

## THE ELECTRICAL THEORY OF DYEING.

BY PROFESSOR W. W. HALDANE GEE, B.Sc., M.Sc.TECH., AND  
WILLIAM HARRISON, ASSOC.M.S.T.

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Dr. J. C. CAIN in the Chair.)

### PART I.

The literature relating to the causes of dyeing reveals great differences of opinion as to the physical and chemical phenomena involved. The main theories are summarised\* in Dreaper's *Chemistry and Physics of Dyeing*, where we read: "Even to-day (September, 1906), with our extended knowledge, we are ignorant of the exact and complete causes which bring about many of the complicated effects which are classified under the comprehensive term, dyeing." To the theories discussed by Dreaper must now be added an electrical one. Its basis is that any two bodies placed in contact are oppositely electrified. In the case of tinctorial chemistry one of the bodies is a non-conducting solid and the other a liquid. There does not seem to be any direct method of obtaining the value of the potential difference between such bodies. We can only avail ourselves of the classic theory of von Helmholtz, which enables the potential difference between a liquid and a porous diaphragm to be deduced.

This may be done in four different ways:—

1. By measuring the rate of flow of the liquid through a diaphragm of the substance under electrical stress (electrical endosmose.)
2. By measuring the mechanical pressure obtained by electrical endosmose.
3. Determining the speed of the solid in the form of small particles, when immersed in the liquid, under electrical stress.
4. Finding the difference of electrical pressure between the two sides of a diaphragm when the liquid is filtered under mechanical pressure.

If  $e$  be the contact difference of pressure between the solid and the liquid we have † (not considering Method 2 at present):—

Method 1—

$$e = \frac{4\pi}{K} \cdot \frac{\eta}{q} \cdot \frac{V}{H}.$$

Method 3—

$$e = \frac{4\pi}{K} \cdot \eta \cdot \frac{V}{H}.$$

\* Also see W. C. M. Lewis, "On the Application of Adsorption to the Theory of Dyeing," *Phil. Mag.*, vol. 15, p. 499, 1908.

† See Helmholtz, *Ann. d. Ph. u. Ch.*, 7, p. 337, 1879; *Memoirs*, London Physical Society, 1888; Lamb, *B.A. Rep.*, p. 495, 1887; Burton, *Phil. Mag.*, 11, p. 425, 1906; Perrin, *Journal de Chimie Physique*, 11, p. 606, 1904.

## Method 4—

$$e = \frac{4\pi}{K} \cdot \frac{\eta}{\rho} \cdot \frac{E}{p};$$

where—

- K is the dielectric constant ;  
 $\eta$  coefficient of viscosity ;  
 V rate of liquid flow or speed of particle  
 $q$  equivalent cross-section of the pores ;  
 H strength of the electrical field ;  
 E e.m.f. produced ;  
 $p$  mechanical pressure ;  
 $\rho$  specific electrical resistance.

USE OF METHOD 3.—This is the most suitable for absolute measurements when the particles are in colloidal solution. It is especially useful in finding the electrical sign of the charged particle by observation of the direction of movement between the electrodes.

The observations may be made by the method of Hardy, using a U-tube

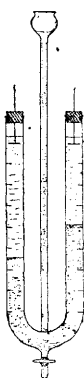


FIG. 1.

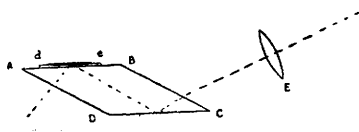


FIG. 2.

length of each limb 25 cms., and diameter of tube 2 cms.) of the form shown in Fig. 1. The colloidal liquid is introduced in the bend of the tube, so that pure water is in the upper parts of the limbs of the tubes. The difference of levels of the colloidal solution, after the electrodes have been connected with the supply voltage for a definite time, is read on the millimetre scales on the tubes. (For further details see Burton, *Phil. Mag.*, 11, p. 425, 1906.)

Instead of the method of Hardy, the direct movement of the particles, observed by the method of dark-ground illumination,\* is sometimes more convenient. The reflecting prism ABCD, each face 4 cms., and height 2 cms. (Fig. 2), which we have used was provided by Messrs. Chance Bros. Light from a Nernst lamp was projected on the rhomb by a lens E, and then was twice totally reflected. The liquid is placed in a cell *d e* made of a slip of glass of the same index of refraction as the prism. The details of the cell are shown in Fig. 3. The copper strips, Cu, and the platinum electrodes, Pt, are cemented to the slip. The liquid is enclosed by an ordinary circular

\* See Cotton and Mouton, *Les Ultramicroscopes*.

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cover-glass. It is necessary to place cedar-wood oil between the lower surface of the cell and the top of the prism.

The nature of the electrical charge of a number of substances has been ascertained either by the U-tube method or by the direct use of the microscope. The results are shown below :—

TABLE I.

A. *Substances giving Positively-charged Particles.*

1. Night-blue Base.—Prepared from the hydrochloride by precipitation with ammonia and washing the precipitate free from chloride. It was dried at  $110^{\circ}$  C., and then 0.1 gm. was dissolved per 100 c.c. of pure alcohol. The solution was filtered and then diluted to a 10 per cent. solution of alcohol. This strength was used in all cases marked with \*. The experiment was performed in a U-tube.

2. Spirit-blue Base.\*—Prepared from the hydrochloride by repeated boiling with ammonia and then washed and treated as above. U-tube used.

3. Crystal-violet Base.\*—Prepared like No. 1. U-tube.

4. Aluminium Hydrate.—Commercial sample, soluble in caustic soda. Washed and ground up with water. Examined by microscope.

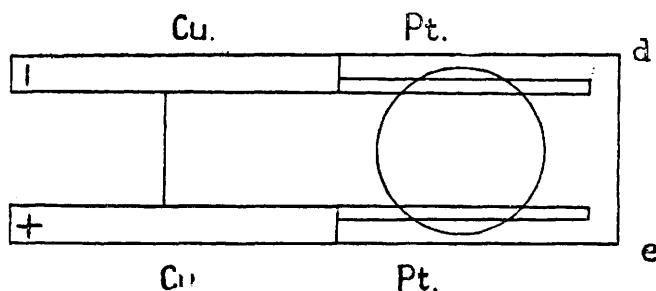


FIG. 3.

5. Magnesium Hydrate.—Prepared from pure Mg. Ground up with water and examined under the microscope.

6. Night-blue Hydrochloride.—Ground up with water in amount insufficient to dissolve the salt. Microscope used.

7. Crystal-violet Hydrochloride.—As in No. 6.

8. Spirit-blue Hydrochloride.—Ground up with water, in which it is insoluble. Microscope used.

TABLE II.

B. *Substances giving Negatively-charged Particles. All Examined by the Microscope Method.*

9. Tannic Acid (Zinsser's).—Boiled up with water and cooled.

10. Rosolic Acid.—Dissolved in alcohol and then poured into water.

11. Uric Acid.—Ground up with water.

12. Silicic Acid.—Precipitated. Treated as in No. 11.

13. Naphthol Yellow (Free Acid).—As in No. 6.

14. Orange II. (Sodium Salt).—As in No. 6.
15. Orange G. (Sodium Salt).—As in No. 6.
16. Naphthol Yellow (Calcium Salt).—As in No. 6.
17. Benzopurpurine 4B. (Potassium Salt).—As in No. 6.
18. Erika B.N. (Potassium Salt).—As in No. 6.
19. Sodium Stearate.—Prepared from pure stearic acid. Boiled with water and cooled.
20. Aluminium Stearate.—Prepared from pure stearic acid. Dissolved in acetone and then poured into water.
21. Latex of *Landolphia Ovariensis*.—This rubber latex was diluted with water, to which a little formalin had been added for preservation.
22. Anthracene.\*—Dissolved in alcohol and poured into water.
23. Naphthalene.\*—Resublimed and then treated as in No. 22.
24. Paraffin Oil (Commercial).—Dissolved in acetone and poured into water.
25. Paraffin Wax (Commercial White).—As in No. 24.
26. Cerasin Wax (Commercial White).—As in No. 24.
27. Beeswax (Brown Commercial).—Dissolved in alcohol and poured into water.
28. Sulphur\* (Precipitated).—Dissolved in acetone and poured into water.
29. Animal Charcoal.—Ground up with water.
30. Nitrocellulose\* (Soluble).—Dissolved in acetone and poured into water.
31. Azobenzene.\*—Dissolved in alcohol and poured into water.
32. Anthraquinone.\*—As in No. 31.
33. Alizarine.\*—As in No. 31.
34. Indigo.—Ground up with water.
35. Starch (Potato).—Boiled up with water and cooled. U-tube used.
36. Paranitriline Red.—Dissolved from dyed cloth with acetone and solution poured into water.
37. Aniline Black (Chrome).—Contains 13 per cent. of Cr. Ground up with water.
38. Compound of Night Blue and Picric Acid.\*—Made from the hydrochloride. Dissolved in alcohol and poured into water.
39. Compound of Chrysophenine and Crystal Violet.\*—Made from crystal-violet hydrochloride. Dissolved in alcohol and poured into water.

In the above thirty-nine cases the substances were either as colloidal solutions or as fine suspensions. They all showed the Tyndall effect in a beam of light from an arc lamp.

An examination of the tables shows that in pure water or in 10 per cent. alcohol all basic substances are charged positively, and all acid substances negatively.\* The hydrochlorides tested are positive, and the metallic salts with complex groups are negative. Further, all the hydrocarbons are negative. The so-called neutral substances and sulphur, as well as carbon, are negative.

#### SPEED OF PARTICLES UNDER ELECTRICAL PRESSURE.

In order to determine the speed of the particles the method of the U-tube or that with the microscope was used.

\* This agrees with some of the work of Teague and Buxton, *Zeits. fur Phys. Chem.*, 60, p. 419, 1907.

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TABLE III.

*U-Tube Method. Temperature 18°C.*

Substance.	Speed. Cms. per second per volt per cm.
Alizarine ... ..	$20 \times 10^{-5}$
Azobenzene ... ..	17
Night Blue Base ... ..	19
Spirit Blue Base ... ..	20
Chrysophenine (Crystal Violet Compound) ... ..	16.5

These were colloidal solutions prepared as previously described.

TABLE IV.

*Microscope Method. Temperature 18–20°C.*

Substance.	Speed, Cms. per second per volt per cm.	
Alizarine ... ..	$26 \times 10^{-5}$	Colloidal Solution prepared as before
Triphenylmethane ... ..	45	Ditto
China Clay ... ..	36	Pure Water Suspension
Silicic Acid ... ..	30	"
Tannic Acid ... ..	27	"
Benzopurpurine 4B. Potassium Salt ... ..	52	"
Erika B.N. Potassium Salt ... ..	60	"
Rubber Latex ... ..	28	"
Sulphur ... ..	27	From Acetone Solution

These results show that the speed of travel in each case is of the same order. In the case of colloidal platinum prepared by Bredig's method we obtained  $20 \times 10^{-5}$ . This agrees with the result of Burton, but is lower than that of Rolla, who gives  $24 \times 10^{-5}$ . The exceptionally high speeds of the salts of benzopurpurine and erika may be due to their partial solubility in the water.

The speed was found to vary directly with the electrical field. This is shown in the following example with triphenylmethane (10 per cent. alcohol) solution, in which the microscope was used:—

TABLE V.

Voltage.	Time. Seconds.	Speed. Cms. per second per volt per cm.
10	32	$47.6 \times 10^{-5}$
20	16	47.6 "
29.7	11	46.6 "
37.0	9	45.7 "

Length of electric field, 1.27 cms. ; measured distance travelled, 0.12 cms.

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The influence of solubility combined with concentration of alcohol in the case of alizarine containing 1 part in 10,000 of varying mixtures of alcohol and water is shown below :—

TABLE VI.

Strength of Alcohol. Per Cent.	Speed. cms./sec.—volt/cm.
2.5	$50 \times 10^{-5}$
5	47
10	28
12.5	22
25	13
50	0

With the 50 per cent. practically all the alizarine was dissolved, only a few particles remaining for examination, and these showed no movement.

## INFLUENCE OF TEMPERATURE ON SPEED.

In the case of dyes it is of the utmost importance to make observations

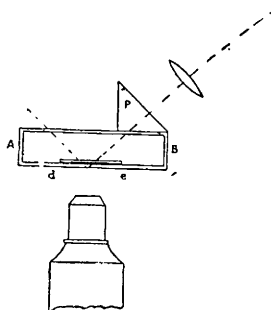


FIG. 4.

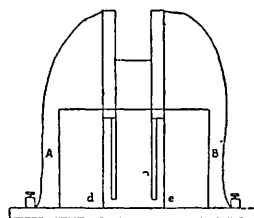


FIG. 5.

at temperatures between 40–100°C., the limits generally used in practice. Experiments made with cold dyes will be of much less value, owing to the destruction of colloidal solutions and the dissociation effects at the higher temperatures.

Great difficulty was found in obtaining speeds by the U-tube method at increased temperatures owing to the convection currents produced. This was also the case when the microscope method was applied to different types of horizontal cells. The best results were obtained with the microscope placed horizontally, as shown in Fig. 4, where *de* is the cell shown in Figs. 2 and 3, placed within a glass tank *AB*, also shown in Fig. 5, having a prism *P* cemented on the back. This prism enabled the particles to be illuminated. The liquid examined was that portion held within a narrow space between the glass slide and the front wall of the tank. The liquid was heated before being poured into the tank, and the temperature observed at the actual time of observation.

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Using the 1 in 10,000 10 per cent. alcohol colloidal solution of pure alizarine the following results were obtained :—

TABLE VII.

Temperature. °C.	Speed. cms./sec. — volt/cm.
16	$21.7 \times 10^{-5}$
22	25.4
30	45.6
33	53.3
40	71.0
45	61.0
48	53.3
60	45.6

## FILTRATION UNDER PRESSURE.

The apparatus used for this purpose is shown in Fig. 6. A glass tube

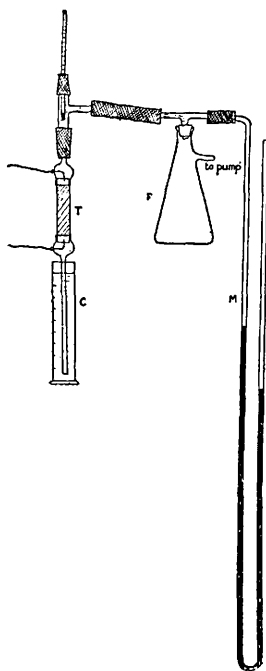


FIG. 6.

10 cms. long and  $1\frac{1}{2}$  cms. diameter was provided with platinum electrodes and ground-glass caps. The cotton or other material was placed within the tube. The lower cap had a piece of glass tubing attached, which had its lower end immersed in a glass measuring cylinder *C*. The upper part of the tube was connected through a filtering flask *F* to a mercury manometer *M* and a vacuum pump. The potential difference produced was measured by

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TABLE VIII.  
*Cotton at 16° C.*

SERIES I.			SERIES II.			SERIES III.				
Pressure, P. (mms. Mercury.)	Voltage, V.	V/P.	Pressure, P.	Voltage, V.	V/P.	Pressure, P.	Flow, F. (c.c.s per min.)	Voltage, V.	V/P.	V/P.
15	—0'005	0'00033	600	—0'92	0'00153	70	3'00	—0'055	0'00079	0'0183
65	—0'04	0'0061	555	—0'85	0'00153	245	8'22	—0'36	0'00147	0'0438
110	—0'12	0'00109	515	—0'78	0'00151	280	10'00	—0'45	0'00160	0'0450
210	—0'27	0'00128	350	—0'53	0'00151	500	20'00	—0'93	0'00185	0'0465
270	—0'37	0'00137	280	—0'39	0'00139	580	25'50	—1'20	0'00207	0'0470
325	—0'47	0'00145	200	—0'26	0'00130					
400	—0'58	0'00145	160	—0'185	0'00115					
485	—0'73	0'00150	110	—0'12	0'00109					
520	—0'79	0'00152	50	—0'03	0'00060					
565	—0'85	0'00150	30	—0'02	0'00067					
610	—0'91	0'00149	10	—0'005	0'00050					
620	—0'92	0'00148								



TABLE IX.  
*Wool at 16° C.*

SERIES I.			SERIES II.			SERIES III.				
Pressure, P.	Voltage, V.	V/P.	Pressure, P.	Voltage, V.	V/P.	Pressure, P. (mm. Mercury.)	Flow, F. (c.c.s per min.)	Voltage, V.	V/P.	V/F.
60	—0'033	0'00055	85	—0'082	0'00096	165	4'28	—0'32	0'00194	0'075
125	—0'142	'00114	105	—0'16	'00153	350	8'00	—0'82	'00234	'102
230	—0'30	'00130	155	—0'31	'00200	360	—	—0'86	'00239	—
290	—0'40	'00138	240	—0'54	'00224	500	—	—1'52	'00304	—
390	—0'54	'00139	300	—0'68	'00227	540	12'5	—1'65	'00306	'132
500	—0'77	'00154	345	—0'80	'00232	565	—	—1'71	'00303	—
650	—1'04	'00160	400	—0'99	'00247	660	14'3	—2'22	'00336	'155
			440	—1'10	'00250					
			490	—1'35	'00276					
			575	—1'77	'00300					
			645	—2'24	'00348					

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TABLE X.  
*Silk at 16° C.*

SERIES I.			SERIES II.				
Pressure, P. (mm. Mercury.)	Voltage, V.	V/P.	P.	Flow, F. (c.c.s per min.)	V.	V/P.	V/F.
110	—0·03	0·00027	95	6·66	—0·22	0·0023	0·033
260	—0·27	·00104	180	11·3	—0·44	·0024	·039
400	—0·75	·00187	200	12·0	—0·65	·0032	·054
490	—1·15	·00235	300	17·6	—1·53	·0051	·087
545	—1·57	·00288	450	25·0	—2·95	·0065	·118
595	—1·94	·00326	480	27·3	—3·24	·0067	·119
660	—2·35	·00356	585	33·3	—3·89	·0068	·120
680	—2·45	·00360	630	35·3	—4·20	·0067	·119

the use of a Carpentier silvered mica condenser, which allowed the capacity to be varied from 0.1 to 2 microfarads. This was charged from the platinum electrodes, and then discharged into a suitable galvanometer.

The materials used were :—

- (1) Cotton yarn, bleached and thoroughly washed.
- (2) Wool sliver, scoured and thoroughly washed.
- (3) Silk yarn, boiled off and well washed.
- (4) Mercerised cotton, bleached and washed.
- (5) Wool sliver, boiled with 1/2 per cent. solution of sulphuric acid and thoroughly washed with cold water.

The results are given in the tables.

TABLE XI.  
*Mercerised Cotton at 16° C.*

Pressure, P. (mms. Mercury.)	Flow, F. (c.c.s per min.)	Voltage, V.	V/P.	V/F.
90	—	—0.065	0.00072	—
110	2.24	—0.093	.00084	0.0415
280	5.00	—0.33	.00118	.0660
400	6.25	—0.49	.00122	.0785
530	7.70	—0.69	.00130	.0895
605	—	—0.81	.00134	—
630	9.54	—0.83	.00131	.0870

TABLE XII.  
*Effect of Temperature.*

COTTON.		SILK.		WOOL.	
P = 150 mms.		P = 150 mms.		P = 210.	
Temp. °C.	Voltage.	Temp. °C.	Voltage.	Temp. °C.	Voltage.
16	—0.090	17	—0.57	16	—0.37
30	.120	19	.60	41	.57
35	.140	30	.62	60	.41
40	.141	35	.67	75	.31
45	.122	45	.62	84	.22
60	.087	55	.55	88	.24
70	.055	60	.49	90	.27
75	.039	65	.44	91 boils	.18
80	.040	75	.33	82	.36
85	.068	80	.24	78	.43
Flow at 16° 10 c.c.s in 130 secs.		90	.22	75	.46
		93	.26	70	.54
				50	.79
				40	.91
				30	.85
				20	.65
				Flow at 40° 10 c.c.s in 38 secs.	

TABLE XIII.  
*Wool Boiled with Acid. Water at Different Temperatures.*

Temperature Rising.	Voltage.	Temperature Falling.	Voltage.
15° C.	+0·099	85° C.	+0·082
20°	+ '093	78°	— '043
25°	+ '092	60°	— '153
30°	+ '087	50°	— '185
35°	+ '086	45°	— '200
40°	+ '082	35°	— '214
50°	+ '080	30°	— '240
60°	+ '088	25°	— '250
80°	+ '110	20°	— '270
95°	+ '160	15°	— '300

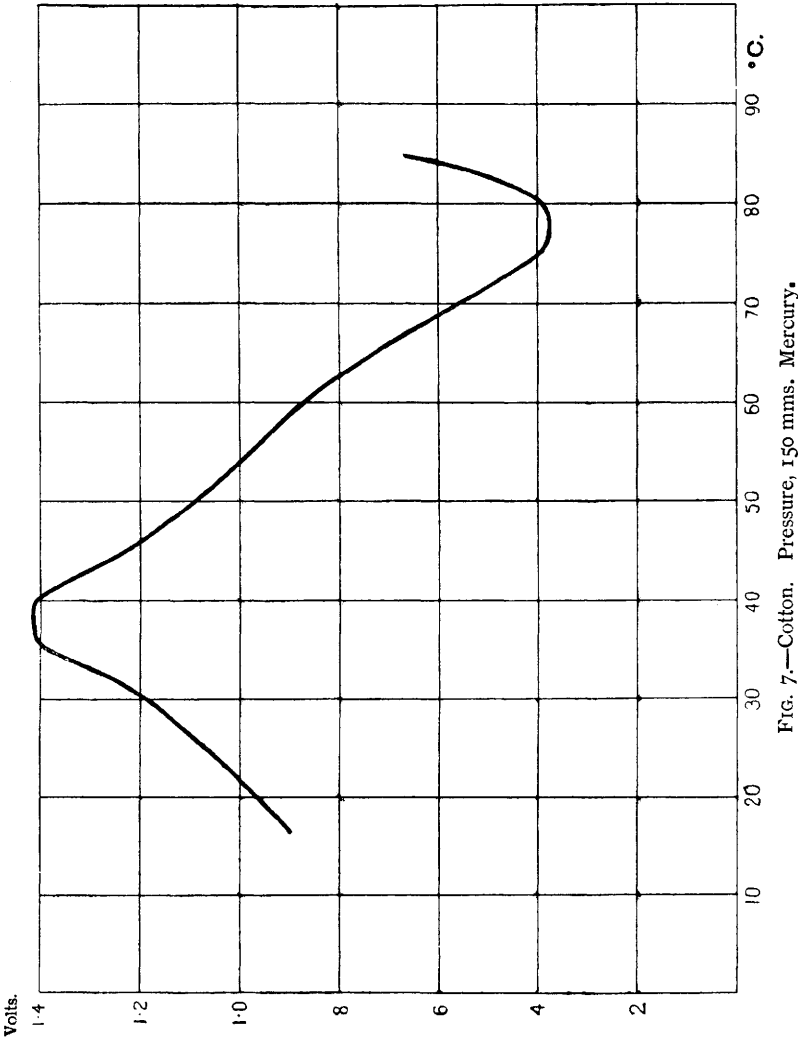


FIG. 7.—Cotton. Pressure, 150 mms. Mercury.

On examining Table VIII., it will be seen that as the pressure increases the ratio  $V/P$  becomes constant after a certain point. In Series III. the rate of flow was also measured, and the value of  $V/F$  is found to be more nearly constant than  $V/P$ .

In Table IX. with wool the value  $V/P$  increases with  $P$ , and in Series III.

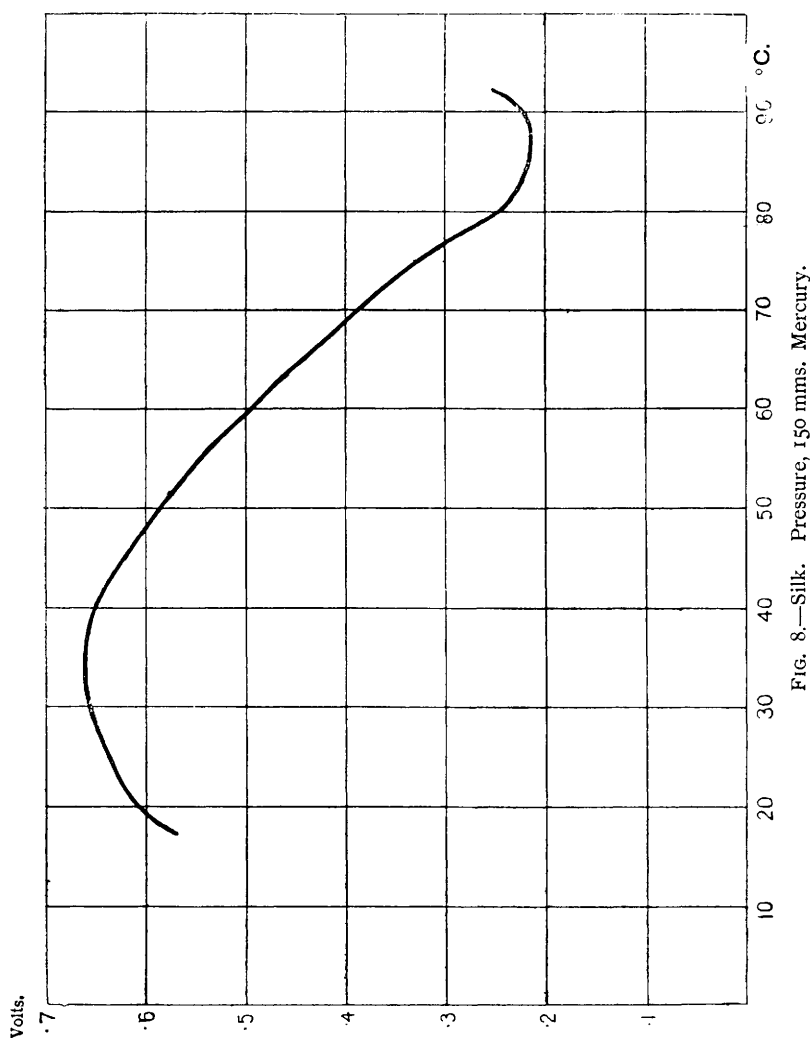


Fig. 8.—Silk. Pressure, 150 mms. Mercury.

$V/F$  increases with the rate of flow. This is also true of Table X. Mercerised cotton behaves like ordinary cotton, as shown in Table XI.

In Table XII. the results are shown of gradually increasing the temperature of the flowing liquid. These results are plotted in Figs. 7, 8, and 9. It will be seen that at 40°C. and 80°C. points of change are indicated.

In Table XIII. the results for wool which has been treated with acid are given for different temperatures.

## CALCULATION OF POTENTIAL DIFFERENCE.

From the formula—

$$e = \frac{4\pi}{K} \frac{\eta V}{H},$$

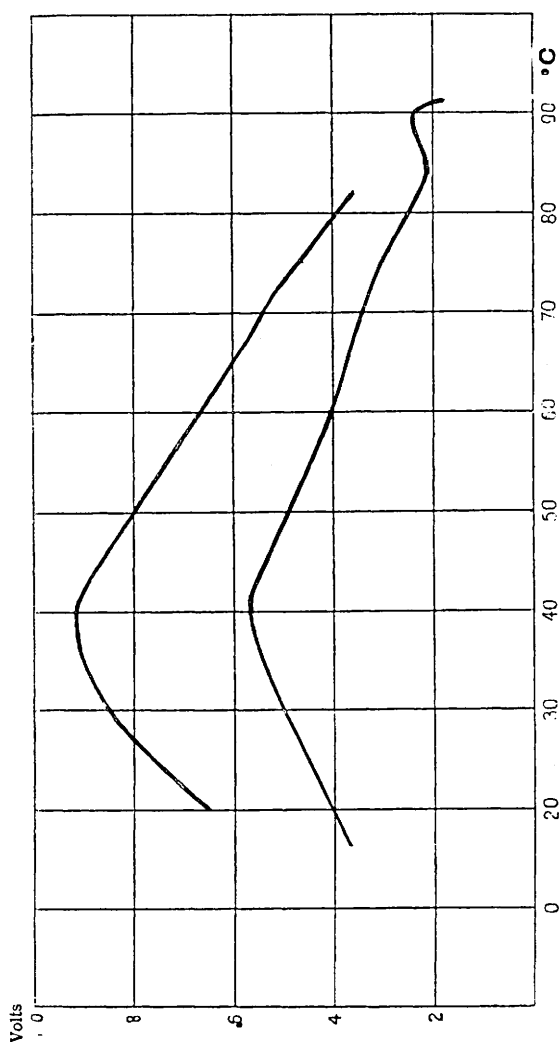


FIG. 9.—Wool. Pressure, 210 mms. Mercury.

which is expressed in electrostatic units, we obtain—

$$e_v = \frac{4\pi}{K} \frac{\mu V}{H_v} \times (300)^2$$

where  $e_v$  and  $H_v$  are in volts. Taking  $K=80$ ,  $H=1$  volt (per cm.), a velocity  $V$  of  $20 \times 10^{-5}$  cms. per second, and for  $\eta$  the value 0.01140, we obtain for the potential difference a value of about 0.03 volt. This value is

about the same for all the colloidal solutions and suspensions examined. It is also the same for colloidal platinum.

In the case for filtration under pressure we have for electromagnetic units of resistance and volts—

$$e_v = \frac{4\pi}{K} \cdot \frac{\eta}{\rho p} \times (3 \times 10^{10})^2$$

This gives for the figures of our experiments the following approximately average values for the contact differences between water and the materials used—

							Volt.
Cotton	...	...	...	...	...	...	0.06
Silk	...	...	...	...	...	...	0.22
Wool	...	...	...	...	...	...	0.09

The endosmose formula can only be approximately applied for finding the value of  $e$ , for the reason that it contains the value of  $q$ , the total cross-section of the capillary tubes. Perrin has obtained an approximate value for the pores in the case of a diaphragm of chromic chloride and dilute acid, between which substances he calculates the potential difference of 0.025 volt. We may, however, eliminate  $q$  if we measure the strength of the current,  $C$ , employed in the endosmose tube, for then the expression becomes—

$$e = \frac{4\pi}{K} \frac{\eta}{\rho C} V$$

We have employed this method, using a modified type of Perrin apparatus into which fabrics could be placed, and find for one sample of cotton 0.02 volt. Further experiments are in progress by this method.

Although the difference of potential is a relatively small value between the fabric and the liquid, yet if the attraction between the two is at all comparable to that between two planes as given by the formula—

$$F = \frac{K}{8\pi t^2} \cdot e^2$$

(where  $F$  is the force per  $\text{cm}^2$  and  $t$  is the distance between the planes), the value is a considerable one, owing to the small value (perhaps only of the order  $10^{-8}$  cms.) between the planes.

It is very important to discuss the influence of temperature on the value of the potential difference. We find that Cruse\* had already obtained an apparent maximum, between  $35^\circ$  and  $40^\circ\text{C}$ ., for the rate of endosmose of water through porous earthenware. This is criticised by M. von Smoluchowski,† for the reason that the rate of increase of the electrical conductivity is not compensated by the decrease in viscosity. We have accordingly examined our results to find what difference will be made in our curves when they are reduced to contact differences. Taking the formula in the form—

$$e = \frac{4\pi}{p} \cdot \frac{\eta}{\rho K} \cdot E$$

in which  $4\pi/p$  is kept constant, then for each value of  $E$ , that of  $e$  will be raised or lowered according as  $\eta/\rho K$  is greater or less than unity.

We have measured  $\rho$  for a sample of the water used in the experiments,

*Phys. Zeit.*, 6, p. 201, 1905.  
*Ibid.*, 6, p. 529, 1905.

adopting the values of  $\eta$  given by Landolt and Börnstein, and those of  $K$  given by Drude, and obtain the results given below :—

Temperature, °C.	$\eta$ .	$\rho$ .	$K$ .	$\eta/\rho$ . Relative Values.	$\eta/\rho K$ . Relative Values.
15	·01134	$10\cdot98 \times 10^4$	82·0	1·03	1·26
20	·01002	10·04	80·1	0·998	1·25
25	·00891	9·25	78·2	·963	1·23
30	·00798	8·50	76·6	·939	1·23
40	·00654	7·30	73·4	·896	1·22
50	·00548	6·45	70·0	·850	1·21
60	·00468	5·70	67·1	·821	1·22
70	·00406	5·02	64·8	·809	1·22
80	·00356	4·50	61·5	·791	1·30

This table shows that unless there is some other factor that ought to be included, our curves indicate fairly well the change of  $\epsilon$  with temperature. It should be remarked that the original formula of Helmholtz did not include the value of  $K$ . It has been introduced by Perrin in accordance with the suggestion of Pellat.

## PART II.

The first question which requires an answer in considering the electrical theory is, "What is the nature of the dyeing solutions?" Pelet-Jolivet and Wild\* conclude that they behave as electrolytes, and in the case of benzo-purpurine, chrysophenine, soluble blue, erika, and naphthol yellow, Knecht and Batey† have shown undoubtedly that their solutions are electrolytes. Now since the dyeing solutions are usually employed hot and dilute, the ionisation must be fairly complete. Thus a suitable bath for dyeing wool with crystal scarlet (a sodium salt of the molecular weight of 502) would be: Water 100 times the weight of the wool, and crystal scarlet 5 per cent. on the weight of the wool. This gives a solution about  $\frac{1}{1000}$  normal, and it would be used at 90° C. to 100° C.

The experiments described in Part I. have shown that wool and silk are negatively electrified in contact with water, and the electrification apparently increases up to 40° C. and then decreases. Hence in dyeing wool or silk which are "wet out," before entering the dye vat they must have a negative charge. Suppose the dye be basic and represented by  $n - P$ , where  $n$  is a small *negative* ion, and  $P$  a large *positive* organic basic ion. These ions will be free, and when the wool or silk is placed in the solution the basic ions will be attracted by the negatively electrified fibres, and be fixed by some process which cannot yet be considered as properly understood.

The small ions will combine with the H-ions which are present in the so-called double layer. If inorganic electrolytes are also present in the solution and are of an alkaline nature, they will tend to make the fibre still more negative, and will assist the process of dyeing.

In the case of acid dyes we deal with substances of the nature  $p - N$ , where  $p$  is now a small *positive* ion and  $N$  a larger *negative* ion. In this case acid is either added to the bath or the fabric has been previously boiled with

\* *Rev. Gen. des. Mat. Col.*, p. 9, 1909.

† *J.S.D.C.*, 25, p. 194, 1909.



acid. In each case the fibre takes a positive charge, as shown by our experiments. The result will be that N will be attracted to the positively electrified material, whilst  $p$  will form a salt in the vat.

This alone is a simple statement of the electrical theory, and there are many facts which it seems to explain. Thus Knecht has shown that when wool and silk are dyed with basic colours until the dye bath is exhausted, the whole of the HCl is left quantitatively in the bath. We have found that in dyeing tanned cotton with a colloidal solution of night-blue picrate the picric acid was likewise left quantitatively in the bath. In these cases the negatively charged fabric appears to take up the whole of the positively charged complex ion. Knecht has also shown that in dyeing wool with the magnesium salt of crystal scarlet (an acid dye) in presence of free acid the magnesium was left quantitatively in the bath. Here the + charged fabric attracts the -ve acid and repels the +ve base.

We have not dealt with "Direct Dyeing" because salts are added to the bath. These additions alter the conductivity, viscosity, and dielectric constant, and Perrin states that the "contact-charge" is reduced. We are investigating these points.

The ionising liquids are those which produce strong electrification by contact,\* and it is in such liquids that dyeing is possible. The so-called "dry" dyeing processes are carried on with alcohol, which is an ionising liquid, or more frequently with aqueous alcohol, in which the ionising power is greater. The use of benzole for dyeing is only possible when water is present either in the solution or the fabric, for benzole is a poor ionising liquid. On the other hand, the bleeding or even complete removal of the dye from a dyed fabric is only possible by ionising liquids. A good example is wool dyed with picric acid. This acid can be extracted from the fibre by alcohol but not by benzene. It is also interesting to note that dry wool will not dye from a benzene solution of picric acid.

It has been shown by Burton† that alcohol favours the production of positive ions only, and therefore when added to wool the negative charge is likely to be destroyed, and so prevent the assimilation of a positive base.

When acid (such as  $\text{H}_2\text{SO}_4$ ) is used in dyeing it is required to set free the colour acid, but in practice it is known that an excess of acid is very desirable. The reason of this has not been satisfactorily explained.‡ If we accept the electrical theory, then the extra acid will be required to make the fibre take a positive charge. It is possible that in the case of a very strong acid colour the colour acid may itself be sufficient to produce a positive charge on the fabric.

Another interesting application of the electrical theory applies to the filtration of dyes through various media. Neutral bodies such as sand are able to retain certain dyes. Since these bodies take a negative charge in pure water they ought to be able to absorb—and not simply filter off—basic colours in neutral solutions. The case of animal charcoal, which absorbs acid colours in acid solution, is likewise explained, since this takes a strong positive charge, probably owing to nitrogenous substances § present. It will appear from the experiments of Lewis || that adsorption does not explain the large amount of dye that is taken up. No doubt surface action will be sufficient to explain the relatively small amount of dye adsorbed in the case of sand and graphite when acid colours are used.

\* Perrin, *Four. Chim. Phys.*, **2**, p. 619, 1904.

† *Phil. Mag.*, **11**, p. 445, 1906.

‡ See Dreaper, pp. 89-91.

§ Knecht, *J.S.D.C.*, **25**, p. 266, 1909. || *Phil. Mag.*, 1908.

A strong confirmation of the electrical theory is afforded by the amount of absorption of dye stuffs at different temperatures. Brown\* has shown that with basic colours the maximum amount of dye stuff absorbed is at about 40° C., and is a minimum at about 80° C. Our results show that the maximum negative charge is apparently attained at about 40° C., and the minimum at about 80° C., the nature of the fibre having but little effect. A comparison of the curves, Figs. 7, 8, and 9, with the curves given for the dyeing with basic colours† shows very marked similarity.

It is known that the dyeing of acid colours on wool is best performed at a boiling temperature. In one of our experiments on wool boiled with acid we found that the wool had a positive charge at 85°, which decreased and changed to negative on cooling. This may help to explain why wool boiled "with acid and subsequently washed has a considerably decreased affinity for basic dyes, but its affinity for acid dyes is increased."‡

The effect of the addition of Na<sub>2</sub>SO<sub>4</sub> to acid dye baths is to cause a restraining action and diminish the rate of the absorption of colour, and this continues after the amount of sulphate added has been sufficient to form bisulphate. This is evidence that the salt diminishes the positive character of the charge, as Perrin proves.

#### COLLOIDS IN DYEING.

*Ultramicroscopic Examination.*—Teague and Buxton§ and L. Pelet-Jolivet and Wild|| have given classifications of dyestuffs as colloidal, slightly colloidal and non-colloidal, and amongst those of a distinctly colloidal nature are Congo red and benzopurpurine. Michaelis¶ also states that benzopurpurine is colloidal.

We have examined solution of a pure sample of benzopurpurine 4B (K salt)—as used by Knecht and Batey\*\* in their experiments—in the ultramicroscope of Siedentopf and Zsigmondy made by Zeiss. The greatest difficulty in all ultramicroscopic examinations is the preparation of water free from particles. The best results we have obtained have been by distilling the water twice and then filtering through a Pukall filter with a vacuum pump, until a sample examined in the ultramicroscope showed not more than two particles in the field at the same time. As the volume examined was  $3.5 \times 10^{-6}$  c.c., each particle corresponds to about  $3 \times 10^8$ , or three hundred million particles to the litre.

A solution of benzopurpurine 1 part in 100,000 was filtered through the same filter, the strength of the filtered solution being ascertained by comparison with the original solution in a tintometer. Although this method is not exact, it is sufficient for our purpose. The solution contained one part of benzopurpurine in about 125,000 water, and the number of particles found was the same as that in the water. The addition of filtered sodium sulphate solution did not produce any visible particles. The benzopurpurine is therefore either not colloidal or its particles are too small to be resolved by the arc-light.

Taking the mass of the hydrogen atom as  $10^{-24}$  grams, the mass of a molecule of benzopurpurine (mol. wt. 756) will be  $7.5 \times 10^{-22}$  grams.

\* *J.S.D.C.*, 17, p. 92, 1901.

† Dreaper, p. 99.

‡ *Ibid.*, p. 91.

§ *Zeit. für Phys. Chemie*, 1907, p. 469.

|| *Comptes Rendus*, October 19, 1908.

¶ *Colloids and the Ultramicroscope*, Zsigmondy, p. 206.

\*\* Soc. Dyers and Col.

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Zsigmondy\* places the limit of visibility by the arc-light as a linear dimension of  $15 \mu\mu$ , or  $1.5 \times 10^{-6}$  cms. diameter. This corresponds to a spherical † volume of  $18 \times 10^{-19}$  c.c., and if the sp. gr. is taken as 1.5, corresponds to  $27 \times 10^{-19}$  grams. Each visible particle would therefore represent 3,600 molecules; any particle containing a less number of molecules than this would be invisible by arc-light.

The limit by sunlight on the brightest possible days is given as  $5 \mu\mu$ , corresponding to a volume of  $7 \times 10^{-20}$  c.c., or a mass of  $10 \times 10^{-20}$  grams. This represents about 130 molecules. We have been unable to obtain the necessary sunlight to carry the investigation to this point.

To the benzopurpurine solution was added an equal bulk of filtered N/10 sulphuric acid; the colour turned blue-violet, and showed no more particles under the ultramicroscope on examining immediately. On standing, however, particles appeared, and in 20 minutes  $36 \times 10^8$  particles per litre were found.

A flask was prepared by boiling filtered water in it, and when no particles could be perceived in the water by the ultramicroscope the flask was considered suitable for the next experiment. The acid benzopurpurine solution was boiled in this flask; the liquid became red, but returned to blue-violet on cooling. The solution now contained  $500 \times 10^8$  particles per litre.

Allowing for the dilution, the solution contained 1 gram benzopurpurine in 250 litres. There are therefore  $1.25 \times 10^{13}$  particles per gram, and the mass of each particle about  $8 \times 10^{-14}$  grams, assuming all the colour has been precipitated. The mass of a molecule being  $7.5 \times 10^{-22}$  grams, each particle corresponds to roughly  $10^8$  molecules, and taking the specific gravity as 1.5, measures  $60 \times 10^{-6}$  cms. diameter, which is well within the limit of ultramicroscopic vision for arc-light. The sample contained 98.3 per cent. colour, 1.1 per cent. water, leaving 0.6 per cent. impurities; 1 gram thus contained 0.006 grams impurities. As the  $500 \times 10^8$  particles found in the above-mentioned experiment only weighed 0.004 grams, it is obvious how necessary it is to filter the solutions. With commercial samples the results would certainly be unreliable.

A solution of benzopurpurine 8 grams per litre after standing for a month became gelatinous and contained large particles which would not pass through the filter. When 20 c.c. of this solution was diluted to make it 200 c.c. it showed a strong green light-cone when illuminated with a powerful convergent beam from an arc-lamp. On heating, the cone gradually decreased in intensity and at  $80^\circ$  C. had completely disappeared, but did not return on cooling. The cause of the gelatinisation is not known, but it is evident that the colloidal nature disappears on boiling.

*Size of Particles and Speed.*—In the experiments given in Part I. the substances in Tables I. and II. were either colloidal solutions or suspensions, but the results show that the speed does not depend on the size of the particle or its nature so long as no electrolyte is present.

This agrees with the fundamental formula—

$$e \frac{l}{d} = \frac{4\pi \mu v}{K H},$$

where  $\frac{l}{d}$  is a slipping coefficient introduced by Lamb. In this formula the size of the particle does not appear, and if it be assumed that  $\frac{l}{d}$  is equal to

\* *Colloids and the Ultramicroscope*, p. 122.

† The particles are not usually spherical.

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unity, then the only variables in the experiment will be the dielectric constant  $K$  and the viscosity  $\mu$ . The speeds were approximately the same in all the experiments, any variation being probably due to traces of electrolytes, which have such a great influence.

It is interesting to compare these speeds with the speeds of ions in electrolysis—

Copper,  $30 \times 10^{-5}$  cms. per second per volt per cm.

$\text{Cr}_2\text{O}_7''$ ,  $47 \times 10^{-5}$  cms. per second per volt per cm.

## GENERAL CONCLUSIONS.

The electrical theory as so far developed explains how one type of colouring matter is selected in preference to another by the fabric, but how the colour is actually fixed to the fabric still remains in doubt. Provisionally we may adopt the view that the primary action depends upon electrical attraction, which is followed by mechanical actions and the colloidal precipitation with the formation of aggregates of a complex character. Adsorption is an insufficient explanation, as Lewis\* has shown, and a solid solution theory † is also not applicable.

Perrin ‡ has shown that there are important parallel relations between the phenomena of contact electricity and colloidal precipitation, and Pelet-Jolivet § has extended this to the amount of dyestuff taken up by the fabric and also to the capillary ascension of the dyes in the fibres. In the latter case the experiments of Pelet-Jolivet consisted of measuring the final height of the colouring matter reached when a band of the absorbent material was suspended vertically in the dye-bath. Here we have a mixed phenomenon depending on surface tension and absorption.

All these phenomena are modified by the action of temperature, which has a most important relation to the dyeing processes. The ascertained facts are collected in the instructive table given on p. 62.

## DYEING WITH COLLOIDAL SOLUTIONS.

From colloidal solutions of the positive substances:—night blue, spirit blue, and crystal violet, all the negative fibres were dyed, the most strongly negative fibres, like tanned cotton and wool, taking the colours up best. From a colloidal solution of the compound of night blue and picric acid which was negative, the negative fibres took out the positive part of the compound and left the negative part in the bath. The same effect was produced with the compound of chrysophenine and crystal violet.

Our thanks are due to Dr. Knecht for samples of pure dyes used in the experiments, and to Principal J. H. Reynolds and the Committee of the Manchester School of Technology for the facilities placed at our disposal.

\* *Phil. Mag.*, vol. 15 (6), p. 499, 1908.

† Walker and Appleyard, *Four. Chem. Soc.*, vol. 69, part ii., p. 1334, 1896.

‡ *Four. Chem. Phys.*, vol. iii., p. 85, 1905.

§ *Rev. Gen. Mat. Color.*, vol. 13, p. 257, 1909.

TABLE XIV.

Laws of Contact Electricity.	Laws of Colloidal Coagulation.	Laws of Dyeing.	Laws of Capillary Ascension in Absorbent Materials.
Dissociating liquids electrify fibres strongly by contact.	Dissociating liquids produce colloidal solutions.	Dissociating liquids are best for dyeing processes.	—
Acids increase the charge of a fibre already positive.	Acids make the positive colloids more difficult to coagulate.	Acids diminish the dyeing with basic colours.	Acids increase the rise of basic colours.
Acids diminish the charge of a fibre already negative and may reverse its sign.	Acids coagulate negative colloids.	Acids increase the dyeing with acid colours.	Acids diminish the rise of acid colours.
All the acids act with the concentration of the H ions.	Acids act according to the concentration of the H ions.	Acids act according to the concentration of the H ions.	—
Bases act in the reverse way to acids.	Bases act in the reverse way to acids.	Bases act in the reverse way to acids.	Bases act in the reverse way to acids (bases do not increase the rise of acid colours).
By addition of salts— 1. The ions of reverse sign to that of the fibre diminish the charge of the fibre. 2. The charge of the fibres may be reversed. 3. Polyvalent ions have the greatest effect. 4. A polyvalent ion does not generally increase the charge of a fibre already of the same sign as itself.	By addition of salts— 1. The ions of reverse sign produce colloidal coagulation. 2. The <i>gel</i> may take a reverse sign to the colloidal particle. 3. Polyvalent ions have the greatest effect. 4. The ions of the same sign render colloidal solutions more stable.	By addition of salts— 1. The ions of reverse sign increase the dyeing power. 2. The fibre may dye best with the opposite kind of colour. 3. Polyvalent ions have the greatest effect. 4. Ions of the same sign as that of the fibre increase the dyeing effect.	By addition of salts— 1. The ions of reverse sign diminish the rise. — 3. Polyvalent ions have the greatest effect. 4. Ions of the same sign increase the rise of basic colours but not of acid colours.
The charge of a negative fibre is greatest at about 40° C.	The mobility of a negatively charged particle is greatest at about 40° C.	The dyeing of a negative fibre with positive dye is greatest at about 40° C.	—

*Other Temperature Effects.*

1. Rise of temperature increases dissociation.
2. Rise of temperature increases conductivity.
3. Rise of temperature diminishes the dielectric constant.
4. Rise of temperature increases fluidity.
5. Rise of temperature diminishes surface tension.
6. Rise of temperature increases diffusion.
7. With other colours than basic colours rise in temperature increases the amount of dye taken up.
8. Adsorption is probably diminished by increase of temperature.
9. The solubility of most substances is increased by temperature.
10. Irreversible colloids are coagulated by rise in temperature; reversible colloids are generally converted from the "gel" state to the "sol" state by rise in temperature.