities of particles suspended in water (cataphoresis).

From the beginning it has been recognized that electrical endosmose is greatly affected by changes of temperature. Perrin found that, with rising temperature, the volume of liquid transported under otherwise constant conditions increased very rapidly, and he reported *that temperature had about the same effect on the rate of endosmose as it had on the fluidity (reciprocal of viscosity) of the liquid.* Equation 1 indicates that this condition is plausible (since D does not change rapidly with the temperature), provided ϵ remains practically constant as the temperature changes. Perrin's conclusion that the

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[50] Note that Bethe and Toropoff maintain that the 'indifferent' point (zero flow) and the isoelectric point do not necessarily coincide exactly. *Zeit. Phys. Chem.* **89**, 597 (1915).

[51] Schwerin has applied this principle in Brit. Pat. 2379 (1911), where in order to obtain stable suspensions he adds acids to those substances which migrate to the cathode and bases to those which migrate to the anode. In 27930 (1911) he adds adsorbed positive or negative colloids (alumina, humic acid, silica, etc.) to obtain the same results.

[53] Freundlich, *Kapillarchemie*, 227 (1909).

[52] Data compiled by Burton, *Physical Properties of Colloid Solutions*, 135 (1916).

temperature coefficient of viscosity determines very largely the value of the temperature coefficient of electro-osmose, is strengthened by experiments of Coehn and Raydt,[54] Cameron and Oettinger,[55] and of Briggs, Bennett and Pierson.[56]

On the other hand Cruse[57] found an apparent maximum in the rate of electro-osmose, this maximum occurring between 35° and 40° C. Briggs, Bennett, and Pierson have shown that Cruse's maximum was probably due to the diaphragm not being in equilibrium with the liquid phase. They have carried out determination of the temperature coefficient and find that with diaphragms of asbestos, cellulose (filter paper) and carborundum, the rate of flow increases with rising temperature slightly less rapidly than the viscosity decreases; the rate for a given diaphragm at constant temperature is also very exactly proportional to the applied external potential. It is only fair to point out, however, that since adsorption varies with the temperature, and since the temperature coefficients for anion and cation are not necessarily equal, ε may also vary with the temperature and might even change its sign. In the cases just discussed, ϵ is probably very nearly constant.

6. *Related Phenomena.*—Cataphoresis is the reverse of electrical endosmose. One is dealing here with a mobile or "floating" diaphragm. The fundamental theory is without question the same; such differences as appear to exist between the two processes being due, in all likelihood, to flocculation complicating the phenomena of cataphoresis. The particles are positive if they migrate to the cathode, negative if they migrate to the anode. Acid-alkali reversals are known, and strongly adsorbed ions determine the charge on the particles. As the subject constitutes a separate report in this series, it will not be considered further at this time.

Perrin[58] has pointed out that the curious Bose-Guillaume phenomena is a special case of Quincke's "diaphragm currents," and is an electro-osmotic phenomenon. Guillaume's data[59] are evidence in favour of the adsorption theory. Electro-stenolysis is another phenomenon dependent upon contact electrification.

When certain aqueous solutions are separated from water by a porous plate of porcelain, for instance, a slight but measurable osmosis is often observed. In some instances the osmotic flow occurs from the solution into the water and not from the water into the solution as one would expect it to do. Such apparently abnormal osmosis is termed "negative osmose."[60]

According to Bartell the most plausible way of accounting for osmosis of this type is to assume that it is caused by the "polarization" of the membrane. The membrane being in contact with different liquids, the adsorption potential will be different for each

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[54] *Drude's Ann.*, **30**, 797 (1909).

[55] *Phil. Mag.* (6) **18**, 586 (1909).

[56] *Jour. Phys. Chem.* **22**, 256 (1918).

[57] *Phys. Zeit.*, **6**, 201 (1905).

[58] *Comptes rendus*, **147**, 55 (1908).

[59] *Ibid.* **147**, 53 (1908).

[60] Bartell, *Jour. Am. Chem, Soc.* **36**, 646 (1914); Bartell and Hocker, *Jour. Am. Chem. Soc.*, **38**, 1029 (1916); Freundlich, *Zeit. Kolloidchemie*, **18**, 11 (1916); Girard, *Comptes rendus*, **146**, 927 (1908); **151**, 99 (1910) *et seq.*

face and there will be established a difference of potential between the ends of the capillaries. This difference in potential causes electrical endosmose to take place in one direction or the other and an apparent osmotic action results. That a difference of potential really does exist between the water side and the solution side of the diaphragm has been demonstrated experimentally. The explanation outlined above is an ingenious one, but the problem is by no means solved as yet.[61]

SUMMARY.

Electro-osmotic phenomena with pure liquids and solutions have been described and the various theories discussed critically. The most plausible hypothesis seems to be the Freundlich-Bancroft theory of selective ion adsorption. The effect of temperature changes and other influences have been considered and in conclusion mention has been made of negative osmosis and other phenomena related closely to electrical endosmose. Cataphoresis and electrostenolysis have not been included.

RECENT PAPERS ON ELECTRICAL ENDOSMOSE.

'Electric osmosis and concentration of electrolytes.' J. O. WAKELIN BARRATT and ALBERT B. HARRIS, *Zeit. Elektrochemie*, **18**, 221 (1912).

Authors have studied electrical endosmose through diaphragms of gelatin, parchment and agar. Rate of flow and direction of osmose appear to be determined by the nature and valence of the ions in solution. See next reference for more comprehensive article.

'Electro-osmosis.' J. O. WAKELIN BARRATT and ALBERT B. HARRIS, *Biochemical Jour.*, **6**, 315 (1916).

See preceding reference. Article gives data for a large number of diaphragm substances, describes ingenious apparatus and discusses the hydration theory. Electro-osmose into human forearm studied.

'The effect of electrolytes on electrical endosmose.' G. VON ELISSAFOFF, *Zeit. Phys. Chem.*, **79**, 385 (1912).

Very important article showing where Perrin's valence rule holds and where it fails. In an appendix written with Freundlich, the author argues very effectually in favour of the ionic adsorption theory.

'Electrical endosmose.' WILDER D. BANCROFT, *Jour. Phys. Chem.*, **16**, 312 (1912); *Trans. Am. Electrochem. Soc.*, **21**, 233 (1912).

Proposes ionic adsorption hypothesis and applies it to some hitherto unexplained experiments of REED, *Trans. Am. Electrochem. Soc.*, **2**, 238 (1902). Article includes discussion of addition agents in electroplating.

'Determination of the valence of radium by means of electrical endosmose.' HERBERT FREUNDLICH and G. VON ELISSAFOFF, *Phys. Zeit.*, **14**, 1052 (1913).

Radium appears to be divalent and closely related to barium. Method depends upon application of Perrin's rule and requires less than 0·01 milligram of substance.

'Hydration of organic colloids under the influence of electrolysis.' E. DOUMER, *Comptes rendus Soc. Biol.*, **76**, 40 (1914).

Some curious hydration and dehydration effects observed during electrical endosmose with gelatin.

'Negative osmose.' F. E. BARTELL, *Jour. Am. Chem. Soc.*, **36**, 646 (1914).

Author accounts for positive and negative osmosis through porcelain by assuming that selective adsorption polarises the membrane and that the osmosis is really electrical endosmose.

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[61] Cf. Bancroft, *Jour. Phys. Chem.*, **21**, 441 (1917).

'Electrolytic endosmose.' HORACE G. BYERS and CARL H. WALTER, *Jour. Am. Chem. Soc.* **36**, 2284 (1914).
Complicated endosmotic experiments with three and six compartment cells.

'Electrolytic processes of diaphragms.' I. Disturbance of Neutrality. ALBRECHT BETHE and T. TOROPOFF, *Zeit. Phys. Chem.* **88**, 686 (1914).
With organic diaphragms electro-osmose causes H* concentration to decrease at anode side and increase at the cathode side. Electrolytes in solution affect the speed with which the neutrality is disturbed. The order of anions and cations recalls the Hofmeister series.

'Electrolytic processes at diaphragms.' II. The dependence of the magnitude and direction of the concentration changes and the water movement upon the hydrogen ion concentration. A. BETHE and T. TOROPOFF, *Zeit. Phys. Chem.*, **89**, 637 (1915).
Article includes a number of experiments on electrical endosmose with gelatin, albumin, collodion, animal and other membranes. Interface potential is an ionic adsorption phenomenon ; electrical endosmose depends both upon interface potential and the relative hydration of mobile ions.

'The relation of osmose of solutions of electrolytes to membrane potentials.' Theoretical. F. E. BARKER and C. D. HOCKER, *Jour. Am. Chem. Soc.*, **38**, 1029 (1916).
Author combines ionic adsorption theory with Nernst diffusion theory to account for polarization of membrane.

'The osmose of some solutions of electrolytes with porcelain membranes and the relation of osmose to membrane potential.' F. E. BARTELL and C. D. HOCKER, *Jour. Am. Chem. Soc.*, **38**, 1036 (1916).

'Negative osmosis.' HERBERT FREUNDLICH, *Zeit. Kolloidchemie*, **18**, 11 (1916).
(Original article not available.)

1917.

'Electrical endosmose,' I. T. R. BRIGGS, *Jour. Phys. Chem.*, **21**, 198 (1917).
Complete historical summary with references to literature. Critical study of different theories of electro-osmose and contact potentials. Author prefers ionic adsorption hypothesis of Freundlich and Bancroft.

'Electrical endosmose and adsorption.' T. R. BRIGGS, H. L. PIERSON, and H. S. BENNETT, *Trans. Am. Electrochem. Soc.*, **31**, 257 (1917).
See below.

1918.

Electrical endosmose,' II. T. R. BRIGGS, H. S. BENNETT, and H. L. PIERSON, *Jour. Phys. Chem.*, **22**, 256 (1918).
Authors describe new and convenient electro-osmometer and study the relation between the rate of endosmose and voltage, temperature and other factors. Data tend to confirm ionic adsorption theory.

ELECTRICAL ENDOSMOSE. II. INDUSTRIAL APPLICATIONS.

By T. R. BRIGGS, *Cornell University.*

INTRODUCTION.

During recent years increasing attention has been paid to the possibility of making some practical application of electro-kinetic processes, including electrical endosmose.[1] It is proposed in this report to indicate to what extent and in what direction these industrial applications have been attempted and to elucidate, wherever necessary and whenever possible, the principles involved. Owing

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[1] Cf. Foerster : *Elektrochemie*, 116 (1915); Kruyt : *Chem. Weekblad* **14**, 766 (1917); *Chem. Abstr.*, 11, 2984 (1917) ; Lewis : *Jour. Soc. Chem. Ind.*, **35**, 575 (1916).

to the close relationship existing between electrical endosmose and cataphoresis and because of the not very surprising fact that cataphoresis plays a very important part in many so-called "electro-osmotic" processes in practice, no attempt will be made to exclude technical cataphoresis from this discussion or to limit it strictly to electrical endosmose.

DEWATERING PEAT BY ELECTRICAL ENDOSMOSE.

The possibility of using electrical endosmose and cataphoresis in the removal of water from muds, pulps and jelly-like or spongy masses containing materials in suspension, has been considered in some detail during recent years, especially by Count Botho Schwerin in Germany. The peat bogs of the latter country and of Ireland offer a very great potential source of fuel provided only a sufficiently economical method can be devised for dewatering the material. Filtration and centrifuging are not applicable because of the slimy nature of the peat pulp, which causes an impervious layer to form on the filter or in the centrifuge. Attempts have been made to submit the peat mud to stream evaporation combined with drying in the air. The mud as it comes from the bog contains approximately 90 per cent. of water and to evaporate a pound of this material containing 50 per cent. of water (which can then be cut into blocks and dried in the air) approximately 880 B.T.U. are required. After air-drying the intermediate 50 per cent. material, a final product results, containing about 20 per cent. of moisture and possessing a calorific power of about 8100 B.T.U. per pound. As one pound of the original mud yields rather less than one-eight pound of dried peat, yielding not more than 1000 B.T.U., it is evident at once that the problem cannot be solved by a direct dehydration process such as the one outlined above. But it might be possible in such a duplex process to substitute electro-osmose for the preliminary evaporation and so either to remove mechanically a large part of the water or else to concentrate the suspended particles in the pulp by causing them to migrate by cataphoresis to the electrodes. It is well to bear in mind, in this connection, that the electro-osmotic process cannot possibly *dry*[2] anything; it can at best remove water only to the extent that filter presses or centrifuges do.

Count Schwerin was granted his first British Patent[3] in 1900. Various types of apparatus were disclosed, in all of which the peat was treated between a suitable anode and a perforated cathode. On passing a direct current between the electrodes, water was forced out of the spongy or semi-liquid mass and escaped through the perforations in the cathode. At the same time some of the suspended peat migrated to the anode and formed there a fairly dense layer. Schwerin called this the "motorial" action of the electric current.

He next patented an apparatus[4] consisting of a series of superposed horizontal partitions, corrugated to allow liquids to flow away, and supporting boxes containing raw peat. These boxes were filled with

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[2] Cf. Nernst and Brill: *Verh. Deutsch. phys. Ges.*, **11**, 112 (1909).

[3] Brit. Pat. 12431 (1900).

[4] Brit. Pat., 22301 (1901).

pervious metallic bottoms serving as cathodes and the anodes pressed down from above upon the peat. The Höchst Color Works experimented with Schwerin's process on a semi-commercial scale and took out several additional patents[5] on improvements of apparatus and procedure. Other patents were taken out in Great Britain by Siemens and Halske,[6] Doull,[7] Kittler,[8] Verey and Downes[9] and Simm,[10] although the last named inventor really used the current for heating purposes only.[11]

Schwerin,[12] addressing the Bunsen Society at the Fifth International Congress at Berlin in 1903, discussed some of the preliminary experiments made with his process and attracted at the time a good deal of attention. Starting with a peat mud containing originally nearly 90 per cent. moisture, it was claimed that a volume of water equal to three-fourths the volume of the mud could be removed and that this could be done with an expenditure of only one-fifth part of the energy available in the recovered peat. The most suitable potential gradient through the peat was stated to be 4 or 5 volts per centimetre and 13 to 15 kilowatt-hours were required in removing one cubic metre of water. Unfortunately, the peat obtained at the end of the treatment contained as high as 65 per cent. of moisture, although the material itself was easily amenable to moulding into bricks or other shapes. It was therefore necessary to subject the moulded peat to prolonged and tedious drying in the air, in order to reduce the water content to the permissible maximum of 20 per cent.

Promising as Schwerin made his process appear, it proved a failure when tried out on a commercial scale apparently because air-drying the material with 65 per cent. moisture proved to be far more tedious and costly than experience with 50 per cent. material had led those interested to expect.[13] Nevertheless, it is possible that the method may some day prove feasible if the electro-osmotic treatment can be improved to yield a product with less than 50 per cent. of moisture ; such an improvement might be brought about, as Foerster suggests, by previously disintegrating[14] the jelly-like aggregates in the original peat and thus permitting closer packing of the peat solids. A very large proportion, however, of the water in peat is *adsorbed*, and the difficulty as I see it lies in the removal of this adsorbed moisture ; only water held *mechanically* can be removed by electro-kinetic processes.[15]

In recent years Schwerin has endeavoured to improve things by applying to his purposes some of the newer knowledge gained from

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[5] Brit. Pats., 3795, 24670 (1904) Farbwerke, vorm. Meister Lucius u. Brüning.

[6] Brit. Pat., 14195 (1903).

[7] Brit. Pat., 1717 (1903).

[8] Brit. Pat., 126 (1904).

[9] Brit. Pat., 2226 (1907).

[10] Brit. Pat., 4792 (1905).

[11] Cf. Davis : *Bull. U.S. Bur. of Mines*, **16**, 122 (1912).

[12] *Ber. V. int. Kong. angew. Chem.*, **4**, 653 (1903) ; *Zeit. Elektrochemie*, **9**, 739 (1903).

[13] Cf. Foerster : *Elektrochemie*, 118 (1915).

[14] Cf. Brit. Pats. 6993, 6995 (1914).

[15] The same difficulty arises in the removal by cataphoresis of iron oxide from clay. Cf. the "osmose" process of clay purification.

the researches of Perrin and others. By adding a trace of caustic alkali to the peat mud, the dewatering is greatly hastened.[16] He has also devised an interesting electro-osmotic filter press[17] in which peat or clay are dewatered under pressure between filter diaphragms and an electric current sent through. It is claimed that by continuous pressure and electrical endosmose, the pressure necessary to filter clay or peat suspensions may be reduced twenty fold. Further improvement is said to be gained by disintegrating[18] in a ball mill the peat as it comes from the bog and adding the electrolyte to the mill.

THE "OSMOSE" PROCESS OF PURIFYING AND DEWATERING CLAY.

The electro-osmose process was next applied to the dewatering and purification of clay,[19] for the purpose of transforming a low grade and impure material into something approximately in quality ball-clay or china-clay. In the older processes the impure clay is first made into a thin slip with water, the slip is allowed to stand until the coarser particles (usually silica) have had time to settle, and the fine particles of clay still remaining suspended in the slip are removed by gravity settling, filtration or centrifugal separation. The settling process is very tedious, and the difficulties of filtering or centrifuging are very great.

Schwerin proposed to hasten and improve the process by dewatering the suspended clay by means of cataphoresis. The crude clay substance is made into a slip with water in the usual way, the kaolin is deflocculated (peptized) by the addition of a little sodium hydroxide or other agent such as humus or sodium silicate, and the coarser particles are allowed to settle. If the impurities such as silica or iron oxide happen to consist of relatively coarse particles unadsorbed by the clay itself or even if they are finely divided but are not deflocculated (peptized) by the addition agents, the crude clay is purified to a certain extent and is usually improved in plasticity and firing qualities. The clay suspension, after settling, is pumped into the "osmose" machine where it is dewatered by cataphoresis.

According to Ormandy[20] the "osmose" machine consists of a semicircular trough, in the center of which a revolving metal drum serves as anode and outside of this drum and distant about half an inch from it is a cathode of wire netting, surrounding the anode drum on the under side. When the suspension is pumped between the electrodes, the impurities are said to settle on or under the wire cathode, whence they are removed, while clay is deposited on the slowly revolving drum in a blanket $4\frac{1}{2}$ feet wide and $\frac{1}{4}$ inch thick, containing not more than 20 per cent. of moisture. For other details

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[16] Cf. Brit. Pats. 3364, 11626 (1911).

[17] Cf. Brit. Pats. 14369, 23545, 24666 (1912); 10873 (1913); Ulzer: *Zeit. angew. Chem.*, **28** (1), 308 (1915).

[18] Brit. Pats. 6993, 6995 (1914).

[19] Cf. Brit. Pats. 10024 (1907); 28185 (1911) and others.

[20] *Brit. Clayworker*, **22**, 9 (1913); *Pott. Gaz.*, **38**, 1162 (1913); **40**, 178 (1915). Cf. Stoermer: *Tonindustrie Zeit.*, **36**, 178 (1915); also Hopkins: *Brit. Clayworker*, **22**, 62 (1913), Cf. Brit. Pats. 725 (1912); 3434 (1913), etc.

as to operation, size of plant, costs and other matters, Ormandy's article and the interesting discussion on the part of members of the Ceramic Society should be consulted.

Among the advantages claimed for the method are (1) greater ease and steadiness of operation; (2) smaller plant-space; (3) lower labour cost; (4) process not only dewaters clay but purifies it as well, thus supplementing the preliminary settling treatment, (5) clay after treatment is very plastic and sinters at a temperature far below the melting point.[21]

Schwerin's "osmose" method has been discussed critically by Bleininger[22] who points out that the "osmose" machine is merely a substitute for the filter press or centrifuge, having the advantage over most filter apparatus of being automatic and continuous. By experiments of his own Bleininger assured himself that no measurable purification occurred during the cataphoretic separation of the clay and that such change as the clay finally underwent was due to the preliminary deflocculation and settling. At the present time Bleininger[23] is of the opinion that, although the "osmose" process can be made to work satisfactorily, the same results can be obtained without the use of the electric current by deflocculating the clay with caustic soda, thus removing the granular impurities, coagulating the suspension with acids or aluminum chloride and filtering out the precipitated material. At any rate no electro-osmose plants are in operation in the United States, while the precipitation process is giving satisfaction at the Saylersburg, Pa. plant of the Miner-Edgar Company, Brooklyn, N.Y., and that of the Georgia Kaolin Co., at Macon, Georgia.

There seems to be a great deal of misunderstanding with regard to the extent to which the "osmose" machine acts as a purifier. Ormandy points out that clay or kaolin particles are electro-negative, silica is more or less neutral while oxides of iron and titanium are positive. Hence only kaolin migrates to the anode, silica settles out and the iron collects at the cathode. In the first place, suspended ferric oxide, although called a positive colloid, is not necessarily positive against an alkaline solution and probably is electronegative[24] unless there happens to be present in the solution some strongly adsorbed cation, such as calcium or magnesium, to counteract the effects of hydroxyl. Another point which has been overlooked is the condition of the iron oxide in the clay—if the oxide is adsorbed by the kaolin the electrical treatment cannot remove an appreciable amount of iron from the clay. To be sure, Schwerin[25] claims that adsorption compounds can be broken up by electrical endosmose or cataphoresis, but this can occur only when there is a relatively large amount of one substance in the liquid phase *and in adsorption equilibrium with the solid phase.* As to the results actually obtained, it is interesting to note that of 25 clays reported

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[21] Cf. Brit. Pat. 3434 (1913).

[22] *Trans. Am. Cer. Soc.* **15**, 338 (1913); *Techn. Paper U.S. Bur. Standards* **51**, (1915).

[23] Private communication to the author, June, 1918.

[24] Ferric oxide peptized by glycerine and NaOH is negative and migrates to the anode. Fischer and Kusnitzky: *Biochem Zeit.*, **27**, 311 (1910).

[25] Brit. Pats. 14369 (1912).

by Ormandy, 15 contained less iron after purification while 8 contained more.

Shortly before the war, Schwerin organized the Elektro-osmose Aktien Gesellschaft of Frankfort-on-the-Main, for the purpose of developing his multiplicity of inventions, commencing operations with a capital of three million marks.[26] Several improvements and changes have been made in the clay process since that time, along the lines of adding negative colloids (silica, humus) to the clay suspension,[27] employing electro-osmotic pressure filters,[28] using diaphragms[29] differing (1) in size of pores, (2) in sign and intensity of interface potential, and making several changes in the "osmose" machine itself. There is not enough available information for one at the present time to evaluate those modifications. The process as a whole appears to be far the most promising one Schwerin has developed.

ELECTRICAL TANNING.

Electrical tanning[30] of leather is the oldest practical application of electrical endosmose, having been originated, according to Buse, by Grosse in 1849. In 1874 de Meritens at Petrograd used electricity in 600 tan pits, employing a layer of carbon at the bottom as anode, placing on this alternate layers of hides and tan bark and concluding with a sheet of zinc as cathode. Buse decribes other systems (Groth, Worms and Balé, etc.) and reports that the electric current increased the rate at which tannin was taken up from 338 to 533.

So far as one is able to judge, electricity has been applied to tanning processes for two purposes (1) to hasten the process by heating the bath electrically, (2) to hasten the process electro-osmotically by the tan liquor into and through the skins. For the first purpose either direct or alternating current may be used, but for the latter only direct current can be employed. It seems incorrect to advocate as Williams does the use of an alternating current to produce the endosmotic effect of a direct current without at the same time causing electrolytic decomposition of the tannins.

The electro-osmotic method of tanning is decidedly more rapid than the ordinary diffusion process and would be a distinct success were it not for anodic oxidation of the tannin. Schwerin[31] has endeavoured to prevent this by surrounding the electrodes with diaphragms but his process and apparatus appear to be excessively intricate. It ought, however, to be possible to solve all these difficulties, for it is undoubtedly in this field and in impregnation in general that electrical endosmose should find widest and most successful application.

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[26] *Elektrotechn. Zeit.*, **35**, 860 (1914).

[27] Brit. Pats. 27931 (1911), etc.

[28] Brit. Pats. 23545 (1912).

[29] Brit. Pats. 2466 (1912).

[30] Folsing: *Zeit. Elektrochemie*, **2**, 167 (1893); Rideal and Trotter: *Jour. Soc. Chem. Ind.*, **10**, 425 (1891); Buse: *Ibid.*, **19**, 57 (1900); Rideal and Evans: *Ibid.*, **32**, 633 (1913); Williams: *Jour. Am. Leather. Chemists. Assoc.*, **8**, 328 (1913); Groth: Brit. Pat. 19239 (1912).

[31] Brit. Pat. 21190 (1914).

Preservation of Timber. Electro-osmotic Impregnation.

At various times it has been proposed to dry timber by electro-osmotically removing the sap. While electrical endosmose can scarcely prove suitable for this process alone, it might be very effective in replacing the sap juices with liquid disinfectants. Alcock and Company, Proprietary, Ltd.,[31a] of Melbourne, propose to impregnate timbers electrically, by placing them on end in a shallow cathode vessel containing a conducting liquid and driving into the upper ends hollow metal anodes filled with the liquid preserving medium with which the wood is to be impregnated. On passing a current, electrical endosmose to the cathode takes place, sap is forced out of the timber and into the lower receptacle and its place is taken by the liquid preservative forced in at the top. If the consumption of electric power is not too great, the method ought to prove a success. In this connection it is interesting to find a note[32] to the effect that the injury to trees caused by stray currents may be due to electrical endosmose. This is quite possibly true in case the electric current is a direct one.

Manufacture of Bricks. Lubricating Metal Surfaces in Contact with Clay.

A very effective and apparently mysterious process which is unquestionably an application of electrical endosmose was announced by Dawkins[33] in 1913 at the Chicago Convention of the National Brick Manufactures Association. Wet clay has a distinct tendency to adhere to smooth metal surfaces. To prevent this a lubricant is used, the lubricants including oils, emulsions and water itself. Water is particularly useful because a layer of it on the metal prevents the clay from sticking, softens the surface of the clay as it is being cut or moulded and gives the brick a smooth finish. It was found that if metal in contact with the clay is made cathode and a current is passed, the clay no longer tends to adhere and all the effects of lubrication are duplicated. In making wire cut bricks electrical "lubrication" is said to reduce the power consumption by 25 to 30 per cent.

It has been suggested that the current forms a layer of hydrogen over the electrode and that this causes the apparent lubrication. What really happens is this: when the current flows water is carried through the clay to the cathode (the metal) and forms a layer between it and the clay; it is this layer of water which prevents the clay from sticking and acts as a lubricant.

ELECTRO-THERAPEUTICS. ELECTRO-OSMOTIC INFILTRATION OF DRUGS.[34]

Shortly after the early experiments, especially those of Wiedemann, had demonstrated the ease with which electrical endosmose

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[31a] Brit. Pat. 25175 (1910).

[32] Schneckenberg: *Elektrochem. Zeit.*, **19**, 151; Chem. Abstr.

[33] Clayworker 57, 426 (1912) Cf. Brit. Clayworker: **22**. 91, 92 (1913).

[34] Morton: *Cataphoresis* (1898); Herdman: Bigelow's *Internot. Sys. of Therapeutics*, **30**, (1894); Peterson: *Ibid.* C 1 (1894); Jones: *Med. Electricity* (4th Ed.) 230 (1904); Traube and Berczeller: *Internat. Zeit. Biol.* **2**, 107 (1915).

occurs through animal membranes, attempts were made to apply the process to living membranes and tissues. In 1859 Richardson produced what he termed "voltaic narcotism" or local anæsthesia produced electrically by forcing morphine through the skin and into the tissues of the subject. The process appears to have been a combination of electrolysis and electrical endosmose. Since Richardson's time a great deal of interesting work has been done on the subject and it has been quite conclusively demonstrated[35] that liquids bearing narcotics or drugs of all kinds can be forced by the electric current into and through living skin and tissue. Electrical endosmose has been applied in dentistry as well, in the local anæsthesia[36] of sensitive dentine and in bleaching teeth with hydrogen peroxide.[37] Electric transference of ions in solution complicates most of these so-called "cataphoretic" experiments (such as Edison's[38] on the infiltration of lithium chloride) as Leduc has shown.[39]

MISCELLANEOUS.

Schwerin has patented an electro-osmotic process[40] of extracting sugar from beet. Sliced beet roots were placed between pervious walls and electrolyzed. The sugar solution containing the soluble albumenoids was driven through the cathode diaphragm and in this manner the beets were extracted. By placing water between the anode and the anode diaphragm the soluble acids in the beets were said to be removed by electrolysis and collected—an improvement which prevented the sugar from inverting. The process appears to have been electrically accelerated dialysis, except in so far as the acidic impurities were more or less segregated. In more recent years Schwerin through the Elektro-osmose A.G. has been granted a large number of patents dealing with the purification of colloidal and non-colloidal mixtures and the resolving of such mixtures into their constituents. By using diaphragms impervious to the colloid but pervious to dissolved ions, the latter may be driven out by electrolysis and collected about the electrodes which are usually surrounded in the beginning by pure water. A simple example is the case of extracting sugar and acids from beets, which we have just mentioned. Suspended colloids may themselves be fractionated by using diaphragms (1) the pores of which vary in size (Cf. ultrafitration) (2) the interface potentials of which are different. When the diaphragm operates because of differences in permeability (size of pores) one is dealing with ultrafiltration accelerated by electrical endosmose. In the other case negative diaphragms are said to hold back positive colloids or vice versa and here the process is analogous to the mutual precipitation of electrical suspensions. It is doubtful, however, whether really satisfactory separations can be made by this

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[35] Cf. Barratt and Harris: *Biochem. Jour.*, **6**, 315 (1912); Morton: *Cataphoresis* 89 (1898).

[36] Morgenstern: *Electrochem. Zeit.*, **15**, 189, 214, 240; *Cf. Chem. Abstr.* **3**, 1203 (1909).

[37] Morton: *Cataphoresis*, 41 (1898).

[38] Peterson: *Bigelow's Internat. Sys. of Therapeutics* 613 (1894).

[39] Jones: *Med. Electricity* (4th Ed.) 228 (1904).

[40] Brit. Pat. 8068 (1901); 14195 (1903).

second method because the adsorption of the suspended colloid may change the sign of the diaphragm. Schwerin claims to apply the method in the production of pure colloidal silica,[41] in the tanning of leather, in the purification of gelatine (glue)[42] dyes,[43] metal sols[44] and alumina[45] and in the treatment of serum.

SUMMARY.

In this report there have been described applications of electrical endosmose or of electrical endosmose and cataphoresis in the processes of dewatering peat and other substances ; treatment of clay ; tanning ; filtration ; medicine ; separation of colloidal and non-colloidal mixtures ; and so forth. No mention has been made of certain processes, such as the electrical treatment of emulsions and the use of addition agents in electro-plating, which are clearly instances of applied cataphoresis and are so recognized.

British Patents. Electro-osmotic Processes.

In the case of Patents dated as of the years 1900 to 1913 inclusive the original Specifications have been consulted. The information contained in the more recent patents has been obtained from Chemical Abstracts and other sources.

1900.

12431, July 10. B. Schwerin, Munich. "Improvements relating to the extraction of water or other liquid from mineral, vegetable and animal substances." Evidently first British patent. Discusses electrical endosmose, the utilization of the "motorial" action of the electric current in removing water from peat and describes apparatus for so doing.

1901.

8086, April 19. B. Schwerin, Munich. "Improvements relating to the extraction of sugar. Sliced beet-roots placed between pervious walls and submitted to electro-osmose and electrolysis. Sugar, soluble albumin and water driven to cathode. Places water between solid material and anode ; the acids in the beets collect by electrolysis in the anode liquid and are prevented from inverting sugar. Describes apparatus.

22301, November 5. B. Schwerin, Berlin. Cf. 12431 (1900). Describes apparatus for dewatering peat.

1903.

1717, Jan. 23. J. Doull. Use of electric current in drying materials.

14195, June 25. C. D. Abel for Siemens and Halske A. G., Berlin. Elaborate discussion of electrical endosmose and

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[41] Brit. Pat. 9237 (1914).

[42] Brit. Pats. 21448, 21483 (1914).

[43] Brit. Pats. 9565, 9566 (1915).

[44] Brit. Pat. 9261 (1914).

[45] Brit. Pats. 6727, 7212 (1915).

cataphoresis. Use of diaphragm aids in removing water from peat. Interesting to note that water passes to *anode* when current is passed through a porous cup containing iron "oxychloride" (colloidal ferric hydroxide) and the "oxychloride" is reduced to a jelly (dewatering of colloidal suspension with subsequent formation of an iron oxide jelly). Purification of "saccharine juices."

1904.

126, Jan. 4. B. Kittler, Memel, Germany. Apparatus (continuous) for dewatering peat.

3795, Feb. 16. Imray for Farbwerke, vorm. Meister, Lucius u. Brüning Höchst, a/M. Dewatering peat. Heats apparatus and material. Cf. 12431 (1900).

24670, Nov. 14. Imray for Farbwerke, vorm. Meister, Lucius u. Brüning Höchst, a/M. Dewatering peat. Ingenious apparatus for continuous operation, consisting of two endless belt conveyers, one of which may be an electrode.

1905.

4792, March 8. W. Simm. Dewatering peat. Doubtful if Simm really uses electrical endosmose at all as he specifies alternating current. Mentions heating effect of the current.

1907.

2226, Jan. 29. J. C. Verey and L. Downes. Electric-osmotic apparatus for dewatering peat.

10024, Apl. 30. Farbwerke, vorm. Meister, Lucius u. Brüning, Höchst a/M. Depositing suspended particles on electrodes by cataphoresis. Fractional cataphoresis, with especial emphasis on purifying and dewatering clay. Better results are obtained by causing fresh suspension to enter cell by passing close to a cathode of large surface. In this way the suspension passes through a diluted region and settling out of impurities is facilitated.

1909.

10793, May 6. B. Schwerin. Production of electric current by Quincke's method (diaphragm currents). Claim is made of the use of suitable electrolytes to increase effectiveness of process. Importance of making certain that diaphragm and liquid are in equilibrium. "Action of electrolytes is so great, it seems generation of current is dependent upon presence of ions." With diaphragms of quartz, an alkaline liquid (pyridine and water), pumped through under pressure gave the following results:

Pressure.	Volts.	Amperes.	Watts.
10	4	0·01	0·04
20	8	0·02	0·16
40	16	0·04	0·64
80	32	0·08	2·56

The efficiency was calculated from the formula:

$$\text{Efficiency} = \frac{\text{volts} \times \text{amperes}}{\text{pressure} \times \text{discharge of water}}$$

It was found experimentally that the efficiency remained the same for each of the above pressures but increased as the pores in the diaphragm became finer because the discharge of water at constant pressure was thereby lessened.

1910.

132, Jan. 3. F. Arledter, Hamburg. Electric sizing of paper (cataphoresis ?).

25175, Oct. 29. Alcock and Co. Proprietary Ltd., Melbourne. Drying timber by electrical endosmose. Stand timber on end in shallow vessel as cathode containing a small quantity of conducting liquid and connect top of timber with suitable anode. Sap is driven endosmotically out of timber into lower vessel, following which solutions of resin, sugar or creosote may be driven in from above and the timber impregnated with preservative.

1911.

3364, Feb. 9. B. Schwerin. Accelerates process of electro-osmose (cataphoresis) by adding *acids* (acetic acid, CO_2, etc.) to those substances which migrate to cathode and *bases* ($NaOH$, NH_4OH) to those substances which migrate to anode. Hastens draining of peat by adding a little alkali to the pulp. An interesting application of Perrin's rule. In 2379 (1911) Schwerin patents use of *acids* to peptize substances (elutriate) which wander to cathode and *bases* to peptize substances which wander to anode.

11626, May 13. B. Schwerin. Adding electrolytes, especially Na_2SO_4 to peat. Data on improvement which results are not particularly convincing.

17597, Aug. 2. Felten and Guilleaume Carlswerk A. G., Carlswerk. Claim use of non-aqueous solvents in electro-osmotic (cataphoresis) separations. Separation of dyes in alcohol, etc

27931, Dec. 12. B. Schwerin. In 3364 (1911) use of electrolytes has been claimed. In order to cause deposits at electrodes to adhere more firmly to latter add electro-positive or electro-negative [adsorbed] colloids. For example, peptizes clay with a little sodium silicate, allows coarse particles to settle out and electrolyzes. With 100 volts and 1·6 amps., obtains 140 g., containing 65 per cent. clay, in 5 minutes. Clay adsorbs electro-negative colloidal silicic acid from water glass and is carried to the anode.

28185, Dec. 14. Gesellschaft für Elektro-osmose (Schwerin). Frankfurt a/M. Dewatering and purifying clay. Deflocculates clay with dilute NaOH, allows thin slip so made to settle in vats, and finally treats in "electro-osmose" machine. Electrolyte added supposed to peptize clay and coagulate impurities.

1912.

725, Jan. 9. Gesellschaft für Electro-osmose. Frankfurt a/M. Apparatus (osmose machine) for purifying and dewatering clay. Rotating cylinder anode and wire gauze cathode. Circulating device to prevent impoverishment of suspension between anode and cathode.

10370, May 1. J. E. Jameson and O. H. Valpy, London. Electric current passed into peat at 100°C. and under pressure (10 Atm.). Current may be "continuous or alternating" (*sic*), and "decomposes hydrocellulose." It is possible that the alternating current in some manner breaks down the jelly of peaty material.

14235, June 18. B. Schwerin. Use of electro-osmose in connection with manufacture of refractory articles, baked without binder.

14369, June 19. B. Schwerin. Separates mixtures of different substances in suspension by fractional cataphoresis. Also separates by means of diaphragms of different permeability; Apparatus really a kind of electric "ultrafilter."

19239, Aug. 22. L. A. Groth, London. Electric tanning. Details of apparatus.

23545, Oct. 15. Gesellschaft für Elektro-osmose (Schwerin). Drying peat, clay, kaolin, etc. by pressure combined with electro-osmose Electro-osmotic filtration. Pressure may be reduced from 20 atmospheres to 1 atmosphere by combining electro-osmose (cataphoresis) with it. The higher the voltage used the more rapid the filtration. Apparatus.

24666, Oct. 28. B. Schwerin. Use of electrically charged diaphragms in the fractional separation of suspended colloids, depending upon

1. Difference in size of pores
2. Differences in interface potentials.

Electro-negative diaphragms tend to hold back electro-positive colloids and vice versa.

29826, Dec. 27. Gesellschaft für Elektro-osmose and H. Illig. Improved apparatus for dewatering and purifying clay. Cf. 725 (1912).

1913.

3434, Feb. 10. Gesellschaft für Elektro-osmose (Schwerin). Making ceramic articles without adding flux to cause sintering at temperatures below melting point. No flux (steatite, magnesium silicates) necessary with clay purified by electro-osmose, owing to the extreme fineness of the particles. In one case a clay treated by the osmose process sintered at a temperature more than 300° C. below its melting point, and did this without the addition of a flux.

6668, Mar. 18. A.L.C. Nodon, Bordeaux. Electrical preservation of railway sleepers (ties). Uses alternating current (?) and 1 per cent. $ZnCl_2$ solution.

10873, May 8. Gesellschaft für Elektro-osmose (Schwerin). Cf. 23545 (1912) Electro-osmotic filter with electrodes of hard lead.

26061, July 21. Gesellschaft für Elektro-osmose (Schwerin). Further mechanical improvements in osmose machine for clay.

1914.

6993, Mar. 19. Elektro-osmose Akt. Gesellschaft (*Schwerin*). Facilitates dewatering of peat by previously subdividing material in a ball mill and adding electrolyte such as NaOH to increase the rate of cataphoresis and endosmose.

6995, Mar. 19. Elektro-osmose Akt. Gesellschaft (*Schwerin*). Cf. 6993 (1914). Adds adsorbed colloid before grinding peat. Colloidal silicic acid or humic acids are suitable. By adding sodium silicate obtains both a suitable electrolyte (NaOH) and colloidal silica. Adsorbed colloid peptizes the solid and being strongly electro-negative in dilute NaOH hastens the migration to the anode.

9237, Apr. 14. Gesellschaft für Elektro-osmose (*Schwerin*). Electro-osmotic preparation and purification of colloidal silicic acid. Places 5 to 10 per cent. sodium silicate solution between two porous diaphragms—one around cathode and the other around anode. By using a *neutral* diaphragm (composed of carborundum plus alundum) about the cathode, the alkali is electrolyzed out of the sodium silicate, and no silica is carried into the cathode compartment, since no electrical endosmose takes place through the cathode diaphragm. With parchment above anode, no colloidal silica can get into anode compartment but soluble acids can do so. Obtained colloidal solution of silica in the middle compartment. Platinum or lead-antimony anodes; brass gauze cathodes. Typical "electro-osmotic" multiple diaphragm process. Cf. German Pat. 283,886, Apr. 15, 1913.

9261, Apr. 14. Gesellschaft für Elektro-osmose (*Schwerin*). Making stable metal sols by using colloidal silicic acid as protecting agent, reducing metal salt with hydrazine hydrate and purifying subsequently by process such as specified in 9237.

11823, May 13. Gesellschaft für Elektro-osmose (*Schwerin*). Separating colloids, etc. by electrical endosmose and cataphoresis.

19849, Sept. 16. Gesellschaft für Elektro-osmose (*Schwerin*). Tanning and dyeing by electro-osmose. Places leather or adsorbing substance together with tannin solution in compartment between two or more diaphragms, impervious to tannin but pervious to dissolved electrolytes. Claims simultaneous purification of tannin solution by electrolysis and impregnation of leather.

21189, Oct. 19. Gesellschaft für Elektro-osmose (*Schwerin*). Changes interface potential of diaphragms by addition agents. Thus Cr_2O_3, makes a leather diaphragm more positive (leather adsorbs Cr_2O_3 which is distinctly electro-positive). Methylene blue (basic dye) makes viscose positive (viscose adsorbs the dye cation). Adsorbed acid dyes make diaphragms electronegative. Interesting patent based on selective ion adsorption or on the adsorption of charged colloids.

21190, Oct. 19. Gesellschaft für Elektro-osmose (*Schwerin*). Modifies 19849 to allow preliminary purification of tan liquor.

Uses three diaphragms instead of two and places tan liquor next the hides in a separate compartment between the hides and the cathode. Anode, cathode and hides are immersed in water. On passing current acid and basic impurities in the tan liquor are electrolyzed out and carried into the anode and cathode compartments, after which tannin is said to migrate into compartment containing hides. Process seems hopelessly complicated and not at all practical. Theory of process not very clear.

21448, Oct. 23. B. Schwerin. Gelatin or glue placed between diaphragms impervious to glutin and electrolyzed a cell containing anode, cathode and gelatin compartments. Soluble electrolytes removed and albumins precipitated. Other complicated modifications are described. Combined electrical dialysis and ultrafiltration process.

21483, Oct. 24. Gesellschaft für Elektro-osmose (Schwerin). Cf. 21448 (1914). Uses hide or leather waste between diaphragms instead of glue.

1915–1916.

6727, May 5. Elektro-osmose, Akt. Gesellschaft (Schwerin). Electrical purification of alumins. Cf. 21448 (1914).

7212, May 13. Elektro-osmose Akt. Gesellschaft (Schwerin). Cf. 6727. Electrical purification of alumina.

7590, May 20. Elektro-osmose Akt. Gesellschaft (Schwerin). Use of centrifuge to hasten preliminary settling process in the "electro-osmotic" purification of clay.

9565, 9566, June 30. Elektro-osmose, Akt. Gesellschaft (Schwerin). Electrical purification of dyes. Dye suspension placed in inner compartment and shielded from oxidizing and reducing action of electrodes, by means of diaphragms impervious to dyes. Cf. 21448 (1914).

11659, Aug. 12. Elektro-osmose, Akt. Gesellschaft (Schwerin). Treatment of clay.

COLLOID-CHEMISTRY IN THE TEXTILE INDUSTRIES:

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Introduction.

Although a considerable amount of research work has been done on the chemistry of textile fibres, particularly cotton, no definite information has been obtained on the chemical constitution of the substances composing them. The colloidal nature of these substances always stands in the way of pure chemical research. There are many processes used in the textile industry where a knowledge of the chemical constitution of the substances composing fibres is unnecessary, the changes produced being more physical than chemical. Chemists are naturally attracted by the idea that all the physical properties of a substance are dependent on the chemical constitution of its molecules, but the properties of colloidal barium sulphate are quite different from those of the crystalline substance although the chemical constitution is considered to be the same in the two cases. The suggestion has been made[1] that colloidal barium sulphate consists of extremely minute crystals, but this does not explain the difference in physical state. The chemist's idea can only be upheld by a considerable modification in the conception of molecules as present in solid substances. The Braggs[2] have established beyond doubt that the fundamental units of a crystal are atoms, not molecules. Many chemists[3—8] have cast doubt on the crystal models of the Braggs', except that of the diamond, simply because they are against the generally accepted ideas on valency. It has been suggested[9] that one of the interesting problems of the future will be to reconcile the X-ray crystal models with the molecular hypothesis. Since the X-ray models have been deduced from positive evidence whereas no positive evidence has ever obtained in favour of the molecular hypothesis as applied to solids, the author considers that it is the molecular hypothesis which requires broadening. The original definition of a molecule was the smallest particle of a substance which could exist; with the discovery of chemical polymerisation this definition has been narrowed somewhat. The author considers that the difficulty of reconciling the X-ray models with the molecular hypothesis disappears if one admits a crystal to be a polymeride or single molecule as suggested by Langmuir.[13] This idea has far-reaching consequences of very great importance in colloid chemistry, since the necessity for admitting a high molecular weight as a special characteristic of colloids disappears. A single crystal may be considered as a single molecule since it consists of atoms bound together by the same forces which bind together the atoms in the simple molecules found in gases. The molecular weight of the crystal is then proportional to its size. This view is entirely in agreement with the observations in brownian movement of particles in different degrees of dispersion which were shown by Perrin[10] to be explained by the kinetic theory of gases. There are numerous other consequences of the idea of considering crystals as polymerides which it is not intended to discuss here.

Regarding the chemical nature of fibres, chemists have divided opinions, some considering them to be very complex bodies of high molecular weight, others to be physical forms of insoluble substances of possibly low molecular weight. These opinions may be taken to be identical in the light of the idea discussed above.

In the case of vegetable fibres, the suggestion has recently been made[11] that the fibre substances, celluloses, are liquid systems; this brings forward the question of reconsidering the definitions of liquid and solids. At present, these are somewhat rigid and bodies possessing properties of both states of matter are considered to be mixtures. The author does not hold this view, but considers that there is no distinct line of demarcation between the solid and liquid states any more than there is between colloidal—and true—solution. The semi-solid state of many colloids does not necessarily imply the presence of both solid and liquid phases. It is, therefore, still an open question whether the celluloses are mono--or diphasic systems.

The fibres possess many physical properties in common with other colloids such as indiarubber and gelatine.

When subjected to stress in a dry condition they become deformed and acquire increased double refraction which persists when the stress is removed.[12] This increased double refraction shows the presence of extra internal stresses resulting from the deformation. When placed in a solvent which tends to produce swelling—water in the case of fibres—these extra internal stresses disappear and the fibres regain their original shape. When compressed under boiling water most fibres become permanently deformed, no internal stresses being produced.

These theoretical points have an important bearing on many of the phenomena met with in the treatment of textile materials.

(A) *Introduction.*

[1] Von Weimarn, *Grundzuge der Dispersoid chemie.*, Leipzig (1912).

[2] W. H. Bragg and W. L. Bragg, *Proc. Roy. Soc.* **A. 87**, 277 (1914), etc. See also *Trans. Chem. Soc.*, p. 252 (1916).

[3] A. Smits and F. E. C. Scheffer, *Proc. K. Akad Wetlensch*, Amsterdam, **19**, 432 (1916).

[4] A. Fock, *Centr. Min.* 392 (1916).

[5] J. Beckenkamp, *ibid.* 97 (1917).

[6] J. Stark, *Jahr. Radioaktiv. Electonik*, **12**, 280 (1915).

[7] F Rinne, *Zeit anorg. Chem.*, **96**, 317 (1916).

[8] P. Pfeiffer, *ibid.*, **92**, 376 (1915) ; **97**, 161 (1916).

[9] H. M. Dawson, *Annual Report Chem. Soc.* (*Physical Chemistry*) (1917).

[10] J. Perrin, *Brownian Movement and Molecular Reality.*

[11] C. F. Cross, *Presidential Address to Soc. Dyers and Colourists*, **34**, 19 (1918).

[12] W. Harrison, *Proc. Roy. Soc.* **A. 94**, 460 (1918).

[13] I. Langmuir, *Journ. Amer. Chem. Soc.*, **28**; 2221 (1916).

[14] Tinker, *Proc. Roy. Soc.* **A. 92**, 357 (1916).

[15] W. Moeller, *Koll. Zeit.* **19**, 205, 213 (1916) ; **20**, 242, 257 (1917) ; **23**, 11 (1918).

[16] J. R. Katz, *Koll. Ch. Beith.*, **9**, 1 (1917).

[17] Bachmann, *Koll. Zeit*, **9**, 312 (1911) ; **11**, 150 (1912) ; **12**, 204 (1913) ; **23**, 85, (1918) ; also *Zeit. anorg. Chem.*, **73**, 125–172 (1911) ; **79**, 202 (1912) ; **100**, 76 (1917).

[18] Debye & Scherrer, *Phys. Zeit.*, **18**, 291 (1917).

Cotton.

Regarding the chemical constitution of the substance of the cotton fibre, six formulæ have already been proposed, but none of these have been established. (Refs. [10–16]).

Cross originally held that the cellulose molecule was large, being composed of units of a certain type bound together ; Green favoured a simple formula. In a recent address (Ref. A.[11]) Cross stated that there are no grounds for the assumption of large molecules in the strict chemical sense. He considers that the celluloses are liquid systems capable of large volume changes and also solution-aggregates of amphoteric character. He suggests that the units in the cellulose aggregate may have dimensions less than C_7. One difficulty in the way of the acceptance of a very simple formula for cellulose is the number of hydroxyl groups which chemical methods prove to be present ; all the bodies of the same chemical composition, known up to the dimension C_7, having a corresponding number of hydroxyl groups are soluble in water.

It is quite likely that the units in the cellulose aggregate are bound together in a similar manner to the units in a crystal, although perhaps not in a regular formation. As already suggested, there is no necessity to discuss the molecular weight of the cellulose colloid since it only exists in the solid state. The fibre itself may be considered to be a molecule in so far as the atoms composing it are bound together in the same way as in any other molecule.

Mechanical disintegration produces changes corresponding to depolymerisation, B[25. 26. 31. 34. 35] in the same way that mastication is considered to produce depolymerisation of rubber. (Compare *Journ. Soc. Chem. Ind.*, **37**, 313A (1918).)

The substance of the cotton fibre is known in many colloidal states; in the fibre itself it exists as a porous, adherent mass, showing turbidity in the ultramicroscope, which indicates amicroscopic structure. Treatment with sulphuric acid of 1·70 Sp G causes the fibre to swell and eventually pass into solution. In the swollen state the fibre shows a distinct granular structure, which the author succeeded in photographing.[22-23] Since the acid acts in the direction of solution and not coagulation, the author is of the opinion that the structure of the swollen fibre is an extension of that of the original fibre, this extension allowing the structure to be resolved.

The double refraction of cotton fibres has been shown to be due to the presence of internal stresses, which become active when the fibre is softened.[22–23] There is no doubt that the cellulose is in different colloidal states in different parts of the cotton fibre, the outer portions being more solid than the inner. There are markings on the fibre (Refs. [9–19]) which have physiological importance which it is not proposed to discuss in this review. The colloid chemical investigation of cotton indicates that it is first formed in somewhat gelatinous filaments which harden from the outside by drying or by some chemical change.

The following extract from W. L. Ball's observations on the development of cotton appear to be in agreement with the view just expressed :—

"The full diameter of the seed hair is attained almost at once, when its length is only $\frac{1}{10}$ m.m. while its length continues to increase until the 25th day of development after which its wall begins to thicken, giving strength to the lint. This thickening is not uniform but leaves simple pits in the wall set obliquely, and the closure of these pits when the wall dries after the boll opens, gives twist to the fibre. The uninucleate cell contents remain alive until the boll begins to open, when they die from desiccation."

"The cell wall is extremely thin for the first three weeks and the cuticle which covers it can scarcely be differentiated unless the wall has been swollen with Schweitzer's reagent when (being unaffected by the ammoniacal copper oxide) it causes the familiar beaded appearance, the cellulose of the wall swelling through the torn places in the cuticle."

The difference between the outer cell wall or cuticle and the inner portions of the fibre is most probably one of colloidal state[23] and not of chemical nature. A similar difference exists between the outer layers of starch granules and the inner portions and it has been shown that this difference is one of colloidal state.

The colloidal state of cellulose is modified in the direction of distension by treatment with strong alkalies, caustic soda, caustic potash tetramethyl-ammonium-hydroxide and by several other substances. A still greater degree of swelling is produced when cotton is overworked in the hollander used in the paper-making industry.[25] [26] The maximum degree of dispersion is attained when the cotton is treated with cellulose solvents.

It has been observed that freshly precipitated cellulose is soluble in caustic soda but that this solubility disappears when the cellulose is dried. A similar change is produced when precipitated starch is dried. These changes are the common result of gel-dehydration.

Iodine forms a useful reagent in conjunction with hydrating agents such as potassium codide, zinc chloride and sulphuric acid, for indicating the different colloidal states of cellulose. The strength of hydrating agent required to give the blue colour indicates the degree of dispersion of the cellulose. It is interesting to note that starch celluloses can be prepared which give the blue colour with iodine under the same conditions as cellulose.[22] This does not necessarily imply that there is any chemical relationship between starch and cellulose since the blue colour has been shown to be due to colloidal iodine and numerous substances have been found which give the reaction.

(B). *Cotton :*

Books of Reference.

[1] Cross & Bevan, *Cellulose and Researches.*
[2] Schwalbe, *Die Cellulose.*
[3] Worden, *Nitrocellulose Industry.*
[4] O. N. Witt, *Chem. Tech. der Gespinnst-fasern Braunschweig*, (1888).
[5] Monie, *The Cotton Fibre, London*, (1890).
[6] Bowman, *The Structure of the Cotton Fibre.*
[7] H. Kuhn, *Die Baumwolle.*
[8] Flatters, *The Cotton Plant*, (1906).
[9] W. L. Balls, *The Development and Properties of Raw Cotton*, (1915).

References.

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[11] Vignon, *Bull. Soc. Chem.*, **21**, 599, (1899).
[12] Bernadou, (Compare (2), p. 349).
[13] Cross & Bevan, *Trans. Chem. Soc.*, **79**, 366, (1901).
[14] A. G. Green, *Journ. Soc. Dyers & Cols.* **20**, 117, (1904).
[15] Cross & Bevan, *Ibid.* **32**, 135, (1916).
[16] A. E. Sunderland, *Ibid.* **32**, 230, (1916).
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[18] Muller Jacobs, *Journ. Soc. Dyers & Cols.*, **11**, 95, (1885).
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[20] Haller, *Zeit. für Farben u. Textil Chem.*, **8**, 125, (1907).
[21] Herzog, *Koll Zeit.*, **5**, 246, (1909).
[22] W. Harrison, *Journ. Soc. Dyers & Cols.* **31**, 198, (1915).
[23] W. Harrison, *Trans. Nat. Assoc. Cotton Manfrs.*, **101**, 201, (1916).
[24] Haller (Structure of Cotton), *Koll. Zeit.*, **20**, 127, (1917).
[25] Cross, *Papier Zeitung*, **33**, 3246, (1908).
[26] Briggs, *Papier Fabrikant*, **5**, 2644, (1907) ; 46, (1910).
[27] Fenton (Action of hydrochloric acid), *Trans. Chem. Soc.*, **73**, 554, (1898) ; **75**, 427, (1899) ; **79**, 361, 807, (1901) ; **99**, 1193, (1911).
[28] Erdmann & Schaeffer, *Ber.*, **43**, 2398, (1910). (Dry distillation of cellulose).
[29] Pictet and Sarasin, *Comp. Rend.*, **166**, 28, (1918). (Dry distillation of cellulose and starch).
[30] Sarasin, *Arch. Sci. phys. Nat.* (1918) pp. 5–32.
[31] Fort, *Journ. Soc. Duers & Cols.* **34**, 9, (1918).

[32] S. Judd Lewis, *Ibid.* **34**, 167, (1918).
[33] W. L. Balls, *Journ. Soc. Arts.* p. 389, (1918).
[34] C. F. Cross, *Journ. Soc. Dyers & Cols.* **34**, 215, 247, (1918).
[35] W. Harrison, *Ibid.* **34**, 218, (1918).
[36] Knecht & Hall, *Ibid.* **34**, 220, (1918).

Compound Celluloses:

[37] Cross & Bevan, *Cellulose*, pp. 89–232.
[38] Schwalbe, *Die Cellulose*, pp. 366–483.
[39] Stocks, *First Report on Colloid Chemistry*, pp. 58–64.

Animal Celluloses:

[40] Worden, *Nitrocellulose Industry*, p. 1.
[41] Irvine, *Trans. Chem. Soc.*, 95, 564, (1909).

Cellulose Solutions.

The so-called solutions of cellulose are really colloidal solutions. The best known solvents are Schweitzer's reagent,[6 18 21] zinc chloride solution and sulphuric acid. Numerous other solvents have been found in recent years.[7] Recently,[8] it has been stated that cellulose can be dissolved in solutions of most salts when heated under pressure.

Regarding the solution of cellulose in ammoniacal copper solution Cramer[9] came to the conclusion from osmotic measurements that it was a true solution. Erdmann,[10] on the other hand, considered it to be a very highly hydrated gel. Cross & Bevan[11] expressed the view that the copper compound combined with the cellulose to form a colloid double salt.[19–20] The dialysis of these copper solutions has been studied by Grumaux[12] who came to the conclusion that it was the non-dialysable portion of the solution of copper hydrate in ammonia which acted as a solvent for cellulose.

It is important to note that cuprammonium hydroxide is not so strong an alkali as caustic soda.[13]

The solution of cellulose in ammoniacal copper solution has been stated to be optically active[14–15] a view which does not appear to be substantiated.[16] The solution of cellulose in hydrochloric acid is optically inactive.[17]

(C) *Cellulose Solutions.*

[1] Compare B.[1]
[2] Compare B.[2]
[3] Compare B.[3]
[4] Czapek, *Biochemie der Pflanzen*, Jena, 1905.
[5] Abderhalden, *Biochem Handlexikon*, Berlin, 1911 (II) Cellulose.
[6] Schweitzer, *Journ. für prakt. Chem.* **72**, 109. 3441 (1857).
[7] Deming, *Journ. Amer. Chem. Soc.*, **33**, 1515 (1911).
[8] Weimarn, *Koll Zeit*, **11**, 41 (1912).
[9] Cramer, *Journ. für prakt. Chem.*, **73**, 1 (1858).
[10] Erdmann (Compare B[1], p. 11).
[11] Cross & Bevan, Textbook of Papermaking, p. 8.
[12] Grumaux, *Comp. Rend.*, **98**, 1885.
[13] H. M. Dawson, *Trans. Chem. Soc.* **89**, 1666 (1906) ; **95**, 370 (1909).
[14] Levallois, *Bull Soc. Chem.* (2) **43**, 83, 616 (1885).
[15] Levallois, *Comp. Rend.*, **98**, 372, 732 (1884) ; **99**, 431, 1027 (1884).
[16] Bechamp, *Ibid.* **99**, 1027, 1122 (1884) ; **100**, 279, 368 (1885).
[17] Willstatter & Zechmeister, *Ber.*, **46**, 2401 (1912).
[18] Schlossberger, *Journ. für prakt. Chem.* **73**, 373 (1858).
[19] Lehner, *Zeit. für angew. Chem.*, **19**, 1584 (1906).
[20] Mulder, *Jahr. der Chem.*, 566 (1863).
[21] Haller, *Zeit. für Farben Ind.* **6**, 126 (1907).

Mercerised Cotton.

It was first observed by Mercer [3–4] that cotton fibres shrink when they are treated with concentrated solutions of caustic soda. This shrinkage has been shown [7] to be caused by the action of internal stresses present in natural cotton fibres. If prevented from shrinking while under treatment with the alkali, the fibres acquire an increased lustre. [5–6] Lange [8] considered this lustre to be due to the smoothness of the surface of the mercerised fibres as compared with untreated cotton. Hübner & Pope [9] suggested that the formation of regular spiral grooves in the fibre during mercerisation was the cause of the lustre. This theory has been shown [7] to be untenable, Lange's theory being substantially correct. The shape of the cross-section of the mercerised fibres has been shown to have an important bearing on the lustre. [7]

The amount of caustic soda absorbed by cotton during mercerisation has been investigated by several workers.[11–15] [38] Vieweg[13] observed change points in the curve of absorption but Miller [14] found the curve to be continuous. Clayton Beadle & Stevens [15] made some interesting observations on the absorption of caustic soda by regenerated cellulose which have an important bearing on this subject.

Mercerised cotton has properties which differ from those of ordinary cotton in the following manner:—

It grinds more pasty in the hollander, [16–17] dissolves quicker in solvents, gives a greater yield of benzoyl derivative, [18] gives nitrates more soluble in solvents [19] but giving less viscous solutions [20] and gives a blue colour with iodine with a less concentrated solution of sulphuric acid than ordinary cotton. [7] In the last case, the application of tension during mercerisation has been shown to modify the reaction.

All these properties are in agreement with the view that mercerisation produces distension of the fibre—colloid.

Mercerised cotton appears to revert towards its original condition on drying,[21] [24] [36] or on treatment with alcohol.[23] Green[22] considers this reversion to be due to anhydride formation, but the author thinks it is an ordinary case of gel-dehydration, since the same effect is produced by pressure without the application of heat or chemical re-agents.[25] A similar change is produced by pressure on wet unmercerised cotton,[26] the effect being much greater when heat also is applied.[26] [27]

The internal structure of cotton fibres,[28–33] and the internal stresses present in them (A 12) are considerably modified by mercerisation: these changes persist when the fibres are dried.

The dyeing properties of cotton,[34] [35] and its re-activity towards certain re-agents, are modified in a similar manner to that produced by caustic alkalies, when treated with solutions of sulphuric, hydrochloric[36] and nitric acids[37] and zinc chloride.[3] [4]

(D) *Mercerised Cotton.*

[1] Cross & Bevan, *Researches*, I. p. 26.
[2] Gardener, *Mercerisation.*
[3] Mercer, *Life and Labours of John Mercer*, Parnell (Longmans, Green), 1884.
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[7] Harrison, *Journ. Soc. Dyers & Cols.* **31**, 198 (1915).
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[9] Hübner & Pope, *Journ. Soc. Chem. Ind.*, **22**, 70 (1903) ; **23**, 410 (1904).
[10] Hübner, *Ibid.* **27**, 110 (1908).
[11] Gladstone, *Trans. Chem. Soc.*, **17**, (1862).
[12] Crum, *Ibid.*, **16**, 406.
[13] Vieweg, *Ber.*, **40**, 3876 (1907) ; **41**, 3269 (1908).
[14] Miller, *Ber.*, **40**, 4903 (1907) ; **41**, 4297 (1909) ; **43**, 3430 (1910).
[15] Clayton Beadle & Stevens, *Journ. Soc. Dyers & Cols.*, **30**, 244 (1914).
[16] Briggs, *Papier Fabrikant*, **5**, 2644 (1907).
[17] Cross, *Papier Zeitung*, **33**, 3246 (1908).
[18] Wichelhaus & Vieweg, *Ber.*, **40**, 441 (1907).
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[21] Copley, *Journ. Soc. Dyers & Cols.*, **24**, 72 (1908).
[22] Green, *ibid.* **24**, 72 (1908).
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[24] Miller, *Ber.*, 728 (1911).
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[30] Minajeff, *Zeit. Farben. Ind.*, 1 and 17 (1908).
[31] Minajeff, *Zeit. fur Farben and Textile Chem.*, **2**, 257 (1903) ; **4**, 81 (1905) ; **6**, 309, 345, **15**, 233, **16**, 252, **19**, 309 (1907) ; **7**, 1 (1908).
[32] Haller, *ibid.* **8**, 125 (1907).
[33] Haller, *Koll. Zeit.*, **20**, 127 (1917).
[34] Justin Mueller, *Zeit. fur Farben and Textile Chem.*, **3**, 251, 332 (1904).
[35] Knecht, *Journ. Soc. Dyers & Cols.*, **24**, 68 (1908).
[36] Knecht, *ibid.*, **24**, 107 (1908)
[37] Knecht, *ibid.*, **12**, 89 (1891).
[38] Leighton, *Journ. phys. Chem.* **20**, 32, 188 (1916).

Hydrocellulose.

Hot dilute mineral acids hydrolyse cellulose forming a pulverulent substance termed 'hydrocellulose' [1–14] and a sugar having the same reducing power and optical activity as glucose.[16, 18]

Denham and Woodhouse[17] by the hydrolysis of methylated cellulose have obtained methyl glucoses. This points definitely to the conclusion that glucose is formed by the hydrolysis of cellulose, although Cross[19] considers this to be still an open question.

The author[15] has shown that hydrocellulose may exist in several different colloidal states and has suggested that it is a form of cellulose containing adsorbed reducing bodies. Guignet's soluble cellulose[20] is probably a similar form of cellulose not containing reducing agents.

The action of chemical reagents on a solid structure would obviously be to attack the exposed surfaces and dissolve them away, gradually reducing the size of the solid particles, with consequent modification in colloidal state.

(E) *Hydrocellulose.*

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[2] Schwalbe, *Die Cellulose*, p. 211.
[3] Girard, *Ann. Chem. Phys.* (5) **24**, 342–370 (1881).
[4] Flechsig, *Zeit. Physiol Chem.* **7**, 523 (1883).
[5] Vignon, *Comp. Rend.* **126**, 1355 (1888).

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[7] Cross & Bevan, *Journ. Soc. Chem., Ind.* **12**, 966 (1893).
[8] Stern, *Trans. Chem. Soc.* **67**, 74 (1895).
[9] Tollens & Murmurow, *Ber.* **34**, 1431–4 (1901).
[10] Morck & Walker, *Journ. Franklin Inst.* 136 (1907).
[11] Schwalbe, *Zeit. fur angew Chem.* **20**, 2170 (1907).
[12] Buttner & Neumann, *ibid.* **21**, 2609 (1908).
[13] Ost. & Wilkening, *Chem. Zeit.* **34**, 461 (1910).
[14] Cross & Bevan, *8th Int. Congress Applied Chem.* **13**, 101 (1912).
[15] Harrison, *Journ. Soc. Dyers and Cols.* **28**, 238 (1912).
[16] Willstatter & Zechmeister, *Ber.* **46**, 2401 (1913).
[17] Denham & Woodhouse, *Trans. Chem. Soc.* 1735 (1913); 2357 (1914); 244 (1917).
[18] Cunningham, *ibid.* 173 (1918).
[19] Cross & Bevan, *ibid.* 182 (1918).
[20] Guignet, *Comp. Rend.* **108**, 1258.
[21] Fort & Pickles, *Journ. Soc. Dyers & Cols.* **31**, 255 (1915).
[22] Briggs, *Journ. Soc. Ch. Ind.* 78 (1916).

Oxycellulose.

Oxidising agents attack cellulose, producing bodies[1–3 7 11–24] similar in many respects to hydrocellulose, [6 8 9 10 24 25 26] in fact no test has yet been found which definitely distinguishes between these substances. The suggestion has been made[26] that oxycellulose consists of a form of cellulose containing adsorbed reducing substances which may or may not be similar to those present in hydrocellulose.[15] It is interesting to note that oxycellulose is formed by the action of light on cellulose.[37 38]

Cross and Bevan[27 28] observed that bleached cotton retained the power of liberating iodine from potassium iodide much longer than the presence of a trace of hypochlorite would account for.[30] They considered that a peroxide was formed. Ditz[29 32] made a similar observation in the action of ammonium persulphate on cotton. This effect may be due to adsorption by the fibre-colloid.[31 33]

A similar effect has been noticed in the action of ozone on cellulose.[34]

(F) *Oxycellulose.*

[1] Cross & Bevan, *Cellulose.*
[2] Schwalbe, *Die Cellulose*, pp. 221–257.
[3] Witz, *Bull Rouen*, **10**, 447 (1882) ; **11**, 2210 (1883).
[4] Vetillart, *ibid.*, **11**, 234 (1883).
[5] Permetier, *ibid.*, **11**, 236 (1883).
[6] Schmid, *Dingler's Journ.* 250, 278 (1883).
[7] Cross & Bevan, *Trans. Chem. Soc.* **43**, 22 (1883) ; **46**, 206, 291, 897 (1884).
[8] Witz & Osmond, *Bull. Soc. Chem.* **45**, 309–15 (1886).
[9] Witz & Osmond, *Ber.* **19** (3), 318 (1886).
[10] Nastjukoff, *Bull Mulhouse*, **62**, 493–510 (1892).
[11] Cross, Bevan, & Beadle, *Ber.* **26**, 2520 (1893).
[12] Bull, *Trans. Chem. Soc.* **71**, 1090–1097 (1897).
[13] Vignon, *Bull Soc. Chem.* (3), **19**, 790 (1898).
[14] Von Faber & Tollens, *Ber.* **32**, 2592 (1899).
[15] Bumcke & Wolffenstein, *Ber.* **32**, 2493 (1899).
[16] Nastjukoff, *Ber.* **33**, 2237 (1900).
[17] Nastjukoff, *Ber.* **34**, 719 (1901).
[18] Murmurow, Sack & Tollens, *Ber.* **34**, 1427 (1901).
[19] Vignon, *Bull Soc. Chem.* (3) **25**, 136 (1901).
[20] Kurz, *Ziet. fur Farb. and Textilchemie*, **1**, 46 (1902).
[21] Vignon, *Bull Soc. Chem.* (3) **29**, 513 (1903).
[22] Berl & Klaye, *Zeit Schiess and Sprengwesen*, **2**, 381, 387 (1907).
[23] Ditz, *Journ. Prakt. Chem.* **78**, 348 (1908).

[24] Scholl, *Ber.* 1312 (1911).
[25] Ermen, *Journ. Soc. Dyers and Cols.* **26**, 266 (1910) ; **27**,(1911).
[26] Harrison, *Journ. Soc. Dyers and Cols.* **28**, 359 (1912). 132

Cellulose Peroxide.

[27] Cross & Bevan, *Zeit. angew. Chem.* **19**, 2101 (1906).
[28] Cross, Bevan & Briggs, *ibid.*, **20**, 570 (1907).
[29] Ditz, *Chem. Ziet.* **31**, 833, 844, 857 (1907).
[30] Heinke, *ibid.*, **31**, 974 (1907).
[31] Zimmermann, *Ziet. fur angew. Chem.* **20**, 1286 (1907).
[32] Ditz, *Journ. prakt. Chem.* **78**, 343 (1908).
[33] Grandmougin, *Chem. Zeit.*, **32**, 242 (1908).

Cellulose Ozonide.

[34] Dorée, *Trans. Chem. Soc.* **101**, 497 (1912).

Action of Light on Cellulose.

[35] Hartley, *Proc. Roy. Soc.* **B 78**, 385 ; **80**, 376.
[36] Hartley, *Trans. Chem. Soc.* **63**, 243 (1893).
[37] Harrison, *Journ. Dyers and Cols.* **28**, 225 (1912).
[38] Dorée & Dyer, *ibid.*, **33**, 19 (1917).

Cellulose Nitrates.

When cellulose is treated with a mixture of sulphuric and nitric acids, esters are formed containing nitrogen in quantities varying with the conditions of treatment.[1–5 7 9 11 12 14 23] Many authors[6 8 9] have attempted to classify the products, according to degree of nitration, into nitrates of definite molecular composition but there seems to be no break in the curve representing the amount of nitrogen introduced by different concentrations of acid.[11 15 17] The suggestion has been made[16] that nitrocelluloses are adsorption compounds but this view does not appear to have been substantiated.[17] There is little doubt that true esters are formed, but as the cellulose is solid during treatment, the reaction must take place from the exposed surfaces, whether external or within the porous structure of the fibre, and the degree of nitration must be dependent on the colloidal state of the fibre substance.

The viscosity of solutions of nitrocellulose[11 13 18 19 20 21] vary with the conditions of preparation. A nitrocellulose after solution and reprecipitation has been shown to give a less viscous solution than one directly dissolved.[18] Similar changes have been observed with rubber solutions.

The behaviour of nitrated cotton towards polarised light has been investigated by several authors [13 18 21 22] and many interesting points brought forward.

(G) *Cellulose Nitrates.*

[1] Cross & Bevan, *Cellulose*, p. 38.
[2] Schwalbe, *Die Cellulose*, p. 270.
[3] Schonbein, *Comp. Rend.* **23**, 678 (1846).
[4] Otto. *ibid.*, **23**, 807 (1846).
[5] Crum, *Proc. Phil. Soc. Glasgow*, 183 (1847).
[6] Eder, *Ber.*, **13**, 169 (1880).
[7] Knecht, *Journ. Soc. Dyers & Cols.*, **12**, 89 (1891).
[8] Veielle, *Comp. Rend.*, **95**, 132 (1883).
[9] Liebschutz, *Mon. Sci.*, p. 119 (1891).
[10] Vignon, *Comp. Rend.*, **126** (1898).

[11] Lunge, *Journ. Amer. Chem. Soc.*, **23**, 527 (1901).
[12] Berl & Klaye, *Mon. Sci.* (4), 23, 103.
[13] Mosenthal, *Journ. Soc Chem. Ind.*, 292 (1904).
[14] Cross & Bevan, *Cellulose* (pp. 38–41) *Researches*, 1895–1900, p. 43 ; 1900, 3, p. 97.
[15] Saposchnikow, *Journ. Russ. Phys. Chem. Soc.*, **35**, 669, (1904) ; **36**, 518, (1905) ; **38**, 1186 (1906).
(See also *7th Internal Cong. Appl. Chem.*, London, p. 19).
[16] E. Justin Mueller, *Koll. Zeit.*, **2**, 49 (1907).
[17] Arthur Muller, *ibid.*, **2**, 173 (1907).
[18] Mosenthal, *Journ. Soc. Chem., Ind.* 443 (1907).
[19] Piest, *Zeit. angew. Chem.*, **22**, 1215 (1908) ; **23**, 1009 (1910).
[20] Berl, *Zeit. f. Scheiss and Sprengwesen*, **4**, 81 (1909) ; **5**, 254 (1910).
[21] Schwartz, *Koll. Zeit*, **12**, 32 (1913).
[22] Ambronn, *Koll. Zeit*, **13**, 200 (1913),
[23] Knecht & Lipschitz, *Journ. Soc. Chem. Ind.* **33**, 116 (1914).

Organic Esters of Cellulose. Cellulose Acetates.

Cellulose forms esters of acetic acid when treated with acetic anhydride in presence of condensing agents.[1–12] The maximum amount of acetyl groups which can be introduced without modification of the cellulose complex corresponds to one half of the number of carbon atoms present in the cellulose. It is possible to introduce more acetyl groups but considerable modification in the cellulose is produced.

The solubility of cellulose acetates and the viscosity[10] of its solutions varies with the conditions of preparation in a more irregular manner than the nitrates. Even under apparently identical conditions, different results are sometimes obtained. The ease with which the colloidal state of the cellulose in cotton fibres is changed is possibly the explanation of these differences.

Cellulose Formate.

Cellulose forms derivatives with formic acid quite readily in the presence of condensing agents.[14–19] It has been stated[20] that cellulose formate is produced when oxalic acid solution is dried on cotton.

The properties of cellulose formates have not yet been thoroughly studied.

Of other esters of cellulose the following have been prepared :—

Cellulose propionate,[21] butyrate,[22] aceto-butyrate,[22] palmitate,[22] phenyl-acetate,[22] phospho-formate,[23] aceto-nitrate,[24] aceto sulphate,[25] nitro-sulphate,[26 27 28] sulphonates, etc.

Recently, methylated celluloses[30, 31] have been prepared, and their products of hydrolysis carefully studied. Nastjukoff[32] claims to have prepared phenylated celluloses.

(H) *Cellulose Acetates.*

[1] Cross & Bevan, *Cellulose*, p. 34.
[2] Schwalbe, *Die Cellulose*, p. 316.
[3] Worden, *Nitrocellulose Industry*, pp. 984–1004.
[4] Schutzenberger, *Comp. Rend.* **61**, 488 (1869); **68**, 814 (1870).
[5] Franchimont, *Ber.* **12**, 1264, 1941, 2099 (1879).
[6] Cross & Bevan, *Trans. Chem. Soc.* **57**, 1 (1890); **67**, 433 (1895)
[7] Thiele, *Journ. Soc. Dyers & Cols.* **24**, 294 (1908).
[8] Cross & Briggs, *ibid.* **24**, 189 (1908).
[9] Schwalbe, *Zeit. angew. Chem.* **23**, 435 (1910).

[10] Knoevenegal, *ibid.* **24**, 504 (1911).
[11] Patents. Compare Suvern, *Die kunstliche Seide*, Berlin (1900).
[12] Compare Marsden, *Journ. Soc. Dyers & Cols.* **21**, 103 (1905).
[13] Compare Worden, *Journ. Soc. Chem. Ind.* **31**, 1064 (1912).

Cellulose Formate.

[14] Berl & Smith, *Ber.* **40**, 903 (1907).
[15] Woodbridge, *Journ. Amer. Chem. Soc.* **31**, 1070 (1909).
[16] Deming, *ibid.* **33**, 1519 (1911).
[17] Worden, *Journ. Soc. Chem. Ind.* **31**, 1064 (1912).
[18] Worden, *Nitrocellulose Industry*, pp. 1004–1006.
[19] Cross, *Trans. Chem. Soc.* **99**, 1450 (1911).
[20] Knecht, *7th Int. Cong. App. Chem., London*, 1909.
[21] Cellulose Propionate. See refs. 14 & 15.
[22] Cellulose Butyrate. *Aceto-Butyrate, palmitate and phenyl-acetate. Henckel*, D.R.P. 12817/00
[23] Cellulose Phospho-formate. *Vereinigte Glanzstoff Fabr.* E.P. 29246/10; 309/11.
[24] Cellulose Aceto-Nitrate. Berl. & Watson Smith, *Ber.* **40**, 903 (1907).
[25] Cellulose Acetosulphate and Acetobenzoate. Cross, Bevan, & Briggs, *Ber.* **38**, 1859, 3561 (1905).
[26] Cellulose Nitrosulphate. Cross & Bevan, *Researches*, 1900–5, pp. 51–53.
[27] Cellulose Nitrosulphate. Cross, Bevan, & Jenks, *Ber.* **34**, 3496 (1908).
[28] Cellulose Nitrosulphate. Hake & Lewis, *Journ. Soc. Chem. Ind.* **24**, 374, 914 (1905).
[29] Benzoate. Cross & Bevan, *Cellulose.* p. 32; *Researches*, I. p. 34.
[30] Methylated Celluloses. Denham & Woodhouse. *Trans. Chem. Soc.*, 1735 (1913); 2357 (1914); 244 (1917).
[31] Ethylated Celluloses. Lilienfeld, F.P. 447974 (1912).
[32] Phenylated Celluloses. Nastjukoff, *Journ. Russ. Phys. Chem. Soc.* **34**, 231, 505 (1902). Compare *Journ. Soc. Chem. Ind.* Abstracts 1302 (1902); 414 (1903); 282 (1907).

Viscose.

When treated with caustic soda and carbon disulphide cellulose forms a xanthogenate soluble in water.[1–7] A solution of this substance increases in viscosity on standing and eventually sets to a jelly. This change is known as ripening and is considered by Cross and Bevan to be due to the formation of compounds of increasing complexity. This phenomenon appears to be quite analogous to the setting of a gelatine jelly, although recent patents[8] indicate that the oxygen of the air may play some part in it. It is interesting to note that if the cellulose is left in contact with the caustic soda for some time before conversion into viscose a less viscous solution is produced.[9]

(I) *Viscose.*

[1] Cross & Bevan, *Cellulose*, p. 25; *Researches*, pp. 27, 107.
[2] Schwalbe, *Die Cellulose*, p. 332.
[3] Cross, Bevan, & Beadle, E.P. 8700 (1892).
[4] Cross, Bevan, & Beadle, *Trans. Chem. Soc.* **63**, 837 (1893).
[5] Cross, Bevan, & Beadle, *Journ. Soc. Chem. Ind.* **12**, 498 (1893).
[6] Cross, Bevan, & Beadle, *Ber.* **34**, 1513 (1901).
[7] Beltzer, *Koll. Zeit.* **8**, 177 (1911); **9**, 76, 120 (1911).
[8] Courtaulds, Glover, & Wilson. E.P. 13, 005 (1914); 14675 (1914).
[9] Cross & Bevan, *Researches* (1900–5), p. 107.

Artificial Silk.

The preparation of artificial silk[1] is dependent on the coagulation of a cellulose solution, and it is found that the viscosity of the solution influences the nature[2] [3] of the fibres obtained.

An interesting investigation has recently been carried out by Clayton, Beadle & Stevens on the swelling of artificial silk in caustic soda solutions.[4] [5] It was found that the swelling increased with the concentration of alkali up to a certain point and then decreased. This change is very similar to that observed by Procter with gelatine and hydrochloric acid. Procter's method of investigation cannot be applied in this case since the concentration of alkali used is too high. It was shown that the addition of sodium chloride to the caustic soda diminished the swelling and adsorption of alkali. The author found that if the artificial silk was first treated with the caustic soda and then with a salt solution the amount of swelling was considerably decreased, but practically no caustic soda passed into the salt solution. It is, of course, known that sodium chloride 'salts out' caustic soda from solution.

(J) *Artificial Silk.*

[1] Suvern, *Die Kunstliche Seide*, Berlin (1900).
[2] Herzog, *Untersuchung der naturlichen und Kunstlichen, Seiden* (1910).
[3] Gaidukow, *Koll. Zeit.*, **6**, 260 (1910).
[4] Clayton, Beadle & Stevens, *8th Int. cong. Chem.* 13, p. 25.
[5] Clayton, Beadle & Stevens, *Journ. Soc. Dyers and Cols.*, **30**, 244 (1914).
[6] Ost, *Zeit. f. angew. Chem.*, 31, p. 141 (1918).
[7] Wilson, *Journ. Soc. Chem. Ind.*, 817 (1917).

Wool.

The products formed by the hydrolysis of wool have been determined,[1] but nothing is known of the constitution of the substances of the wool fibre itself. The presence of a free amido group in the substance of the wool fibre has been discussed from time to time without any very definite conclusions being arrived at.[2] [3] [4] [13] It has recently been shown that wool fibres are not chemically homogeneous, the outer layers being more resistant to the action of chemical reagents than the inner parts.[5] [6]

By treatment of wool with solutions of caustic alkalies a colloidal solution is obtained,[7] which forms precipitates with dyestuffs.[8–14] These precipitates have been considered to be definite chemical compounds. The process of precipitation reminds one more of the coagulation of colloidal solutions than of chemical combination.

The colloidal state of wool fibres is considerably changed by boiling in water, the fibres becoming more plastic; changes in the internal strains are also produced.[9] [10]

When subjected to beating in presence of solutions of soap or of acids, wool fibres become matted together, the process being known as felting, fulling or milling. For many years felting has been considered to be due to the interlocking of the serrations present in wool fibres. This theory was supported by the fact that in some cases fibres with less serrations felted less easily than others with more, and that treatment with chlorine[11] removed the serrations and prevented felting. There are, however, wool fibres having practically no serrations which can be felted, although with difficulty, but which are also prevented from felting by treatment with chlorine. Another theory has been brought forward[17] that the wool fibres become plastic and adhere together when subjected to beating. The fact that a fabric made of tightly-spun, straight wool fibres is very much more difficult to felt than one made of more loosely-spun material appears against this theory, since the closer contact obtained in the first case should assist this adhesion of fibres.

The author is of the opinion that felting is due mainly to the interlocking of fibres caused by the beating of the wool while in an elastic condition. Chlorine reduces this elasticity and makes the wool more plastic.

Mechanical pressure produces considerable changes in wool, particularly when containing moisture and at a high temperature.[9]

The adsorption of acids by wool has been determined by numerous workers.[12–16] The work of Procter (*see* First Report) on the action of acids on gelatine led other chemists[13] to consider that wool formed definite compounds with acids. Exactly as in the case of the adsorption of caustic soda by cotton and the nitration of cotton, peaks were noticed in the curve of adsorption.[13] In the two examples of cotton more recent work has shown that the curves are continuous, and it is certain that the same will apply to wool. The author attempted to apply Procter's methods to wool, but no results of any value were obtained. The amount of swelling in the case of wool is very small compared with that shown by gelatine. The osmotic effect which was expected from Procter's theory did not produce any changes in volume of the wool fibre; it may, however, have produced a change in the internal stresses present in the fibre, but this could not be determined.

(K) *Wool:*

[1] Abderhalden, *Journ. Physiol. Chem.* 46, p. 31.
[2] Prudhomme, *Rev. Gen. Mat. Col.* 209 (1898).
[3] Kann, *Färber Zeit.* 25, 73 (1914).
[4] Gabhard, *Färber Zeit.* 25, 279, 283 (1914).
[5] Naumann, *Zeit. fur angew. Chem.* 30, 135, 297, 305 (1917).
[6] Allworden, *Zeit. angew. Chem.* 29, 77, 78 (1916).
[7] Champion, *Comp. Rend.* 72, 330.
[8] Knecht & Appleyard, *Journ. Soc. Dyers & Cols.* 15, 71 (1889). (Dye compounds).
[9] Harrison, *Proc. Roy. Soc.* A. 94, 460 (1918).
[10] Herzoz, *Chem. Zeit.* 40, 528 (1916).
[11] Pearson, *Journ. Soc. Dyers & Cols.* 25, 81 (1909).
[12] Georgievics, *Zeit. Physiol. Chem.* 87, 669 (1914).
[13] Fort & Lloyd, *Journ. Soc. Dyers & Cols.* 30, 5, 73 (1914).
[14] Fort & Lloyd, *Ibid.* 30, 297 (1914). (Indigo compound).
[15] Harrison, *Ibid.* 34, 57 (1918).
[16] Gee & Harrison, *Trans. Faraday Soc.*, (*April*, 1910).
[17] Justin Mueller, *Koll. Zeit.* 114 (1909).
[18] Miller & Tallmann (Strength & Elasticity of Wool), *J. agric. Res.* 4, 379 (1915).
[19] Hardy, *Ibid.* 14, 285 (1918).
[20] Hartshorne, *Trans. Nat. Assoc. Cotton Manuf.* 79, 194-225 (1905); 90, 281-319 (1911).
[21] Woodmansey, *Journ. Soc. Dyers & Cols.*, 34, 227 (1918).

Silk.

A large amount of work has been carried out on the products of hydrolysis of different kinds of silk.[1–2] The silk fibre in its natural condition consists of two substances, sericine and fibroine, very similar in chemical nature. The sericine is dissolved from the fibroine by the action of dilute alkalies. Attempts have been made from time to time to fix this sericine by means of formaldehyde[3–4] in order to avoid the loss in weight of the silk, but little is known regarding the value of this process.

Silk is modified by boiling in water in a similar manner to wool.[5] The effect of mechanical pressure is also similar with these two fibres.

Colloid chemical investigations have been made[6] with the substance present in the glands of the silk worm from which the silk is spun. The colloid present in these glands coagulates on standing, more quickly on heating or freezing or by treatment with dilute acids, a tough gelatinous mass being formed. It is interesting to note that the coagulation is accelerated by mechanical strain, and the suggestion has been made[6] that the solidification of the silk as spun by the silkworm is due to the mechanical strain exerted during ejection of the viscous secretion of the silk gland through the spinning orifices. This may have some connection with the double refraction shown by silk fibres.[5]

(L). *Silk:*

[1] Fischer, *Zeit. Physiol Ch.* p. 126 (1907).
[2] Abderhalden, *Zeit. Physiol Chem.* **66**, 13—18 & 910 and numerous other articles.
[3] Clavel & Lindermeyer, F.P. 451, 897 (1912).
[4] Cardazzi, F.P. 457, 326 (1913).
[5] Harrison, *Proc. Roy. Soc.*, **A.**, **94**, 460 (1918).
[6] Foa, *Koll. Zeit.* **10**, 7—12 (1912).
[7] Farrell, *Journ. Soc. Dyers & Cols.* 70 (1905). (Action of hydrochloric acid.)
[8] Sansone, *Rev. Gen. Mat. Col.* 194 (1911). (Action of formic acid.)
[9] Hohnel, *Journ. Soc. Chem. Ind.* **2**, 172. (Diameter of silk fibres.)
[10] Wardle, *Tussur Silk.*
[11] Vignon, *Recherches sur la soie, Lyon* (1892).
[12] Rossinski, *Bull. du Labor de la soie, Lyon* (1895).
[13] Franceson, *Etudes sur la filature de la soie, Lyon* (1890).
[14] Collomt, *Journ. de Physik.* (1785).
[15] Bolley & Schoch, *Dingl polyt Journ.* 196 (1870).
[16] Cramer, *Journ. fur prakt. Chem.* **96**.
[17] Persoz, *Mon. Sci.* **1**, 597.
[18] Mills & Takamine, *Trans. Chem. Soc.*, p. 142 (1881). (Absorption of acids.)
[19] Silberman, *Die Seide.*

Sizing.

Very little work of any importance has been done with respect to the sizing of textile materials, but a considerable amount of work has been done on the materials used in this process. The work carried out on glue and gelatine has been fully dealt with by Procter in the first report. Practically all the work done on starch has been considered by Brown[1] and by Stocks.[2] The characteristic blue colour produced when iodine is added to starch has been shown to be due to colloidal iodine,[3] and many other substances have been found to give the same reaction.[14]

The changes undergone by starch during boiling are of great importance in relation to sizing and finishing and have received considerable attention.[4–12] The addition of salts has been shown to influence these changes.[5–6]

The so-called sizing properties of starch are somewhat obscure. The process of sizing is carried out for the specific purpose of assisting in the weaving of fabrics, and the advantages of any particular sizing material can, at present, only be determined by a practical test.[13] The relationship between the mechanical properties of the sized yarns and the physical properties of the sizing materials has never been determined. This is mainly due to the difficulty of measuring those mechanical properties of sized yarns which determine their value in weaving.

(M) *Sizing, Starch, &c.*

[1] *See* Brown, First Report, p. 38.
[2] Stocks, First Report, p. 46.
[3] Harrison, *Koll. Zeit.* 9, 5 (1911)
[4] Harrison, *Journ. Soc. Dyers & Cols.*, 27 p. 84 (1911).
[5] Samec, *Kolloidchem. Beiheft.* 3, 123 (1911).
[6] Samec, *ibid.* 4, 132 (1912).
[7] Samec & Hoefft, *ibid.* 5, 141 (1913).
[8] Samec, *ibid.* 6, 23 (1914).
[9] Samec & Jencic, *ibid.* 7, 137 (1915).
[10] Samec, *ibid.* 8, 33 (1916).
[11] Rakowski, *Koll. Zeit.* 9, 225 (1912); 10, 22 (1912); 11, 19, 51, 269 (1913).
[12] Harrison, *Journ. Soc. Dyers & Cols.*, 32, 40 (1916).
[13] Whowell, *Text. Inst. Journal* 2, 43 (1911).
[14] Barger & Starling, *Trans. Chem. Soc.*, 441 (1915).
[15] Barger & Field, *Trans. Chem. Soc.*, 1394 (1916).

Scouring (Soap, &c.).

The scouring of textiles is mainly a colloid-chemical process. In the case of cotton the impurities to be removed are fats and colloidal matters usually termed pectic substances. These latter form colloidal substances in alkali, by which they are removed from the cotton. In recent patents[24] substances of colloidal character, starch and albumenoids, are used in conjunction with caustic alkalis as scouring agents, and apparently these substances act as protective colloids during the scouring process.

In the case of wool the impurities consist mainly of fat, although some protein matters are present in the "suint." The removal of this fat is effected by a dilute solution of soap.

The nature of the process of scouring has recently been investigated from the colloid-chemical standpoint[20] and numerous important points deduced.

The impurities in silk consist mainly of albumenoid and are removed by dilute solution of soap.

(N) *Scouring Soap, &c.*

[1] Chevreul, *Recherches sur les Corps gras d'origine animale Paris* (1823).
[2] Krafft, *Ber.*, 27, 1747 (1894); 28, 2566 (1895); 29, 1328 (1896); 32, 1584, 1899.
[3] Kahlenberg & Schreiner, *Zeit. f. Phys. Chem.*, 27, 559 (1899).
[4] Cornish, *ibid.*, 31, 42 (1899).
[5] Donnan, *ibid.*, 31, 44 (1899).
[6] Donnan & White, *Trans. Chem. Soc.*, 1668 (1899).
[7] Browden, *ibid.*, 191 (1899).
[8] Goldschmidt, *Seifen fabr.*, 1247 (1902).
[9] Smits, *Zeit. f. Phys. Chem.* 45, 608 (1903).
[10] Leimdorfer, *Seifenseider Zeitung Ausgberg*, (1906).
[11] Meyer, Schaeffer & Terroine, *Comp. Rend.*, 146, 484 (1907).
[12] Spring, *Koll. Zeit.*, 4, 162 (1909); 6, 11, 109, 164 (1910).
[13] Leimdorfer, *Kolloidehem. Beihefte*, 2, 243 (1910).
[14] Donnan & Potts, *Koll. Zeit*, 7, 208 (1911).
[15] Reychler, *ibid.*, 12, 18, 277 (1913); 13, 252 (1914).
[16] Arndt & Schiff, *Kolloid. Beihefte*, 6, 201 (1914)
[17] Kurzmann, *ibid*, 5 433 (1014).
[18] McBain, *Trans. Faraday Soc.*, 9, 99 (1913).

[19] Fischer & Hooker, *Koll. Zeit.* 18, 129 (1916). (Casein Solutions.)
[20] Shorter, *Journ. Soc. Dyers & Cols.*, **31**, 64 (1915); **32**, 90 (1916); **34**, 136 (1918).
[21] Shorter & Ellingworth, *Proc. Roy. Soc.*, **A. 92**, 232 (1916).
[22] Pickering, *Trans. Chem. Soc.*, **111**, 96, (1917).
[23] Shorter & Harrison, *Journ. Soc. Dyers & Cols.*, **34**, 163 (1918).
[24] McPherson & Heys, *E.P.*, 5620 (1909); 20089 (1909); 8478 (1915).
[25] McBain & Taylor, *Ber.* **43**, 321 (1910).
[26] McBain & Taylor, *Zeit. phys. Chem.*, **76**, 179 (1911).
[27] Bowden, *Chem. Soc. Trans.*, **99**, 191 (1911).
[28] McBain, Cornish & Bowden, *ibid.* **101**, 2042 (1912).
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Dyeing.

The large amount of work carried out on dyeing has already been fully considered by King in the first report. The electrical theory of dyeing has recently been discussed at some length.[3] In its present condition[2] four factors are taken into account.

1. Molecular movement, by which dye molecules or particles transport themselves on to the fibre or into its pores. In true solution, this process is usually known as diffusion and must be taken into account in all theories of dyeing. In colloidal solutions the same thing occurs but to a less extent.

2. The electrical charge on the fibre and on the dye. The potential of this charge has been measured under several conditions as regards nature and concentration of added electrolytes. The nature of this contact potential has received much discussion; some chemists consider it to be due to residual valency. The opposite view that valency is the direct result of the electrical construction of elements is more likely to be true. In any case, Bragg's models of crystals show that the surfaces of solids must behave differently from the bulk of the material.

3. The size of the pores in the fibre.

The presence of these pores has been directly proved by ultramicroscopic examination and indirectly by the fact that colloidal solutions can penetrate to a considerable extent into the fibres. The idea that dyes are imbibed into the cavities and pores of fibres by capillary attraction was put forward by Crum more than 50 years ago. The manner in which the dyes were fixed in those pores was, however, not explained by Crum, but has been explained as a case of electrical coagulation.

The increased dyeing produced with cotton on mercerisation has been shown to be due to changes in the colloidal state of the fibre as well as electrical charge. The effect of drying on mercerised cotton is to reduce its dyeing capacity; this has been explained as being due to reversion of the changes produced by mercerisation.

4. The size of the dye particles.

It is obvious that the extent to which dye particles can penetrate into porous substances must depend on their size. The rapidity of coagulation is also dependent on the size of the particles.

By the inclusion of these four factors, the electrical theory appears to explain most cases of dyeing; its value is recognised mostly in the case of direct colours where chemical theories have failed.

Printing.

The printing of textile fabrics is carried out by applying a viscous solution by means of an engraved roller to the fabric. Many interesting colloid-chemical phenomena are met with in the preparation of the viscous printing pastes. Even to-day there is a considerable amount of secrecy exercised in the preparation of these pastes, partly as regards the materials employed, but more particularly in the manner of mixing them. There is little difficulty in ascertaining the ingredients by chemical analysis, and by the help of colloid-chemistry the order in which the ingredients must be mixed can readily be decided. Materials which precipitate one another should first be mixed with the protective colloid, starch, tragacanth, &c.

The subsequent fixation of the printing colour by steaming, particularly in the case of non-mordant dyes, has been shown to be due to the swelling of the fibre by the action of the steam.[1, 2 and 4] The fixation of colours from pastes containing both colour and mordant is undoubtedly due to coagulation, as the result of reduction in the protective power of the colloids at high temperature.[Compare 3]

Finishing.

The finishing of textile fabrics is an art to which very ltttle science has been applied. The effects of the mechanical treatments to which fabrics are subjected during finishing[1] have only recently been investigated.[2] The main factors are mechanical pressure, heat and moisture. The effect of moisture is to increase the degree of swelling of the fibre, and this is greater the higher the temperature. Pressure decreases the swelling in the direction at which it is applied. Permanent finishes are produced by processes which reduce the swelling capacity of the fibre colloids.

(O) *Dyeing.*

[1] Compare King, *First Report*, p. 20.
[2] Harrison, *Journ. Soc. Dyers and Cols.*, 27, 279 (1911).
[3] Harrison, *ibid.* 34, 97, 127 (1918).
[4] Craven, *ibid.* 34, 128 (1918).
[5] Fort, *ibid.* 34, 124 (1918).
[6] Haller, *Koll. Zeit.*, 23, 100 (1918).

(P) *Printing.*

Compare *First Report* Article by Stocks, 46–78.

[1] Justin Mueller, *Koll. Zeit.*, 5, 233 (1909).
[2] Justin Mueller, 7, 40 (1910).
[3] Harrison, *Koll. Zeit.*, 9. 5 (1911).
[4] Haller, *Kolloidchem. Beihefte*, 8, 1 (1916).
[5] Haller, *Koll. Zeit.*, 23, 100 (1918).

(Q) *Finishing.*

[1] See Article in *Journ. Soc. Dyers and Colourists*, 29 117 (1913)
[2] Harrison, *Textile Inst. Journal* (1916).

REPORT ON THE PART PLAYED BY COLLOIDS IN AGRICULTURAL PHENOMENA.

By E. J. Russell, D.Sc., F.R.S., *Director of the Rothamsted Experimental Station.*

Agricultural chemists only slowly recognised the part played by colloids in the soil. For many years the soil was regarded as a mass of crystalloid mineral matter, and in discussions of its properties it was treated as if it were sand mingled with certain soluble salts and organic matter. Sand cultures were commonly adopted in pot work; sand particles were used in experiments on the physical properties of the soil; and in the early attempts at mathematical analysis the particles were supposed to be spherical and impenetrable, though this assumption was recognised as an approximation only. As experimental results and deductions accumulated, it became obvious that there was a wide discrepancy between the properties expected and those actually found in natural soils. It therefore became necessary to re-examine the fundamental propositions.

The first demonstrations of the unsoundness of the old views came from the Dutch investigator van Bemellen. It had long been known that soil possessed the remarkable property of absorbing certain soluble substances from their solutions: ammonia was taken from ammonium sulphate solution, potash from potassium sulphate, and so on. It was this property that justified the use of soluble salts as artificial fertilisers. The first explanation was offered by Way, who supposed that the process was a simple chemical reaction of the double decomposition type, and he assumed the existence in the soil of a series of reactive silicates in order to account for the observed phenomena. Subsequent writers, adopting the simple expedient of keeping away from the soil, elaborated the properties of these double silicates; and when, at a later date, mineralogists directed attention to the zeolites, some of the agricultural chemists assumed that these substances existed in quantity in the soil and were the reactive constituents in question.

Shortly after Way had offered his chemical hypothesis Liebig advanced a physical explanation. He supposed that soil had some power of attracting dissolved salts similar to the power possessed by charcoal for condensing gases. Only the substances physically held in the soil were considered of immediate value to the plant, although the chemically combined substances might be a reservoir in maintaining supplies.

Further investigations showed that neither explanation was quite sufficient: Knop therefore combined the two hypotheses and explained the absorption of acids as a chemical combination with iron or aluminium oxides, and the removal of bases partly as a physical attraction and partly as a chemical combination with silica or double aluminium silicates. But the compromise was not very satisfying and aroused little enthusiasm; moreover, it did not help to account for the ever increasing number of apparently abnormal phenomena. Later on van Bemmelen proved that the phenomena were precisely similar to those shown by colloids, and argued that the soil must be treated as a colloid. This view was generally accepted by those who read his papers. Unfortunately, van Bemellen's work was published in German, and the translation from his own language was not altogether happy—rather giving the impression of a long drawn tedious memoir on an unimportant subject. A good English translation is very desirable: the papers belong to the classics of agricultural chemistry. Van Bemellen did not at once arrive at the colloid explanation; he first accepted Way's chemical explanation, and, indeed, devised a method for estimating the double silicates present. Later on, however, he made extensive studies of absorption by simple gels, silica, alumina, ferric hydroxide, tin hydroxide, etc., and found it closely to resemble absorption by soils: other studies of colloids were made, and in each case the similarity to soil phenomena was so close as to leave no doubt that soil was essentially a colloid and soil absorption simply a manifestation of its colloidal properties.

This new idea was soon found to explain many of the old discrepancies. Chemists had several times attempted to bring the phenomena of absorption equilibrium into line with those of chemical equilibrium, but the equations would not fit except for a narrow range of concentrations.

When, however, the adsorption formula is used, a much closer fit can be obtained: Wiegner has gone over the recorded data and shown that they all agree with the ordinary equation,

$$\frac{y}{m} = Kc^{\frac{1}{p}}$$

the constants having the following values:—

Absorbent.	Solute.	K	$\frac{1}{p}$	Worker.
Garden soil	NH_4Cl	0·0948	0·039	Henneberg and Stohmann.
" "	NH_4Cl	0·131	0·424	
Nile sediment	NH_4Cl	0·489	0·399	Armsby.
Permutite ... artificial	NH_4Cl	2·823	0·398	Wiegner.
Sodium zeolite	$CaCl_2$	2·487	0·317	Armsby
Zeolite ...	$LiCl$	24·419	0·414	Campbell.
Soil	NH_4OH	0·0994	0·434	Brustlein.
"	NH_4OH	0·147	0·461	
"	NH_4OH	0·054	0·386	

It is still, however, necessary to account for the fact that the absorbed bases displace an equivalent amount of some other bases from the soil—a procedure which would be unnecessary if nothing but adsorption were involved. This is done by supposing that only the hydroxide is absorbed: the acid radicle in general is not: it therefore dissolves out some of the bases from the soil. As this is a purely chemical reaction the amount of base brought out is equivalent to the acid set free, *i.e.*, to the amount of base adsorbed.

This view is found to account for all the phenomena as yet recorded. Moreover, it explains the difficulties that have attended the study of the soil solution or the liquid phase in the soil. Chemists now realise that the colloids profoundly affect the composition of the liquid phase, and they are devoting considerable time and ingenuity to the problem of extracting typical samples for investigation. Centrifugal methods have been tried, but they are troublesome in application. Displacement methods would be easier if one could be sure that the adsorption relationships were not being disturbed. Morgan claims that paraffin oil is both effective and simple in use. A pressure method is in use in Ramann's and also in van Zyl's laboratories, especially for soils containing much clay or humus: 3 kgms. of soil are subjected to a pressure of 300 kilos per sq. cm. In view of the great importance of the soil solution in the nutrition of plants, it is a matter of vital necessity to discover the laws governing its composition, the influence of manuring, climate and soil treatment.

Thus it is known that sodium salts liberate potassium from the soil: lime also has the same effect. Regarded as adsorption effects the phenomena are much easier to explain than as simple chemical reactions. The technical importance of a full understanding of the phenomena is considerable. There is, however, a school of chemists who regard the whole phenomena as chemical, and adhere to the hypothesis of reactive zeolites: Gedrortz in Russia, and von Rothmund and Kornfeld in Germany.

The action of Acids on the Soil.

Agricultural chemists have long hoped that soil analysis might guide the farmer in drawing up a system of manuring. Unfortunately, this hope has proved largely illusory; the problem is complicated by the fact that at least five or six factors enter into soil fertility, of which the chemical composition of the soil is only one. But there is another source of trouble well recognised by agricultural chemists: the selection of a method for the extraction of the plant nutrients in the analytical process.

The first methods, founded wholly on mineral analysis, involved the use of strong acids and proved of little value in this country. A marked improvement was effected when dilute acids were substituted for strong acids, but many anomalous cases still arose: in particular, no two acids ever gave the same result, nor even did different concentrations of the same acid. The underlying assumption always was that the soil was a mass of mineral fragments with the phosphates, etc., in the ordinary mineral form. All attempts to interpret the action of dilute acids on soil phosphates as an ordinary chemical reaction failed.

Russell and Prescott have studied the reaction between dilute acids and the phosphates in the soil and find that it can be interpreted satisfactorily as a simple solvent followed by an adsorption. The solvent action is practically the same for nitric, hydrochloric and citric acids of equivalent strengths, and appears to be the normal action of an acid on a phosphate. The reverse reaction is the typical adsorption shown by colloids, and can be expressed by the equation which has been found to fit so many of them. It is considerably influenced by the acid, being greater in the presence of the mineral acids than of the organic acids. The amount of phosphorus compound actually brought out is the difference between the direct and the reverse action. Thus, hydrochloric acid dissolves out a certain amount of phosphate, but considerable adsorption takes place, so that the net amount left in solution is only small. Citric acid dissolves out the same amount of phosphate, but there is much less adsorption, and therefore the amount left in solution is markedly greater. The difference between the various dilute acids lies not in their solvent power, which is similar for all, but in their influence on the adsorption process. The observed net effect of the acid on the soil is therefore expressed by the ordinary adsorption curve.

The reaction between dilute acids and soils thus appears to be essentially a displacement of absorbed material by something which is itself absorbed; and it falls into line with other displacements from colloids.

If this view is correct, it follows that acids need not be used in soil analysis, at any rate for the extraction of bases: any agent capable of being absorbed by the soil would serve equally well. Ramann has used a solution of ammonium nitrate and finds it dissolves at least as much potassium, calcium, etc., as an acid, and in some respects is more satisfactory. This method of extracting the bases from soils promises to be useful and to clear up many of the difficulties in soil analysis.

The water relationships of soils.

The earlier soil physicists, regarding soil as a mass of mineral matter, began their studies of the water relationships of soils by treating soil as a mass of sand, or, in mathematical analysis, of small bullets or marbles, and investigating the distribution of water by surface tension. The conclusions obtained were not wholly in accordance with facts. The facts observed in the evaporation of water from soil were particularly difficult to fit in with expectations, and numerous breaks in the curves seemed to indicate the existence of a variety of critical points and co-efficients. Keen has shown, however, that the phenomena become much clearer when regarded as colloidal effects. He found that the relationship of water to soil differs considerably from its relationship to sand. The evaporation of water from sand, silt, china-clay, and ignited soil proved to be relatively simple, and could be explained by the known laws of evaporation and diffusion. But the evaporation of water from soil could not: it was more complex. Instead of the simple proportionality between water content and time observed in the case of sand, the curves for soil were more exponential in type. The difference was traced to the soil colloids, and it disappeared when the soil was ignited and the colloidal properties lost: the curve then became identical with that obtained for sand. The influence of the colloids has so far only been expressed empirically, but it is probably connected with the relation between vapour pressure and moisture content. But there is clearly something else at work, for the curve is not of a simple exponential type. It is necessary to allow for another factor: the effect on the rate of evaporation of the water surface in the soil, which obviously diminishes in area as evaporation continues.

The equation finally developed by Keen is:—

$$A\frac{dw}{dt} = \left(\sqrt[3]{\frac{ws}{100}} + 1\right)(\log_e(w + K) - \log_e K),$$

where $\frac{dw}{dt}$ = rate of evaporation.

w = percentage of water present by weight.
s = specific gravity of the soil.
A and K = constants.

This relationship holds without any break, proving that all the water in a normally moist soil is held in the same way without change in physical state. At one end of the curve the water is more easily given up than at the other, and in the competition for water between soil colloids and plants or micro-organisms some kind of equilibrium may be attained under definite conditions: this equilibrium is the "wilting point" of the physiologist. On this view the other constants and critical points that have been indicated by various investigators are all equilibrium points and do not represent breaks in the condition of water in the soil.

The retention of liquid water by soil, or, in other words, the resistance to drainage, is no doubt influenced by soil colloids. Attempts have been made by Alway and McDole to trace some connection between the amount of water absorbed by dry soil from a moist atmosphere and its water-holding capacity: in so far as these phenomena are related it is probably through their relationship to the soil colloids. The influence of salts on the permeability of soil to water, which is probably as much physical as chemical, has been studied by Hissink.

Soil Acidity.

It has long been known that some soils are acid to litmus paper, but become neutral on the addition of calcium carbonate. Acidity is not tolerated by most cultivated plants, and the agriculturist has therefore to guard carefully against it: the problem is one of high technical importance.

The older chemists took the obvious view that acidity was due to some special soil acid or acids, to which various names were given: humic acid, ulmic acid, crenic acid, apocrenic acid, etc. But no acid satisfying the modern chemist could be isolated, and when the colloid conception was introduced Cameron pointed out that the phenomena could all be explained as simple colloidal manifestations and did not require the assumption of soil acids at all. It was only necessary to suppose that the soil colloids absorbed the base more readily than the acid from blue litmus and the whole phenomena are explained. In support of this view Cameron showed that cotton and other absorbents behaved exactly like "acid" soils, slowly turning blue litmus red; the phenomenon was therefore a general property of a class of absorbents.

Baumann and Gully applied this idea to the case of peat and showed that it fully explained all the known facts.

In the first instance they pointed out that it was not necessary to assume that the "acid" was a decomposition product because the original sphagnum was almost as "acid" as the peat.

Secondly, the acid if it exists must be insoluble because the water extract of the peat is practically neutral to litmus.

It must, however, be very potent because solutions of neutral salts such as calcium chloride, sodium nitrate, etc., are decomposed with liberation of free hydrochloric and nitric acids when treated with peat or sphagnum.

Baumann and Gully argue that no acid of this character is known to chemists, and it involves less strain to conceive of a physical adsorption of the base from the dissolved salt with liberation of the acid than to imagine an insoluble organic acid capable of decomposing simple salts in solution.

The view that acidity of the mineral acid soils is due to preferential absorption of the base was developed by Harris in an investigation of Michigan soils. The phenomena are substantially the same as for peat: the soil turns blue litmus red; an aqueous extract is neutral, while an extract made with a solution of a salt, *e.g.*, calcium nitrate, is acid. We must therefore assume either an insoluble but very potent mineral acid, or a preferential absorption of the base over the acid. The latter is indicated because, as in the case of peat, the amount of acid liberated from equivalent quantities of different salts is not the same, as it should be in a chemical reaction.

Daikuhara has applied this view to the case of the acid mineral soils of Japan and Korea, but he has modified the explanation and made it more easily intelligible to the chemist, who finds it difficult to understand why an unparalleled physical decomposition of a simple salt should be accepted, and the assumption of a difficultly soluble but potent acid rejected. Daikuhara shows that the development of acidity in the salt solution is due to an exchange of bases and not to simple absorption of the base from the salt. If the acid solution is analysed it is found to be really a solution of an aluminium salt: aluminium being given up from the soil in amount approximately equivalent to the base absorbed. Aluminium salts, as is well known, turn blue litmus red, and therefore are indicated as acids. The phenomenon is still essentially an absorption, but the seat of the reaction is located.

This view is supported by Rice's experiments, which have demonstrated the substantial identity in hydrogen ion concentration of a solution of aluminium nitrate and the solution obtained by treating an "acid" soil with potassium nitrate solution.

Ramann adopts this view and gives up the expression "acid soils," using instead "absorptiv ungesättigte Boden." Kappen confirms the observations without entirely accepting the explanation.

The physical explanation of acidity has not passed unchallenged. Rindall of Helsingfors, Sven Odén of Upsala, Tacke and Ehrenberg have each argued in favour of definite humic acids in peat. Truog finds, in the case of mineral soils, that equivalent amounts of different bases are required to neutralise the acid properties of the soil—which, if generally true, would be easier to explain by assuming an acid than an adsorption.

It is always possible that both factors are at work. Evidence has been adduced by Christensen and by Schollenberger to show that acidity and base-absorbing power are not quite the same thing. Still more significant, measurements of the hydrogen ion concentration of soil extracts have been made, and show definite acidity.

Pan formation.

A pan is a layer of hard impermeable rock that gradually forms below the surface of the soil under certain conditions. Its effect is to cut off the soil above from the material below, and therefore to modify profoundly the movements of water and air, leading often to swampy conditions. The effect on vegetation becomes so marked that in agricultural practice the pan has to be removed, often at considerable trouble and expense.

The conditions determining the formation of pan seem to be a supply of organic matter, permeability of soil, low content of soluble mineral matter, and absence of calcium carbonate. These conditions occur most frequently on light sandy soils where, for some reason, the water is held sufficiently near the surface.

The older chemists explained the phenomena on purely chemical lines; it is unnecessary to go into the details of the various hypotheses put forward: in the main they involved alternate reductions and oxidations, or else solution in carbonic acid, and subsequent deposition. These hypotheses broke down on further examination, some necessary links failing to be realised when the experiment was made under natural conditions.

Recent workers, therefore (Munst, Ramann, Morison, Sothers and Stremme) regard the whole process as a formation first of a "sol" and then of a "gel," and Morison and Sothers suggest the following as the most probable course of events.

It is well known that "sols" change to "gels" in presence of small quantities of electrolytes, and conversely "gels" often change to "sols" when electrolytes are removed. In normal soils the conditions are favourable to gel formation, but when in these particular soils the upper layer of sand becomes denuded of its soluble material by the persistent washing of rain water, the conditions become favourable for the formation of sols of ferric hydroxide and of humus—or ferric humate, if one likes to put it in that way. Morison and Sothers actually obtained such sols[*] by persistent washing of ferric-humus gels.

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[*] As might be expected these did not give the ordinary iron reactions.

As the sol is washed down most of it passes to the permanent water level, where it remains and accumulates, diffusion being practically non-existent. During the dry months a certain amount of dessication takes place, involving a deposition of the sol as a gel: there is also a certain amount of transformation of sol to gel through the presence of electrolytes in the ground water.* Some of the humus gels become oxidised, some of both humus and ferric hydroxide gels change their colloidal properties in other ways. When wet weather comes on again it is no longer possible for the whole of the deposited gel to change back to a sol. Deposition has begun, and the place where this happened serves as a seat of further action.

This view seems more in accordance with the facts than the older one, in that it does not involve any unproved assumptions—such as reduction of ferric to ferrous iron and presence of ferrous iron in the pan.

Flocculation and Deflocculation.

Clay possesses well marked colloidal properties. If rubbed with water it becomes plastic, sticky and impervious: it shrinks on drying and absorbs heat: on moistening, however, the process is reversed and there is considerable swelling and evolution of heat. The importance of these observations is equally great in agriculture and in the ceramic industry.

Two hypotheses have been put forward to account for plasticity. Rohland attributes it to hydrated colloids present in the clay: Atterberg to minute flake-like particles which are able to slip over one another without difficulty.

Another property of clay is of great importance to agriculture, and has received much attention from agricultural chemists. Addition of a trace of electrolyte—acids or salts—to puddled clay causes considerable change in properties: the temporary loss of plasticity, impermeability and the power of remaining long suspended in water without settling; the clay is now said to be flocculated. The change can be watched if a small quantity of any flocculating substance is added to the turbid liquid obtained by shaking clay with water; the minute particles are then seen to unite to larger aggregates which settle, leaving the liquid clear. There is, however, no permanent change, deflocculation takes place, and the original properties return, as soon as the flocculating agent is washed away. Alkalis (caustic soda, caustic potash, ammonia, and their carbonates) produce the reverse effect: they deflocculate clay, intensifying its stickiness and impermeability, and causing it to remain suspended in water for long periods.

These properties are of considerable importance in devising schemes of manuring for soils: it is obvious that alkaline substances are to be avoided on clay soils, however rich they might be in plant nutrients, as they would produce undesirable

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* Ramann lays stress on this, Morison and Sothers do not because their sols were very stable in presence of electrolytes.

physical effects. On the other hand, slightly acid substances such as superphosphate have no bad effects, but rather the reverse.

Clay is thus an electro-negative colloid, its reaction probably being conditioned by a trace of potash liberated by hydrolysis. It shows the general properties of electro-negative colloids as elucidated by Schulze and by Hardy: thus it is flocculated only by a solution containing ions or particles of opposite electrical sign, and the extent of flocculation increases rapidly with the valency and concentration of the ion. No quantitative relationships, however, could be found by Hall and Morison.

Pickering throws over the electrical hypothesis and attributes flocculation to a combination of the clay with the flocculant and the solute, whereby the aggregation of molecules increases so much that it loses its power of Brownian movement and soon settles.

Other effects of Colloids.

Various obscure changes are brought about on drying the soil. There is a marked increase in the proportion of water-soluble material, and, as Buddin has shown, in the ease with which nitrates are formed. Changes in the micro-organic population no doubt account for some, but not all, of these effects, and the simplest explanation is to attribute them to the changes in the colloids. Again, soil has a remarkable power of decomposing hydrogen peroxide, which is affected by small quantities of various substances, and may be a colloidal phenomenon. The decomposition of cyanamide in the soil has been attributed to colloids.

The influence of Colloids on Bacterial and Plant Life.

Plants and bacteria draw from the soil their water and their nutrient salts, and are therefore profoundly affected by anything that retards delivery of these essential substances. Inasmuch as colloids possess markedly absorbent powers they might serve as reservoirs to protect against loss by evaporation or leaching, or, on the other hand, they might actually compete against the plant and hold some of the supplies the plant ought to obtain.

As yet there is insufficient experimental evidence to show how the various factors are likely to interact. Fortunately ecologists, both in this country and elsewhere, are fully alive to the possibilities: Gola has discussed the influence of the colloidal complex in determining plant habitats, and Söhngen its effects on the activities of micro-organisms; an illuminating résumé by Cavers has also appeared. It is interesting to note that soils destitute of colloidal properties are often infertile.

The Estimation of Soil Colloids.

Many efforts have been made to estimate the amount of colloidal matter in the soil. They fall into two groups based on the absorption of dye stuffs and of water vapour respectively. Methods based on the absorption of dye-stuffs have been elaborated by Sjollema, Endell, Ashley, König, Hasenbäumer and Hassler, Hanley and Tadokoro, the last named giving other references also. Methods depending on the absorption of water vapour have been suggested by Mitscherlich. Different methods do not give altogether concordant results, nor is it to be expected that they should; it is highly improbable that any sharp dividing line exists in the soil between the typical colloids and the typical non-colloids; intermediate substances are to be expected showing colloidal properties only to a slight extent. It is certain, however, that the finer particles of the soil—the clay and fine silt—show much more marked colloidal properties than the coarser particles—the coarse silt and the sands.

The Constitution of the Soil.

Soil consists mainly of disintegrated and decomposed rock fragments of all sizes, varying from 1 mm. diameter downwards; these may be said to constitute its skeleton. Intimately mingled with these are the decaying remains of past vegetation. It seems necessary further to suppose that the particles are coated with a gel composed of silica, oxides of iron and aluminium, soluble organic matter, and a smaller quantity of lime, magnesia and potash, traces of ammonia, etc.: this gel being spread relatively more thickly on the small particles than on the larger ones. This view of the constitution of the soil fits in with the known facts, and it has the further advantage of offering a definite starting point for further investigations.

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SEWAGE PURIFICATION WITH REFERENCE TO COLLOID CHEMISTRY.

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Although the problem of sewage purification, as it is known to-day, dates back to the introduction of the water-carriage system in the early part of the nineteenth century, the significance of colloid chemistry in relation thereto has only been observed within comparatively recent years.

Even at the present time, although certain theories have been elaborated with respect to the fate of the colloid matter during the purification process, in the main such theories have been established by analogy from the known characteristics of organic colloids and their behaviour under certain conditions rather than from any systematic study of the colloid matter actually present in sewage. So far as the writer is aware, no reliable data are available with respect to the separation, estimation and identification of the actual colloids present originally in the sewage and during the various stages of the purification process.

With the view, therefore, of indicating the present position in regard to the subject it is proposed (*a*) to state briefly the problem and (*b*) to give a résumé of the chief theories advanced with respect to the mechanism of the changes involved in the purification process, with special reference to the points of contact with colloid chemistry.

Briefly, ordinary domestic sewage may be said to be the water supply polluted by human excremental matter, kitchen and other domestic waste products. As in the majority of cases a combined drainage system is adopted, road detritus and washings must be added.

The character and strength of domestic sewage varies very considerably, dependent on the following factors:—

(i) The extent to which the water carriage system has been adopted.
(ii) The water consumption per head of population connected to the sewer.
(iii) Whether a combined, separate or partially separate system is in vogue.

(iv) Length of travel of outfall sewer.
(v) Rainfall, contour of district, nature of subsoil, and character of sewers, &c.

In industrial areas the character of the sewage is altered to an extent dependent on the nature and relative volume of the trade wastes admitted to the sewers.

In certain districts, *e.g.*, in woollen districts (Bradford, Huddersfield, &c.), or centres of chemical industry (Manchester, Birmingham, &c.), these are such as to alter very materially the character of the sewage, and consequently to vary the problem of its purification.

The main constituents of domestic sewage have been summarised by Fowler as follows:—

1. Matters in actual suspension:
    - (*a*) Sedimentary matters, such as silt and sand, &c.
    - (*b*) Floating and finely divided suspended matters (paper, rags, faeces, animal and vegetable debris, &c.).
2. Colloidal matters in pseudo solution or emulsion:
    Products of faecal emulsion, soaps and fatty matters, &c.
3. Matters in true solution:
    Ammonium salts resulting mainly from the hydrolysis of urea. Nitrogenous substances—urea, products of the decomposition of albumen—peptone like bodies, carbohydrates; mineral salts—chiefly sodium chloride, with phosphates mainly derived from urine.

It will be understood that on account of its complex character and the unstable nature of its organic contents it is practically impossible to differentiate with anything like a high degree of accuracy the various states of the organic matter present in sewage which under physical and biological action is subject to transition from one form to the other.

O'Shaughnessy has shown that the colloid matter in pseudo solution is derived mainly from the faecal matter present, and that although there is a limit to the amount that can be taken up, the actual quantity (as measured by the 4 hours' oxygen absorption test) varies with the volume and character of the diluting water, the time of contact and the amount of agitation.

It is thus evident that the amount of organic "hydrosols" varies very considerably in different sewages. For an average domestic sewage it may be taken that roughly one-half of the soluble organic matter is present in pseudo solution.

Sewage is such a heterogeneous mixture of complex and varying character that apart from such determinations as chloride content, ammonium salts, organic nitrogen, total suspended and dissolved (true and pseudo solution) solids, its chemical examination is usually confined to certain empirical tests such as "albuminoid ammonia" resulting from the distillation of the sewage with an alkaline solution of permanganate of potash after removal of the ammonium salts, which is taken as a measure of the albuminous bodies present, and "Oxygen absorption" from an acid solution of permanganate (usually $\frac{N}{80}$ K MnO_4) under stated conditions, which gives an indication of the amount of oxidisable matter present.

For the purpose of controlling purification plants, in addition to the above tests, the amount of oxidised nitrogen (Nitrite and Nitrate) is determined in the effluent.

Incubation will show whether the effluent is putrescible, and determination of the amount of dissolved oxygen absorbed by the effluent from aerated water, as recommended by the Royal Commission on Sewage Disposal as a Standard Test, will afford valuable information with respect to the matter still capable of fermentation, and consequently of the extent to which the oxidation change has been carried.

With the object of obtaining information in relation to what happens to the colloidal matters during the purification process, at any rate so far as the "hydrosols" are concerned, these tests have been supplemented by submitting the sewage and effluents to dialysis and thus determining the proportion of dialysable to non-dialysable matter and their respective oxygen absorption and albuminoid ammonia content, *see* Rivers Committee Report, Manchester, 1901, Kröhnke & Biltz, Fowler & Ardern, Travis & Johnston, O'Shaughnessy & Kinnersley (1901–1906).

An objectionable feature of this method of attack is the time required by the dialysis operation, which is usually not less than 24 hours, even where the determination is stopped when equilibrium is attained (as measured by the chloride content) on either side of the membrane employed, during which period there are many possibilities of change of character in an unstable liquid like sewage. In the method employed by Johnston for the complete separation of the non-dialysable from the dialysable constituents of the sewage, a period of 6 days usually elapsed. The sewage and effluents were sterilised by the addition of acid with the idea of obviating changes due to bacterial action, but it is obvious that mere acidification is likely to alter the character of the samples under examination.

The method proposed by Rübner of coagulating the colloidal matter by precipitation with acetate of iron surmounts this difficulty but introduces other errors with respect to the removal of organic matters in true solution. Fowler and others elaborated this test and called it the "clarification test," while Rolants compared the effect of acetate of iron with that of calcium chloride and sodium phosphate, alumina, and powdered talc, respectively, the latter material being employed with the idea of avoiding precipitation of organic matter from crystalloidal solution.

A difficulty common to both these methods of investigation is the character of the preliminary treatment of the sample, undertaken for the removal of the finely divided non-colloidal matter. The method of procedure is either to allow the sample to stand for a stated period and to work with the supernatant liquid, or to filter the original sample through filter paper. The first procedure is open to the objection that matters in what may be termed 'macroscopical' suspension are incompletely removed, while filtration through paper, in addition to the removal of such matter, may also remove actual colloids by the absorptive action of the film of suspended matters formed on the filter paper. It will thus be seen that it is difficult to differentiate between particulate suspended matter in a state of fine division and actual colloidal matter.

The object of sewage purification is primarily to obtain an effluent which will not pollute the water course into which it is discharged.

An effluent may be said to be entirely satisfactory which avoids the following:—

1. Secondary decomposition which may give rise to aerial nuisance.
2. Deaeration of the body of water into which it is discharged.
3. Deposition on the bed of the watercourse.

Having regard to the conditions usual in this country of the relative volumes of the stream and sewage, the production of such an effluent involves the removal of suspended matters and of the putrescible organic matter in colloidal and crystalloidal solution.

In the following paragraphs is given a brief account of the methods generally adopted to effect this object.

The sewage as it arrives at the outfall works is usually passed through a detritus and screening chamber, where the heavier sedimentary matters, road detritus, &c., are removed, together with floating matters, such as rags, paper, &c., and a proportion of the non-disintegrated faecal matter.

Apart from the treatment of sewage on land by broad irrigation, or in some cases of intermittent filtration, or by the activated sludge process, which will be briefly considered later, the screened sewage then receives preliminary treatment by one of the following alternate methods:—

1. Plain sedimentation tanks.
2. Chemical precipitation tanks.
3. Specially designed tanks such as the Hampton (Hydrolytic) or Emscher tank.
4. Specially constructed contact beds, such as the Dibdin slate filter.

The main object of this preliminary treatment is to remove, as far as possible, the actual suspended matters in order to facilitate the subsequent filtration of the sewage.

In septic tank treatment, anaerobic fermentation of the sewage is encouraged, with the view of reducing the volume of sludge to be dealt with, while the double-decked tanks of Travis (Hampton) and Imhoff (Emscher) are designed to confine such anaerobic action to the deposited sludge and so avoid a septic effluent.

Except in special cases where the sewage itself contains trade waste which may coagulate colloidal matter, simple sedimentation of the sewage, while doubtless effecting removal of a considerable proportion of the organic colloidal matter in the 'gel' form, is practically without effect on that in the 'hydrosol' condition.

A certain proportion of the 'hydrosols' will be carried down by chemical treatment, but unless a fairly heavy dose of salts of iron or alumina with or without lime is employed, when the process becomes expensive and in many cases impracticable, the tank effluent still contains appreciable quantities of organic colloidal matter.

Kröhnke and Biltz, Rolants and others have shown that in the main the sewage colloids possess a negative charge which very probably is not without effect in regard to the value of the salts of trivalent metals of opposite charge, such as those of iron and alumina, in coagulating the colloidal matter present in sewage. Purely chemical reactions and the effect of the extended surface afforded by the precipitate formed, cannot, however, be neglected in considering the process of chemical precipitation.

While considering this question, mention should be made of the suggestion of Rohlands to use plastic clay as a means of separation of colloid matter. Polz, however, reports that as the result of large scale trials with dyeworks effluent, the process is both unsatisfactory and impracticable.

Reference should also be made to Degener, who, arguing by analogy from the absorptive action of the 'humus' in soil, worked out a method of purifying sewage by precipitation with powdered lignite and iron salts, which it is claimed is capable of removing not only the suspended solids, but also the colloid and other putrescible matters in the sewage to the extent of producing a non-putrescible effluent. Dunbar, however, reports that it is only applicable in certain special cases, and that its cost is too great for general adoption.

Effluents from ordinary septic tanks usually contain appreciably more finely divided suspended matter than the effluent resulting from either chemical treatment or simple sedimentation, as the result of the constant rising and falling of particles of sludge due to the gas evolved consequent on the anaerobic decomposition of the deposited sludge.

It has been found generally that as a result of septic treatment there is a small though appreciable reduction in the amount of oxidisable matter in true solution.

With regard to the action on the matter in pseudo solution, this seems to vary with the character of the sewage treated with particular reference to its original colloid content.

O'Shaughnessy, working with a mixed trade sewage of low colloidal content, concluded there was a slight increase in the oxidisable matter in pseudo solution as the result of treatment in septic tanks, and Fowler and others have stated that where septic action was vigorous as the result of higher temperature there is evidence of some slight increase.

On the other hand Rolants, employing a precipitation method for removal of colloids, found that while the percentage of the total oxidisable matter present in pseudo solution was slightly higher in septic tank effluent than in the sewage treated, the actual amount of colloidal matter (as measured by the permanganate test) was, if anything, rather less. On determining the organic nitrogen and organic carbon contained in the colloids present, which was considered to give a better appreciation of the colloid matter than does the oxygen absorption test, he found in every case a diminution of colloid matter in the septic tank effluent as compared with the original sewage.

On the whole, it may be considered that septic action as exhibited during septic tank treatment has no material effect on the amount of matter in pseudo solution, the differences found being very little more, if any, than the errors in the method of estimation.

The chief object of preliminary treatment in slate beds is to keep the solids deposited therein under aerobic conditions as far as possible, and Dibdin has shown that if operated in a proper manner a considerable destruction of the deposited sludge is brought about by the agency of bacteria, moulds, and higher organisms such as protozoa, worms, &c.

While it is possible that contact with the slates will tend to flocculate, by surface action, some of the matter in pseudo solution, the filters are too open to be very effective in this respect, and it is understood that the effluents obtained are still turbid and contain appreciable quantities of colloidal matters.

It can be stated that with properly designed plant, having regard to the maximum permissible velocity of flow, a more or less complete removal of the grosser suspended solids can be obtained, and that, dependent on the character of the sewage, a considerable proportion of the more finely divided solids, including, doubtless, colloids in the ‘ gel ’ condition, may be effected.

It is, however, evident that none of these preliminary processes, except heavy chemical treatment, affect appreciably the organic matter in pseudo solution.

The resultant effluent, therefore, contains practically the original sewage solids in solution together with a varying proportion of the finely divided suspended solids, and its subsequent purification involves the application of extended surfaces.

This is usually effected by distribution on land or on artificial filters composed of various inert media of different grades, in which the liquid is held in contact with the filtering media (placed in water-tight tanks), or is allowed to percolate through, either intermittently or continuously.

Briefly, it may be said by the adoption of any of these methods no difficulty need be experienced in obtaining a satisfactory effluent, provided due attention is paid to the design of the purification works and to its capacity in relation to the volume and character of sewage treated.

With the object of dealing with the mechanism of the complex changes, physical, chemical and biological, which take place during the oxidation or purification process, it is proposed to consider briefly the three main theories which have been advanced in explanation of the purification phenomena, more particularly with reference to the fate of the colloid matter.

The earliest theory advanced with respect to the mechanism of the purification changes effected by the filtration of 'sewage' was based on the work carried out at the Lawrence Experimental Station, Mass., in respect of the development of the intermittent sand filters as advocated by Frankland, as a practical means of sewage purification.

According to this theory, the suspended solids applied with the sewage or tank effluent are arrested mechanically in the filter by virtue of its fine pores, and subsequently oxidised, and the organic matter in solution is directly oxidised and mineralised by bacterial agency during the course of its passage through the filter with the accumulation within the filter of small quantities of 'humus,' which is very resistant to further fermentation. Presumably colloids are included in the organic matters in solution, although they are not referred to specifically.

This simple representation of the purification process received almost universal support, notably by Stoddart as recently as 1909.

Dunbar assumed that it was not possible to bring about the complete oxidation of the complex organic matter present in solution in sewage during the short period of time taken by the liquid in passing through the filter, and as the result of a series of experiments extending over a considerable period (1897–1900) carried out by him and his colleagues at the Hamburg Hygienic Institute (*vide* 'Principles of Sewage Treatment') he advanced what is known as the "absorption theory" of sewage purification.

This theory explains the mechanism of the purification changes as follows:—

1. The actual suspended matters are removed by attraction of the filtering media, &c.
2. The dissolved matters (true and pseudo solution) are retained by absorption phenomena, which is accelerated and increased as the slimy matter, or what is termed the bacterial film, accumulates on the media as the filter becomes mature.
3. That the matters thus retained are oxidised by chemical action (condensed oxygen, &c.), and by the agency of bacteria and higher forms of life. The resultant soluble products—mineral salts, amino-acids, &c.—are subsequently washed out of the filter by succeeding quantities of sewage treated.
4. That this absorption process is prevented from ceasing by the action of micro-organisms, &c., in the presence of atmospheric oxygen.
5. There is a residue of organic matter, &c., which is very resistant to further oxidation changes, which either accumulates in the filter or is discharged with the effluent.

It will be noted that this theory draws no distinction between matters in true and pseudo solution so far as the mechanism of the purification changes is concerned.

Experience with the operation of the Hampton sewage works, where relatively large quantities of sludge accumulated in the filtration area, led Travis to study the question of sewage colloids in relation to sludge production. As the result of a series of experiments carried out in conjunction with Johnston, he advanced in 1905 what is known as the Hampton Doctrine.

According to this theory the purification process is primarily and essentially a de-solution effect brought about purely by physical causes and that any bacterial or biological action is definitely ancillary.

Unlike Dunbar's theory, a distinction is drawn with regard to the mechanism of the purification process as between organic matter in colloidal solution and matter in true solution.

It is held that whereas 'organic matters and products in actual solution, *e.g.*, ammonia, sulphuretted hydrogen and volatile products, are absorbed by the accumulated deposits in the filter,' the solids in colloid solution are coagulated or precipitated 'in virtue of a physical action'—effect of extended surface contact, &c.

These coagulated colloids are either retained in the filter or discharged with the effluent from the filter, and any biolytic action on them is a very slow and prolonged process, and consequently in addition to the actual suspended solids in the sewage or tank-effluent treated, the amount of such coagulated colloids which have been termed 'ultra sludge,' must receive attention in considering the amount of the total sludge to be dealt with.

In discussing these theories, it is proposed to confine attention as far as possible to the purification effect on matters in colloidal solution.

Briefly, it may be said that—

(i) In the earlier theory, especially as propounded by Stoddart, that such matters are held to be oxidised directly by bacterial agency during the passage of the liquid through the filter.

(ii) That Dunbar's theory provides for their preliminary absorption by the filtering media and the gelatinous coating thereon, with subsequent more or less rapid oxidation by agency of condensed oxygen, bacteria and higher forms of life.

(iii) That according to the Hampton Doctrine, such absorptive processes are confined to the matters in true solution, and that the matter in pseudo solution is coagulated by virtue of a physical action. That the subsequent biolytic oxidation of the matter thus deposited is a very prolonged process.

In connection with the question of absorption, it may be mentioned that Clark, and later Clifford, have demonstrated that the mean time of passage of sewage through a filter as operated in practice, while it varies considerably, dependent on several factors, is, on the whole, much longer than the few minutes spoken of by Dunbar, and may in some cases amount to more than one hour, which would allow time for appreciable bacterial action.

Also that Harriette Chick, Fowler and Gaunt, and Stoddart have shown that absorption of ammonium salts does not take place under sterile conditions except with material such as clinker, &c., which allows of chemical interaction between the liquid and the media. Stoddart has extended this observation to solutions of albumen and was unable to confirm Dunbar's experiment which shewed 50 per cent. loss of albumen. He suggests either preliminary decomposition (prior to use) with formation of ammonia which would be partially fixed by the clinker, or direct chemical interaction as a possible explanation. It is obvious that experiments designed to shew purely absorptive phenomena should be carried out with material entirely inert, such as pure quartz as used by Fowler and Gaunt.

Stoddart's conclusion that there is no evidence of the preliminary absorption of the soluble constituents of sewage was based on the results of his experiments on the nitrification of solutions of (*a*) ammonium salts (*b*) urea (*c*) albumen and (*d*) of sewage deprived of its suspended matter by filtration through paper, in which the flow through his experimental filter (seeded with a vigorous growth of nitrifying organisms) was interrupted from time to time, and the liquid treated replaced by salt solution of known strength applied at exactly the same rate.

The coincidence of a series of curves plotted with respect to the time taken to attain maximum nitrification and maximum chloride content was claimed to establish that preliminary absorption did not take place.

Stoddart also objects to the absorption theory, developed as it was as the result of studies with contact beds, being applied to the modern percolating filters where the conditions differ very considerably. On the other hand, Dunbar considers that such altered conditions are more favourable to absorptive phenomena.

For a full discussion of the difference between the theory of preliminary absorption of colloidal matter and of its direct coagulation and deposition in the filter, the reader is referred to a paper presented by Travis to the meeting of the Association of Managers of Sewage Disposal Works at Leicester, (July 4th, 1908), which appeared in the July 10th, 1908, issue of the *Surveyor*, and to the discussion thereon which ensued between the author and Lübbert, of the Hamburg Hygienic Institute.

So far as the mechanism of the preliminary removal of the matter in colloidal solutions is concerned, both Dunbar and Travis agree that it is essentially the result of physical action; mention should therefore be made of the work of Fowler and Mumford. They found that under strictly aerobic conditions, a bacterium isolated from a body of water receiving colliery discharges, acting through its enzyme in the presence of small quantities of iron salts, was capable of coagulating sewage colloids in the course of a few hours. Such removal of colloid matter from pseudo-solution is effected without the aid of surface content other than is provided by the air bubbles and the matter precipitated.

The evidence available with respect to the mechanism of the removal from sewage of organic matter in pseudo-solution may be summarised thus :—

(i) The experiments of Stoddart designed to show its direct oxidation by bacterial agency cannot be considered conclusive. On the other hand it has not been demonstrated that under the favourable conditions present in an efficient filter, in which the sewage passes in thin films over a network of media covered with an active bacterial slime, the mean time of passage is insufficient to allow of direct biolytical oxidation of some portions of the organic matter in pseudo-solution.

(ii) While it is accepted that sewage colloids may be precipitated or coagulated by intimate surface contact, this 'de-solution' theory can scarcely represent the whole phenomena of colloid removal otherwise such action would continue in the absence of micro-organisms.

(iii) The conditions met with in a mature and efficient filter are such as to render it most probable that absorption phenomena play an important part in the removal of matters from pseudo-solution.

In considering the final fate of the matters removed from pseudo-solution during the purification process it may be said that, independent of what may occur with experimental filters inoculated with vigorous growths of micro-organisms, and operated under ideal conditions, Stoddart's view that none of the solid matter retained in sewage filters is derived from organic matters originally in pseudo-solution is not consistent with what obtains in actual practice.

On the other hand the contention of Travis that the retained colloids undergo very little change as the result of biolytic action was formulated on entirely inconclusive evidence.

In this connection mention may be made of Dunbar's experiment in which a solution of albumen containing nitrogen equivalent to the organic nitrogen content of an average sewage was applied to a mature filter, with the result that almost quantitative oxidation of the sulphur was obtained, while 58 per cent. of the total nitrogen appeared in the filtrate, 10 per cent. as ammonia, 20 per cent. as nitrate and 25 per cent. as organic nitrogen. Thus 42 per cent. of the nitrogen disappeared either in the gaseous form or accumulated in the 'humus.' A considerable part of the carbon of the albumen also disappeared as gaseous carbonic acid, but a part also went to form the 'humus' which accumulated in the filters.

The Massachusetts intermittent sand filters have demonstrated that the amount of retained nitrogenous matter after 18 years' continuous operation with 'regulation station' sewage containing its original suspended solids only amounts to from 4 to 5 per cent. of the total nitrogen in the sewage applied. Travis estimates this to be equal to about 20 per cent. of the original organic nitrogen.

Recently, Clark in reporting on these filters after they had been at work for 28 years, states that for some years only as much sewage has been applied as can be purified without increasing the amount of organic matter stored in the filters.

Comparison of the conditions obtaining in these filters with those of the modern 'artificial' filters in which sewage is treated at very much higher rates, leads to the conclusion that the results obtained may certainly be considered a maximum effect with respect to the resolution of the organic matter deposited in the filter, at any rate so far as any practicable scheme of sewage filtration is concerned.

The fact that the sewage treated contained its original solids in suspension unfortunately precludes any definite conclusion with regard to the actual resolution of the solids derived from matters in pseudo solution.

In the Second Annual Report of the State Department of Health of Massachusetts (1916), Clark reports the results obtained with the operation of a series of sand filters receiving respectively, (*a*) untreated sewage, (*b*) settled sewage, (*c*) sewage after treatment in straining filter, and (*d*) sewage clarified by precipitation with sulphate of alumina The volume of sewage applied to each filter was varied so that each received as nearly as possible equal amounts of organic matter (measured by the organic nitrogen). It is interesting to observe that working in this manner there was no material difference in the amount of nitrogenous matter stored in the respective filters, measured by determining the amount of albuminoid ammonia in the sand.

It would thus appear that the nitrogenous organic constituents of sewage whether in actual suspension or in colloidal solution are more or less equally amenable to biolytic action, and consequently the percentage resolution of total organic matter observed in connection with the sand filters treating crude sewage should apply fairly well to the matters coagulated from pseudo solution.

In conclusion it is evident that the total unresolved organic matter either retained in the filter or discharged with the effluent, will depend on the character (suspended solids and colloid contents) of the sewage treated and the rate of application with respect to the capacity of the filter, which will vary according to the type employed.

A survey of the subject would not be complete without reference to the large scale operations developed by O'Shaughnessy with reference to the subsequent treatment of the sludge removed from the Birmingham sewage by treatment in sedimentation on septic tanks.

This sludge is submitted to prolonged anaerobic fermentation, whereby appreciable auto-digestion of the sludge occurs with loss of colloidal character. By this treatment a dense and granular material is produced without nuisance. (*Vide* Reference, 1914, J.S.C.I., No. 1, vol. xxxiii.)

The following reference to the "Activated Sludge" process of sewage purification is made on account of the rapid removal of oxidisable matter in pseudo-solution, which is effected without the aid of actual surfaces, other than is provided by the particles of sludge.

An "active" sludge is built up as the result of the oxidation by aeration of successive quantities of screened and detritus free sewage.

This sludge is flocculent in character, has a very high bacterial content and contains numerous higher forms of life especially ciliated protozoa.

When sewage is aerated in intimate contact with from 20 to 25 per cent. (by volume) of activated sludge there is a rapid initial removal of oxidisable matter from pseudo-solution, with the production of a well clarified effluent, which is nitrified on further aeration.

Judging by the volume of sludge produced it is presumed that the colloidal matters are removed from solution either by the absorptive action of the flocculent sludge or coagulated by intimate contact with the sludge particles, or as the result of enzymic action.

While Bartow has shown that large quantities of carbonic acid are produced during the purification process, which is indicative of vigorous biolytic action, the high proportion of organic matter in the resultant sludge appears to preclude any material destruction or resolution of the organic matter present in the original sewage either in actual suspension or in colloidal solution although it is evident from its appearance there has been a considerable alteration in its physical character.

The high nitrogen content of activated sludge, which varies from 4 to 7 per cent. (dry matter) dependent on the character of the sewage treated, leads to the same conclusion, as Clark has shown that the sewage colloids contain much more nitrogen than do the grosser suspended solids.

There is however an undetermined factor, viz. :—to what extent, if any, is there any fixation of atmospheric nitrogen ?

Ardern and Lockett have studied this question but further information is required before any definite pronouncement can be made.

As previously stated, the sludge is quite flocculent and readily separates out from the purified sewage.

Presumably on account of its gelatinous condition, the water content of the sludge is very high and cannot be reduced below 95 per cent. by simple sedimentation.

When this percentage has been reduced to from 88 to 90 per cent., either by centrifuge, or by treatment on drainage filters, the sludge is of the consistency of a fairly stiff jelly, whereas ordinary sludge obtained from the sedimentation of sewage, containing a similar amount of water, is quite fluid and can be readily carried and discharged through pipes.

The solution of the problem of the best means of preliminary de-watering of this sludge, prior to drying, involves a study of the conditions favourable to the removal of water retained by colloids in the "gel" state.

Chalkley Hatton has shown that such de-watering can be effected by treatment in a modified type of filter press, with the production of a cake containing 75 to 80 per cent. moisture.

There is, however, room for research, with special reference to electrical effects, in regard to the most economical method of de-waterising and drying the sludge.

The problem is one of considerable importance to agriculture, involving as it does the utilisation of the full value of the sludge as a fertiliser.

A complete bibliography of the activated sludge process will be found in Porter's publication, given in the list of references submitted.

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'36th Annual Report of State Board of Health,' Mass.

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'A Study of the Process of Nitrification with Reference to the Purification of Sewage.'

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'The Behaviour of Colloids in Sewage.'

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TRAVIS, OWEN, 'The Surveyor,' vol. xxxiv., 63–66.
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and vol. xxxv., 7–10.

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(1909), vol. xxxvi., 109–111.

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'Physical and Biolytic factors in Purification of Sewage.'

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Stoddart, F. W., reference as previous p. 183–210.
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Colloids determined by absorption of aniline blue.

Polz, 'Farben-Zeit,' 1913, 24, 395–6. Abst. 'J.S.C.I.', vol. xxxii., p. 940.
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Fowler & **Clifford**, 'J.S.C.I.', vol. xxxiii., p. 815.
'Notes on the composition of Sundry Residual Products from Sewage.'
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Marc and **Sac**, 'Koll. Chem. Beihefte,' 1914, 5, 375–410. Abst. 'J.S.C.I.,' vol. xxxiii., p. 564.
'Determination of Colloids in Effluents.'
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COLLOID PROBLEMS IN DAIRY CHEMISTRY.

(*Milk, Butter, Cheese, Margarine, and Ice-cream.*)

By WILLIAM CLAYTON, M.SC., *Chief Chemist, Calders Margarine Co., Liverpool.*

In this paper it is proposed to treat of Dairy Chemistry under special headings, drawing particular attention to the colloid phenomena and problems involved. Milk (the basis of all the other products), butter, cheese, margarine, and ice-cream, each receive special consideration :—

MILK.

Milk contains substances which are inherently colloidal in nature, *e.g.*, casein and albumen, and also materials which behave as colloidal systems by virtue of their fine state of subdivision, *e.g.*, the fat present as emulsion, the cell-content of milk, and the enzymes of milk.

The casein of milk, a protein combined with phosphates of the alkaline earths, is present to the extent of about 3 per cent., whilst the second protein body, albumin, is present to about 0·5 per cent. Casein is so important from the standpoint of the colloid chemistry of milk, that a separate section of the paper has been devoted to it. The albumin, known as lact-albumin, is separated from casein, by precipitating the latter with acetic acid. Pure lact-albumin is an amorphous, tasteless powder. In aqueous solution it is coagulated by heating to 70° C., but only about 85 per cent. to 90 per cent. is thus precipitated. [*See* Rupps. U.S. *Dept. Agri. Bureau of Animal, Ind. Bull.* 166. Pp. 1–15. (April, 1913).] Lact-albumin is soluble in saturated aqueous $Mg\ SO_4$, but is precipitated if acetic acid be added. A crystalline form of this albumin is obtained if the saturated $Mg\ SO_4$ solution has an equal volume of water added, a little acetic acid being present, and then allowed to stand.

Amongst other reactions given by the albumin proteins, lact-albumin is thrown out of solution by saturation with ammonium sulphate, or by addition of tannin, or phosphotungstic acid. It is insoluble in alcohol.

Some evidence has been obtained for the existence in milk of a third protein, lacto-globulin, present to the extent of about 0·15 per cent. It is soluble in acidified NaCl solutions, is coagulated at 72°C., is not coagulated by rennet, and is precipitated by sodium sulphate, and tannin.

See { Hammarsten, *Z. f. physiol. Chemie*, **8**, 467 (1183–4).
Sebelien, *Z. f. physiol. Chemie*, **9**, 445 (1885).
Schlossmann, *Z. f. physiol. Chemie*, **22**, 197 (1896).

The colloid chemistry of milk chiefly centres round the phenomenon of "protection," in this case, the protective action exerted by lact-albumin on casein. The subject has been well investigated, and is fairly involved ; for its complete understanding, the compositions of various milks must be studied. The following table of the average composition of various milks is Leach's compilation from Koenig's, "Chemie der mensch-Nahrung und Genussmittel."

Constant.	*Cow.*	*Human.*	*Goat.*	*Ewe.*	*Mare.*	*Ass.*
S.G.	1·0316	1·03	1·0305	1·0298	1·0347	1·036
Water per cent.	87·27	87·41	85·71	80·82	90·78	89·64
Casein.	3·02	1·03	3·20	4·97	1·24	0·67
Albumen.	0·53	1·26	1·09	1·55	0·75	1·55
Fat.	3·64	3·78	4·78	6·86	1·21	1·64
Milk Sugar.	4·88	6·21	4·46	4·91	5·67	5·99
Ash.	0·71	0·31	0·76	0·89	0·35	0·51

It has long been known that infants can digest human and asses' milk more easily than cows' milk cf. Jacobi, *Journ. Am. Med. Assocn.* 51, 1216–1219 (1908). "Asses' milk has always been recognised as a refuge in digestive disorders, when neither mothers' or cows' milk, or its mixtures, were tolerated."

From the above table we see that in cows' milk the ratio of albumen to casein is only 0·53 to 3·02, whereas in human milk it is 1·26 to 1·03, and in asses' milk 1·55 to 0·67 (or over double the amount). "In cows' milk the casein forms 5/6ths of the total proteids in the milk, whereas in women's milk the casein forms 2/6ths of the total proteids." (Koplik, "*Diseases of Infancy & Childhood,*" 1902.)

Human milk is hardly curdled at all by acid or rennin, the reverse being true with cows' milk. We see then, that the ratio of protective colloid (albumen) to the irreversible coagulative colloid (casein) is a most important factor.

"Cows' milk precipitates or coagulates very early with the aid of acids or salts; women's milk quite late or not at all. Hence in the infant stomach, cows' milk does not take up much acid of the gastric juice and soon coagulates in large masses. Women's milk, on the other hand, takes up a large amount of acid of the gastric juice, and coagulates late in small masses. The differences in the modes of coagulation in the two caseins are of great importance in the study of infant feeding." (Koplik, *loc. cit.*)

Cows' milk can be made to resemble human or asses' milk in protective qualities by the addition of such colloidal subtances as gelatine, gum-arabic, cereal gruel, or barley water (a starchy solution). Very interesting observations with the ultra-microscope were made by Alexander and Bullowa on this subject:—*see Chem. News*, 101, 193 (1910). These authors followed the coagulation of milk by heat, rennin, and acids, with and without the addition of protective colloids, by the aid of the ultra-microscope. They concluded that "the casein of milk is an irreversible or coagulating or unstable colloid, which is protected by lact-albumen, a reversible or stable colloid," and further that "in the modification of cows' milk for infant feeding, it is necessary not only to consider the per cent. of total proteids, fat, etc., present but to see that the casein is adequately protected." (*Loc. cit.*, p. 195.)

The fat present in milk is carried down by the curd resultant upon milk-curdling. The greater the extent of coagulation, the larger is the amount of fat carried down with the curd, and since such fatty curds tend to coalesce and give rise to large masses little amenable to the action of the digestive juices, it follows that protection of the casein by some agent such as albumen or gelatine is most advantageous.

cf. {
Alexander, *J. Am. Chem. Soc.* **32**, 680–87 (1910).
Auzol, *These de Paris* (1907).
U.S. Pub. Health and Mar. Hosp. Serv., Washington, Hyg. Lab. Bull. **41**, p. 658.

A most interesting and comprehensive study of "The Coagulation of Cows' Milk in the Human Stomach" has been made by Brennemann (*Arch. Pediatrics* **34**, 81–117 (1917)).

He found that when fresh milk is drunk, the curds formed in the stomach are very large and hard, whilst milk boiled for 5 minutes gives rise to small soft curds. The curds become harder and bigger as the fat content of the milk is decreased. An increased fat content leads to smaller and softer curds, but their digestion is less rapid. A rapid ingestion of milk produces larger curds than does the sipping of milk.

Diluted milk leads to finer, flakier, and more porous curds. Lime water and milk do not easily coagulate, even if at all. Barley water and other starchy decoctions, when added to the milk, lead to smaller curds, more easily digested; they exert a "protective" influence over the casein.

Another phenomenon of great interest in colloid chemistry is exhibited when milk is boiled, or made into milk puddings etc., namely, the formation of a skin or membrane at the surface. This subject has been investigated by Ramsden:—

Archi. f. Anat. u. Physiol., pp. 517–534 (1894).
Proc. Roy. Soc. **72**, 156–164 (1903).
Zeit. phys. Chem. **47**, 336 (1904).

Ramsden asserts that for this membrane formation there must be present a free (gas) surface, and a general system as follows:—

$$\text{water} \rightleftharpoons \text{dissolved colloid} \rightleftharpoons \text{gas}.$$

Particles of the dissolved colloid passing spontaneously out of the solution give rise to a delicate surface pellicle or membrane. Ramsden found that all albumins in time can form such a skin at the still surface of their solutions. The colloid lowers the surface tension of the liquid and passes into the surface layer (adsorption), the process being an irreversible one. Even dilute solutions can yield a highly concentrated surface layer, following definite mathematical relations; *see* Milner (*Phil. Mag.* 1907 (vi) **13**, 96).

The Fat in Milk Cream.

Milk contains about 3·6 per cent. of fat, present as an emulsion of fair stability. On standing, the greater portion of the fat rises to the surface, as cream, and the milk then contains about 0·2 per cent. fat (water = 90·4 per cent.). Much argument has taken place as to whether the fat globules in milk are surrounded by a membrane, or by a gelatinous mucoid substance, semi-liquid, usually referred to under the Danish name "slim-membran". Storch claims to isolate this mucoid body by treating cream until all the lactose, casein, etc., has been washed away. Staining milk with ammoniacal picro-carmine, Storch examined the fat globules under the microscope and observed a stain layer enveloping each globule. Though he claims this fact as additional evidence for his "slim-membran" theory, the modern notion of adsorption can account for such staining without assuming a mucoid surface at all.

A milk from which the cream has been separated may be used as the medium for emulsifying such oils as coconut oil, and cotton-seed oil, to yield artificial milks, emulsions of great stability. Such a result decidedly tends to disprove the notion of a mucoid substance being necessary for the existence of the fat in milk as small globules.

Cream is formed by the rising of the fat globules through the denser milk serum to the surface. The density of the liquefied fat is about 0·92, whilst that of the milk serum is over unity. The diameters of the fat globules vary between 0·01 mm. and 0·0016 mm. Thick cream contains about 56 per cent. fat and 39 per cent. water, whilst thin cream contains about 29 per cent. fat and 64 per cent. water. The fat content varies between very wide limits, and the percentage of fat is in inverse ratio to the density of the cream.

The purchase of cream is based on its thickness, which is usually measured by its viscosity. Thickness is often induced by the aid of such substances as gum tragacanth, gelatine, starch, "viscogen" (lime and sucrose-syrup), or by the process of homogenising, *i.e.*, forcing the cream through minute orifices (at a suitable temperature below 60°C.) under pressure. (*See* section on homogenised milk.)

Since it is impossible to whip cream which has undergone homogenisation, gelatine, agar-agar, or gum tragacanth is added to the extent of about 0·1 per cent., so as to induce permanent frothing on beating up the cream. It is interesting to note that homogenised cream cannot be churned into butter.

Butter.

When milk or cream is churned, the globules of fat coalesce and granules are formed, which are then worked together to give a mass of apparently homogeneous texture. The average fat content of butter is 83·5 per cent. fat and the water content about 13 per cent. When examined under the microscope with crossed Nicol prisms, a uniformly dark field is viewed, whereas margarine under similar conditions presents a dark field containing bright portions and indistinct crystalline structures. The fat in milk, on churning into butter, has no crystalline structure, whilst margarine fats have, owing to their repeated melting and cooling.

As to the exact changes occurring when milk fat is churned into butter, there is still divergence of opinions. The upholders of the "slim-membran" theory, argue that the mucoid substance enveloping the fat globules is rubbed off, and the globules thereupon coalesce. Fleischmann inclines to regard the process of churning as being the solidification of superfused fat globules, but this theory is discredited by the fact that the fat globules in milk are rapidly solidified by mere cooling.

It is very likely, however, that there is an adsorption layer of some kind around the fat and that during churning this layer is continually thinned out by the impacts of the various globules, eventually permitting coalescence to small nuclei, which grow by degrees until that particular moment arrives when the butter particles suddenly become visible. There is still room for considerable physico-chemical research in connection with this long-known but little-elucidated phenomenon.

The butter nuclei are worked up to a homogeneous mass, which the microscope shows to be a solid emulsion of fat, with fat the continuous medium, and water the disperse phase, an exact reverse of the system occurring in milk. (Compare section on "Margarine.")

The physical conditions of churning, especially the temperature, exert a profound influence on the butter, particularly with regard to its moisture content. The main factors to be considered in this connection are the fat content, the acidity, and the viscosity of the cream, and the agitation employed. A cream containing 30 to 45 per cent. of fat churned at a temperature ranging from 13°C. to 18°C. should give good results. As cream ripens, lactic acid is produced, the viscosity of the cream diminishes and churning becomes easier. In this connection it is interesting to note that acids tend to make emulsions "break," *i.e.*, separate into oil and water, probably by some action on the protective (emulsifying) agent present. Here the casein is coagulated and precipitated if the acidity is too pronounced, and casein clots may be found in the butter mass. Churning must not be conducted too rapidly and violently, for then the moisture content will be too high owing to the enclosure of buttermilk within the nuclei. Also churning must be stopped as soon as the butter granules reach the size of small peas, otherwise the granules will coalesce and retain an excess of buttermilk which cannot be washed out again.

The physical chemistry of butter as a solid emulsion has been little studied, as indeed have any cases of solid emulsions, a matter which is referred to in more detail when discussing "Margarine."

Casein.

Casein is a phosphoprotein occurring to the extent of about 3 per cent. in cows' milk and about 1 per cent. in human milk. It is combined with the phosphates of the alkaline earths yielding a pseudo-solution or very fine colloidal suspension. Some writers adopt Halliburton's nomenclature and use the name "caseinogen," reserving the term "casein" for the curd produced by the action of rennet on milk. In this paper the term "casein" is used throughout (following Hammarsten).

Casein is precipitated from milk by saturating with NaCl, MgSO4, $(NH_4)_2SO_4$, and mineral acids; also by tannin, metaphosphoric acid, phosphotungstic acid, $CuSO_4$, $ZnSO_4$ and by rennet. It is soluble in alkalies and in solutions of salts which hydrolyse to alkaline solutions, *e.g.*, phosphates, and it is insoluble in alcohol and ether.

When pure, casein is a white amorphous, odourless, tasteless solid, soluble in water to about 0·1 per cent. Though precipitated by mineral acids, it redissolves in excess of acid. Opalescent solutions are obtained when casein is dissolved in just the necessary quantity of sodium phosphate and a little $CaCl_2$; some investigators believe this condition prevails in milk itself.

The elemental analysis of casein derived from Cows' and from Human milk respectively are :—

	Casein.		
	Cows'.	*Human.*	
C	52·69 per cent.	52·24 per cent.	cf. Lane — Claypon "*Milk and its Hygienic Relations*" (1916), p. 37.
H	6·81 ,,	7·32 ,,	
N	15·65 ,,	14·97 ,,	
S	0·832 ,,	1·12 ,,	
P	0·877 ,,	0·68 ,,	

Casein is amphoteric in reaction, though its acidic functions are more pronounced, when it behaves as a tri-basic acid. When dissolved in dilute alkali a *l*-rotatory solution ensues.

Exactly as to how casein exists in milk is still a debatable point. Some authors believe it exists as a salt of lactic acid, casein-lactate. That lactic acid and casein do unite was shown by W. Van Dam (*Chem. Weekblad.* 7, 1013 (1910)). This author, using Bredig's ethyl diazo-acetate method, determined the reduction of the H ions in solutions of lactic acid produced by adding various amounts of casein. The casein combined with a constant amount of lactic acid, viz., 4·25 per cent.

Revis and Payne infer a combination of casein with calcium phosphate. Richmond adduces evidence "that casein exists in milk as a calcium sodium salt, combined with one molecular proportion of tricalcium phosphate." (*Dairy Chemistry* (1914), p. 30).

Casein is not coagulated when milk is boiled, but alterations occur in the molecule affecting the action thereon of digestive ferments, and in all probability increases the digestibility.

At higher temperatures than boiling, casein suffers partial coagulation, e.g., at 130°–140° C., and Jensen and Plattner are of the opinion that the browning of milk so heated, is caused by the incipient breaking down of the casein." (*Rev. gen. du Lait* IV, 361–388 (1904–5).)

Cf. Also Conradi "Ueber den Einfluss erhöhter Temperaturen auf das Casein der Milch." *Münch. med. Wochensch.* 48, 175 (1901).

The estimation of casein in milk is made as follows :—10 grs. of milk are diluted to 100 cc. and warmed to 42° C. 1·5 cc. of a 10 per cent. solution of acetic acid are added, and the mixture well stirred. The precipitated casein is allowed to settle for about 10 minutes, filtered on to a tared filter paper, dried at 105° C. and weighed. Ignite, and subtract the ash, plus the ash of the filter paper, from the total weight.

Casein is typically colloidal in nature as may be inferred from its behaviour in solution. It acts as a protective colloid, and stable sols of silver or cadmium sulphides are readily prepared by passing H_2S through solutions of silver or cadmium salts containing casein. Its gold number (determined in solution in ammonia) is 0·01, which stands quite high in the list of protective colloids arranged in the order of their gold no., i.e., power of protection.

Casein combines with a fixed amount of NaOH (1 gr. requiring 0·88 millimol of NaOH) yielding a solution which has a normal electrical conductivity, but which does not pass through parchment when dialysed.

Chick and Martin showed that both acid and alkaline solutions of casein show an increase in viscosity as the amount of acid or alkali present is increased, indicating the greater adsorption of water by the casein-salt particles than by casein alone. (Cf. *Z. Chem. Ind. Koll.* **11**, 102–105 (1912).)

Casein adsorbs acids, the amount adsorbed being almost directly proportional to the acid concentration. (Cf. TANGL, *Chem. Zeit.* (1908) **1**, 1288.)

The part played by casein in the colloid reactions of milk is very pronounced, and is discussed under "The Coagulation of Milk."

The Coagulation of Milk.

The coagulation or "curdling" of milk can be brought about by addition of acids, or by means of rennet, an enzyme obtained from the stomach of the calf. The casein in the milk is not acted upon by rennet in alkaline solutions, but only in acid or neutral solutions, and the greater the degree of acidity of the milk, the more rapidly does the rennet act. Dilution of the milk with water inhibits the action.

The natural curdling of milk is due to the acidity produced by bacterial action, which sets free lactic acid. Various investigators have proved that it is the actual hydrogen ion concentration that matters, and not the nature of the acid. The time required for clotting is proportional to the hydrogen ion concentration. (Cf. Michaelis and Mendlessohn, *Biochem. Zeit.* **58**, 315 (1915).)

These investigators found that the optimum concentration of hydrogen ions required for the precipitation of casein by acids in pure solutions or in milk $= 2{\cdot}5 \times 10^{-5}$. The minimum concentration required was found by Allemann to be $1{\cdot}3 \times 10^{-5}$. (Cf. *Biochem. Zeit.* **45**, 346–358 (1912).)

Orla-Jensen showed that equivalent quantities of different acids are necessary to curdle equal quantities of the same milk at a given temperature, but the acids act at a different rate. (Cf. *Oversigt. K. Danike. Vidensk. Selsk. Forh.*, pp. 287–309 (1914).)

The whole question of the coagulation of milk by acids, and especially by rennet, is intimately connected with the question of the calcium content of milk, and any complete discussion must commence from this point.

In milk about 76 per cent. of the total calcium is combined with the casein; the total calcium content amounts to about 0·18 per cent. That calcium which is not united to the casein (about 24 per cent.) is present as phosphate and citrate. (Cf. Trunz, *Zeit. f. physiol. Chem.*, **40**, 263 (1903–4), Rona and Michaelis. *Biochem. Zeitsch.*, **21**, 114 (1909).)

When milk is heated, the calcium content falls. Thus Söldner showed that a milk containing 18 mgms. of Ca. per 100cc. when cold, lost 14 mgms. (*i.e.*, 17·5 per cent.) on boiling; in two other instances the loss amounted to 18 per cent. and 24 per cent. respectively. A similar decrease took place in the content of P_2O_5. Söldner inferred that the Ca. was united with phosphorus as mono- and di-calcium phosphate; this on boiling was converted into the insoluble tri-phosphate, and so precipitated. (Cf. Söldner, *Landw. Versuchs.* (1888), p. 351, Boekhout and de Vries, *Landw. Versuchs.* (1901), p. 221.)

Grosser, *Biochem. Zeit.*, **48**, 427 (1913) took a sample of milk and filtered it through a Bechold filter under a six atmospheres pressure of nitrogen, thus removing the colloidal constituents. The filtered milk was analysed raw, and also after being boiled for 15 minutes. The CaO content of the raw filtered milk was 23·4 per cent. of the initial (unfiltered) sample, and after 15 minutes boiling, only 18·0 per cent., or a loss due to heating of 5·4 per cent. of CaO. Repeating this experiment with butter-milk he found no change in the CaO content of the raw and the boiled filtrate, and inferred that the phosphorus and calcium had been spilt off from the casein owing to the acidity.

When milk is boiled the decrease in the calcium content is accompanied by a rise in the hydrogen ion concentration; see Milroy, *Biochem. Jour.*, **9**, 215 (1915). Approximately 8 per cent. of the total crude protein of fresh milk is not recovered by acid precipitation or heat coagulation. Cf. Palmer, *J. Ass. Off. Agric. Chemists*, **2**, part I., 144 (1916).

Rennet Coagulation.

When rennet is added to milk a separation into a precipitate (curd) and liquid (whey) takes place; the casein is transformed to a dyscaseose, "curd" being the insoluble calcium compound of this, and to a caseose (soluble). Rennet can clot 400,000 times its weight of casein in milk (Hammarsten), but it is a most remarkable thing that shaking the rennet renders it inactive. Cf. Schmidt-Nielsen, *Zeit. f. physiol. Chem.*, **60**, 426–62 (1909). An aqueous solution of rennet can be separated into fractions, having varying capacities for curdling milk by filtration through porous clay. See Korschun, *Zeit. f. physiol. Chem.*, **37**, 366–76 (1902).

Rennet acts best at 41° C., and the curd is then very firm; a fluffy, soft curd results at temperatures between 15° C. and 20° C. (at which temperature only 18 per cent. of the milk is curdled), and also at 50° C. (where 50 per cent. of the milk is curdled). The optimum range of temperature is from 36° to 45°.

Rennet is rendered inactive by prolonged storage, by shaking, by heating to temperatures over 60° C., and by addition of alkalies.

When milk is heated the action of the rennet is delayed, owing to the precipitation of calcium, but if $CaCl_2$ be added, the coagulation occurs in the normal way. Milk deficient in calcium salts requires a longer time for rennet-coagulation to take place. Cf. Söldner, *Landw. Versuchs.* (1888), p. 351; Ringer, *Journal of Physiology*, **11**, 464 (1890); Conradi, *Münch. med. Wochensch.*, **48**, 175 (1901); Kreidl and Lenk, *Biochem. Zeit.*, **36**, 357 (1911).

Interesting observations were made by Rupp, who observed that curdling by rennet was more rapid than with raw milk at temperatures between 55° C. and 65° C., but slowed down at about 70° C. to nearly double the time; in this case, however, a finer grained coagulum resulted. Cf. *Bureau of Animal Ind. Bull.*, p. 166 (1913).

Although boiled milk is not curdled by rennet, a coagulation occurs on the addition of small amounts of $CaCl_2$. Lindet (*Comptes Rendus*, **157**, 381 (1913)), suggests that this is due to the interaction of the $CaCl_2$ with the alkali phosphate and citrate in the milk, thus reducing the content of these, and rendering the casein less soluble.

During the action of rennet there is no change in the hydrogen ion concentration, but this is raised by addition of soluble calcium salts, and decreased by addition of ammonium oxalate. It is interesting in this connection to recall the fact that rennet acts best in acid solution, i.e.. in the presence of hydrogen ions. It was shown by Van Dam by the determination of electrical conductivity that the coagulation time varied inversely as the hydrogen ion concentration, see *Zeit. physiol. Chem.*, **58**, 295 (1908).

Mellanby has advanced an interesting theory for the rennet coagulation of milk, assuming it is due to the adsorption of the enzyme by the casein, and the subsequent precipitation of the enzyme-casein complex by the bivalent Ca ions of the milk. The quantity of ionised Ca salt required to effect precipitation is intimately related to the quantity of the enzyme adsorbed. Cf. *Jour. of Physiol.*, **45**, 345 (1912).

Bang observed that by adding rennet in fractions to milk, summation is noted, e.g., the coagulation time on adding 0·1 cc. of rennet to 10 cc. milk is 8 minutes, and on adding 0·2 cc. four minutes. If, however, 0·1 cc. is added, and 4 minutes later another 0·1 cc., then clotting occurs two minutes after the second addition. No such summation occurs if the milk, after the first addition of rennet, is heated to 65° C.

Bang's many experiments led him to conclude that rennet is not a coagulating enzyme, since rennet of itself does not produce curdling, and the final act of curdling is not true coagulation, but is more akin to the precipitation of protein by neutral salts. Cf. Ivar Bang, *Skand. Archiv. Physiol.* (1911), **25**, 105–144.

Another conception of the rennet coagulation of milk is advanced by Schryver, *Proc. Roy. Soc.* (1913), **B. 86**, pp. 460–481. When solutions of calcium salts and sodium cholate are mixed, a clot results on heating. For salts which increase the surface tension of water, the greater their amount present, the shorter will be the time required for clotting to take place. Salts which decrease the surface tension decrease the time for coagulation, only up to a certain limit of concentration, above which the time is increased, or the coagulation entirely prevented. The inhibition of coagulation is attributed to the adsorption of simple molecules by the more complex colloids which are thereby prevented from coalescing. In milk the necessary materials exist, but the adsorption of simple molecules from the solution stops the coalescing. Schryver assumes that the enzyme clears the surface of the colloid from the absorbed substances thus permitting coalescence to occur. He asserts that in milk the clot formation depends on the presence of four series of substances present, viz., simple inhibitory substances, colloids, enzymes, and calcium salts.

Alexander advanced a somewhat similar notion, his view being that the casein is "protected" or held in stable suspension by the hydrophile colloid, lact-albumin, which rennet destroys, thus permitting the coalescence and precipitation of the casein particles. Cf. *8th Int. Cong. App. Chem.*, **6**, 12–14 (1912).

A very remarkable observation has been made by Kredil and Lenk (*Biochem. Zeit.*, **36**, 357, (1911)). They assert that sterile milk contained in sterile vessels will not clot when treated with sterile rennet. If, however, one dips into the mixture a non-sterilised body such as the finger or a glass rod, clotting sets in. A few drops of ordinary milk will also cause clotting.

In conclusion attention is directed to a most interesting paper by Bordas and Touplain on "Reactions of Curdled Milk due to the Colloidal State" (*Comptes Rendus*, **150**, 341 (1910)), where the view is advanced that the reactions of curdled milk hitherto attributed to the presence of enzymes may be explained by the colloidal state of the casein.

The Cellular Content of Milk.

Milk contains a large number of cells, falling into three main classes:—

(1) large uninucleated cells;
(2) multinucleated cells;
(3) small uninucleated cells.

These cells are formed either from the epithelium of the gland, or from blood and lymph. They may be estimated by centrifuging a given quantity of milk, *e.g.*, 10 cc. (preferably warmed to about 70° C.) and examining the sediment by a microscope. Very varied results are given, thus Russell and Hoffmann obtained figures varying between 4,000 and 1,000,000 cells per 1 cc. milk.

Cf. Hewlett, *Jour. of Hyg.*, **13**, 87 (1913); Howlett and Revis, *Lancet*, p. 855 (1915); Ross, *Jour. of Inf. Diseases*, **10**, 7 (1912); Russell and Hoffmann, *Jour. of Inf. Diseases*, **8**, Suppt. (3), 63 (1910).

Detailed knowledge of the nature of the cellular content of milk is still meagre, and the subject is only referred to here, as indicating another factor in the very complex colloidal nature of milk, since modern colloid chemistry is no longer the study of undialysable or glue-like substances, but of matter in a finely divided form, thus embracing grains, bubbles, capillary structures, animal cells, etc., and indeed any system of at least two phases, involving extensive surface areas.

The cell content of milk is mainly of interest to histologists who are investigating its relation to disease in the cow. *See* "*Public Health Dept.*, Washington. *Report No.* 78 (1912)."

Homogenised Milk.

Homogenised milk is the term given to milk which has been heated to 50–60°C, and then forced under great pressure through very small orifices, thus reducing the fat particles to very small diameters, *e.g.*, 1/100th of the original size. When such a milk is allowed to stand, practically no cream separation occurs at all, the milk remaining a homogeneous system.

This change in the dispersity of the fat leads to phenomena well known in colloid chemistry. The extension of surface area of the fat leads to greatly increased adsorption of the milk serum, and the fat globules bear a "condensed layer" which is very tenaciously held. The rising of the fat globules is thus inhibited and no cream separates. Again, one cannot churn homogenised milk, since churning really implies the coalescing of the fat particles, and the separation of the milk serum.

The density of milk suffers no change on homogenising. The viscosity increases, due to casein adsorption by the fat globules, and the milk is thicker than ordinary milk of the same fat content. Wiegner reduced the average diameter of fat particles in milk by homogenising from $2 \cdot 9\mu$ to about $0 \cdot 27\mu$. From viscosity measurements he calculated that in ordinary milk about 2 per cent. of the casein is adsorbed, whilst the casein adsorbed by the fat in homogenised milk is about 25 per cent.

No change is produced in the molecular disperse constituents of the milk, as is indicated by the fact that the electrical conductivity, and the osmotic pressure (determined by F. Pt.) show no change.

If the homogenised milk is kept at a low temperature for some time the viscosity rises, and the fat particles do aggregate somewhat. Skim milk cannot be homogenised since it is nearly fat-free, and the casein present is already in a high degree of dispersity. Although mechanical means are of no avail, chemical means allow of this further dispersion of the casein, *e.g.*, when NaOH is added to skim milk, the viscosity increases rapidly with the concentration of the alkali.

Homogenised Cream.

When cream is forced through an homogenising machine at a pressure of from 3,000 to 4,000 lbs. per square inch, the fat particles become extremely small, and the product is very viscous. Separation of the fat again is rendered almost impossible, even on centrifuging; also it admits of neither churning nor whipping, and a colloid substance such as gum tragacanth must be added (*e.g.*, 0·1 per cent.) before a permanent foam can be produced. (Cf. *Koll. Zeit.*, **15**, 105–123 (1914).) Owing to its excessive thickness, homogenised cream is utilised in making ice-cream, since a cream containing about 17 per cent. of fat will, if homogenised, serve in an ice-cream as effectively as an ordinary cream of fat content 25 per cent., the final product having as good a body and texture, as well as "creaminess." An objection to homogenised cream is its peculiar "starchy" flavour, this being more apparent, the higher the temperature at which homogenisation is conducted.

The surface tension of homogenised milk is lower than that of the normal sample of milk.

Artificial Milk.

Of late years artificial milk has been prepared, and numerous patents taken out in this connection. It is simple enough to make a solution containing all the inorganic constituents of milk, but the organic (colloidal) constituents present a more difficult problem.

Certain nuts and beans contain proteid substances closely akin to gluten or casein in properties, *e.g.* soya beans contain about 37 per cent. of such proteid matter, which can be brought into colloidal solution by boiling with alkali, or salts which react alkaline, *e.g.*, sodium phosphate.

Thus, von Riegler [Fr. Pat. 461131 (1913)], prepared an artificial milk by dissolving gluten in caustic potash. It is usual, however, to emulsify a small quantity of oil (say 3 per cent.) with this colloidal solution of casein, and then to add small quantities of lactose, lactic acid, citric acid, etc., to render the similarity to milk more complete. Other ingredients which find their way into artificial milks are dextrin, malt extract, sucrose, dextrose, honey, NaCl, NaH CO_3, egg yolk, and preservatives.

Artificial milk can be "soured" by inoculation with lactic bacilli, and may be condensed, or made into artificial cream, butter, or cheese. Undoubtedly, a big future awaits this product, and it marks an especial advance in its use in margarine manufacture.

For further details cf. :—

Melhuish, Brit. Pat., 24572 (1913) ; Gossel, Fr. Pat., 451447 (1912), and Eng. Pat., 27860 (1912) ; Monahan & Pope, U.S. Pat., 1104376 (1914) ; Y.Y. Li, Eng. Pat. 30275 (1910) ; Kaufmann, Eng. Pat., 7296 (1913) ; Liebrich, Eng. Pat., 12355 (1898) ; Melhuish, Eng. Pat., 9626 (1915) ; Beckmann & Dyck, U.S. Pat., 1216052 (1917).

The Enzymes of Milk.

Enzymes are colloids, constituting a special class of catalysts, the catalysts being living organisms. Their presence in milk gives rise to some interesting facts explicable along the lines of our modern notions concerning colloid phenomena. The following enzymes are present in cows' milk :—

(*a*) Peroxidase.
(*b*) Reductase (indirect).
(*c*) Catalase.
(*d*) Amylase.

There is no conclusive evidence of the presence of proteolytic enzymes, lipolytic (fat-splitting) enzymes, or of lactase.

(a) *Peroxidase.*

This enzyme is always present in cows' milk, and its destruction by heat furnishes the basis of numerous tests devised to distinguish between pasteurised and unpasteurised milks. The first test used was to add tincture of guaiacum and H_2O_2 to milk, when, if peroxidase was present, a blue colour appeared. This test depended on the fact that guaiaconic acid (present in guaiacum) oxidises to a blue compound. It is noteworthy that H_2O_2 alone does not give this coloration with guaiaconic acid ; an activator must be present to give the activating impulse to H_2O_2 and then oxidation can take place. Such an activator is peroxidase the enzyme of oxidation. The active system, peroxide plus peroxidase, is termed an "oxidase."

The enzyme is destroyed by heat ; also it behaves catalytically, since extremely large amounts of peroxides can be acted upon, provided an oxidisable body be present.

The guaiacum test is replaced to a large extent by Storch's more reliable test involving the use of para-phenylene-diamine, and H_2O_2.

Cf. *Ber. des. Versuchst. d. K. Vet. u. Landb. Hochs.*, Kopenhagen ; *Milchztg.*, **27**, 374 (1898).

A grey-blue coloration is given. It is necessary for this test, however, to use only 1 drop of H_2O_2 inasmuch as boiled cows' milk gives a blue coloration with p-phenylene-diamine and H_2O_2, if the latter is present in sufficient quantity. This is owing to the fact that the casein interacts with an oxidation product of the amine giving a blue compound. Such a milk would not respond to the guaiacol test, unless a peroxidase were added. Cf. Nicolas, *Bull. Soc. Chim.* **9**, 266–269 (1911–14).

The importance of the "peroxidase reaction" in the colloid chemistry of milk lies in the fact that most investigators now believe peroxidase to be a peculiarly active form of colloidal iron or manganese hydroxide, held in solution by a protective (hydrophile) colloid.

This protective colloid or emulsoid stabilises the system, and very likely confers specific properties such as coagulation by heat, acids, alcohol, etc. See Perrin, *J. de Chim. phys.*, **3**, 103 (1905) ; also, Röhmann and Shnamine, *Biochem. Zeits.*, **42**, 235–249 (1912).

Wolff, in his "*Contributions à la connaissance de divers phénomènes ozydasiques naturels et artificiels*" (1910), describes the full reproduction of all the actions of peroxidase with colloidal ferrocyanide of iron. Similarly, Sjolleman made an artificial oxidase with a colloidal solution of manganese hydroxide.

Lactic acid and hydrogen peroxide only interact very slowly ; if now, a trace of ferrous sulphate be added, oxidation proceeds very rapidly indeed. A similar acceleration of oxidation can be brought about by addition of peroxidase. Thus the close similarity between the true inorganic colloid and the enzyme is shown clearly. In fact an artificial peroxidase of marked activity was described by Dony-Henault, *Bull. de la classe d. Sciences, Acad. roy. de Belgique*, pp. 105–163 (1908), viz., A solution of 10 grs. gum-arabic, 1 gr. manganese formate and 0·4 gram. sodium bicarbonate in 50 cc. water, is treated with alcohol. The ppt. is redissolved and reprecipitated by alcohol. The precipitate contains colloidal manganese hydroxide kept in stable solution by the "protecting" gum-arabic.

The "peroxidase reaction" is, no doubt, very closely connected with the iron content of milk, and it has been shown that there is quite sufficient iron in cows' milk to produce the reaction. The amount of iron in milk varies from 0·4 to 0·7 mg. per litre. Cf. Edelstein and von Csonka, *Biochem. Zt.*, **38**, 14–22 (1912).

Sarthou, *Jour. de Pharm.*, **2**, 583 (1910), and **3**, 49 (1911), showed that the peroxidase reaction can result when as small a quantity as ·0002% of iron is present.

The reaction is used in dairy laboratories to detect between raw and pasteurised milk, and although great differences of opinion are held as to the temperature at which the reaction is no longer given, it is generally agreed that milk pasteurised by heating to at least 70° C. for about 15 minutes, renders the peroxidase inactive. Cf. van Eck, *Zeit. f. Unters. Nahr. u. Genussm.*, **22**, 393 (1911).

Other papers of much interest in the elucidation of the peroxidase reaction :—

Fenton, *Trans. Chem. Soc.*, **65**, 899–910 (1894).
Euler and Bolin, *Z. f. physiol. Chem.*, **57**, 80–98 (1908).
Herzog and Meier, *Z. f. physiol. Chem.*, **73**, 258–262 (1911).
Bach and Chodat, *Berichte d. Chem. Ges.*, **37**, 1342–1348 (1904). *Arch. d. Sciences Phys. et Nat., Geneva*, **37**, 477.
Arnost, *Z. f. Unters. Nahr. u. Genussm.* (1905), **10**, 309.
Bertrand, *C. Rendus.* **124**, 1355 (1897).
Kastle and Porch, *J. of Biol. Chem.*, **4**, 301 (1912).
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Sarthou, *Journ. de Pharm.*, **3**, 49 (1911).
Seligmann, *Z. f. Hyg.*, **50**, 97 (1905).
Utz, *Z. f. angew. Chem.*, **16**, 871 (1903). *Oesterr. Chem. Ztg.* (1904), p. 916.
Waentig, *Arb. a. d. kaiserl. Gesundh.*, **26**, 464 (1907).
Weber, *Milchztg.* (1902), pp. 657, 673.
Wirthle, *Chem. Ztg.* (1903), p. 432.

(*b*) *Reductase.*

It has long been known that if methylene blue be added to milk, the blue colouration produced could often be destroyed by incubating the milk for a while, the time required varying with the samples of milk taken. The action is recognised as a bacterial one, and great efforts have been made to utilise it to measure the bacterial content of milk, but owing to the fact that only some, and not all, of the bacteria in milk are concerned in the reaction, the method was found very unreliable.

Schardinger (*Zeit. Unters. Nahrungs- und Genussmittel* 5, 1113–1121 (1902)) made some notable observations on the milk-reduction of methylene blue, establishing the following facts :—

(1) Fresh milk alone does not reduce methylene blue.
(2) Fresh milk to which an aldehyde (*e.g.* formaldehyde) has been added reduces methylene blue to the leuco or colourless base.
(3) This decolouration does not take place if the milk has been boiled.
(4) If bacterial development be permitted, there is no need to add aldehyde to milk to obtain the reduction of methylene blue.

The reaction in the absence of aldehyde is now termed the "direct reductase reaction," and in the presence of aldehyde, the "indirect reductase reaction."

Shardinger's M.B. reagent is obtained by diluting 5cc. of a saturated alcoholic solution of methylene blue with 195cc. of water. His F.M.B. reagent contains 5cc. saturated alc.; methylene blue + 5cc. of 40 per cent. formaldehyde + 190cc. water. In each case one uses 1cc. of the reagent to 20cc. of milk warmed to 45° to 50° C.

The specific enzyme causing the reaction is termed "aldehyde-reductase" or "formaldehydase."

It is interesting to note that analogous reactions in inorganic chemistry are obtained, using the colloidal solutions of metals of the platinum group. Thus aqueous solutions of hypophosphites are oxidised on the addition of finely-divided palladium :—

$$H_3PO_2+2H_2O \qquad H_3PO_3+H_2+H_2O.$$

Formaldehyde is unaffected by colloidal palladium, but in the presence of methylene blue, nitrates, indigo, or other easily reducible bodies, the aldehyde is oxidised, and the reducible bodies act as "receivers" for the hydrogen.

Bach, *Arch. Sci. phys., Génève*, **32**, 27–41 (1911), assumes the existence of a perhydride of oxygen in the water, H_4O, analogous to peroxides in the peroxidase reaction. Such a compound has never been isolated, and one feels that its assumption is not required, since the theory of the activation of the water by the enzyme amply meets the case.

An enormous mass of work has been done on the Schardinger reaction, but a recent paper by Lee and Mellon (*J. Ind. Eng. Chem.* **9**, 360 (1917)) ably summarises the present position. The conclusions reached are :—

(A) Methylene blue as it occurs in Schardinger's reagent F.M.B. is not decolourised by :—
  (i) Normal fresh milk in less than 20 minutes. When decolouration was effected in 10 mins. or less, the milk was found to contain 1,000,000 or more micro-organisms per 1cc.
  (ii) Milk pasteurised at 70° C. for 10 mins., unless approx. 48 hours have elapsed since the milk was pasteurised, or until the bacteria have had time to multiply sufficiently.
  (iii) Old milk in which formaldehyde had inhibited the growth of bacteria.

(B) Schardinger's reagent, F.M.B., is as a rule decolourised by normal milk allowed to "age" under ordinary conditions of temperature for 24 to 48 hours.

(C) Pasteurisation increases the time required for the decolourisation of the reagent.

(D) In general, no proportionality exists between the time required for the decolourisation of the reagent and the number of bacteria in milk. In a given sample, however, a general relation seems to exist between the two up to a given point of acidity.

(E) Inasmuch as there is no absolute parallelism between the *number* of bacteria in the milk and the *time* required to decolourise the reagent, but that the relationship seems to exist in a given sample of milk, it would indicate that reductase is of bacterial action, but that not all bacteria found in milk produce this enzyme.

(F) It seems probable that formaldehyde either gradually retards the action of the reductase or destroys it.

Several very interesting observations on the Schardinger reaction have been made by various investigators. Thus :—

Utz (*Zeit. f. angew. Chemie* (**16**), 871 (1903)) showed that sour milk could be made to give the reaction by adding to it NaOH or other alkalies.

Rullmann (*Biochem. Zeit.* (**32**), 446 (1911)) showed that instead of HCOH one could use formic acid for the F.M.B. test.

Römer and Sames (*Zeit. f. Unters. Nahr- u. Genussm.*, (20), 1 (1910)) showed that milk which failed to respond to the Schardinger test would do so if a small quantity (less than 1 per cent.) of ferrous sulphate were added. The ferrous sulphate solution must not be boiled.

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Smidt, .*Arch. f. Hyg.* **58**, 313 (1908).
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(*c*) *Catalase.*

This very remarkable enzyme is universally present in cow's milk. It acts on hydrogen peroxide to produce *molecular* oxygen, this result being very unique, since one usually obtains 'active' or atomic oxygen when H_2O_2 is decomposed. The generally-accepted explanation is that the enzyme attacks two molecules of H_2O_2 simultaneously, thus:—

$$2HOOH = 2H_2O + O_2$$

Catalase in milk is estimated by measuring the volume of oxygen liberated when a given quantity of H_2O_2 is added to a given quantity of milk. Usually one takes 20cc. of milk and 5cc. of a 3 per cent. H_2O_2 solution, using a special apparatus, which is kept in the water-bath during the course of the test.

The catalase is most probably of bacterial action, and its amount increases when the milk grows stale. Cream contains a larger percentage of catalase than the rest of the milk. So far no figure for the normal catalase content of milk is agreed upon, though such a standard is desirable as an indication of the bacterial content of a given sample.

Oxidising agents such as chlorates, nitrates, and hydrogen peroxide, and poisonous bodies like HCN or mercuric chloride are especially harmful to catalase ; indeed, Euler has shown that a strength of 1 in 1,000,000 of HCN reduces the reaction velocity of catalase by one half.

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For a detailed study of the enzymes of milk cf. Lane-Claypon, 'Reports to the Local Government Board on Public Health and Medical Subjects' (New Series), No. 76 (1913).

(*d*) *Amylase.*

This enzyme is only present in small amount, *e.g.* Lane-Claypon found that 10cc. of cow's milk at 37°C hydrolysed about ·001 to ·002 grm. of starch in three hours. The starch is converted to dextrins.

Koning found the amylase activity of milk to be destroyed on heating to 68° C. for 45 minutes.

MARGARINE.

Margarine technology presents many questions of great interest to the Colloid Chemist, and offers a wide field of research in pure physical chemistry.

Margarine is a substitute for Butter, certain animal and vegetable oils and fats replacing the familiar butter fat. Thus stearine, oleo, lard, cocoanut oil, palm kernel oil, cottonseed oil, and arachis, kapok, maize, and wheat oils are all in present use. The oils and fats are liquefied together in certain proportions, depending on the quality of the margarine required, and then churned with soured milk to form an emulsion. This emulsion is rapidly cooled, either by means of a spray of iced water under pressure, or by flowing on to well-cooled revolving drums. The product in each case is then worked up in drums or rollers to the required buttery texture and consistency.

For an account of modern Margarine Technology, cf. Clayton, J.S.C.I., 36, 1205–1209 (1917).

In the manufacture of margarine, the process of emulsification is of first importance. "The object of churning is to imitate the emulsion found in cream and milk, where the fat globules have diameters ranging from 0·01 m.m. to 0·0016 m.m. and remain as discrete particles. The general theory of emulsification indicates that with two immiscible or only partly miscible liquids, two types of emulsion are possible, each constituent being in turn the disperse and then the continuous phase. For concentrated solutions a third (emulsifying) agent is required. Where oil is to be the internal or disperse phase, the emulsifying agent should be capable of lowering the surface tension of the external or continuous medium, and should be viscous, as is glycerin, or an emulsoid, like gelatin. If oil be dispersed in water, a stable emulsion can be made, the stability depending on the minuteness of the oil drops, this in turn being a result of the efficiency of the emulsifying apparatus. If, however, water be dispersed in oil, a very unstable system is produced, separation into two layers taking place as soon as beating-up ceases. Now milk by virtue of its colloidal content is an excellent emulsifying agent, when oil is the disperse phase. Consequently if milk be in a churn in bulk, and oil is slowly fed in, with continuous agitation, an excellent emulsion of great oil concentration can be produced, and will set to a homogeneous mass afterwards. But if the oil be in the churns in bulk, and milk is fed in, a very unstable system results, which easily separates into layers on stopping the agitation for a while. This has been proved many times and the explanation seems clear :—To get a suitable emulsion of water in oil, one would require an emulsifying agent which should form an *oil*-soluble colloidal solution but in milk the colloids are *water*-soluble. Both theory and practice condemn any form of churning which would lead to emulsion with oil as the continuous medium. Such emulsions when cooled by iced water, or on drums, solidify with clot formation, and the resultant margarines are 'spotted' in texture." (Clayton, *Loc. cit.*).

In order to aid emulsification many colloidal substances have been proposed for use in making margarine, *e.g.*, starch, gelatin, glycerin, egg-yolk, lecithin compositions, etc. These agents are added to the milk, and certainly do have a most helpful effect when churning. So small a quantity as 0·1 per cent. of glycerine added to the milk or oils (since it mixes with oils) leads to much improved emulsification. The usually-accepted theory accounting for this phenomenon is that the emulsifying agent forms a membrane or film around the oil globules and so prevents their coalescence.

Egg-yolk, usually compounded in Sesame Oil, has been fairly widely used in margarine works as an aid to churning, and it is very interesting to note that egg-yolk, containing about 10 per cent. of lecithin, and 15 per cent. albumen, both colloids, is an exceptionally stable emulsion, not separating into phases even on long standing or centrifuging.

Practically all the physico-chemical questions relating to margarine involve discussion of emulsions, and unfortunately rather too little is understood concerning them, whilst the physical chemistry of a *solid emulsion*, such as margarine as a finished article presents, is only in its infancy.

The first question which arises is concerned with the determination of the nature of the external, and disperse phases of a given sample of margarine, *i.e.*, is it a solidified oil-water or water-in-oil emulsion ? That is a hard question to answer. With liquid emulsions the problem is easier, and three methods at least may be employed to differentiate :—

(1) By a *Kataphoresis test*, since the internal phase being negatively charged will wander to the anode.

(2) *Indicator Method.* This method depends on the fact that if one adds an oil-soluble dye to an emulsion, the dye will spread if the oil be the continuous medium. Thus Robertson used Sudan III, a red dye, in his work on emulsions of olive oil in water (*cf. Koll. Zeit.*, 7, 7-10 (1910).) With an emulsion of oil in water, the colour would not spread, but be confined to those globules of oil with which the colour grains were actually in contact.

(3) *Drop Method.* The principle involved is that one can dilute an emulsion by adding more of the continuous medium. (*See* Newman, *Journ. Phys. Chem.*, **18**, 34–55 (1914).)

Now these methods are not suitable for a solid emulsion such as margarine, though the staining with dyes, followed by an examination of a thin film under the microscope, sometimes gives valuable indications. The electrical conductance of margarine, the heat conductance, and the viscosity would seem to offer suitable lines of research in this problem of distinguishing the nature of the phases.

If the margarine were an oil-in-water emulsion, one would anticipate a possible electrical conductance (since there is at least 1 per cent. NaCl present), on the same lines as the conductivity through a set jelly, *e.g.*, gelatine. But with a water-in-oil emulsion, the conductivity (if any) would be very small indeed, inasmuch as the contiguous particles are now fat, which is characterized by its insulating properties.

Again, it would be most interesting to investigate the heat conductivity of two solid emulsions having inverted phases. The corresponding case of the heat conductivity of a set jelly still remains for research.

Possibly information would be afforded by the viscosity of a solid emulsion. The rôle ef viscosity in colloid researches is increasingly manifested, and "the great importance of viscosity measurements as the most delicate means of tracing slight changes in colloidal solutions is fully recognized" (E. Hatschek). Indeed, with an emulsion like margarine, with an average ratio of oil to water, 3·6 : 1, one would anticipate notable variations in viscosity depending on whether the oils and fats constituted the disperse or continuous medium.

There are many other problems of a colloid nature connected with margarine, but they are only apparent to one actually in contact with the entire process. Thus, why does soured milk yield a better emulsion with the oils and fats than sweet milk? Certainly, no very sound theory is as yet proposed, though it is interesting to note that oils and fats containing a small percentage of free fatty acids will much more easily emulsify with water than will neutral oils or fats. Since sour milk is distinctly acid (lactic acid), there would seem to be some connection here, but mineral acids cause emulsions to "break."

Finally, in connection with margarine manufacture, one research of great importance is suggested by the use of the various emulsifying agents previously referred to. So far, little work has been published describing what one may term the 'emulsifying efficiency' of such an agent. Thus, to make a concentrated stable emulsion of an oil in water, one adds gelatine, starch, gum, flour, etc. It would be very interesting to arrange these substances in the order of their capacity or power of stabilising a standard-strength emulsion, and then investigating the possible connection between the "emulsifying efficiency" and the gold number, viscosity, surface tension, etc., of their pure solutions in water (cf. Moore & Krombholz, *Brit. Journ. Physiol.* **22**, 54 (1908)).

CHEESE.

Cheese is obtained by the rennet curdling of milk. The curd is cut up small and the whey expressed from it; the mass is then salted and allowed to ripen by bacterial and enzymic action. There are many kinds of cheeses, but for the purpose of this paper their description is unnecessary. Very little indeed is known of the colloid chemistry of cheese, except that portion relating to the action of rennet on milk and the subsequent production of curd.

The following are some typical analyses of hard cheeses :—

	H_2O.	Fat.	Protein.	Ash.
	Per cent.	Per cent.	Per cent.	Per cent.
(*a*) Stilton....	20·30	44·00	23·70	2·75
(*b*) Cheshire	34·70	33·30	26·10	4·30
(*c*) Cheddar	33·90	29·05	27·37	4·05

The structure of cheese varies from a dough-like to a granular texture, and it is in this connection that the only colloid researches have been made on cheese.

Van Dam investigated the swelling of casein under the influence of common salt and lactic acid. He ascertained the solubility of casein in solutions of NaCl (5, 3, and 1 per cent.) containing lactic acid, and obtained curves showing the relation between the dissolved casein and the concentration of the hydrogen ions. Cf. van Dam, *Gedenkboek aan J. M. van Bemmeln* (1910), pp. 102–107.

Chick and Martin published results on the viscosity of casein sols, which bear somewhat on this problem. In the case of both alkaline and acid casein solutions, the viscosity increases with the quantity of alkali or acid present, which indicates that the casein-salt particles have a greater adsorptive power for water than has casein itself. Cf. *Z. Chem. Ind. Koll.* **11**, 102–105 (1912).

The most important contribution to the subject, however, has been made by Allemann and Schmid (*Landw. Jahrb. Schweiz.* **30**, 357-383 (1916)). They investigated 'the elasticity of the coagulum produced in milk by rennet.'

An apparatus was employed which measured the resistance which the curd offered to a vertical rod carrying three concentric rings. Thus they were able to investigate the effect of time, concentration of rennet, concentration of acid, and other factors, on the curd produced. It was found that the elasticity of the curd increased in direct proportion to (*a*) acidity of milk, (*b*) concentration of the rennet, (*c*) addition of soluble calcium salts, (*d*) rise in temperature. No apparent maximum of elasticity was ascertained with ascending temperatures, though the time required for coagulation reached a maximum at 41° C. Agitation during curdling inhibits the velocity about 8 per cent. With cold milk, a longer time was required for curdling, and the resulting curd had a decreased elasticity.

The whole question of the structure of cheese still remains open for research, as also does the question as to the physical state of the fat globules present. *See* Stocking, '*Manual of Milk Products*', chap. 9 (1917).

ICE-CREAM.

Ice-cream manufacture provides an interesting case of the practical value of the so-called 'protective action' of colloids.

Alexander (*J.S.C.I.* 28, 284 (1909)) writes :—'It is a well-known fact to practical ice-cream makers and amply proven by experience, that ice-cream made without eggs, gelatin, or some similar colloidal ingredient, is gritty, grainy, or sandy, or else soon becomes so on standing, whereas ice-cream made with small quantities of colloids possesses that rich, mellow, velvety texture, so much in demand.' (Cf. also Alexander (*Zt. Chem. Ind. Koll.*, Feb., 1909).)

Now ice-cream contains casein, and the action of the added (hydrophile) colloid is to 'protect' it from coagulating. Gelatin is especially advantageous, and as little as 0·5 per cent. suffices to render the ice-cream smooth in texture. Incidentally, the digestibility is increased too by addition of gelatin. (Cf. discussion on the digestion of milk curd in the stomach.) Besides the protection of the casein, it is most interesting to note that the small ice crystals are also 'protected' by the colloidal binders added. An ice-cream having been whipped during freezing, contains numerous small ice crystals which on standing coalesce to form coarse grains. This coalescence is decidedly inhibited by gelatin, gum tragacanth, and starches, thus retaining the smooth texture so desirable in a first grade product. (C.f. Stocking '*Manaul of Milk Products*,' Chap. 14, (1917).)

An interesting paper on 'The Effects of Binders upon the Melting and Hardness of the Ice-Cream,' was published by Holdaway and Reynolds (*Virginia Expt. Stat. Bull.* 211, 3 (1916)). It is here shown that as the per cent. of fat in plain ice-cream increases, the cream becomes softer, and if too much fat is present a soft fluffy product results owing to 'whipping.' Ice-cream made from 8 per cent. cream was no harder than from 19 per cent. cream, while 30 per cent. plain cream was much softer than either. The fat, however, raises the melting point.

Now if gelatin be added a harder ice-cream results, with a higher melting point. The hardest and most heat-resisting cream is given by a medium per cent. of fat and a large amount of gelatin. Gum tragacanth (also a protective agent) may be used, in which case the ice-cream produced is harder than usual (plain) but softer than when gelatin is used. One would expect this result, since the protective powers of the two colloids are very different, as will be seen by a comparison of their gold-numbers, viz.:—

Gelatin	0·005 to 0·01.
Gum tragacanth	about 2·0.

If too much gum tragacanth is used, a very slimy cream results; in any case it is far inferior to gelatin ice-cream of any composition.

Some manufacturers use starch as the agent to 'smooth' their ice-cream, but although a better product than normal (plain) cream results, the texture is much more grainy than the ice-creams containing gelatin or gum. One expects this to be the case, since starch is only a poor protecting colloid, the gold value of wheat starch being about 5, and of potato starch about 25.

Eggs are, of course, good binders, since egg-albumen (with a gold value of 0·15 to 0·25) is a strongly-protecting colloid.

In the literature concerning ice-cream one finds the term 'filler' applied to these added colloids, but the term 'binder' is probably to be preferred.

This problem once again opens up the question as to the ultimate action of a protecting colloid; the usually-accepted idea is that the colloid forms a membrane around the particles of the suspension material and so prevents the coalescence. This is Bechold's adsorption view. (Cf. *Zeit. phys. Chem.* 48, 385 (1904)).

[The question of 'protection' is considered in detail in W. D. Bancroft's report upon Peptization and Precipitation, Cf. p. 2. W. C. M'C.L.]

COLLOID CHEMISTRY IN PHYSIOLOGY.

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Introductory.

Since all physiological processes occur in complex heterogeneous systems, both coarsely heterogeneous and colloidal, it is clear that a complete discussion of the subject would include practically the whole of the science. Even in the functions of the central nervous system, which might seem most distant from colloidal chemistry, we have to take account of the properties of the membranes which intervene between the component elements, and certain observations made on these elements themselves will be referred to incidentally in the following pages. There are, however, some regions in which colloidal properties play a more obvious and better known part. These concern especially the nature and properties of protoplasm itself, including the membrane which surrounds it, and the relationship of their constituents to electrolytes. Another problem that will appropriately be considered is the nature and functions of enzymes, which regulate the chemical reactions of the living organism. And finally, the remarkable properties of haemoglobin in relation to the transport of gases require brief consideration.

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I. Protoplasm and Cell Contents.

When a simple unicellular organism, such as amoeba, which consists of so-called "naked" protoplasm, is examined under the microscope, it is seen to contain a variety of granules and other inclusions of comparatively large size. These lie in a clear, apparently structureless, substance which is in contact with the water in which the animal lives. For this latter reason, the protoplasm is said to be naked, in contradistinction to vegetable cells, such as algae, which are clothed with a cellulose coat.

Since the amoeba and the water are two distinct phases, which do not mix, there is a surface tension at the interface of contact. Owing to the curvature of the surface being concave towards the animal, this surface tension results in a pressure exerted on the contents. Now the tension can be lessened by the addition of various substances to the water and, when this takes place locally, a protrusion is brought about by the internal pressure due to the higher tension of other parts of the surface. Under the ordinary microscope, these protuded portions, "pseudopodia," appear to be clear and structureless like water. This fact can be seen in the drawings made by various observers. But when they are examined by the brilliant lateral illumination of ultra-microscopic methods, light is diffracted by minute particles which are present in great number. These become visible as bright shining dots against the dark background. The general effect, when the illumination is at its best, is that of a multitude of brilliant points in rapid, shimmering motion, occasionally more distinctly vibratory. This is the phenomenon first seen by the botanist Robert Brown in 1828 and hence called "Brownian movement." Its nature has been cleared up by Perrin, in a masterly series of researches, now well known. It was shown to be due to irregular bombardment by molecules of the liquid in which the particles are immersed and only present when the mass of a particle is small enough to enable the difference between the resultants of the unequal bombardment on opposite sides to be great enough to move it. The chief observations on Brownian movement in protoplasm are due to Gaidukov (1910) and to Price (1914).

The observation shows at once that protoplasm in its simplest form is a liquid, because otherwise particles present in it would not be free to move. The existence of these particles in the liquid shows that we have a colloidal solution of the kind called by Graham a hydrosol, which consists of a suspension of minute particles of a solid in water, or of an immiscible liquid in water. In other words, protoplasm is a dispersion of a more solid phase in a more liquid or watery phase.

It is necessary to emphasise this fact, because earlier observations, made on cells which had been coagulated by the action of heat or of precipitating reagents, were believed to show the presence of a continuous network. Although it is possible that a network might be produced under such conditions, it is to be remembered that, owing to the similarity in refractive index and in colour of the two phases, it is impossible to examine such preparations under conditions of illumination adequate to eliminate diffraction images, which readily take the form of networks when a regular series of dots is examined. The work of Hardy (1899) and of Alfred Fischer (1899) has shown, moreover, that a great variety of structures can be produced by the action of fixing reagents on cell protoplasm. It is impossible to say which of these corresponds to the living state. Most probably none do so, since we know that living protoplasm is a liquid.

There is further evidence that this is the correct statement. When the cell of an alga is taken in as food, water is either taken with it or is excreted around it. Whatever may be the shape of the particle itself, the shape of the liquid drop in which it floats is always spherical. In other words, it takes the form conditioned by the free play of its surface tension. This would not be possible unless it were free from the constraint exerted by solid structures. A similar conclusion may be drawn from the shape assumed by a mass of protoplasm when stimulated in any way; this is also spherical. Arthur Lister (1888), again, found that *Badhamia*, an organism which, at one stage of its existence, takes the form of masses of flowing protoplasm, filled with the brown spores of a fungus on which it feeds, can be filtered clear through wet cotton wool. It seems impossible that anything but a liquid could be separated up into the fine threads necessary to pass through the cotton wool and reunite again into its original form. Chambers (1917) has introduced some beautiful methods of micro-dissection. He finds that the needle can be repeatedly drawn through protoplasm without injuring it in any way. Very little resistance due to viscosity is experienced, as shown by the fact that it is only the granules in immediate contact with the needle that are displaced. There is no trace left behind in the track of the needle.

It is remarkable that the only constituent cells of the tissues of higher animal organisms that have been examined in the living state by ultra-microscopic methods are those of the central nervous system. This has been done by Mott (1912) and by Marinesco (1912), independently. They agree in the statement that the protoplasm of these cells shows numerous particles in Brownian movement and is therefore a liquid. There is no sign of the large masses ('Nissl granules') nor of the 'neuro-fibrils' seen in fixed and hardened preparations. According to Mott, the "granules" themselves consist of a hydrosol, surrounded by an envelope which stains deeply with methylene-blue. Marinesco was able to see local reversible changes taking place spontaneously. Areas of more brilliant, that is, larger, particles appeared now at one part, now at another of the cell.

While the state in which protoplasm usually is seen is that of a hydrosol, certain observations made by Kühne (1864), by Gaidukov (1910), and by Price (1914) indicate that it may take on, temporarily, the state of a gel. In this state the Brownian movements are arrested, because the particles become fixed in position. It is evidently related to functional activity. I have myself been able to produce it by weak electrical stimulation. What one sees is a sudden cessation of the shimmering movement, as if frozen solid. The condition is very transitory and requires careful adjustment of the illumination to show it. Price (1914) describes the protoplasm of a resting spore as being in the gel state, changing to the hydrosol on germination. When a cell dies it passes to the hydrogel condition. It is of some interest to note that the protruded pseudopodium of an amoeba remains in the hydrosol state, a fact which suggests that it is produced by external influence rather than by a "vital" reaction on the part of the animal.

What do we know of the mechanism by which such changes might be produced? There are two researches in particular which throw light on the question—that of Hardy (1900) on gelatin and that of Clowes (1916) on emulsions of oil and water. Hardy examined under the microscope the phenomena which occur when a warm gelatin sol sets to a gel on cooling; the first sign of change is that the ultra-microscopic droplets of the dispersed phase unite to form larger drops. If the solution is moderately concentrated, these drops unite together to form a network, but the watery phase is still continuous. On the other hand, if we begin with a solution of high concentration, the drops which first separate can be seen by their refraction to consist of the watery phase, so that the phase relations are reversed when compared with the former kind of gel. Thus the network may consist either of the more solid or of the more liquid phase. The properties vary accordingly. If the liquid phase is the continuous one, it can be pressed out by squeezing. If the more solid constituent is the continuous phase, liquid cannot be pressed out except by a pressure sufficient to filter it through the more solid phase.

The work of Clowes took its departure from an observation of Bancroft (1913) that a mixture of oil and water can be made into a permanent emulsion in two ways. One of these consists of drops of oil suspended in a continuous watery phase, as in cream; the other is of drops of water suspended in a continuous phase of oil, as in butter. The former system is produced when sodium soaps are used as emulsifying agents; the latter if calcium soaps are used. Clowes (1916) showed that an emulsion of the former kind could be converted into one of the latter by shaking with a solution of calcium chloride, while the latter could be changed into the former by shaking with sodium hydroxide. The changes may perhaps be realised by the illustration of a set of islands joining together so as to be transformed into a series of lakes surrounded by land. Clowes describes further experiments which will be more appropriately discussed in the section dealing with the cell membrane. He shows how the nature of the system depends on the relative surface tension at the two sides of the soap film which is formed by adsorption at the boundary surface between the two phases. It will be obvious that the physiological properties of the two kinds of system, the liquid and the gel, with the possibility of converting one into the other by phase reversal, must play an important part in cell life.

That there are possibilities of the formation of membranes, doubtless of a gel nature, within the protoplasm of a cell is shown by the fact that different reactions can take place at the same time in different parts of the cell, notwithstanding the general liquid nature of its contents. The view that the organization of the cell is of the nature of many minute factories, in which various operations are being carried on under the influence of the structure of the cell, is at the present time rapidly displacing that of "giant" molecules with "side-chains," which were supposed to be continually split off and exchanged for other chemical groups. The question is discussed in the British Association address of Prof. Hopkins (1913). Put in another way, limitation of the point of view to that of pure structural organic chemistry is showing itself to be incapable of explaining physiological reactions. Protoplasm is an extraordinarily complex heterogeneous system of numerous phases and components, continually changing their relations under the influence of electrolytes and other agents.

It has frequently been felt to be a difficulty, from the standpoint of energetics, that cells use energy for purposes in which it is not easy to make out what has become of it. Warburg (1914) suggests that it may be required for the keeping apart of substances which would mix by diffusion, for the preservation of semi-permeable membranes, the restriction of osmotic interchange and so on, all of these phenomena being manifested in microscopic or even ultramicroscopic dimensions. A discussion of phase relations in protoplasm in connection with equilibrium and energy will be found in the essay by Zwaardemaker (1906).

A property of emulsoid colloids which has its importance in the present connection is their capacity of taking up water by what is often called "imbibition." The distribution of water between the two phases can be varied to a large extent by the presence of electrolytes and other agents. Whether imbibition is mainly or entirely an adsorption of water at the *surface* of the constituent elements, as is indicated by the experiments of Posnyak (1912) and by some which I did myself on gelatin ("General Physiology," p. 101), it is clear that the concentration of solutes in the liquid phase must be raised thereby. Since the position of equilibrium in reversible hydrolytic reactions, catalyzed by enzymes, depends on the concentration of water present, we see how at one time a synthetic product, such as glycogen, is hydrolyzed, and at another time glucose is synthesized to glycogen by the same enzyme. What is required is merely a means of varying the free water, and the possibility of this is provided by the presence of highly dispersed emulsoid colloids.

In addition to the highly dispersed systems discussed above, protoplasm usually contains various larger aggregates and structures. Chambers (1917) calls the small particles visible under the ordinary microscope, "microsomes," and the larger ones, "macrosomes." He shows that the former are stable, the latter very sensitive to injury. There are also certain granules, of various forms, called 'mitochondria.' Cowdry (1916) has devoted special attention to these and finds that they are stained in the living state by dyes which contain a diethyl-safranin group, such as Janus-green B, and are apparently composed of albumin and lecithin. Ih the living state they are continually changing shape, and especially in cells during activity.

In the present state of knowledge, it would be unprofitable to speculate further on the functions of these different inclusions. The same may be said of the *nucleus* of the cell. That this is essential to continued life, growth, and subdivision is clear. Much attention has been given to the series of changes which it undergoes in the last process, called "mitosis," or "karyokinesis." They are obviously due to the ordered arrangement of certain vectorial forces, having a definite focus of origin, but we are still in the dark as to their meaning. Much importance has been attached to the number of distinct staining elements, "chromosomes," produced at a particular stage of the process.

Unwarranted conclusions are sometimes drawn as to the chemical nature of substances found in cells from their behaviour to dyes.

The theory of dyeing has been described in an earlier report by King (1917) to which the reader may be referred. There are many factors which play a part in addition to chemical composition. Fischer (1899) has shown that the same substance stains differently according to the size of the particles in which it is found. The sign of the electric charge is also of importance. The meaning of the facts is still obscure. Nervous substance has a special "affinity" for methylene-blue and other thiazine dyes, but also for some safranin-azo dyes, which have no chemical relationship to the former.

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II. The Nature and Permeability of the Cell Membrane.

Although protoplasm is a hydrosol of low viscosity, it does not mix with water, remaining, while alive, as a separate phase. If "killed", as by an electrical shock or the application of an anæsthetic, it freely mixes with the surrounding watery solution. In the normal state, it must be surrounded by a film or membrane of some kind, which prevents escape of the cell contents. We may draw a similar conclusion from the fact that the products arising from digestion of the food particles in protozoa, although consisting of such freely diffusible substances as glucose and amino-acids, are not washed out. Much discussion has arisen as to the nature and even the existence of such a membrane. In the present Report, space will not permit of discussion of all the work which has been devoted to the problem. Attention must be directed to those aspects of it which appear to the writer to be of essential importance and to the conclusions to be drawn therefrom. These conclusions will sometimes differ from those of the investigators themselves and the reader may not always be inclined to agree with the interpretations given in this place.

It has been pointed out (Bayliss, "General Physiology" p. 128) that, according to the Principle of Willard Gibbs, which is a consequence of the tendency of free energy to decrease, as stated by the second law of energetics, if there are in the cell contents any substances which lower surface tension, these must be concentrated at the interface between the protoplasm and the surrounding liquid. Moreover, Ramsden (1904) has shown that, in many cases, as solutions of bile salts, quinine or saponin, this concentration at the surface may be so great as to exceed the solubility of the substance in question, which is then deposited in a solid form, producing a film of more or less rigidity. In addition to this, Chambers (1917) finds that the extreme outer layer of the protoplasm has the properties of a gel. The change from sol to gel has been discussed in the preceding section. In the present case, it is doubtless due to the molecular forces at the surface. It should be noted that this outer layer of the protoplasm is not identical with the membrane to which the cell owes its semi-permeable properties. When a dye is unable to enter a cell, it does not stain this "hyaloplasm" stratum, so that the membrane which stops it has a more external situation. We see that there is every reason to expect the presence of a film on the surface of cells and that it would be reversible, existing only on the boundary surface and formed anew whenever any fresh surface is produced. These considerations also give us a clue as to the chemical composition to be looked for. In addition to the components of the hydrogel, whatever they may be, but almost certainly protein of some kind, we shall expect to find more especially those constituents of the cell which lower the surface tension of water to a marked degree; in other words, all compounds of a fatty nature, and of these lecithin is known to be universally present.

If we add certain dyes, such as aniline-blue or congo-red, to the water in contact with the protoplasm of a cell, we notice that it does not enter; the cell remains unstained. That this is not due to an obstruction anywhere but on the surface is shown by the fact observed by Kite (1913) that, if introduced by a capillary tube into the interior of a cell, congo-red freely and rapidly diffuses throughout the contents. Now it was observed by Nägeli (1855), and confirmed by Pfeffer (1890) and others, that if a mass of protoplasm be broken up into several smaller pieces, these parts when free assume a spherical shape, and form at once on their surfaces a layer with the same properties as regards permeability as the original protoplasmic membrane had.

If the cell substance is in contact with a liquid containing various substances in solution, as in the tissues of the higher plants and animals and in the case of the vacuoles in the interior of the cell, then the surface film will contain constituents of both phases and its properties will not be identical with those of a membrane formed in contact with water only. Evidence of this was found by Osterhout (1913).

It is obvious that the properties of the cell membrane as regards permeability to solutes both in the external liquid and in the interior of the protoplasm must play an important part in the life of the cell. While it is impossible to deny that a film of some sort must be formed, it is held by some investigators that sufficient evidence does not exist that it is possessed of the property of semi-permeability, at all events as regards crystalloids (see especially Moore and Roaf, 1908). If this be so, it is clear that the escape of such constituents from the cell must be prevented by their existence therein in fixed combination with solid parts. The evidence on this question must be examined.

There is no doubt that the salts present inside a cell may differ, not only in concentration, but in their chemical nature, from those in the external liquid. Perhaps the most striking case is that of the red blood corpuscles of the rabbit. Abderhalden (1898, p. 100) found that the blood serum contains 0·44 per cent. of sodium salts, while the corpuscles contain none at all; whereas the corpuscles contain twenty times as much potassium salts as the serum does. Similar facts have been described in the case of the muscle cells. The behaviour towards acid and alkali is interesting. Neither hydrochloric acid nor sodium hydroxide is capable of entrance into the uninjured cell. If jellyfish are allowed to swim in sea water to which neutral red has been added, they take up the dye into their cells, where it has the orange-red colour of the neutral solution. Bethe (1909) added hydrochloric acid until the colour of the dye in the water was changed to the cherry red of the acid solution. But the contents of the cells underwent no change in colour until enough acid had been added to stop the movements and kill the organisms. Warburg (1910) showed that the colour of neutral red inside the eggs of the sea urchin, which are acid, was unchanged by the addition of sodium hydroxide to the water, but immediately changed to yellow by a small quantity of ammonia.

But, it may be said, no evidence has been given that the electrolytes inside the cell are free to diffuse, even if the membrane allowed them to pass. The fact that the osmotic pressure inside cells is too great to be accounted for except by the presence of small molecules in the free state is indirect proof. Animal cells require, to prevent their swelling and rupture by osmosis, an external solution equivalent to 5·4 per cent. glucose or 0·9 per cent. sodium chloride; that is, a solution of 0·3 molar concentration. The osmotic pressure of this is 6·7 atmospheres. If we take a colloid which has as great an osmotic pressure as hæmoglobin has, we find, on calculation, that a solution of the necessary molar concentration would be solid. Even congo-red would require to be 21 per cent., a value far exceeding its solubility in water.

Höber (1910–1912) has shown, moreover, that there are free electrolytes present in cells. He made use of two methods. The first was by determining the increase in capacity of a condenser when a conductor is placed between its plates. Red blood corpuscles showed a conductivity about equal to that of deci-normal potassium chloride. The second method depends on the damping of the vibration of a rapidly alternating current in a coil by the presence of a conductor in the axis of the coil. By this method the blood corpuscles had the conductivity of a solution of potassium chloride between 0·1 and 0·4 per cent., muscle between 0·1 and 0·2 per cent. Although the methods are probably not sufficiently sensitive to give exact measurements of the concentration, they show clearly that free electrolytes are actually present.

Another experimental result pointing to the same conclusion may be referred to. When cells are immersed in dilute copper sulphate, alcohol, acetone or aniline, there is a marked increase in the conductivity of the outer solution, as shown by Stiles and Jörgensen (1915 and 1917). The additional ions must have come from the interior of the cells.

Living cells oppose an enormous resistance to the passage of an electrical current and if it were possible to examine them free from external electrolytes, it is probable that they would be found to be non-conductors in respect of currents applied by electrodes external to them. But, if they contain free electrolytes, it seems to the writer that the only satisfactory explanation of inability to conduct electrical currents is that the cell is surrounded by a membrane impermeable to these electrolytes, so that there is no possibility of their conveying charges from one electrode to the other. This phenomenon is shown in an interesting way in the method used by Morse (1914, p. 83) to prepare his copper ferrocyanide cells by electrolytic deposition. As the membrane becomes more perfect, the resistance goes up steadily and may amount, after soaking in water, to a million ohms.

The cell membrane can be deprived of this property, of resistance to the passage of currents, by the action of heat, of anæsthetics and so on. After this treatment the cells conduct currents readily.

We may conclude that, when examined under normal conditions and at rest, living cells are surrounded by a membrane impermeable to most salts, to strong acids and bases, and also, as shown by osmotic experiments, to glucose and to amino-acids. There are, however, certain crystalloids to which the cell appears to be permeable under all conditions. These are urea, ammonium hydroxide and some other ammonium salts, certain dyes of low molecular weight, alcohols, etc. But in some of these cases, it is not clear that no damage has been done to the membrane by the solution applied, a difficulty not always taken into consideration.

But the physiologist will raise an objection. If the membrane is impermeable to glucose and sodium chloride how does the cell ever obtain these materials for its active processes? The answer is to be obtained from the mode of production of the membrane. If it is composed of materials contained in the protoplasm of the cell it will naturally vary its nature according to the state of the cell, while, being a complex colloidal mixture, it will be easily accessible to the influence of electrolytes. But what actual evidence have we that it may become permeable to electrolytes under any conditions?

Direct proof of such changes under natural conditions is clearly difficult, but Lillie (1913) noticed that the cells of the larva of *Arenicola* when in a state of contraction lost their normal pigment, which is usually in solution in the cell contents. Garmus (1912) found that certain secreting cells became less permeable to dyes under the influence of atropine, more permeable under pilocarpine. The point of these observations is that pilocarpine excites glands to activity; atropine stops their activity. Indirect proofs are more in number. The change of electrical conductivity already referred to is a convenient means of detecting changes of permeability. The egg cell on fertilization increases in conductivity (McClendon, 1910, Gray, 1916), as also does the muscle cell on contraction (McClendon, 1912). The movements of the sensitive plant are usually ascribed to an increase of permeability of the cell membranes of the lower side of the "pulvinus." In this way the cells, which are normally distended owing to the osmotic pressure of certain solutes in their interior, lose these solutes and thus the distension due to their osmotic pressure. Blackman and Paine (1918), however, show that, although there is evidence of a very small escape of electrolytes, it is too small to account for the phenomenon, which can be repeated many times with the tissue immersed in warm water. They consider it more probable that the loss of turgor is due to a sudden decrease in concentration of osmotically active substances in the cell.

The effects of certain agents on the cell, producing a temporary, reversible increase in permeability of the membrane, show how the necessary changes might be produced. The most instructive are those produced by inorganic salts. Ringer (1882) was the first to show that the frog's heart is incapable of continued activity in a pure solution of sodium chloride, even of the correct osmotic concentration, whereas the addition of salts of calcium and of potassium in relatively small amount enabled the beats to continue indefinitely. A large number of experiments on such "balanced solutions" were made by Loeb (1901 and onwards) and brought into relation with changes in the permeability of the cell membrane. The experiments of Osterhout (1911) on the seaweed, *Laminaria*, showed that the tissue increased greatly in electrical conductivity when immersed in a solution equivalent to sea water, but containing sodium chloride only, returning to its normal state on the addition of a certain proportion of calcium chloride. No permanent damage was done to the cells (Osterhout, 1915) by repeating the experiment many times. The explanation given by the investigator himself is not quite clear, but to the present writer it seems to be as follows: As we saw above, the cells in normal conditions are non-conductors because their surface membranes do not permit the passage of ions. Under the influence of sodium ions these membranes become permeable and allow free movement of ions carrying electric charges through them. Calcium ions restore the normal state of semi-permeability. In this connection, the experiments of Clowes (1916), referred to in the preceding section, are significant. We have seen that the constituents of the cell membrane are most probably fatty substances, since they lower surface tension, together with concentrated solutions of emulsoid colloids in water, perhaps in the gel state, but certainly forming a watery phase. In other words, we have a system similar to that of oil and water in the experiments of Clowes, but more complex. Under the influence of sodium salts, Clowes' emulsion was one of oil drops in a continuous watery phase and therefore permeable to water and to solutes therein. On the other hand, under the influence of calcium salts, a phase reversal occurred, so that there was then an emulsion of water drops in a continuous oil phase. Such a system would be impermeable to water, but permeable to substances soluble in oil. A change of this latter kind, if complete, would not give us the properties which the normal cell membrane possesses. It would be impermeable to water, as well as to solutes in water. These solutes would not be able to manifest their osmotic pressure and the volume of the cell would not have any relation to the osmotic pressure of an external solution, as we find that it actually has. Incidentally, however, it appears from some experiments by Lillie (1917), on the changes of permeability in fertilized egg cells, that, under exceptional conditions, the production of a "waterproof" membrane may be possible. But what we have to explain is the change from a membrane permeable to salts, sugar, &c. to one impermeable to them, while remaining permeable to water. It is clear that the "Clowes effect," as we may call it, must be only partially effected. The way in which Bancroft explains the mode in which it takes place is summarized by Clowes as follows:—"The soaps present in the system tend, as stated above, to concentrate at the interface between water and oil and to form a coherent film. Soaps of monovalent cations, being readily dispersed in water but not in oil, form a film or diaphragm which is wetted more readily by water than by oil, consequently the surface tension is lower on the water than on the oil side. Since the area of the inside face of a film surrounding a sphere is obviously smaller than that of the outside face, the film tends to curve so that it encloses globules of oil in water, in this manner reducing the area of the side of higher surface tension to a minimum as compared with that of lower surface tension. On the other hand, a film composed of soaps of divalent or trivalent cations, being freely dispersed in oil but not in water, is wetted more readily by the oil than by the water, the surface tension is lower on the oil than on the water side, and the film tends to curve in such a manner as to enclose the globules of water in an outer or continuous oil phase." The process is dependent on the presence of a film of soap between the phases and it is interesting to note the powerful effect of sodium oleate in destroying the membrane of the red blood corpuscles, while pure olein has not this effect.

During the process of phase reversal, as described above, there is a stage in which one of the two phases is drawn out into elongated drops with narrow films or channels of the other phase between them. This is shown in Figure 2 of the paper by Clowes. Now, if these pores were small enough, we have the possibility of the production of a membrane with the structure that Traube held that of the copper ferrocyanide membrane to be, namely, a sieve whose holes were of dimensions such that water molecules could pass through, while larger molecules, such as those of calcium chloride or potassium sulphate, could not. Here we meet with the disputed question of the *nature of the semi-permeable* membrane in general. It seems to the writer that the evidence in favour of Traube's original view is very strong, although further evidence on the point is much required. In the case of membranes such as those of parchment paper or collodion, which are permeable to water and the small molecules of crystalloids, impermeable to the large molecules or aggregates of colloids, the degree of permeability appears to be strictly in proportion to the dimensions of the particles of the solutes. In the case of the copper ferrocyanide membrane, some observers hold that the passage of water depends on the different degrees of hydration of the colloid material of the membrane on its two faces. Even Morse (1914, p. 87) appears to hold this view, but the degree of hydration of colloids follows quite a different law from that of osmotic pressure. While the osmotic pressure of a solution is directly proportional to the molar concentration, not the chemical nature, of the solute, the hydration by salt solutions follows the series known as that of Hofmeister, where sodium and lithium salts, for example, behave differently from one another. Some investigators, moreover, state that non-electrolytes have no influence on the amount of water taken up by colloids. Objection also may be made to the theory of the production of osmosis by surface tension effects. Surface tension is not a function of molar concentration only, whereas osmotic pressure is. But, however this may be, Tinker's (1916) photographs show a definitely porous structure in the copper ferrocyanide membrane. The measurements given by him of the dimensions of the pores must be received with caution, since the published photographs show obvious diffraction. Indeed, the method of illumination used, a narrow cone of light, is not in agreement with the recognised methods of "critical" illumination, with a wide angled cone, adopted by the microscopists. The conclusions drawn as to adsorption of water molecules on the walls of the pores are also open to question. Further discussion of the problem is beyond the scope of this report, but we have seen how a sieve-like membrane might be formed on the surface of protoplasm, whereas a membrane which owed its semi-permeable character to its behaviour as a solvent for some solutes and not for others is much more difficult to imagine.

At this place a few words are desirable with respect to the Overton (1899) theory of the membrane as composed of lipoid material. It is a striking fact that the cell membrane is always permeable to those substances which are soluble in fats, such as the alcohols are. But, when we extend this statement and make it to apply generally, we meet with difficulties. For instance, certain dyes, such as methylene blue, are found to penetrate the cell membrane, while others, aniline blue, do not. Methylene blue is insoluble in chloroform, but if a solution of kephalin (a lipoid allied to lecithin) in chloroform be shaken with a solution of methylene blue in water, the chloroform phase is found to be coloured blue. In order to understand what this really means, we must refer to the work of Loewe (1912). He shows that kephalin is not in true solution in chloroform, but in large colloidal aggregates, since no measurable change in the boiling point of chloroform is produced by dissolving kephalin in it. The second point brought out is that, when methlene blue is present in the two phases, water and lipoid-chloroform, in contact, if it were a case of true solution in the latter, there would be a definite "partition-coefficient," independent of the absolute concentration. This is not the case. There is relatively *less* in the latter phase as the concentration rises, and the law followed is the parabolic law of adsorption. The actual ratio is such as to involve a high polymerization of the dye in both solvents, whereas electrical conductivity measurements indicate normal molecular weights in water. Again, if the dye were dissolved in the lipoid, a notable proportion of it would escape to water if placed in contact with it. Only a very minute amount leaves the lipoid. In fact, it behaves just like a negatively charged surface such as that of paper in water, to "basic" dyes, which are hydrolyzed in solution, and whose coloured base becomes a positively charged colloidal particle. As Freundlich has pointed out, the adsorption in such cases is so great that equilibrium is only effected when a very small amount of the dye is left in the water. Further confirmation of the view that we have to deal with a surface condensation only is that, if a mass of kephalin be placed in contact with a solution of methylene blue in water, the dye does not pass into the lipoid. Similar evidence was obtained in the cases of other "lipoid-soluble" substances, such as the alkaloids and certain narcotics. It is impossible to accept the view that the cell membrane is a lipoid film, and that the passage of substances into and out of the protoplasm depends on their solubility in lipoids.

It is also easy to show that a membrane of pure protein, as held by some, has not the requisite properties. Nothing but a complex system of more than one phase will suffice to explain the changes in permeability which are shown by the surface membrane of the cell.

We have already spoken of the effect of certain electrolytes on the membrane. Further discussion as to the meaning of "balanced" action will be found in the following section of this report. A few more facts in connection with permeability may be given here. Newton Harvey (1914) was unable to find any general law as to the relation of cells to acids, except that if an acid is soluble in lipoids it penetrates freely ; if not, the cell surface must be changed before it can enter. Strong bases do not enter ; weak bases do. This fact suggests that the permeability is in respect of one ion only. Since weak bases enter, OH′ ions must do so. Therefore, when sodium hydroxide does not, it must be that the sodium ion is obstructed. This point was indicated by Ostwald (1890). It is sufficient for a membrane to be impermeable to one of the oppositely charged ions of an electrolytically dissociated solute in order that the solute may be completely kept out. The reason is because the two ions cannot be separated without the expenditure of a large amount of energy on account of electrostatic forces. We shall see presently that this fact plays an important part in the electrical behaviour of living cells.

The action of *anæsthetics* is of interest. Osterhout (1916) has shown that there are two stages in this action, of opposite nature. The first one is a *decrease* in permeability, the second an *increase.* The former is recovered from on removal of the anæsthetic, while the latter is a toxic effect, irreversible and leading to death. Remembering that the characteristic action of anæsthetics is to make a cell unable to enter into a state of excitation, and that the state of excitation is associated with an increase of permeability, we see that the first stage is the real anæsthetic action. Whether the state of excitation is a consequence of the permeability change, or *vice versa*, is not certain, but it may well be that the prevention of the permeability change also removes the possibility of excitation. The pronounced "lipoid-solubility" of the volatile anæsthetics suggests that their action is on the lipoid constituents of the membrane, but magnesium salts have a similar action, so that it seems probable that the relationship to lipoids may be merely incidental.

The interesting observations of Meigs (1915) on the permeability of membranes of colloidal calcium and magnesium phosphates show that such membranes may be impermeable to sugar, phosphates, &c., but highly permeable to ethyl alcohol. Hence this latter property is not limited to "lipoid" membranes.

As pointed out previously, calcium salts decrease, while sodium salts increase the permeability of the cell-membrane, so that the effects may be balanced. Anæsthetics also decrease the permeability. Hence they should oppose the effect of sodium salts. This has been shown by Lillie (1914) to be the case.

Since the membrane is a local concentration of components of the protoplasm of the cell, there must always be an equilibrium between the two. Hence a change in either involves a change in both. It is not a matter of surprise, therefore, to find that substances applied to the outside of a cell may effect marked changes in its chemical behaviour, even when they are unable to pass through the membrane. Thus, as mentioned above, sodium hydroxide does not enter the living cell, but it increases greatly the rate of its oxidation processes. Newton Harvey (1914, p. 142) finds that although weak alkalies (ammonia and amines) enter muscle cells almost instantly, as shown by the change in colour of neutral red within the cells, their contraction does not cease until some time later. Strong alkalies (sodium hydroxide) abolish contractile power at once, but do not enter the cell until long afterwards. The effect of electrolytes on the beat of the heart and on muscular contraction in general is on the cell membrane (*see* Straub, 1912, p. 14, and Overton, 1904, p. 202). A somewhat remarkable phenomenon occurs in the case of such drugs as muscarine and pilocarpine, which produce their effects while passing through the membrane in either direction, whether entering or leaving the cell. When in equal concentration on both sides their effect is nil (Straub, 1907, Neukirch, 1912).

In order that the cells of the tissues of the higher animals shall maintain their normal water content and volume, it is necessary that they be surrounded by a solution of the same osmotic pressure as their own contents. The fact that whatever be the chemical nature of the solute, so long as it does not injure the cell, its osmotic pressure must be of the same definite value, unless either swelling or contraction of the cell is to occur, is in itself proof of the semi-permeability of the cell membrane. The facts are so simply explained on this view that it is somewhat puzzling to understand why elaborate theories should be invented to explain the phenomena otherwise. The question naturally arises, nevertheless, how do organisms like amœba, living in water, avoid swelling up and disintegration on account of the osmotic pressure of their contents? We have no accurate knowledge of the value of this osmotic pressure, but we know that it must be higher than that of the extremely dilute solution in which they live. It is pointed out by Stempell (1914) that the well-known *pulsating vacuole* of protozoa is the means of removing excess of water taken in by osmosis. A minute drop of water makes its appearance at a particular place in the protoplasm, gradually increases in size until it touches the outer surface of the organism and bursts to the exterior. The process is continually repeated.

The taking up of *solid particles* and small organisms, such as algæ and bacteria, by living cells, as in the process of 'phagocytosis,' seems at first sight to be difficult to understand. If molecules of sodium chloride are unable to pass through, how do such large masses manage to do so? The writer has suggested in another place ('General Physiology,' p. 144) that the membrane is actually perforated in the latter process, as when a needle is dropped through a soap film, the film closing up again as the object passes through. As we have seen, the cell-membrane is not a fixed structure, and the difference between the impermeability to salts and the permeability to large particles is that in the former case the molecules would have to pass through pores which are too small for them; in the latter case they break the film mechanically, but it is formed again behind them.

It will be of some interest, in conclusion, to refer briefly to some typical physiological phenomena in which membranes of variable permeability are believed to play an essential part. A limited selection is all that is possible, since, as pointed out above, the properties intervene in nearly all vital processes.

I. *The Stimulation of Nerve.* Nernst (1899) was the first to suggest that the electrical stimulation of nerves is conditioned by the concentration of ions of a certain sign of charge in the neighbourhood of a semi-permeable membrane. He made no statement as to the situation of such a membrane, nor did he claim that his theory was more than an approximation. A more complete extension of this theory was made by A. V. Hill (1910) and found by Keith Lucas (1910) to satisfy experimental results. There is no evidence of the existence of membranes within the nerve fibre itself, the contents of which, so far as can be made out, are liquid. Hence the membrane in question must be that on the exterior of the central core, that is, the cell-membrane. The relation of increased permeability to the condition of excitation has been emphasized by Lillie (1914) and the manner in which it is possible to explain the conduction along a nerve fibre on the basis of the disappearance of the electrical charge described below is explained (1915).

II. *Electromotive Phenomena.* If a membrane is permeable to ions of one sign only, a Helmholtz double layer is established, such that the opposite sides of the membrane obtain opposite charges, owing to the ions held there. In other words, the membrane is polarized. It has been known for many years that muscle and nerve fibres show, on testing, that their outer surfaces have a positive charge. This can be most satisfactorily accounted for on the hypothesis that the cell-membrane is impermeable to certain anions, permeable to the corresponding cations. In the address to the Physiology Section of the British Association in 1915, I showed how this view explains the phenomena met with and may venture to repeat the paragraph here :—

"Suppose that we lead off, to some instrument capable of detecting differences of electrical potential, two places on the outer surface of a cell having the properties referred to. It will be clear that we shall obtain no indication of the presence of the electrical charge, because the two points are equipotential and we cannot get at the interior of the cell without destroying its structure. But if excitation means increased permeability, the double layer will disappear at an excited spot, owing to indiscriminate mixing of both kinds of ions, and we are then practically leading off from the interior of the cell, that is, from the internal component of the double layer, while the unexcited spot is still led off from the outer component. The two contacts are no longer equipotential. Since we find experimentally that a point at rest is electrically positive to an excited one, the outer component must be positive, or the membrane is permeable to certain cations, impermeable to the corresponding anions. Any action on the cell such as would make the membrane permeable-injury—certain chemical agents and so on—would have the same effect as the state of excitation." The point of view taken here is practically identical with that of Bernstein (1913). Loeb (1915) has brought some objections to this view, based mainly on the fact that the application of salts to one of the places led off results in a change of the potential difference of such magnitude as to follow the well-known Nernst formula for concentration cells. I may point out that I have been able to show, both experimentally and by calculation (1911 and 'General Physiology,' pp. 648–650), that one can imitate the muscle cell by means of an osmometer, closed by a parchment paper membrane and filled with a solution of congo-red. This membrane is permeable to the sodium ions resulting from the electrolytic dissociation of the dye, but impermeable to the anions. The only difference is in the sign of the charge on the inside and outside, the latter being negative in this case. The potential difference between the two sides, which can be modified or abolished by the addition to the outer liquid of a solute giving sodium or other cations, is found to be in accordance with the Nernst formula. In fact, a cell of the kind described is a model of the rationale of the electrode potential of the concentration battery. It seems that there is then no real opposition between the results obtained by Loeb and Beutner (1912) and the hypothesis advocated here. The potential difference between two liquid phases, referred to by Loeb, has clearly the same origin as the membrane potential of the cell. The former has been investigated by Haber and Klemensiewicz (1909) in a well-known paper. If the salt is hydrolytically, as well as electrolytically, dissociated, a more complex state of affairs exists, which has been investigated thermodynamically by Donnan (1911). If, for example, we are dealing with a sodium salt of a weak acid, there are no forces to restrain the free diffusion of sodium hydroxide through the membrane, so that the alkali would be detected on the outer side, while the colloidal acid inside might be precipitated. Moreover, when no hydrolysis is present, if an acid, even as weak as carbonic, is present outside, the sodium ions at the membrane are partially replaced by hydrogen ions, the sodium combines to form carbonate and, by renewal of the outer fluid, all of the sodium can in time be removed.

III. *Secretion.* Although it is clear that complex changes of permeability occur in this process, too little definite knowledge is at hand to make detailed discussion of profit. The reader may be referred to my "General Physiology," pp. 163 and 334, for a brief statement. The point of immediate interest is that, suppose we have an inverted U-tube with a semi-permeable membrane at both ends and filled with a solution of cane sugar. If we immerse both ends in water in two separate vessels, a large osmotic pressure will develop inside the tube, but no liquid will escape, provided that the membranes can withstand the pressure. Now imagine the semi-permeable membrane at one end to become permeable to the sugar. A current of water, carrying sugar in solution, will pass through the tube from one vessel to the other, as long as there is any sugar left in the tube. This tube may be compared to the cells of a secreting gland, one end being in contact with lymph, filtered from the blood, the other end with the watery secretion in the duct. Water can be conveyed in the way described by a change in the permeability of the end bordering on the duct. Cases of this kind have been described by Lepeschkin (1906) in plant mechanisms.

IV. *The Blood Vessels.* Scott (1916) showed that when liquid is absorbed into the blood from the tissue spaces, this liquid, while containing all the crystalloids, is free from the colloids. The walls of the blood vessels are therefore impermeable to colloids. If, then, these colloids are such as have an osmotic pressure, the conditions are such that it can be manifested and it will play an important part in the passage of water from the blood to the tissues, and *vice versa.*

A few words are necessary therefore on the osmotic pressure of colloids. Starling (1896) showed that those present in the blood have an osmotic pressure of about 30 to 40 mm. of mercury at room temperature. Later work by Moore and Roaf (1907), Donnan and Harris (1911), Sörensen (1918) and myself (1911) showed that there are many colloids whose active elements are sufficiently small to give a fairly high osmotic pressure. When the colloid is an electrolytically dissociated salt of a diffusible ion with one to which the membrane is impermeable, as in the case of congo-red with a parchment paper membrane, an interesting question arises, whether the diffusible ions, which are held only by electrostatic forces, play their part in the osmotic pressure. I showed (1911), by determinations of the osmotic pressure of congo-red solutions by a vapour pressure method, that the values were the same as those given by the parchment paper membrane. Therefore, all the elements present in the solution, including the sodium ions, gave their proper contribution to the osmotic pressure measured by the osmometer method; otherwise, the vapour pressure measurements would have been much higher than those with the latter method. Theoretical considerations and calculations based on them (Bayliss, "General Physiology," p. 649) confirm the fact. Owing to the osmotic activity of all the ions formed by an electrolytically dissociated colloid comparatively high osmotic pressures may be manifested. This is the cause of the large rise in osmotic pressure produced by the addition of sodium hydroxide to a protein solution.

In order that we may realize how the osmotic pressure of colloids is of importance in problems of the circulation of the blood it is necessary to remember that the pressure in the arteries is something over 100 mm. of mercury, falling regularly to about 8 mm. in the capillaries, and to zero in the small veins. Since the osmotic pressure of the colloids in the blood is only 40 mm. of mercury, and the walls of the blood vessels are freely permeable to water and crystalloids, it is clear that the osmotic pressure of the colloids, which tends to draw water in, is overpowered as far as the commencement of the capillaries. Thus a filtration outwards of blood, minus its colloids, takes place in that part of the vascular system in which the pressure exceeds 40 mm. The same process occurs in a part of the kidney, resulting in the production of what is a very dilute urine, being the first stage in the complete process. The blood then is continually losing liquid to the tissues up to a certain region in its course. But, as we follow the gradual fall in the blood pressure along the capillaries, we come to a point where the osmotic pressure of the colloids, which has risen somewhat owing to the loss of water, is higher than the blood pressure. From this point onwards water is taken in again from the tissue spaces by osmosis. This latter process, however, does not usually suffice to balance the loss completely, and the difference is carried away by the lymphatic channels, and finally returned to the blood by the thoracic duct. Consider next what will happen when a dilute salt solution is introduced into the veins in order to replace blood which has been lost by escape from injured blood vessels for example. It is clear that the concentration of colloïds in the blood is lowered, and therefore their osmotic pressure. The result is that more rapid loss of liquid by filtration occurs, while the region travelled before the blood pressure falls sufficiently to permit osmotic inflow is lengthened, leaving a less distance in which reabsorption takes place. The net effect is that much more liquid escapes to the tissues, while the blood quickly loses that which has been put in. In practice this is found to be the case. Simple saline solutions are useless. The present writer has shown (1916), however, that if a colloid, such as gelatin, or better, gum acacia, be added in such amount to the solution injected as to raise its colloidal osmotic pressure to that of the blood, then it remains in the blood vessels raising the blood pressure and forming an effective substitute for the blood lost. Indeed, a gum solution of this kind was in extensive use during the war.

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III. The Relation of Biochemical Colloids to Electrolytes.

We have already met with several instances in which the interaction between colloids and electrolytes plays an important part. In the present section, further analysis of such phenomena will be attempted.

It is necessary to take account of the fact that the greater number of the colloids occurring in living organisms are proteins. These, being conjugated amino-acids, behave as amphoteric electrolytes, able to combine with strong acids by their NH_2 groups and with strong bases by their carboxyl groups. Electrolytically dissociated salts are thus formed, the protein ion being the cation in the former case, the anion in the latter. Although there is no doubt of this fact, it is sometimes forgotten that the protein itself is present in solution in the form of an anhydride, the NH_2 and $COOH$ groups are not free to combine with ions until hydrolyzed by the action of strong acids or bases. Nevertheless, various statements have been made to the effect that not only are chemical compounds formed with weak acids, but even with neutral salts. That this is not so is shown clearly by the results of Bugarsky and Liebermann (1898), who found no change in the freezing point on adding egg albumin to sodium chloride, whereas there was a marked depression with hydrochloric acid or sodium hydroxide. The evidence brought by Pfeiffer and Modelski (1912), to the effect that amino-acids form definite chemical compounds with calcium and lithium chlorides and other salts, is not convincing and the present writer was unable to confirm their statements.

Hardy (1905–6) finds that globulins form non-ionized complexes with neutral salts. On the other hand, Loeb (1918) holds that neutral salts with a univalent cation form highly ionizable salts with gelatin. The evidence is that powdered gelatin, after washing with m/8 or m/4 solution of sodium chloride, shows a further swelling when afterwards put in contact with a more dilute solution of a neutral salt with a univalent metal. There is a critical concentration above which this additional swelling is absent. And this concentration is half as great if the anion is bivalent, regardless of the nature of the anion and cation. The evidence is somewhat indirect, but it indicates an electrical effect independent of the chemical nature of the ion. Whether the conclusion is justified that it implies the production of a definite salt seems doubtful. The difference between the osmotic pressures of equimolar solutions of sodium salts with uni-and bivalent anions must not be forgotten. A further difficulty is presented by the fact that calcium salts were not found to form ionizable compounds, whereas in the experiments of Pfeiffer and Modelski (1912), the "compounds" of amino-acids with calcium chloride were some of the easiest to prepare. If the contrast is due to the colloidal nature of gelatin, it is an additional reason to doubt the adequacy of explanation on pure electro-chemical lines. Why does Loeb speak of proteins as "so-called colloids"?

If a salt of a protein with a strong base or strong acid is exposed to an electric field between electrodes, the colloidal ion is deposited at one pole or the other according to whether it is anion or cation and the protein is naturally said to have a charge of the sign opposite to that of the pole at which it is deposited. But the sign of the charge on such a surface as that of paper can be changed by electrolytes, even by weak acids and by neutral salts. In such cases, it seems that something other than actual salt formation must be the cause. Whatever may be the way in which the electric charge on the surface of insoluble particles or colloids is produced, whether by electrolytic dissociation at the surface, one ion being insoluble and fixed (see Hardy, 1910), or by other causes more allied to the phenomena of static electricity (Lewis, 1909), as appears to be the case with drops of petroleum in water, it is clear that the surface energy due to this charge would be reduced if ions of the opposite sign were deposited on it. The second law of thermodynamics would allow us to predict this fact, which has been called "electrical adsorption." It is shown in a striking way by the opposite effect of bivalent ions on the adsorption of colloidal dye ions by paper, when these have a different sign of charge. Some data on this point will be found in a paper by myself (1906). I was inclined to attribute the effect to a reversal in sign of the charge on the colloidal particles, but it is more satisfactorily explained as exerted on the paper. While, however, it is comparatively easy to see why the charge should be reduced to zero, it is not quite so easy to see why it should be replaced by a charge of the opposite sign, as Perrin, (1904, 1905), Mines (1912) and others have shown to be the case. Freundlich (1909, p. 245) has suggested that certain ions may be adsorbed in the mechanical way to a much greater extent than certain others with an opposite charge. The result would be a deposition on the surface in amount greater than merely necessary to neutralize the existing charge and sufficient to confer a charge of the opposite sign. (See especially the experiments of Freundlich and Schucht, 1913, and of Ishizaka, 1913.)

We have, then, in addition to the chemical compounds of certain amphoteric electrolytes with strong acids and bases, as association of electrolytes with the surfaces of colloids in general, a relationship which appears to be of the nature of adsorption. This is indicated by the law which expresses the proportion of electrolyte held by the colloid to that in the external phase. The law is expressed by the equation to one of the higher orders of parabolas. This is the reason why it is so difficult to remove, by repeated changes of water or dialysis, the last traces of electrolytes attached to colloids or coarsely heterogeneous systems.

This difficulty of removing all electrolytes and other crystalloids from a colloidal solution has led some workers in the past to the belief that the osmotic pressure shown by some of these solutions was due to the electrolytes present. There are several reasons, theoretical and experimental, that make this view inadmissible. In many cases, such as gelatin and congo-red, the more effectively these impurities are removed, the higher is the osmotic pressure. If the crystalloid is in any form of combination with the colloidal particle, chemical or by adsorption, it forms one indivisible system with it, so that if a colloidal particle is too large to possess the kinetic energy requisite to give an osmotic pressure, it would be even less able to do so if attached to another molecule. In fact, the association of a colloidal particle with an electrolyte would decrease the osmotic pressure given by it. If, on the other hand, the electrolytes are free, they must be removed by repeated dialysis. The osmotic pressure of hæmoglobin (Hüfner and Gansser, 1907) is that which it should have in accordance with its molecular weight as determined by chemical analysis. It is true that certain colloids, such as ferric hydroxide, become unstable if the last traces of ferric chloride are removed, but the particle consists of a complex of a variable number of ferric hydroxide molecules in adsorption with one or more ferric chloride molecules. The latter are not free.

The greater number of the colloids of biochemical interest belong to the class called *emulsoids.* Their characteristic is that the two phases are not solid and liquid, but both contain solvent in different amounts. The two phases in these biochemical colloids may be described as being, on the one hand, a solution of a small amount of the solvent in the solid, and, on the other hand, a dilute solution of the solid in the solvent. They may also be regarded as being both liquid, one of them possessed of a very high degree of viscosity. Such systems would not show a high surface tension at the interface, nor a high electrical charge. They are, accordingly, relatively to the suspensoid class, somewhat insensitive to the precipitating action of ions. At the same time, as Mines has shown (1912, p. 211), the difference is not a fundamental one and is merely one of degree. Egg white is at once thrown down by a simple trivalent ion, such as lanthanum, even in a concentration of only 0·0016 molar. The complex trivalent ion of the luteo-cobalt salts (Mines, 1912) does not precipitate emulsoids, although it is nearly as effective on suspensoids as the simple lanthanum ion. The fact appears to be related to the low density of the charge on the large ion.

On the other hand, these particular emulsoid colloids react in an important way to another property of salts, that property called by Freundlich (1909, pp. 54 and 412) "*lyotropic.*" It is manifested by changes in the distribution of the solvent between the two phases, dependent on changes in the solvent itself. In the case of water, we speak of the hydration of the ions and changes in the equilibrium between the various states of water itself. These give rise to alterations in the internal pressure, compressibility, viscosity, solubility, &c. The phenomena are not in relation to the valency of either ion, but follow a series known as that of Hofmeister (1888). The order of activity in anions is :—

$$SCN < I < ClO_3 < NO_3 < Cl < CH_3COO < SO_4 < \text{tart.} < \text{citrat.}$$

In cations .—

$$NH_4 < Li < Cs < Na < Rb < K.$$

But the difference between individual cations is less marked than that between anions. This series is met with in many phenomena in which emulsoid colloids play a part. The action appears to be preceded by adsorption.

The effect of acid and alkali in increasing the amount of water taken up in the swelling of emulsoid colloids has been the subject of experiments by Martin Fischer and G. Moore (1907), Chiari (1911) and others. According to Pauli (1912), the swelling is due to the formation of electrolytically dissociated salts and the affinity of the protein or other colloidal ion for water. If this be the case, we see how little importance the process can have in the phenomena of œdema or of "acidosis," where the possible increase in hydrogen-ion concentration is far too small to result in any salt formation with proteins. The experimental results of Fischer and Moore show, moreover, that a fairly high degree of acidity is necessary to produce any significant effect. Pauli's point of view is rendered doubtful also by the fact that the swelling occurs in solids, as well as dispersed molecules. It seems more likely that it is due to a change in the properties of water at the surfaces of the constituent elements of the colloidal masses, a change conditioned by the adsorption of inorganic ions at this situation.

The opposite effects which sodium and calcium salts have in reversing the phases of oil and water systems and on the permeability of the cell membrane have been referred to in the preceding section, together with the necessity for the presence of both for maintenance of the normal cell processes. If we confine our attention only to the cation in its action on emulsoid systems, it is difficult to understand why there should be, not merely a quantitative difference between univalent and bivalent ions, but an opposite effect. Clowes (1916, p. 408) holds that the opposition is really one between anions and cations, a more intelligible view. In the case of calcium chloride, for example, the cation is more powerfully adsorbed and reactive than the anion ; in that of sodium chloride, the anion is adsorbed to a greater degree than the cation. Hence the possibility of obtaining a balance between the two effects and the reason why a small concentration of calcium chloride balances a much larger one of sodium chloride. This view is confirmed by the fact that much less sodium citrate than of sodium chloride is required to counteract the effect of calcium chloride, because the citric anion is more powerfully adsorbed than the chlorine ion. But the possibility of the production of complex ions, containing calcium and the citric ion, must not be overlooked.

A certain difficulty arises with regard to potassium. It is found that to maintain normal cell processes and to permit growth the presence of a small concentration of potassium salt is necessary in addition to that of sodium and calcium. We may perhaps be satisfied with the statement that potassium is required on account of particular chemical properties. This appears to be the view taken by Loeb and Cattell (1915), but, as we have no idea as to what these properties are, very little is gained. Some recent work by Zwaardemaker (1918) is of importance with respect to the elucidation of the problem. This observer noticed that the elements which Ringer found to be able to replace potassium, namely, rubidium and caesium, are, like potassium, weakly radio-active and he proceeded to test other substances more powerfully radio active, such as radium itself, emanation, uranium, and thorium. It was found that equally radio-active concentrations of all the elements named were equal in their capacity of replacing potassium in a solution adequate to maintain normal cell life.

Sodium salts are chosen to make up the correct osmotic pressure of these fluids because they are the least toxic salts. But Clark (1913, p. 77) found that a better solution was obtained if a part of the sodium chloride was replaced by its osmotic equivalent in cane-sugar.

Some very interesting conclusions have been drawn by Macallum (1904) from the fact that the salts present in sea water form an appropriately balanced mixture for the cells of the higher vertebrates, when the sea water is diluted to the correct osmotic concentration. It seems evident that the electrolyte composition of the blood of the present land vertebrate is that of the ocean at the close of the Cambrian period, when their ancestors left the water and took to the land. The Cambrian period was an extremely long one and the colloidal systems of the cell were developed in adjustment to this balanced mixture of salts. But at the same time, it is a remarkable fact that the particular mixture arising from the dissolving of constituents of the earth's surface should be that of a "balanced" solution, not only for protoplasm, but also for emulsions of oil and water.

There is another interesting way in which the relationship of colloids to electrolytes meets us in physiological phenomena, namely, the mechanism of *muscular contraction*. Blix (1891) and A. V. Hill (1913) have shown conclusively that the tension developed is proportional to the area of certain surfaces arranged longitudinally in the muscle and is not a volume effect. Fitzgerald (1878) and Bernstein (1901) had already suggested surface tension at the contact between the fibrillæ and sarcoplasm as the mode of production of the muscular force, and there are other facts which confirm the view that surface phenomena form a component part of the complex of events. Surface tension has the peculiarity of possessing a negative temperature coefficient, doubtless connected with the absence of any boundary surface at the critical temperature. The contractile stress produced by muscle has a negative temperature coefficient (Bernstein, 1908), as also has the heat produced in the initial stage. Lactic acid is one of the chemical products of the muscular process, and Haber and Klemensiewicz (1909) put forward the hypothesis that the acid alters the electrical forces at the boundary between the fibrillæ and the sarcoplasmic liquid. This again involves a change of surface tension, which brings about the mechanical shortening of the fibres. The negative temperature coefficient excludes swelling of colloidal fibrils under the influence of acid as accounting for the muscle process as suggested by some. The imbibition of water has a positive coefficient.

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IV. Enzymes.

In the present report, that aspect only of the action of enzymes which is related to their colloidal nature will be discussed.

The fact that enzymes are present in their solutions in the colloidal state is shown by their non-diffusibility through parchment paper, and is now generally recognized. Taking this fact into consideration, together with the form of the relation between the concentration of the substrate and enzyme and the velocity of the reaction, the present writer (1906) put forward the hypothesis that the chemical decomposition of the substrate is preceded and controlled in rate by adsorption. Not only, however, are enzymes in the colloidal state, but they are able to act in a medium in which they are insoluble and present as coarse particles which can be filtered off, leaving the filtrate inactive. This has been shown in the case of lipase by Dietz (1907), in that of emulsin by Bourquelot et Bridel (1913), by myself (1915) for lactase, papain, peroxidase, catalase, urease, and invertase, with great probability for trypsin and pepsin. Armstrong, Benjamin and Horton (1913) came to the conclusion that urease acts by its surface. A similar conclusion may be drawn from the fact that invertase may be adsorbed by charcoal and nevertheless remain active (Nelson and Griffin, 1916). We may conclude, then, that enzymes belong to the class of catalysts present as a separate phase and acting in a heterogeneous system.

The next question that arises concerns the mechanism of their action.

There are two theories of catalysis in heterogeneous systems: one of these assumes the formation of an intermediate unstable chemical compound between the catalyst and substrate, the reaction following the ordinary laws of mass action ; the other regards the chemical change as being brought about, or rather greatly accelerated by close approximation of the reacting substances by condensation on the surface of the catalyst by adsorption. An intermediate position is taken by those who regard the rate of the reaction as conditioned by the amount of reagents present on the surface at any given time, but hold that the actual chemical change is due to formation of a chemical compound with the substance of the catalyst itself, occurring as a second stage of the complete process. This process may be expressed as made up, in order, of adsorption, combination with enzyme, decomposition of intermediate compound, with enzyme left finally as at first.

As a typical instance of the first view, we may take Van Slyke and Cullen's (1914) account of the kinetics of urease. These observers state that the action consists of two consecutive reactions : (1) combination of enzyme with urea, and (2) breaking up of the compound, the urea being freed in the form of ammonia and carbon dioxide. They formulate an expression of two factors, each with an empirical constant, which, by proper choice of the two constants, satisfies the experimental data. This fact, however, does not prove that the first stage is a chemical combination. Indeed, it is stated that the first stage, combination between enzyme and urea, is so rapid that no appreciable time is lost. If this be so, it is difficult to see why it appears in the equation at all. The authors seem to hold that physical phenomena, such as adsorption, diffusion and so on, follow indefinite laws only. in contradistinction to those of chemical combination. Further remarks with reference to formulae based on mass action alone, will be found below. Although the work in question is the most clearly expressed statement of the particular point of view, the theory itself is probably the most widely accepted one as applying to enzymes. Incidentally, we may remark that the fact that a particular reaction appears to follow the ordinary unimolecular law of velocity, deduced from mass action, is no guide to the nature of the process as a whole. Denham's (1910) reaction, in which a sheet of platinum is the catalyst, follows this law.

For the first statement of the other view, we must go back to Faraday (1834). The experiments and conclusions to be found in his paper, 'On the Power of Metals and other Solids to Induce the Combination of Gaseous Bodies,' are apt to be forgotten, so that I make no excuse for referring to them in some detail. The phenomena in question are the combination of oxygen (and nitrous oxide) with hydrogen, induced by the surface of metallic platinum and other solids. In paragraph 619, Faraday states 'All the phenomena connected with this subject press upon my mind the conviction that they are dependent upon the *natural conditions* of gaseous elasticity, combined with the exertion of that attractive force possessed by many bodies, especially those which are solid, in an eminent degree, and probably belonging to all; by which they are drawn into association more or less close, without at the same time undergoing chemical combination, though often assuming the condition of adhesion; and which occasionally leads, under very favourable circumstances, as in the present instance, to the combination of bodies simultaneously subjected to this attraction.' That the phenomena are regarded as a condensation *on* the surface, not a solution in the substance of the solid, is clear from the reference to hygrometric. bodies which 'condense water vapour around or upon their surface,' and are said to be instances of the same power (par. 621). The absence of chemical combination with the surface is stated clearly in par. 631, 'The platina is not considered as causing the combination of any particles with itself, but only associating them closely around it; and the compressed particles are as free to move from the platina, being replaced by other particles, as a portion of dense air upon the surface of the globe, or at the bottom of a deep mine, is free to move, by the slightest impulse, into the upper and rarer parts of the atmosphere.' Par. 632 calls attention to a fact which is common to adsorption phenomena in general, and is of importance in certain effects of retarding agents on enzymes, as we shall see presently. 'It can hardly be necessary to give any reasons why platina does not show this effect under ordinary circumstances. It is then not sufficiently clean (617), and the gases are prevented from touching it, and suffering that degree of effect which is needful to commence their combination at common temperatures, and which they can only experience at its surface. In fact, the very power which causes the combination of oxygen and hydrogen is competent, under the usual casual exposure of platina, to condense extraneous matters upon its surface, which, soiling it, take away for the time its power of combining oxygen and hydrogen, by preventing their contact with it' (598). Numerous facts are described which show that the only condition necessary is a perfectly clean surface, however produced. One way of doing this is of theoretical importance as showing that the action is not due to chemical combination of either oxygen or hydrogen with platinum. Platinum can be made active by making it either anode or cathode of an electrolytic cell (617). Chemical action is also excluded by the fact that nitrous oxide and hydrogen can be made to combine (572), and also by the fact that the 'effect is produced by most, if not all, solid bodies' in varying degree (618). It may be said that gas reactions only are contemplated in this theory, but statements in pars. 623, 625, and 657 indicate that Faraday had in mind the possibility of similar reactions in liquids. Indeed, the following statement is remarkably like an anticipation of Van Hoff's theory of solutions, 'An analogy in condition exists between the parts of a body in solution and those of a body in the vaporous or gaseous state.'

Denham (1910) brings powerful evidence in support of this theory of catalysis in inorganic heterogeneous systems as being due to the high surface concentration caused by molecular forces at the surface, and the high velocity of reaction as being due to the increased mass action thus brought into play. Bancroft (1918) gives a valuable discussion of contact catalysis.

Denham, however, although he is of the opinion that some enzyme effects may be accounted for in a similar way, hesitates to apply the theory to all enzymes. We may, therefore, proceed to examine the evidence bearing on the question. But before doing this, we should remember that it is possible, as Hardy points out (see paper by Drury, 1914), that there may be, in addition to the simple mass effect, an increased chemical potential of the reacting molecules brought about by the actual process of condensation itself and the stresses which it involves.

That the rate of reaction is controlled by adsorption is evident from various facts. The law expressing the way in which the concentration of enzyme and of substrate is related to the rate of change is not one that could be deduced from mass action. Up to a particular concentration of substrate, which varies with different enzymes, the law followed is that of a parabolic curve, similar to that of adsorption, although this, of course, does not in itself prove that we have to do with adsorption. Beyond this particular concentration, the rate is either constant, whatever the concentration of the substrate, or, owing to some secondary effects of the enzyme, is actually diminished. This fact is easily accounted for by the familiar fact that a surface may become saturated ; so that, above a certain concentration of the substrate, no more can be adsorbed at a given moment of time. On other hypotheses explanation is very difficult. Data showing the fact in the case of enzymes are numerous ; those of Frankland Armstrong (1904) with lactase may be particularly mentioned.

When attempts are made to express in mathematical formulae the velocity of reaction with enzymes, starting with the usual expressions based on mass action, it is found that numerous empirical factors have to be introduced in order to obtain adequate expressions. Since we do not know the meaning of these factors, it seems to the writer that very little is gained by such procedures. The difficulty is to know exactly what is the active mass at any moment. It is clearly some function of the concentration of the substrate, because this determines the amount adsorbed, but it is also related to the adsorbing capacity of the enzyme surface, which is itself affected by numerous influences, probably changing during the progress of the reaction itself.

According to the theory of Nernst concerning reactions in heterogeneous systems, there are three stages—diffusion of the reagents to the surface, adsorption on this surface, and finally chemical reaction with each other or with the constituents of the surface itself. The stage of adsorption is very rapid when the reagents have reached the surface ; so that, since the rate of the reaction as a whole is that of its slowest component, the process of adsorption itself does not control it. When one of the phases is a large mass, the time taken for the reagents to diffuse to it is an important component and usually longer than the actual chemical reaction itself. In such cases, the temperature coefficient of the reaction as a whole is that of diffusion, and is a low one. In the case of a colloidal dispersion, such as an enzyme in solution, the solid phase is evenly distributed throughout the system, so that the paths travelled by the substrate to reach the surfaces of the enzyme particles are very short, and the rate of the reaction is that of the chemical component, with the temperature coefficient of a chemical reaction. It seems likely that the coarsely heterogeneous systems of urease or emulsin in alcohol would be found to have the temperature coefficient of diffusion, but they have not been investigated from this point of view. The failure to realize these various facts has led to confusion of statements regarding the impossibility of an adsorption process having the high temperature coefficient of a chemical reaction. The temperature coefficient of an enzyme reaction is naturally that of whatever chemical change occurs, and it gives us no information as to the other components of the total process.

We know from numerous investigations that when a substance is strongly adsorbed it is capable of displacing another substance to a greater or less degree from its position on the surface. Many of the substances found to retard the rate of enzyme action are of this kind. The alcohols, urethane, saponin and so on lower surface energy markedly. It was natural, therefore, that Meyerhof (1914) should suggest this as an explanation of their action, which was found in a series of related compounds to follow their capacities of lowering surface tension. It is complicated, however, by some other properties of these agents to be referred to below. As was pointed out in the preceding report in connection with muscular contraction, surface energy is peculiar in having a negative temperature coefficient. If the inhibiting effect produced by saponin, etc., has the cause suggested it should be found to be greater at a low temperature, just as the degree of adsorption in general is well known to be greater at a low temperature. The present writer (1918) in experiments with saponin and with amyl alcohol showed that this actually was the case.

A practical point of interest is the effect of alcohol on digestion. As far as the rate of action of the digestive enzymes on food is concerned all experimental evidence shows it to be a retarding one, and the reason is doubtless that given above.

Remembering that the action of enzymes is a surface one it is clear that any agents affecting the *state of dispersion* must affect the intensity of action. Any agent which increases the degree of dispersion increases the total surface and hence the activity of the enzyme. This factor comes in to complicate the case discussed above, since agents lowering surface tension tend to increase dispersion and thus to counteract the inhibiting effect. A particularly marked case is the accelerating effect of bile salts on the action of lipase. It was thought to be due to better emulsification of the oil used as substrate until it was found to be present also when soluble esters, such as ethyl acetate, were used. It seems, therefore, that it must be due in part to greater dispersion of the enzyme itself.

The possibilities of complexity of action are obviously greater in the *action of electrolytes*, because we have in addition the intervention of electrical forces and the effects of electrical adsorption. Some of these may decrease, others increase, the state of dispersion, according to the sign of charge on the enzyme particles. In the investigation of the effects of substances added to solutions of enzymes we have then a multiplicity of factors to take into account, so that analysis of the phenomena is very difficult and much further work is required. The experiments of Onodera (1915) are of interest in this connection.

We may regard it as established that adsorption of substrate by enzyme particles is the controlling factor in the velocity of the chemical reaction that follows. But is this adsorption followed by chemical combination with the enzyme, forming an intermediate compound of an unstable nature which then breaks up into products different from those substances from which it was formed? In the majority of cases, the chemical change involved is one by which the elements of water are either added or removed, but this is not always the case. There is every reason to regard the effect of an enzyme as an acceleration of the rate at which a given system attains its equilibrium position, the final products being the same as those which would have been formed, very slowly, in the absence of the enzyme. There is no inherent difficulty in the view that the concentration on the surface results in the rapid attainment of equilibrium by increased mass action, in the same way as Faraday explained the platinum effect and as Denham regards the inorganic heterogeneous catalysts in general to produce their results. This last observer points out that there is only one case in which evidence of a kind of intermediate compound of a chemical nature has been brought forward. So far as I am aware, no compound between enzyme and substrate has been shown to exist. Adsorption compounds or colloidal complexes have been obtained when the substrate is in the colloidal state, as between starch and amylase, and between trypsin and casein. But such compounds are formed whether the substrate is one capable of attack by the enzyme or not. Thus, amylase forms a similar compound with casein and with starch, and it appears to be a mere physical juxtaposition of the colloidal particles, held together by mechanical or electrical forces.

A certain amount of evidence that adsorption alone can increase the rate of change is afforded by some experiments which the present writer made with powdered charcoal and urea solution. Urea in solution, as Walker and Hambly (1895) showed, is slowly changed into ammonium cyanate, up to a certain equilibrium position. This is followed by a further change into ammonium carbonate. The rate of this change is accelerated to a marked degree by the presence of powdered charcoal.

The absence of an intermediate compound is more definitely indicated in the investigation of Horace Brown (1914) on some Cape wines, where an oxidation proceeds under the influence of a catalyst consisting of iron in the ferrous state associated with tannin and protein. This acts as a 'carrier of oxygen,' as in Fenton's reaction. The observations of Moore and Webster (1918) on the photosynthesis of formaldehyde in presence of inorganic colloids are also to the point. They show that the effects are not due to changes of the catalyst from a higher to a lower oxide, but to a surface condensation of carbon dioxide on the particles. The effect is given indeed by silicic acid, in addition to ferric and uranic hydroxides and beryllium chloride, also, to a less extent, by copper, nickel, palladium, manganese and erbium salts. The bearing of this fact on the problem of chlorophyll assimilation in plants is obvious. It suggests that the function of the pigment in the chloroplasts is to absorb light energy which is then utilized by the aid of an iron catalyst to reduce carbonic acid to formaldehyde.

It has been pointed out to me by Prof. Hopkins that if the process is to be regarded as the rapid attainment of the natural equilibrium in consequence of condensation on the surface of the enzyme, it follows that all the constituents of the system must be adsorbed in the same relative proportion as in the body of the liquid, otherwise there must be a change in the equilibrium position. I have made some experiments to test this deduction, but the difficulties are great and the work is for the present interrupted. I found, however, that a mixture of ethyl alcohol, acetic acid, ethyl acetate and water, after equilibrium had taken place, was unaltered by the addition of powdered charcoal, although charcoal is known to adsorb some of the constituents, at all events. The result indicates that the various constituents must have been adsorbed in the same proportion as that in which they were present in the mixture. But further experiments are desirable and it does not follow that enzymes behave like charcoal. Curiously enough, it appears to be well established that, in the case of esters at least, the equilibrium position is not the same with acid as catalyst as with lipase (Dietz, 1907). In the former case, the equilibrium is with 85·5 per cent. ester (amyl butyrate); in the latter, with 75 per cent. ester. The equilibrium is a genuine one in both cases, since it can be reached from either direction. If water were more highly adsorbed from this mixture than the other constituents, the result, which shows more hydrolysis than in the case of acid, might be explained. The fact has given rise to many conjectures, on account of the fact that it seems to give an opportunity to evade the second law of thermodynamics. The considerations given above add yet another, namely, that the fact may be due to unequal adsorption. Whether the equilibrium on the surface of enzymes is of necessity the same as that in the body of the solution is not yet quite clear and this point requires investigation. At any rate, there seem to be no inherent difficulties in the hypothesis suggested. The relative degree of adsorption of the various constituents of a mixture has received some attention, especially by Arrhenius and others working with him (see Williams, 1913). It is clear that all are adsorbed, including the solvent itself.

Some interesting possibilities are pointed out by Bancroft (1918). If different products can be obtained from a particular substance, it may happen that one catalyst adsorbs certain of them more powerfully than another one does, so that the resulting equilibrium may not be the same in the two cases. Similarly, different catalysts, such as platinum, charcoal, clay, etc., may cause different forms of combination in a mixture of gases, according to their relative adsorption. If one of the products of a reaction is very strongly adsorbed, it may possess the surface to such an extent as to stop further action and produce a false appearance of equilibrium, the position of which will depend on the concentration of the catalyst, contrary to the true equilibrium.

The question of synthesis by enzymes does not properly belong to the scope of this report, but it is clear that, since the characteristic of catalysis is the rapid attainment of a natural equilibrium, depending on the relative concentration of the components of the system, the same enzyme will exhibit either hydrolytic or synthetic activity according to the composition of the mixture. Synthetic action requires a low concentration of water (see especially Armstrong and Gosney, 1914), so that, as pointed out previously, a method is wanted by which the cell can vary the effective concentration of water. No special synthesizing enzymes are called for. The evidence that has been brought for the existence of such agents is not convincing (see Bayliss, 1913).

The chief difficulty in regarding the mode of action of enzymes as consisting merely in a surface condensation of the constituents of the reacting system is the apparently specific nature of these catalysts, although the degree of specificity is probably exaggerated. We must remember that the nature of the surface determines adsorption, since all the physical properties of a substance depend on its chemical nature. The possibilities of different adsorption properties are enormous and the study of the subject is yet in its infancy. One of the most interesting cases of this specific action is that of those enzymes which act on optically active compounds and the synthesis of such compounds by optically active catalysts (see Bredig and Fajans, 1898, and Bredig and Fiske, 1912).

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V. The Transport of Gases in Animals.

Oxygen is continually being used up and carbon dioxide produced by the oxidation of food materials in the tissues of animals. When the current of blood flowing in a given time is compared with the consumption of oxygen and the carbon dioxide produced in the same time it is clear that, in neither case, is the amount that could be carried in solution in the liquid of the blood nearly sufficient to account for that actually transported.

Both these gases, therefore, must be carried in some kind of combination with substances present in the blood. It will clear the way if we exclude certain possibilities at once. Oxygen is taken up by the blood in the air sacs of the lungs, where its partial pressure is about 100 mm. of mercury. The venous blood has an oxygen tension of about 37 mm. of mercury. Accordingly, the substance serving for the transport of oxygen must be one which takes up oxygen when exposed to a tension of this gas of 100 mm. and gives it off again, more or less completely, at 37 mm. or thereabouts. The tension of carbon dioxide in the lungs is 40 mm. of mercury; in the blood arriving from the tissues about 64 mm. or thereabouts. The substance transporting this gas must be one that takes up carbon dioxide at 64 mm. and gives it off at 40 mm. There is only one substance present in the blood that has the requisite properties as regards oxygen, that is the red colouring matter of the red blood corpuscles, hæmoglobin. This has been known for a long time. But some confusion has arisen with regard to carbon dioxide, because sodium bicarbonate is present in the blood plasma, and it was natural to look upon this as the carrier. Bohr (1891), however, had already shown that sodium bicarbonate gives off no carbon dioxide to the gas at a pressure of 40 mm. of mercury, and Buckmaster (1917) has confirmed this statement. The latter observer has also shown that there is no substance present in the blood acting as an acid to drive off the carbon dioxide. There seems to be no possibility of a dissociable compound of carbon dioxide with the proteins of the blood plasma. We have seen that proteins do not combine with weak acids, although a process akin to adsorption may occur, although it is not definitely shown to be present. The part played by the proteins is as yet somewhat uncertain, but the work of Buckmaster has proved that by far the greater part of the carbon dioxide, if not all, is carried by the hæmoglobin in a manner similar to that in which it carries oxygen.

The function of the sodium bicarbonate, as Lawrence Henderson (1908) has so well shown, is to preserve the hydrogen-ion concentration of the blood within narrow limits.

The work of Barcroft and his coadjutors has brought out in detail the relations between oxygen and hæmoglobin, under various conditions, and shown how the facts can be expressed in a mathematical form. A complete account will be found in Barcroft's book (1914). The object of the present report is to point out the difficulties met with when an attempt is made to reconcile the interpretation sometimes given to these expressions with the fact that hæmoglobin exists in the blood as a heterogeneous phase. In the corpuscles the concentration of hæmoglobin is about 30 per cent. No solution of hæmoglobin of this strength can be made. Even in 5 per cent. it forms a colloidal suspension, and it does not diffuse through parchment paper, however dilute the solution may be.

Barcroft explains the phenomena on the basis of chemical combination between oxygen and hæmoglobin, a series of compounds, HbO_2, Hb_2O_4, Hb_3O_6, &c., being formed in different relative proportions according to the electrolytes present in the solution. These electrolytes are regarded as causing aggregation of hæmoglobin molecules; the aggregate Hb_2, when it combines with two molecules of oxygen, leads, by mass action, to a different order of equation from that of Hb and O_2, which is unimolecular. But it is not yet certain that we are justified in applying the law of mass action in a simple form to heterogeneous systems and, if we apply the phase rule, we are at once met with difficulties, as will be seen below. On the other hand, it is not universally accepted that the phase rule can be applied to colloidal solutions, although the hæmoglobin in the corpuscles may reasonably be regarded as a more definitely distinct phase.

Barcroft's experimental results are of so much value that it seems to the writer that there is some risk of the problem being prematurely considered to be solved and the very remarkable character of the phenomena being overlooked.

Assuming that the phase rule applies, what does it tell us? If HbO_2 is a chemical compound, there are three phases present in a solution of it when in contact with an oxygen atmosphere, Hb, HbO_2 and oxygen. There are two components; because Hb and HbO_2 vary inversely; the oxygen is present in unlimited amount. There is therefore only one degree of freedom:

$$F = C + 2 - P = 2 + 2 - 3 = 1.$$

In other words, at a given temperature, say that of the blood, the *whole* of the hæmoglobin is either reduced or oxidized, according to the tension of the oxygen. But this is not the case. It is well known that hæmoglobin varies in its content in oxygen, at the same temperature, according to the tension of oxygen. It is free from oxygen at zero tension and saturated at about 100 mm. of mercury at the temperature of 38° C., while it follows a particular law, expressed by the dissociation curve, between these values.

Apart from this deduction from the phase rule, there are certain chemical systems that have been hastily assumed to be similar to that of oxygen and hæmoglobin. We shall see that they are different and really obey the phase rule.

By a misunderstanding of Le Chatelier's data (1883), the calcium oxide and carbon dioxide system has been supposed to throw light on the hæmoglobin question. But, *at a given temperature*, the calcium is present either entirely in the form of calcium oxide or calcium carbonate, according to the tension of carbon dioxide. At tensions below a certain value, different for each temperature, we have complete decomposition; at all tensions above this value, the whole exists as calcium carbonate, and there are no intermediate stages. At first sight, again, a solution of sodium bicarbonate in water seems more like the one we seek. At tensions of carbon dioxide between 0 and about 3 mm. of mercury, there is a series of intermediate stages in which there are progressively increasing concentrations of the bicarbonate and decreasing concentrations of carbonate. But the explanation of this fact lies in the electrolytic decomposition of the salt. The presence of more HCO_3 ions results in a rounding off of the corner of the curve owing to reduced ionization of the salt. Again, there are some dyes which may exist in a reduced form, capable of taking up oxygen when exposed to the air. Experiments made by W. A. Osborne (not yet published) were unable to discover any one of these which was not either completely reduced or completely oxidized, as the phase rule would predict. All search has hitherto failed to find any chemical system similar to that of oxygen and hæmoglobin.

It will probably occur to the reader that the adsorption of gases by indifferent solids, such as charcoal, is, at a given temperature, in proportion to the tension of the gas. In fact, it was suggested by Wolfgang Ostwald (1908) that the taking up of gases by hæmoglobin is a case of adsorption. But we are met by nearly as many difficulties in this view as in that of chemical combination. The taking up of gases by charcoal follows the usual parabolic law, whereas that of oxygen by hæmoglobin in solution in distilled water follows the rectangular hyperbola of a unimolecular reaction. On the other hand, the curve given by the latter system in the presence of electrolytes, acids or salts, requires a value greater than unity to be given to the exponent of the equation for the reaction velocity, in some cases above 3, an exceptional value for the order of an equation for velocity of reaction. The curve approximates more to that for adsorption.

The fact that there is a saturation point, beyond which increase of oxygen tension gives no measurable increase in the amount taken up by hæmoglobin, is not in itself, of course, inconsistent with adsorption. But, again, it is a remarkable fact that the accurate determinations of Peters (1912) have shown that the amount of oxygen taken up in saturation is exactly that required to combine with the iron in the hæmoglobin molecule to form FeO_2; in other words, one molecule of hæmoglobin combines with one molecule of oxygen. It is natural to associate the iron with the taking up of oxygen, but there is no other compound of iron having the properties of hæmoglobin. Even the hæmatin, which is combined with a protein to form hæmoglobin, behaves in a way similar to the dyes mentioned above. A further difficulty is the fact that hæmoglobin takes up carbon dioxide, carbon monoxide and nitric oxide in a similar dissociable way to that in which oxygen is taken up, although in different amounts. Just as in adsorption, one of these gases drives out more or less completely another one. The absorption spectra of the CO and NO compounds is very like that of oxyhæmoglobin, although there is a difference between all of them and reduced hæmoglobin. In any case it must be a remarkable chemical substance to combine with such dissimilar substances. According to Buckmaster and Gardner (1910–1911), chloroform is also taken up by hæmoglobin, driving off part of the oxygen.

In this connection, the relative adsorbing capacity of charcoal for various gases and vapours, the displacement of a weakly adsorbed gas by a more strongly adsorbed one and the "spoiling" of the surface by adsorbed impurities are problems of much interest and importance, not only in relation to the hæmoglobin question, but especially in relation to the properties of the material used for the box respirator for protection against poison gases. It will be remembered that Faraday showed how readily the activity of platinum was stopped by the deposition of impurities from the air of the laboratory and that they could be driven off by heat. Investigations on these lines, from certain aspects, have been carried out by the Anti-gas Department, but are not yet made public. Bancroft (1918) states that carbon monoxide decreases the action of platinum in causing combination between oxygen and hydrogen gases and that it is tenaciously retained by the surface.

When hæmoglobin "combines" with oxygen, heat is evolved, but the results obtained by different investigators vary so much that it is scarcely worth while quoting them. It is well known that adsorption of gases by charcoal is attended by evolution of heat, so that the fact does not exclude the hypothesis of adsorption by hæmoglobin. The condensation of a gas on the surface is equivalent to a reduction of volume by compression.

The behaviour of the oxy-hæmoglobin system to a rise of temperature is similar to that of an adsorption process. That is, the *rate* at which oxygen is taken up is increased, but the *amount* held in equilibrium is less than at a lower temperature.

There are thus difficulties involved in both views, that of chemical combination and that of adsorption. It may be that the explanation may be found in a double process, such that the amount of oxygen taken up at a given tension is determined by the amount adsorbed, and that the adsorption is followed by chemical combination. But it is by no means easy to understand the mechanism of such a process. At any rate, it is obvious that hæmoglobin is a very extraordinary chemical compound and that its relation to gases is far from being explained up to the present.

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THE ADMINISTRATION OF COLLOIDS IN DISEASE.

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The general trend of pathological research has shown that the human body possesses in a varying degree the power of protecting itself against diseases of a parasitic nature, and that the protective medium is chiefly found in the blood.

Parasites such as bacteria do not usually kill by their mere presence in the body, but because they produce poisons. The body in normal health reacts to these poisons producing an anti-toxin which either neutralises the poison or kills the parasites producing it. If, however, the body is unable to produce such anti-toxins in sufficient quantities it is necessary to supply them artificially.

Some diseases appear to be due to an alteration of the blood owing to the presence in it of an excess of some substance such as uric acid or to a deficiency of certain inorganic elements which appear to be necessary to effect complete metabolism.

Modern methods of treatment therefore tend to follow four lines of development:

(*a*) The use of purer forms of well-known remedies, such as quinine hydrobromide instead of a decoction of cinchona bark, or morphia instead of tincture of opium.

(*b*) The administration of the elements or salts which are temporarily deficient.

(*c*) The use of substances having a selective action on the parasites which have invaded the body (see later).

(*d*) The increased production in the serum of the patient of the protective or curative substances which would be produced in insufficient quantities by the body under normal conditions. For instance, a healthy nurse will not usually be attacked by the disease from which the patient suffers, as the body will produce sufficient protective substances. In a less healthy person insufficient protective material is produced unless the corresponding stimulus is given to ensure its formation.

The medicines in the first group are improved by investigating their chemical composition, isolating the pure alkaloid or other essential ingredient from the mixture ordinarily used or by preparing the drug synthetically. There are obvious limitations to this procedure, and there are strong reasons for supposing that only a portion of even the purest drugs are required by the organism. In other words, the first group tends increasingly to be absorbed by one of the others.

Remedies of the (*b*) group are relatively simple when once the most suitable form of administration has been learned. The chief difficulty of the investigator is to obtain them in a form in which they will react in the desired manner so as to form the correct chemical compound required by the tissues. E. Dubard, for instance, has obtained evidence that a deficiency of magnesia in the system facilitates the development of cancer, but he has been unable to retain the magnesia in the system unless it is administered in such large doses (12 grammes daily) that the excess of it produces undesirable effects. Such a difficulty clearly shows that the medicine has been administered in an unsuitable form.

The chief advances in chemistry during the past thirty years have been due to the development of the theory that chemical reactions occur between the ions or ultimate portions into which compounds are decomposable. Hence, an element in which the body is deficient must eventually be reduced either to its ionic state or to a form of combination which is equivalent to it.

In many cases, substances in a colloidal state react with an activity which is otherwise unobtainable. This may, in part, be due to the fact that when complete dissociation into ions is required the solutions must usually be exceedingly dilute, whereas colloidal solutions may be much stronger. Hence, the use of colloids has proved invaluable as a means of making good the deficiency in certain elements from which some tissues suffer.

Diseases which require selective remedies (group *c*) are chiefly those due to parasites, including the bacilli, micrococci, and other "germs" which produce certain poisons or toxins.

A substance which exerts either a toxic or a healing action on the body usually shows a greater affinity for one set of tissues than for others. Some substances have a greater action on bacteria and other parasites than on the host, and *vice versâ*. In other words, their action is selective, and an ideal medicine would be one which is so powerfully selective as to be absolutely fatal to the parasites it is desired to destroy and yet wholly harmless to the patient.

Ehrlich showed that a toxin is capable of producing disease only in those persons whose body-cells contain substances capable of entering into chemical combination with the particular toxin.

The anti-toxins and bacteriolysins appear to equally definite in composition. Ehrlich found that an aniline dye, to which he gave the name of trypan red, is highly toxic with respect to trypanosomic parasites in blood but relatively harmless to the host.

According to Metchnikoff's popular theory of phagocytosis, the wandering corpuscles or leucocytes in the blood attack the bacteria or other parasites, but this theory has receded in consequence of the discovery by G. F. Nuttall, who, when working in Flügge's laboratory in 1886, found that anthrax and other bacteria died rapidly in fresh blood serum without the interposition of the leucocytes, thus showing that the serum itself contained the (chemical) substances which brought about their destruction. This is to some extent incompatible with Erlich's endeavours to seek a substance which is parasito-tropic without being organo-tropic, because a drug injected into the blood stream—either directly or intramuscularly—does not usually exhibit any action until it has been taken up by the serum. Hence the organo-tropic (as distinct from the organo-toxic) properties of a drug are of great importance. So far, no substances have been found which are highly parasito-tropic and wholly devoid of organo-tropic properties, though many colloidal sols are so feebly organo-tropic as to be devoid of danger in any ordinary doses. In the case of elementary colloids such as mercury or iodine, any toxic symptoms and ill effects may be removed by the administration of a colloid of the opposite electrical charge (a metal to relieve an excess of non-metal and *vice versâ*). Whilst, as a rule, no coagulation occurs when colloidal solutions of the same electric sign are mixed, if a solution of the opposite sign is added coagulation occurs unless one of the colloids is in very large excess. Before the science of chemotherapy had advanced to its present stage, and even now as regards certain diseases, successful remedies were found by what is known as the serum treatment in which the requisite anti-toxins are prepared by cultivating suitable bacteria, etc., and using the products which they have formed. Investigations have also been made with a view to synthesising the anti-toxins (or those portions of them which are required for the purpose) in order to eliminate certain objectionable features of the serum treatment. Endeavours have also been made to simplify the materials used, by supplying the body with just those elements or groups from which it could most rapidly prepare the material which would stop the progress of the disease and facilitate a cure.

Still further investigations have shown that all the normal fluids and secretions of the organism are essentially colloidal in character, the toxins or bacterial poisons appear also to be in the colloidal state and to a large extent the reactions which create immunity to certain diseases are typical of those met with in ordinary chemical absorptions and precipitations. This at once suggests the importance of colloidal substances, both in the maintenance of health and in the cure of disease.

Graham,[1] to whom we owe the conception of the colloidal state, clearly saw the importance of colloids for living matter, when he wrote, "The colloidal is, in fact, the dynamic state of matter; crystalloidal being the static condition. The colloid possesses *energia*. It may be looked upon as the probable primary source of the force appearing in the phenomena of vitality. To the gradual manner in which colloidal changes take place may the characteristic protraction of chemical organic changes be referred." These words are prophetic of what is now recognised with regard to the relation of colloidal and living matter, whether healthy or diseased, and, so far as is known at present, the physico-chemical conditions necessary for life can be accurately summarised in the statement that *all life-processes take place in a colloid system*,[2] only those structures being considered as living which are at all times in a colloidal state.

According to J. Beatty,[3] all enzyme action, whether of hydrolysis, synthesis, oxidation, or reduction, can ultimately be traced to the addition or removal of hydrogen or hydroxyl radicles in hydrolysis or synthesis, and to the replacement of H by OH or OH by H in oxidation and reduction respectively. In the presence of a catalyst the speed of reaction may be increased, or its sphere of action limited, the latter being controlled by the colloidal nature of enzymes, whereby reactions are brought about as the result of surface adsorption.

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[1] Phil. Trans. 1861, **151**, 184.

[2] Wolfgang Ostwald. "Colloid Chemistry," New York, 1917.

[3] "The Method of Enzyme Action," London, 1917.

Many animal organs behave exactly like gels when immersed in water and swell enormously. This swelling is affected by the presence of small proportions of acids, alkalies or salts in the water. Thus, in the case of gelatin, fibrin and egg-albumin, acid solutions of moderate concentration greatly increase the amount of swelling and the amount of water absorbed by the organic substance. This is due to the presence of free hydrogen ions. On the other hand, the addition of a suitable alkali or salt will reduce the swelling and restore the substance to its previous condition, by neutralising the excess of free hydrogen ions. If an excess of hydroxl ions be added in the attempt to reduce the swelling, the gel may be peptised and "dispersed." A typical glaucomatous state may be induced in sheep's eyes *in vitro* by immersing them in very dilute hydrochloric acid. The normal condition may be restored by the addition of ferric chloride or other appropriate salts. Precisely the same phenomena are observable with living tissues, both in health and disease, and any desired colloidal condition may be obtained in the latter by appropriate colloidal treatment. Thus, the administration of salt has been successfully employed in the treatment of nephritis and œdema.[4] The extensive use of salines solutions in various stages of collapse has long been practised in all civilised countries, and its success is due to the action of these substances on the colloidal serum. Such salts prevent the swelling and coagulating effects of the acids formed in the diseased tissues, just as they decrease the effect of other acids, or effect the precipitation of certain colloids *in vitro*.

Inflammation is also a colloidal phenomenon, and is brought about by precisely similar conditions in the living subject, and in artificially prepared plates of non-living materials.[5] It is easy, for example, to produce "artificial flea bites" by pricking a piece of gelatin with a needle dipped in formic acid and then placing the gelatin in water.[6] The remedy—injecting into the swollen portion sufficient alkali to neutralise the acid—is as efficient as when this method is applied to a real bite. The complete comparison of these "bites" with the phenomena observed when a flea bites the human subject is, however, a very difficult matter.

The unknown substance which produces goitre[7] is most probably colloidal in nature. Hence, from one point of view, therapeutics is largely concerned with a study of the formation of colloids which are abnormal in the sense that they do not occur in the natural processes of a healthy body, but which—when regarded as colloids—are no more unusual than the coagulation of a highly dispersed sol or the peptization of a coarser gel. The chief difficulty in the way of experiment or treatment is that in one case conditions are severely restricted owing to the fact that the colloids form part of a living organism.

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[4] M. H. Fischer, *Œdema and Nephritis*, New York, 1915.

[5] A. Oswald, *Zeitsch. f. exp. Pathol. u. Therapie*, **8**, 226, 1910; *Koll. Zeit.* **9**, 251 (1911).

[6] M. H. Fischer, *Œdema and Nephritis*, New York, 1915, pp. 199, 602.

[7] E. Bircher, *Ergebnisse der Chirurge u. Orthopædie*, **5**, 133; *Zeits. f. exp., Pathol.* **9**, etc.

Many of the recognised methods of treating disease are efforts made with a view to altering the colloidal state of some portion of the patient's body, such as the reduction of a swelling by the dehydration of an unduly hydrated gel or varying the amount of dispersion of the colloidal particles in another part of the system. Thus, it is now quite recognised that many of the most familiar medicines are crude preparations of a colloidal character in which the action of the essential ingredient has been largely obscured by the presence of adventitious substances, some of which possess undesirable or even toxic properties. The digestive disturbances caused by the administration of iron compounds, the headaches which accompany the administration of quinine, and the pain resulting from the use of silver compounds are well known examples of the interference of some subsidiary ingredient of an otherwise useful therapeutic agent.

Many attempts have been made to avoid these complications. In some instances, remarkable results have followed the use of extremely dilute (*i.e.*, fully ionised) solutions; other investigators have sought to eliminate the disturbing elements and to produce purer medicines, and others again have endeavoured to counteract the irritants by using two or more drugs in combination. Each of these methods has resulted in a certain amount of progress. For many years, however, the essentially colloidal character of the recognised remedies was overlooked, and the fact was not realised that before a drug can exert its full therapeutic action it must be converted into the colloidal state.

One of the earliest to appreciate the importance of using therapeutic agents in a colloidal state was the late Henry Crookes who, in 1911, after making protracted experiments, found a means of producing stable preparations of colloidal silver, copper, iron and mercury which were not precipitated by saline solutions. To these he gave the name "Collosols." Since that time, stable preparations of colloidal solutions of sulphur, iodine and manganese as well as those of a much more complex character including some of the alkaloids cocaine, etc., have been used extensively by leading medical practitioners with wholly satisfactory results. The use of unstable colloidal sols has, on the contrary, been far from satisfactory and has led to serious misconceptions as to the value of remedies in the colloidal state.

Owing to their condition, stable colloidal sols behave in a manner quite different from other synthetic medicines. The latter—even when dissociated—contains two distinct groups of substances, one positive and the other negative. So far as is at present known, a diseased organism is deficient in either positive or negative ions, or it has an excess of one of these kinds of ion and is unable to get rid of it. The former case is much more common than the latter. The natural remedy is the presentation of further ions of such a character as to make good the deficiency or to remove the excess. If solutions of chemical compounds of a crystalline nature are administered they must first be dissociated and the requisite ions will then be available for use. The action of the ions which are opposite in character to those required by the body may be either disadvantageous or neutral, but as their presence is accidental, if it could be avoided it would clearly be to the benefit of the patient.

By the use of certain colloidal preparations it is possible to attain this desideratum and to restore the organism to its normal state of ionisation in a relatively simple manner, without the complexities caused by the presence of unwanted ions. Thus, an anæmic patient will be assisted by the administration of iron in a form in which the amount of hæmoglobin in the system can be increased, but the administration of excessive doses of an unsuitable compound of iron will be useless for this purpose and will be detrimental in other ways, such as disturbing the digestive functions. The introduction of a soluble salt of iron into the serum will not necessarily increase the amount of hæmoglobin, though the organism has a remarkable power of utilising apparently unsuitable materials. Briefly, it does this by first extracting some of the required agent (as when the gastric juices dissolve the ferrous carbonate in a Blaud's pill), then, as the solution is usually very dilute, the agent becomes dissociated and the required ions are utilised by the organism and unnecessary ones being eventually discharged. It is obvious, however, that if a therapeutic agent is presented in the form in which it is required—which in the case of many substances is in the state of a colloidal sol—much unnecessary waste of vital energy is avoided, the specific action is more direct and efficient, a loss of time which must occur before the body has effected the preliminary conversion is saved, and troublesome, or even dangerous, side reactions are avoided.

The difference between the action of many medicines and the corresponding colloidal sols is remarkable. Thus, a 2 per cent. solution of iodine in either alcohol or potassium iodide stains the skin badly, and when administered internally is very liable to give rise to iodism. This is avoided by using a colloidal solution of iodine of the same or even greater concentration.

It is, of course, of the utmost importance that colloidal medicines shall be in a suitable state. Colloidal gels are of value in certain cases, but far more important are the colloidal sols. The latter are difficult to prepare in a stable form, and unless they are resistant to the action of the electrolytes normally present in serum they are useless for therapeutic purposes, as they would be precipitated before they could effect the desired purpose. Fortunately, it is easy to test the stability of a colloidal sol by examining it under the ultra-microscope after mixing it with various solutions in respect of which its stability may be questioned.

Colloidal medicines which have not been prepared in a proper manner also decompose on long standing. They then show a precipitate, the amount of which increases as the decomposition continues. Properly-prepared, stabilised colloidal sols are quite permanent. The writer has kept collosol iodine and collosol silver for two years at a temperature of 70°F., and on examining them under the ultramicroscope at the end of this period could observe no difference in activity as compared with that of freshly prepared collosol. On the other hand, a colloidal silver prepared by Bredig's method was feeble after four weeks and inert after seven weeks when kept under the same conditions. The existence of the agent in a suitable and permanent colloidal state is, therefore, essential.

In a general sense, sols may be stabilised by preparing them in the presence of an emulsoid, such as gelatin, which appears to surround the particles of sol and renders them less sensitive to salt solutions. Such protected sols may be evaporated to dryness and the residue—which is usually in the form of dark scales—can be brought back into a state of colloidal sols by the addition of water. If such "dried hydrosols" have been prepared from exceptionally pure materials and with unusual care and skill, they form, when dropped into water, colloidal solutions in which the sol has the same properties as those previous to evaporation. The present writer has found, however, that the commercial "dried hydrosols" which he has examined (which are sold under a variety of fancy names) have seldom been prepared with sufficient skill, and therefore do not yield "solutions" of the same power and therapeutic value as can be obtained without evaporation; the advantage of portability gained by the production of the dried product is more than counterbalanced by the uncertainty as to the strength and activity of the sols produced by adding tap water to them in vessels which have not been specially prepared for the purpose, and by their instability in the presence of salts. For these reasons, he does not favour the use of the dried preparations, except in cases where it is impossible to use those which have not been dried. Moreover, the stability of colloidal sols depends more on the mode of preparation than on the presence of a stabilising agent. Hence, excellent therapeutic results have been obtained with some colloids to which no protective has been added.

It was realised about ten years ago that colloidal sols of certain metals inhibit the growth of all known bacteria, and it has since been found that they are harmless to the tissues. For this reason the use of colloidal sols has an enormous field of usefulness. They can be administered orally or injected in any desired quantities without any risk of toxication or undue shock to the system.

The normal effects of colloidal sols on the blood stream is shown by the following experiment[8] :—

"A rabbit, weighing 1 kilo., was injected with 2 c.c. of collosol hydrargyrum in the auricular vein on the 14th of the month; on the 16th of the same month 3 c.c. more were injected. There was no local reaction, no bad symptoms; the rabbit did not go off its food. On the 16th it was killed by the usual method, viz., chloroform. The arterial system of head and neck were perfused with normal saline solution (the eyeballs were very tense). The cerebro-spinal fluid was extracted under somewhat increased pressure. A post-mortem examination of the rabbit showed no change. A sample of the urine was taken, and also a slice of the cerebral cortex, which was emulsified and allowed to settle.

"These three fluids were examined under the ultra-microscope, and the observations made were as follows :—

"The cerebro-spinal fluid showed a distinct cone, with many colloidal particles having a strong Brownian movement.

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[8] H. Crookes, "Recent Work on Metallic Colloids," *Journal of Chemical Technology*, July, 1915.

"The supernatant fluid from emulsion of the brain section showed the cone distinctly with occasional colloidal particles.

"The sediment stirred up with sterile water showed many coarse particles and a large number of colloidal particles, many having a green colour with strong Brownian movement.

"The urine showed a strong cone of light, no coarse particles, but a very large number of colloidal particles with a strong Brownian movement.

"These results prove that when 'collosols' are given by intravenous injections they permeate throughout the entire system, and that the unutilised or excess portion passes off with the urine."

The toxicity of colloidal substances depends largely on the manner in which they have been prepared and on the presence of associated substances. If sufficiently pure and suitably stabilised, many of them appear to be wholly non-toxic ; but impure or unstable preparations are toxic in proportion to their instability or to the adventitious substances present. Colloids such as mercury and arsenic, which are not normal constituents of the body cells, are liable to be toxic in nerve tissue[9] ; but if wholly in the sol state and properly sterilised, their toxic power is insignificant, and they can be injected intravenously or intra-muscularly with impunity, and with extraordinarily good results.

The first effect of injecting a suitable sol into the serum is to break up any large protein particles into small ones, thereby increasing their surface area and activity. After this, the various colloidal materials react, forming the substances required to effect the necessary readjustment of the serum and to restore it and the tissues to a state of normality. When parasites are present, the protein particles in the serum appear to attack them by some form of surface action, the nature of which is not clearly understood though it appears to be analogous to the action of staining by aniline dyes. Hence, the importance of these protein particles being as small as possible and of the metallic colloids in stimulating and accelerating their destructive action.

Expressed in more physico-chemical terms, the blood stream of man, like the contents of the cells of all living organisms, is a peculiarly sensitive fluid. A slight alteration in the fluids which surround it (in adjacent tissues) and even in its own contents brings about changes which are so great as to produce illness or even death.

Lord Lister[10] showed that the introduction of septic material into the blood gives rise to the development of large cells or flocculent matter which partially decompose with the formation of a thick yellow fluid of a highly toxic character.

Blood serum is, in fact, a typical emulsoid colloid though it is characterised by so high a degree of dispersion that it shows the Tyndall cone only feebly.[11] Equally significant is Hardy's observation[12] that protein is electro-negative in an alkaline solution and electropositive in an acid one. The blood serum in normal health is

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[9] J. E. R. McDonagh, *Brit. Med. Journal*, May 19, 1917, p. 648.

[10] Collected Papers (1909), ii. 541.

[11] Winterstein, *Hand. C. d. vergl. Physiologie I*, 415.

[12] *J. Physiol.*, 1899, 24, 288.

alkaline, and has a prevailing hydroxyl concentration. In many diseases this alkalinity is reduced with consequent toxic symptoms. To restore normality it is therefore necessary to reduce the concentration of the hydrogen ions or to increase that of the hydroxyl ions. The choice between these must depend on other circumstances, and especially on the relation of the relative concentrations of the serum of the patient in disease and in health.

An interesting instance of the importance of a knowledge of the properties of colloids in the treatment of disease occurs in anæmia. In the simplest case this disease is due to a deficiency of iron in the hæmoglobin in the blood stream. Hæmoglobin is electro-positive, and to increase its amount without disturbing the general characteristics of the serum, any iron compound administered must also be electro-positive when it enters the blood stream. For this reason iron carbonate and hydroxide are useful whilst such compounds as ferric chloride which are electro-negative and act as coagulants should be avoided. The objection to iron carbonate and hydroxide lies in the fact that they are usually converted into ferric chloride or analogous compounds by the gastric juices and so largely fail to reach their destination in a useful form.

Colloidal iron, on the contrary not being affected by these juices, is able to enter the blood stream in a satisfactory and therapeutically active form.

The retention of an unnecessary amount of any substance in the blood stream or tissues tends to induce toxicity. The extremely minute size of the particles in the colloidal sols is such that they pass readily through the tissues and the chances of their being improperly stored in the system are correspondingly[13] minimised. In view of the foregoing facts it is not surprising that colloids are coming more and more to the front in pharmacology[14], particularly those which approach the state of true solutions. A good example is seen in Fischer's work on œdema[15] in which he has shown that œdema results from the imbibition of water by certain colloids.

The choice of a colloidal sol suitable for a particular pathological condition must naturally depend on the cause of that condition. This can only be ascertained by trial, though certain broad conclusions may be reached with respect to the chemical behaviour of different substances. In the collodial state, however, many substances react entirely differently from what may be regarded as their normal behaviour. Thus, colloidal sulphur sometimes acts indirectly as an oxidizing agent and both metals and non-metals act in a manner which cannot be predicted on general chemical grounds.

The use of colloidal copper injected intravenously can aggravate boils if administered in large doses. In smaller quantities and injected intramuscularly, it has the opposite effect, but is far inferior to colloidal manganese for this purpose. Indeed, colloidal manganese

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[13] Sir J. J. Thomson (Royal Institution, March, 23rd, 1912) stated that one drop of a metallic collosol contains more than 1,000,000,000,000 particles of metal which cannot be detected by ordinary methods and pass readily through the pores of a filter.

[14] Porges, *Koll. Zeit.* 5, 301 (1909).

[15] *Das Odem*; *Eine Expt. u. theor. Untersuchg. d. Physiologie und Pathologie* (1910).

differs from all other remedies in that when it is used for the treatment of boils it is only very occasionally that fresh boils make their appearance during the treatment and these quickly subside without further trouble. Colloidal manganese appears to be particularly indicated in the treatment of staphylococcic infections.

Turning now to the specific effects of various colloidal substances, it should be noted that the following are all in the sol state and that they must (for reasons previously indicated) have been suitably stabilised.

All these colloidal sols are thin fluids containing the colloid in so finely suspended a condition that it passes readily through a filter.

Colloidal silver containing 0·05 per cent. of the metal in a colloidal form and not as a salt, is a clear, cherry-red liquid which has been used by C. E. A. McLeod with marked success in the following cases :—

By local application on septic and follicular tonsilitis ; Vincent's angina ; phlyctenular conjunctivitis ; gonorrhœal conjunctivitis ; spring catarrh ; impetigo contagiosus, acne of face and body ; septic ulcers of legs ; ringworm on body ; tinea versicolor ; soft sores ; suppurative appendicitis after operation (the wounds cleaned rapidly) ; pustular eczema of scalp and pubes ; chronic eczema of meatus of ear with recurrent boils and also chronic eczema of anterior nares ; offensive discharge in case of chronic suppuration in otitis media ; bromidrosis of feet and axillæ ; blind boils on neck. By injection : gonorrhœa and chronic cystitis (local), boils, epididymitis. It has also been injected intravenously in general blood infections, pneumonia, bronchitis and phthisis in doses of 15–45 minims, with marked success.

Sir James Cantlie has found it particularly effective in cases of sprue, dysentery, and intestinal troubles. The dose can be increased from one to two or more drachms twice or thrice daily without danger.

A. Legge Roe regards stable colloidal silver as a most useful preparation[16] in ophthalmic practice and particularly in cases of gonorrhœal ophthalmia, purulent ophthalmia of infants, infected ulcers of the cornea and hypopyon ulcer (tapping of the interior chamber and cautery and other operative procedures being now rarely required, whilst if perforation does occur it is smaller and more manageable), interstitial keratitis, blepharitis, dacryocystitis and burns and other wounds of the cornea.

T. H. Sanderson-Wells used it successfully intravenously in a case of[17] puerperal septicæmia, without any irritation of the kidneys and with no pigmentation of the skin. This physician has found that a series of intravenous injections each of collosol argentum every 48 hours produces no untoward effects and that recovery is rapid.

Sir Malcolm Morris has found that colloidal silver is free from the drawbacks of other preparations of silver, viz., the pain caused

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[16] *Brit. Med. Journ.*, Jan. 16, 1915.

[17] *Lancet*, Feb. 16, 1918.

and the discolouration of the skin[18]; instead of producing irritation it has, indeed, a distinctly soothing effect. It rapidly subdues inflammation and promotes the healing of lesions. He has had remarkable results in enlarged prostate with irritation of the bladder, in pruritis ani and perineal eczema, and in hæmorrhoids. It can be used in the form of suppositories while a solution is applied to the irritated skin. In bromidrosis in the axillæ and feet it quickly gives relief. It causes a rapid disappearance of warts. Being non-toxic, it can be given internally in urticaria and other forms of dermatitis which are suggestive of toxæmia. In such cases it is quickly beneficial.

In ophthalmology, colloid silver has now largely replaced silver nitrate as its use is free from pain and its action more direct.

J. Mark Howell has found colloidal silver beneficial for permanently[19] restoring the potency of the Eustachian tubes and for reducing nasopharyngeal catarrh.

Colloidal silver has also been used successfully in septic conditions of the mouth (including pyorrhœa alveolaris—Rigg's disease), throat (including tonsilitis and quinsies), ear (including Meniere's symptoms and closure to Valsava's inflation) and in generalized septicæmia, leucorrhœa, cystitis, whooping cough, and shingles. Tests made at King's College show that colloidal silver has an inhibitive effect on bacteria equivalent to mercuric chloride, but is non-toxic, non-irritant and harmless to the host.[19a]

A preparation of colloidal silver which is opaque to X-rays has proved invaluable in certain diagnoses.

Colloidal mercury. The curiously different action of mercury salts according as they are given in small or large doses and in a readily or difficult soluble form have long puzzled pharmacologists It has been generally understood that their action is antiseptic and bactericidal, but according to some of the best known authorities, the chief action of mercury is to increase the natural resistance of the body to disease. The chief disadvantage of the less soluble mercury salts, such as calomel, is their delayed and irregular absorption, with subsequent undesirable results. The soluble mercury salts, on the contrary, are dangerous on account of their high toxicity. With colloidal mercury, the diffusion is extremely rapid and chemical affinity low. Hence the toxicity of colloidal mercury (1—2,000) is so low that doses of two teaspoonfuls may be taken twice daily or intravenous injections of 30 c.c. may be given with impunity.

Colloidal mercury has cured persistently relapsing malaria in a few days.[20]

Some of the colloidal preparations of mercury on the market are not suitable for oral administration, but must be injected intramuscularly. Colloidal mercury is chiefly used in syphilis.

Colloidal iron, according to Lyn Dimond, killed within six minutes, such organisms as bacillus typhosus, bacillus coli communis and various pyogenic cocci. The solutions seem to have

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[18] *Brit. Med. Journ.*, May 12, 1917.

[19] *Brit. Med. Journ.*, Dec. 15, 1917.

[19a] *Lancet* (1914), p.

[20] G. Cremonese, *Gazz. d. osp.* (1918) 39, 427.

a definite elective bactericidal action upon such catarrh-causing organisms as pneumococcus and various strains of the micrococcus catarrhalis. Rapid relief followed the topical application of the solution in cases of catarrh of the nose, larynx or pharynx. Colloidal iron is also used, by subcutaneous intramuscular and intravenous injection, in cases of extreme chlorosis, anæmia, erysipelas and cellulitis.

Iron is almost the only metal found in the animal organism which is also obtainable in a colloidal state in the presence of water. The significance of this fact has not yet been sufficiently recognised. In the serum, the iron is probably present as a protein compound the precise constitution of which has not yet been determined. The total iron content of the normal body does not exceed 37 grains, and although several organic compounds of iron have been recommended they are by no means satisfactory, being either too feeble in action or too readily decomposed *in corpore* and so rendered useless. Inorganic compounds of iron are held by many practitioners to be the most efficient in what they consider to be the only true test of the value of an iron preparation, *i.e.*, an increase of hæmoglobin in the blood. The administration of iron in the form of a colloidal sol appears to be a simple means of increasing the amount of the protein compound in the serum, as this form of iron, when administered orally, is rapidly diffused in the stomach and yet it is not absorbed in individual positions. It is found that the amino-acids formed during the process of digestion are readily able to absorb into their complex molecule a large proportion of the iron administered in the colloidal form and from it to effect the synthesis of hæmoglobin. This is in marked contrast to the behaviour of the carbonate, hydroxide and chloride of iron usually administered.

Colloidal antimony has been used in conjunction with manganese with extremely good results in gonococcic infections. In India it has given very satisfactory results in Kala-azar, its administration in this disease being accompanied with less risk than that of arsenic.

Colloidal manganese has been used with remarkable and surprising results in the treatment of coccogenic skin disease, including deep abscesses, boils and deep-seated impetigo. In superficial impetigo, chronic seborrhœic eczema and acute folliculitis it is of little value when used alone, but gives excellent results when employed in conjunction with intramine. The rapidity of its action[21] combined with the saving of dressings render the use of this form of manganese very attractive in deep-seated coccogenic lesions. It is usually injected intra-muscularly in amounts of 3 c.c. every few days. In most cases one injection is sufficient.

J. E. R. McDonagh[22] has also used intravenous injections of 33 c.c. of colloidal manganese with excellent results in the treatment of poisoning by mustard gas (dichlorethyl sulphide) and other cases of sulphur poisoning.

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[21] J. E. R. McDonagh, *Medical Press and Circular*, Dec. 5, 1917; Sir Malcolm Morris, *Brit. Med. Journ.*, Apl. 20, 1918

Medical World (1918), p. 137

Colloidal copper is useful in the treatment of boils, though it is inferior to manganese for this purpose. In malignant diseases, the intra-muscular injection of copper has proved highly beneficial, the metal having been shown to be present in the growth within 24 hours after injection. Copper is known to have a strong inhibitive action on low forms of life. Herschel, de Gres and others have stated that colloidal copper exerts an inhibiting action on all cell metabolism. In this connexion it is important to note that cases of cancer in which copper can be shown to be present in the growth are certainly the ones which are the most amenable to treatment. The difficulty lies in causing the copper to penetrate the periphery of the cancer. Pessaries of colloidal copper in glyco-gelatin have proved serviceable for uterine fibroids.

Colloidal arsenic (0·2 %) in doses of 2 c.c. has an extraordinary effect in pernicious anæmia and herpes deformans. The simultaneous presence of a liquid or colloidal protein appears to be essential to the proper reaction of arsenic. Thus, salvarsan *per se* has no action on the spirochæta pallida, which can move readily for some hours in a solution of salvarsan. Yet the introduction of a little serum or digested protein will cause their immediate death. The elimination of arsenic from the system is usually a matter of difficulty, but in the colloidal form its low toxicity combined with the small dosage reduce the risk of its retention to a minimum.

Colloid palladium oxide has been applied successfully in the treatment of obesity by injecting it hypodermically into the fatty areas.[23]

Colloidal palladium sol has proved of value in gonorrhea.

Colloidal nickel has been used in meningitis.

Iodine was discovered in 1811. In the form of an alcoholic solution it soon became popular, but was afterwards neglected for many years. More recently, it has been brought prominently forward and at the present time[24] it is almost the only chemical antiseptic, except alcohol, employed by a large number of British surgeons.

Colloidal iodine may be obtained in three forms: (i.) aqueous, (ii.) oil and (iii.) paste or ointment. The aqueous colloid (1 in 500) contains the element in its most active form, and is suitable for administration in all cases in which iodine or an iodide is indicated. Its action is more gradual than that of a solution of iodine, but more certain than that of iodides, and there is complete avoidance of "iodism" and nausea. The whole of the colloidal iodine is absorbed, whereas 85 per cent. or more of the ordinary iodides administered are excreted within 24 hours.

When injected intravenously, the action of colloidal iodine is more rapid, and as much as 300 c.c. has been injected with impunity in cases of pyæmia, and also to effect a softening of fibrous tissue, thus showing its absolute nontoxicity. *Per se* colloidal iodine is only slightly parasitotropic and bacteriotropic, but micro-

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[23] M. Kauffman, Münch. Mediz. Wochenschr., 525, 1913.

[24] Sir R. J. Godlee, Lord Lister (1917), 158.

organisms are very greatly influenced by its action and the effect of a subsequently administered remedy is greatly increased.

Colloidal iodine is also indicated in syphilis by prior injection, and also by internal administration, and in cancer by intravenous injection.

In rheumatism, a piece of flannel soaked in colloidal iodine, attached to the positive pole of a battery and applied as near as possible to the affected area has been successful. It has also been used beneficially as a spray in bronchial and nasal catarrh and internally in recovery from alcoholism.

Colloidal iodine oil (3 per cent.) is very useful for eczema and other forms of affections and abnormal conditions of the skin. On application, the iodine particles penetrate the pores of the skin without staining the epidermis, the latter being kept supple and soft by the hydrocarbon oil in which the colloidal iodine is exhibited and stabilised. Thus, the staining and hardening effects of alcoholic and other solutions of iodine are avoided.

In some cases[25] of bad chilblains, colloidal iodine oil was rubbed in four times a day; every trace of the condition disappeared in four days. Equally valuable is this colloid in severe cases of trench feet with ulceration and in the many cases of Charcot's bedsores which are so troublesome a complication of spinal injuries in military hospitals. In the earlier inflammatory stages of lupus erythematosus, before atrophy has supervened, it is far more suitable than the ordinary form of the drug because of the absence of irritation. Similarly, it is to be preferred for internal administration in the later stage of syphilis, because there need be no fear of iodism. Parasitic affections, again, show a striking amenability to this remedy. In a case of dhobie's itch (in which the disease had spread from the groin and invaded the trunk, legs and arms) under the quite painless application of colloidal iodine oil, the extensive lesions all cleared up in three weeks; with ordinary remedies the case would undoubtedly have been more protracted, and the treatment would inevitably have put the patient to a good deal of pain.

Colloidal sulphur (1 per cent.) has proved invaluable in cases where there is a deficiency of this element in the system. The value of sulphur has long been known, but the forms in which it is usually administered are crude. It has been necessary to employ excessively large doses of an insoluble form of sulphur or to administer "Harrogate water" or some equivalent and unpleasant preparation of hydrogen sulphide. There is little doubt that an insufficient amount of available sulphur in the system impairs the action of the liver, with consequent production of intestinal poisoning (constipation, headache, arthritis, etc.).

Colloidal sulphur is extremely active, readily combines with protein and is entirely absorbed in the stomach. The products of this combination are rapidly taken into circulation and those parts of the organism for which sulphur is necessary are thus supplied. Ordinary sulphur is not absorbed in the stomach at all, and passes practically unchanged into the intestines.

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[25] Sir Malcolm Morris, *Brit. Med. Journ.*, May 12, 1917.

In many cases of rheumatism and neuritis and even in "arthritis deformans" relief has been rapidly obtained by its internal administration. In acute rheumatism, the intravenous injection of colloidal sulphur has proved beneficial. Colloidal sulphur has also been found to increase the tolerance to mercury in syphilis when administered orally, and has given relief in some cases of cancer when injected subcutaneously.

Colloidal sulphur baths have been of service in rheumatic conditions and skin affections. The colloidal sulphur content in the bath is far greater than that of natural sulphur water, and as the bath contains no impurities or free sulphuretted hydrogen it is free from the many objections associated with the use of natural sulphur waters.

Sir Malcolm Morris has found that among the affections in which colloidal[26] sulphur is beneficial are various forms of acne (including acne rosacea and seborrhœa), generalised dermatitis, acute psoriasis and painful fibrositis, whether of connective tissue, of muscle, or of joints. Baths medicated with this colloid are, in his experience, at once soothing and quickly curative.

Colloidal alumina (gel)[27] has shown excellent astringent effects in various kinds of diarrhœa and is less toxic than the bismuth compounds usually administered in such cases.

Colloidal quinine (sol) appears to be free from the chief disadvantages of quinine salts, particularly in malaria. The fact that it is not so readily lost in the excretions is important as Hartmann and Zila[28] have found that less than one-third of the quinine salts ordinarily administered are retained by the body and that the amount found in the blood after oral administration did not exceed 3 per cent. of the dose taken. Further investigations are now being made on this colloid.

Production of Colloidal Remedies.

The production of colloidal solutions which are sufficiently stable to be used in medicine is largely a secret, few of the processes having been protected by Letters Patent. No single method either of peptisation or stabilisation is suitable for all the various sols required, and as prolonged and costly investigations are required before a really stable sol of high therapeutic value can be offered to the medical profession it is only natural that the manufacturers should keep the information to themselves. The general methods by which colloidal sols can be produced and rendered more or less stable are well known, and as a still larger number of substances is reduced to this state the number of methods used in their production will also increase. Of the methods which have been disclosed, the following are the most important, but it should be observed that none of these Patent Specifications have been taken out by the manufacturers of commercial available colloids used in medicine in this country and that they do not describe the methods used in producing the highly stable colloids which have yielded the results mentioned in the present report :—

No. 12,037/1911. F. Arledter, Preparation of sols.

No. 1219/1912. A. Dering, Preparation of Colloidal Mercury.

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[26] *Ibid.*

[27] Eng. Pat. 104, 609.

[28] *Arch. f. exper. Path. u. Pharmakol.* 1918, **83**, 221.

No. 11,771/1912. E. Podszus, Preparation of sols.

No. 14,235/1912. B. Schwerin, Preparation of sols.

No. 29,049/1912. Ges. f. Elektro-Osmose, Preparation of sols.

No. 7238/1913. Aktiebol : Kolloid Preparation of Colloidal Sulphur.

No. 9237/1914. Ges. f. Elektro-Osmose, Preparation of Colloidal Silica.

No. 9261/1914. Ges. f. Elektro-Osmose, Preparation of Metal sols with silica.

No. 15,267/1914. Ges. f. Elektro-Osmose, Preparation of Metal sols.

No. 15,127/1915. Soc. Chem. Ind. Basle, Preparation of Colloidal Copper.

No. 104,609 (1917). Monneron & Guye, Preparation of Colloidal Alumina gel.

Colloids and Synthetic Compounds.

There is no necessary incompatibility between colloidal sols and synthetic compounds which are not regarded as being in the colloidal state. Each of these groups of remedies has its own sphere of usefulness, and some of the synthetic drugs are more colloidal than is generally supposed (see section on Dyes in the 1917 B. A. Report on Colloids). In view, however, of the large amount of work which has been done by Ehrlich and others in the preparation of synthetic compounds of arsenic and other metalloids it appears desirable to draw attention to the following facts :—

The action of synthetic compounds is usually due to their high molecular weight and often to the presence of ortho-amino groups. In some cases, a metal or metalloid is separated in colloidal sol form in the blood, the remainder of the drug merely serving as a vehicle. In others, the whole compound acts as a reducing or oxidizing agent. It may or may not be a coincidence that the most effective therapeutic reducing agents contain a metalloid (such as sulphur or iodine) whilst the most effective oxidizing agents contain a metal.

In this connexion it is particularly interesting to compare the almost non-toxic colloidal metals and metalloids with that of the well known salvarsans and their compounds containing phosphorus (galyl), platinum, gold, copper or silver. According to Kolle[29] the following doses are toxic to syphilitic rabbits ; smaller doses are toxic to the human subject :—

	Toxic Dose grms.	*Tolerated Dose grms.*
Salvarsan	0·125	0·1
Neo-Salvarsan	0·25—0·3	0·2
Hexamino-Salvarsan	—	0·15
Galyl	0·125	0·1
Bismethyl-Standard	0·28	0·22
Dichlorarsalyte	0·25	0·2
Dibromarsalyte	0·36	0·3 (?)
Diiodarsalyte	—	—
Copper Salvarsan K_3	0·04	0·035
Platinum Salvarsan	0·07	0·05
Gold Salvarsan	0·03	0·02
Silver Salvarsan	0·3	0·125

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[29] Deutsche Med.-Wochenschr. 1918, **44**, 11 1 ,.11727

It is well known that most of these salvarsan compounds deteriorate and become more toxic on exposure to air. Thus within an hour the toxicity of neo-salvarsan increases 3 to 6 fold, the arsalytes within 24 hours increase 2½ times in toxicity, and the same applies to the metallic salvarsan compounds. Colloidal metal sols do not become toxic, even on prolonged exposure.

Hexamino-salvarsan in the moderate dose of 0·1 grm. has produced grave symptoms and even fatal results which led to its discontinuance. Gold and platinum salvarsan possess too great a toxicity for therapeutic use in man. Silver salvarsan, on the contrary, is 2 to 3 times as potent as old salvarsan and it is by far the most active form of salvarsan for destroying the spirochætes in rabbit syphilis and in curing the lesions. It has likewise been used with excellent results in man in doses of 0·2 to 0·4 grm. Kolle does not state the exact chemical constitution of this substance, but it is highly probable that much of the silver is in a colloidal state, especially as he found that colloidal silver (collargol) alone in doses of 0·03 grms. per kilo caused the rapid disappearance of spirochætes in the rabbit.

Colloids and Physiological Extracts.

The remarkable results which have followed the administration of certain physiological extracts (thyroid, pituitary, etc.) appear to be largely due to the presence, in them, of sulphur or an equivalent element in a suitable form.

The substitution of carefully prepared colloidal sols for such extracts largely avoids the risks of irregular and uncertain composition which inevitably accompany the use of such extracts.

Colloids in Veterinary Practice.

Colloidal silver and sulphur have yielded excellent results in veterinary practice, the former in the treatment of swellings, sprains, bruises, wounds, sores, rheumatism, thrush in the feet, fistula, various skin diseases and inflammation of the eyes, and the latter for cases where a deficiency of sulphur is indicated.

The Limitations of Colloids.

The selection and use of colloidal sols requires the same care and skill as the administration of any other remedies, but with the great advantage of being made specific and rational rather than empiric.

A word of warning may be expressed as to the use of unstable colloids in medicine. A number of colloidal preparations—particularly of silver and iodine—has been placed on the market which have not been properly stabilised. The use of these preparations has been accompanied by disappointing results, as it is essential (as previously mentioned) that the colloids exhibited should be stable in the presence of serum and saline solutions.

The failure of numerous colloidal sols of German (and some of British) origin created, in some minds, a prejudice against all colloidal remedies. The failures have been found, in every case examined, to have been wholly due to the method of preparation. Thus, it has been found that colloidal metals prepared by Bredig's method (dispersion by an electric arc with poles of the desired metal) are unsuitable for medicinal purposes, as they are not only unstable in themselves, but are rapidly decomposed by electrolytes present in the human organism. Where properly stabilised colloidal sols are employed they are as reliable as any of the preparations in the Pharmacopœia.

It should be observed that some so-called synthetic remedies are found to be colloidal sols, though this is not generally known. This has led to some curious misstatements in regard to the relative therapeutic values of colloids and synthetic drugs.

Owing to the impossibility of repressing all side reactions in making experiments on the living subject, pharmacology and chemotherapy are among the most inexact of sciences. Yet the success which has attended investigations on the use of colloids as remedial agents is so great as to call for the sympathetic interest of all who can appreciate what has been accomplished, and affords a basis of hope that further developments will be still more beneficial to suffering humanity. It is highly probable that serum and vaccine therapy will ultimately be resolved into questions of colloidal chemistry, but in the meantime the use of colloidal solutions of certain elements appears to offer a means whereby the various colloids can be accurately prepared and administered with a higher degree of efficiency than is possible with some of the more complex synthetic compounds at present in use.

The ever-increasing use of colloidal sols in military and private practice is a certain indication of their value, and among the indirect results of the World War, the facilities which it has given for the investigation of many hitherto obscure problems of disease and the opportunities which it has afforded for ascertaining the value and *rationale* of many new remedies, will be among the blessings of a catastrophe which is, otherwise, too awful to contemplate.

Literature.

The literature on the applications of colloid chemistry to biology and physiology,[30] and in the "Kolloidchemie Beihefte," "Kolloid Zeitschrift," and "Biochemische Zeitschrift" should be consulted.

Papers on the application of colloids in therapeutics also appear frequently in the "British Medical Journal," "The Practitioner," "The Lancet," and various foreign medical journals. Notwithstanding the voluminous literature on the general subject a vast amount of research into details remains unexplored. In the prosecution of further work, it is well to recall the words of a former president to the effect that "Medicine is no unworthy ally of the British Association and while her practice is ever more and more based on Science, the ceaseless efforts of her votaries are ever largely adding to the sum of abstract knowledge."[31]

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[30] See "First Report on Colloidal Chemistry," British Association, 1917, pp. 85, 86. Also present Report, pp. 117–154.

[31] Sir J. Lister, "Interdependence of Science and the Healing Art." Presidential address to Brit. Assn., 1896.

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