

solidus curves, but these unite to form a single solid solution at points on the solidus curve.

(3) The alloys containing over 80 per cent. of silver do not undergo segregation under ordinary conditions, and are practically homogeneous and uniform in composition. They are well suited as a material for the manufacture of trial-plates.

“On the Wetting of Cotton by Water and by Water Vapour.”

By ORME MASSON, D.Sc., F.R.S. Received April 25, 1904.

Introduction.

If two thermometers, one of which has its bulb protected by a close covering of ordinary cotton wool, be simultaneously immersed in the same water, all being originally at the same temperature, the protected thermometer shows a marked rise, while the naked one undergoes no perceptible change. Heat is, therefore, generated locally by the wetting of the cotton covering.

The maximum temperature is reached in 2 or 3 minutes, after which there is a fall, the rate of which steadily diminishes in a characteristic manner, so that, when all necessary precautions are taken, a difference of temperature between the cotton and the surrounding water is still distinctly perceptible after several hours. Both the extent of the rise and the rate of the whole change depend on several conditions. With a given thermometer the most important factors are the quantity of cotton wool, its initial condition with respect to hygroscopic moisture, and the temperature of the water. Other things being equal, the effect is more marked with a large covering than with a small one and at a higher than at a lower bath temperature, but the previous condition of the cotton is a more important factor than either. If taken in its ordinary state after exposure to the air of the laboratory, when it usually contains about 8 or 9 per cent. of moisture, it may show a rise of 2° or 3° C., but if precautions be taken to insure that it is dry at the moment of immersion in water (at its own temperature), the same sample will show a rise of from $8-12^{\circ}$ or more.

The relatively large amount of air which is always entangled within the cotton wool does not escape during or after immersion, and the bundle presents a glistening appearance under water which suggests that it is not completely wetted. That this fact is important in connection with the observed temperature change is shown by the behaviour of the so-called “medicated” or “absorbent” cotton wool, which differs from the ordinary (nearly pure) material in having been freed by solvents from traces of natural cotton wax. This gives a

much smaller rise, and in its case the glistening appearance is absent. Moreover, the quantity of water which penetrates the cotton wrapping and remains mechanically adherent to it and the thermometer when they are lifted out after, say, $\frac{1}{2}$ hour's immersion, may be determined by weighing, and it is found to be less than the weight of the dry cotton in the case of the ordinary material, but several times greater in the case of the absorbent variety. Obviously, therefore, when they are immersed, the former is both better insulated and has the smaller heat capacity, and will thus show a larger rise of temperature for a given heat production, and the observed difference does not necessarily indicate that the absorbent wool is inherently less susceptible to such action as may be the cause of the phenomenon.

The true nature of this action is indicated in the first place by the observation that immersion in water is not essential, for the covered thermometer behaves in a precisely similar manner when exposed to air saturated with water vapour. The rise of temperature is as great or greater, though it may take 5 or 6 minutes to reach the maximum instead of 2 or 3, and the subsequent slow cooling curve is similar, as well as the effects of varying conditions. In fact it has been proved by the experiments to be described that the whole action is essentially the same, whether a bath of water or of saturated air be employed, and that in both cases the heat production is due, at all events, primarily, to the condensation of water vapour on the surface of the cotton fibres. More strictly, this is proved in the case of saturated air immersion, and its extension to the other case is necessitated by the proof of the complete similarity of the thermal changes. In the case of immersion in water the vapour which condenses on the cotton must be produced by evaporation from the liquid, which is prevented from complete contact with the fibres by the air which adheres to them and fills the interstices. There is, therefore, an automatic distillation from the water on to the cotton which acts as a condenser, and the heat gained there must be matched by an equal loss of heat by the adjacent water, though the large heat capacity of the latter prevents any fall of temperature comparable with the observed rise. "Absorbent" cotton wool is found to behave in saturated air exactly like the ordinary variety, in contrast with its much smaller temperature effect in water. This is in complete accord with the theory. The condensation of vapour that occurs during exposure to saturated air never renders the cotton sensibly moist, though it may absorb over 20 per cent. of its weight in a few hours.

It has long been known that rise of temperature results from the immersion of finely divided solids in water and other liquids. Pouillet* examined a large number of substances, both inorganic and

* 'Ann. de Chim. et de Phys.,' 1822, (2), vol. 20, pp. 141—162.

organic, and showed that the property is a general one, that the state of division and previous dryness of the material are important, and that the phenomenon is much better marked with animal and vegetable substances than with mineral powders. His experiments, however, can hardly be regarded as quantitative, for the temperature rises, of which he records a long list, have no real significance apart from the special conditions under which they were observed, nor do they by themselves throw light on the nature of the process which causes them. Later observers seem to have confined their attention to inorganic materials such as silica and glass, and the recent work of G. J. Parks, which will be referred to later, is specially notable in this connection. But the author is not aware of any previously recorded thermometric investigation on the lines he has adopted, having the following objects in view:—

1. To map the whole course of the observed change of temperature of cotton due to its immersion in water, tracing both the rise to the maximum and the subsequent fall.

2. To do the same for the case of immersion in air saturated with water vapour, and to compare the two results.

3. To examine the effect of varying conditions and particularly of the initial dryness or dampness of the cotton.

4. To determine, in the case of immersion in saturated air, the course of the hygroscopic absorption.

5. To ascertain the relation between this absorption and the temperature change.

6. To examine the information so obtained as to its bearing on the nature of the Pouillet effect.

Apparatus and Methods.

The *thermometers* required to fulfil the two conditions of being short enough to be weighed on an accurate balance and of yet having a sufficient length of scale. As they were likely to be used at various temperatures, a very open scale was out of the question. Those chosen were graduated in whole degrees only, reading from below zero to 100° C. Readings were always made by a telescope with a micrometer scale in the eyepiece. In all the earlier experiments this micrometer scale was used merely for subdividing the degrees, but in those described as Series V it was employed so as to make the readings altogether independent of the thermometer graduations.

Comparison of the instruments with a standard thermometer at various temperatures showed that the capillary was of practically uniform bore, and as all the readings in any experiment were referred to the initial one, so as to give temperature differences, any zero-point error of the thermometer was of no importance.

The *telescope* was generally so placed that one division of the micrometer scale was equal to $0^{\circ}\cdot 2$, and readings were taken to $0^{\circ}\cdot 02$. They may, in the case of Series V, be taken as free from errors as large as $0^{\circ}\cdot 05$, but the earlier observations are less reliable for the reason stated. The actual temperatures of the immersion bath, as given in the tables, were ascertained by a standard thermometer that could be read to $0^{\circ}\cdot 01$, and in all experiments after Series II these temperatures were maintained constant to within $0^{\circ}\cdot 03$ by a thermostat.

The experimental thermometer was provided with a *jacket tube* of sufficient length to enclose the bulb and part of the stem, and a smooth red-rubber cork was fixed at such a position on the stem that the tube, when in use, was closed and air-tight. All that part of the scale which was used in the observations lay above the level of the cork, and there was sufficient length below it to admit of proper immersion of the bulb and cotton covering without submerging the cork itself. The thermometer was provided with platinum loops so that it could, with its tube, be slung slantwise on the balance for weighing.

The *cotton wool* was tightly wound round the bulb so as to efficiently cover it and a small part of the stem, leaving enough room between it and the cork for subsequent operations. From $\frac{1}{2}$ —1 gramme was found to be a convenient quantity. When once properly wound it remains in position without any special fastening, but for a long series of experiments it is safer to secure it with a single turn of cotton thread. After winding, it should be hung in distilled water for a day to remove soluble impurities derived from the fingers or the laboratory air, and should not afterwards be touched.

In the latter experiments (Series V) a *duplicate thermometer* with cork and tube, but without cotton wool, was used as a counterpoise in weighing, and was also put through every treatment in the same way and at the same time as the experimental apparatus. It was hoped by this means to minimise any small errors that might result from hygroscopic changes in the weight of the rubber cork.

The *oven* used for drying the cotton covering before any experiment was an ordinary air bath with temperature regulated to about 110° C. and with a fairly free draught passing through it. The bulb of the thermometer passed through an opening in the roof, and a slotted wooden cover supported the rubber cork outside the bath and protected it from the heat. It was proved that an hour's drying was more than enough to give constant weight.

It may be mentioned here, as a curiously extreme instance of the ordinary wet and dry bulb effect, that the experimental thermometer with its covering, when lifted out of cold water and placed in the oven, rises steadily till it reaches a point some 50° or 60° below the oven

temperature, then oscillates for some time about that point (following the oscillations of the gas regulator) and finally rises steadily to the full temperature. The effect is seen best when absorbent wool is used, as it carries a much larger store of water.

The *immersion bath* varied according to circumstances. In Series II, for water immersion, it was simply a glass jar holding about 3 litres of distilled water. Its temperature was that of the laboratory and was thus not the same throughout the series, but it varied only between 16° and 18° , and during any one experiment it did not alter more than a few tenths of a degree. This last variation was recorded and afterwards approximately corrected for, in plotting the temperature curve of the covered thermometer. The results are, of course, though fairly good, less reliable than those of later series; for in all of these the immersion bath was placed in a thermostat which kept constant to within 0.03. In the later water immersion tests the bath was a wide-mouthed thin glass flask containing distilled water, and it was clamped in the thermostat so that only its open mouth was above the surface of the water in the latter. For immersion in air saturated with water vapour, this flask was replaced by another arrangement which underwent some modification as the work proceeded. In Series III a large wide-mouthed glass bottle was used, with a layer of water at the bottom and with an air current passing through it. This air was previously saturated at the right temperature by passing through a lead worm and a wash-bottle, both submerged in the thermostat, and it was then delivered into the bottle through a tubulated neck near the bottom. In Series IV the air current was sent through additional saturators, and a cover was provided for the bottle so as to close it when in use, except for the opening which admitted the thermometer. In Series V, as some doubts were entertained as to perfect saturation in previous tests, the bottle was replaced by a large cylindrical pot of porous earthenware, with a hole near the bottom through which the air current could be conveyed. The pot was very completely surrounded by the water of the thermostat and was provided with perforated card covers. The infiltration of water through the walls kept the whole inside surface wet and provided a large and constant area of evaporation. At the same time the infiltration was not rapid enough to give any trouble, even in protracted experiments, if the pot was emptied by a syphon at the start. With this arrangement it was found that it made no appreciable difference whether the air current was used or not, and it was not used in the last six experiments of the series.

Hooks, which occupied a fixed position with respect to the telescope so that its distance and the value of its scale did not vary, served for the vertical suspension of the thermometers during immersion. The small water motor which worked the stirrer of the thermostat was connected with the same support as these hooks, and at each rotation

of the belt a slight jolt was thus given to the thermometers which served the purpose of an automatic tapper in preventing the mercury from sticking.

The actual conduct of an experiment is as follows:—The covered thermometer is dried at about 110° for an hour as already described, the jacket tube being placed separately in the oven at the same time. The counterpoise thermometer and tube, if used, are treated similarly in this and in all subsequent operations. The instrument is then removed and quickly inserted into its tube, both being well above 100° , and is left to cool to the temperature of the balance. Its weight is taken after a momentary loosening of the cork to equalise pressure, and it should not vary in a series of tests more than about 0.001 gramme from the mean. In the twenty experiments of Series V, where the duplicate instrument was used as a counterpoise, the variation was only half as much. The weight of the dry wool itself may be obtained by deducting the tare of the instrument, taken before the bulb was covered.

The thermometer, still protected by its tube, is then suspended in the immersion vessel (water or saturated air as the case may be) and the cover put on, and readings are taken by the telescope from time to time till their constancy indicates that the covered bulb has reached the fixed temperature of the thermostat. About an hour suffices. The final reading is noted as the initial temperature of the experiment. The thermometer is then as rapidly as possible withdrawn, removed from its tube, and re-hung in the proper position, and a stop-watch is started at the moment of immersion. The cover is replaced, the telescope is adjusted vertically so that its scale occupies exactly the same position as before with respect to a fixed mark on the thermometer, and readings begin. These are taken at short intervals, and always, except at the maximum temperature and at the finish, at the moment when the mercury is crossing a scale line, the time being noted to the nearest second so long as seconds are of any importance.

Generally the experiment is stopped at an exact pre-appointed time by removing the thermometer as rapidly as possible to its jacket tube, and it is then allowed to take the temperature of the balance and weighed. The difference between this and the original dry weight gives the amount of moisture absorbed during the immersion. As the final temperature cannot be read at the actual moment of stoppage, a very slight extrapolation is generally necessary to complete the curve; for the exact final temperature may be wanted for a purpose that will appear later. Of course, in the case of water immersion the weighing is omitted, as absorbed moisture cannot be distinguished from that which mechanically adheres to the cotton.

At the completion of an air immersion experiment, after the instrument has been weighed, it may be at once used for a second experiment in which

the influence of a known amount of previous moisture is observed, the procedure being similar to that already described. In Series II (water immersion tests) previous moisture was given to the cotton in roughly predetermined quantity by exposing it for suitable times in moist air at the ordinary temperature.

To obtain the curve which shows the progress of absorption of moisture during immersion in air saturated at any fixed temperature, it is necessary not only to accurately maintain the bath at that temperature but to guard against any interference with the temperature of the cotton. It is an essential feature of the process that the cotton shall become hotter than the bath, and the velocity of absorption at any moment must be affected by the magnitude of this difference of temperature. It is, therefore, impossible to trust an absorption curve obtained from one long experiment, interrupted from time to time for the purpose of weighing. After each such interruption the cotton resumes operations at a lower temperature than that at which it left off, and moreover it never again gets back exactly on to its original temperature curve. There are other errors also which result from such a method, but they are of less importance. Therefore the plan was adopted of determining each point on the absorption curve by means of a separate experiment, starting always with dry cotton, and immersing it for different times, but keeping all other conditions the same. The temperature curve was taken simultaneously in each test.

Unfortunately it has not been found possible to so arrange things that each temperature curve follows the exact course of the last, which would be the best proof of the trustworthiness of the absorption curve. The differences, though small, are unmistakable even in the case of Series V, which was the best in several respects. The extent of these discrepancies will be shown in the tables summarising results. The cause of them is not to be found in the drying process, as is proved by the uniformity of dry weight; nor in premature absorption through the corks after weighing, as this was disproved by special tests; nor in incompleteness of saturation of the air, nor in any other circumstance peculiar to the air immersion experiments, for similar small variations occurred in the temperature curves got by water immersion. It is probable therefore that the errors arise at the moment the thermometer is withdrawn from its tube at the start of each experiment, and that this exposure to air of variable temperature and moistness, brief though it is, initiates a disturbance that shows itself later in the manner described. It is not easy to devise a remedy that would not introduce troubles of its own. Finally it may be pointed out that the constancy of the bath temperature, and the fact that the cotton is always hotter than the bath, afford security against any error such as might otherwise be caused by deposition of dew.

Experimental Results.

In what follows and in the curve diagrams—

t is the time measured in minutes from the moment of immersion of the cotton-covered thermometer ;

θ is the temperature of the same at the moment t , in degrees Centigrade, its own initial temperature, which is the constant temperature of its environment, being taken as zero ;

ϕ is the maximum value attained by θ in the course of the experiment ;

τ is the value of t at which $\theta = \phi$;

m is the weight of water vapour, in milligrammes, absorbed in the time t ;

p is the weight of any water vapour, also in milligrammes, absorbed by the cotton prior to the commencement of the experiment ;

A is the area, determined by planimeter, bounded by the curve, the t axis, and a vertical ordinate corresponding to the time t ;

or $A = \int_0^t \theta dt.$

The terms “water immersion” and “saturated air immersion” have already been fully explained. “Previous moisture” serves to designate that of which the quantity is p . The term “dry curve” is used to distinguish one belonging to an experiment in which the cotton is dry to start with from those which show the effect of previous moisture.

It is unnecessary to reproduce here the numerous t and θ readings of the experiments. They are therefore summarised in the following tables, giving the values of τ and ϕ , the final values of t and θ , and the corresponding values of A and m (where determined), and the value of p in cases where previous moisture was present. In Tables III and V calculated values of m are given also. The mode of calculating m from A and θ will be explained later. Some of the curves are shown in the diagrams, and references to these are given in the tables.

The experiments which formed Series I were of a purely preliminary character, and are therefore omitted. Those of Series II were, as already explained, less accurate than later ones ; but they are correct enough for their purpose, for they show by comparison with Series III the general similarity of the temperature change produced by water immersion and by saturated air immersion, both with and without previous moisture. Series III also gave information as to the progress of absorption during exposure to saturated air ; and the main purpose of Series IV and Series V was to trace this more fully in connection with the temperature change. They also supplied some evidence as to the influence of bath temperature and weight of cotton. Finally water immersion tests, carried out in conjunction with Series IV and V, gave

temperature curves capable of accurate comparison with those of saturated air immersion under otherwise identical conditions. The experiments of Series V are probably more exact than any of the others, for reasons already explained.

Table I.—Summary of Series II.

0.55 gramme of cotton wool covering thermometer C. Water immersion at 16–18°. $\tau = 3$ to $3\frac{1}{2}$ minutes.

Order of experiment.	Approximate bath temp.	p .	ϕ .	θ at 30 minutes.	Reference to figure.
1	17.0	0	8.3	1.7	Fig. 1, <i>a</i> .
5	18.0	0	1.55	1.75	
11	17.3	0	8.65	1.8	
6	17.3	9	7.4	1.7	Fig. 1, <i>b</i> .
3	17.7	18	6.15	1.55	
7	17.0	24	4.95	1.5	
4	16.7	33	3.45	1.35	Fig. 1, <i>c</i> .
2	16.1	44	2.3	1.2	
8	16.8	53	1.65	1.05	
12	18.2	68	1.1	0.7	Fig. 1, <i>d</i> .
9	17.2	88	0.6	0.55	
10	17.4	101	0.4	0.35	

Table II.—Summary of Series III.

0.53 gramme of cotton covering thermometer C. Saturated air immersion at 18°. $\tau =$ about 6 minutes, slightly increasing with p .

Order of experiment.	p .	ϕ .	t .	θ .	m .	Reference to figure.
2	0	8.65	6	8.65	17.6	Fig. 2, <i>a</i> .
7	0	8.75	6	8.75	17.8	
3	0	8.8	15	6.8	32.5	
4	0	8.8	35	3.05	48.3	
5	0	8.8	64	1.65	62.7	
6	0	8.7	111	0.95	77.3	
1	0	8.65	185	0.7	93.6	
8	0	8.8	307	0.3	103.0	
2A	17.6	6.15	73	1.2	52.4	Fig. 2, <i>b</i> .
3A	32.5	3.85	73	1.15	41.3	Fig. 2, <i>c</i> .
4A	48.3	1.95	70	1.0	28.4	Fig. 2, <i>d</i> .
5A	62.7	1.15	70	0.75	19.7	
5B	82.4	0.6	72	0.5	12.6	

Under t , in this and the following tables, is given the time at which each experiment was concluded; and the corresponding values of θ , A , and m , are given in the appropriate columns.

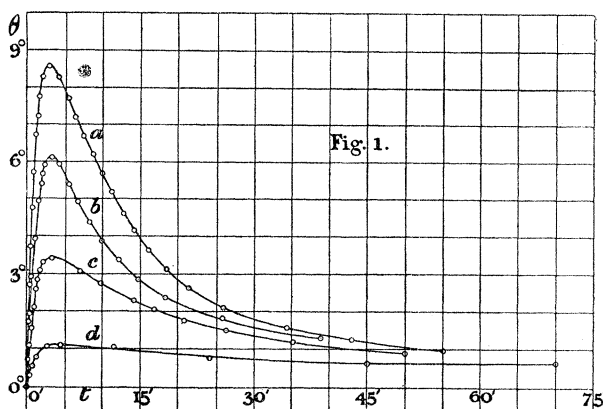


Fig. 1.

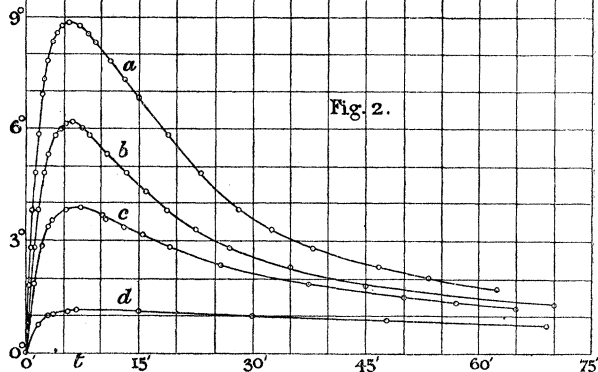


Fig. 2.

Description of Curve Diagrams, figs. 1—4.—Curves showing change of temperature by cotton while absorbing moisture. Time (t) expressed in minutes. Temperature of cotton (θ) in Centigrade degrees, its initial temperature and the constant temperature of the immersion bath being taken as zero. (See Tables I, II, III and IV.)

Fig. 1.—Immersion in water at 16° to 18° C. Cotton = 0.55 gramme.

- (a) Originally dry.
- (b) Containing 18 milligrammes of previous moisture.
- (c) " 33 " " "
- (d) " 68 " " "

Fig. 2.—Immersion in saturated air at $18^{\circ} 0$. Cotton = 0.53 gramme.

- (a) Originally dry.
- (b) Containing 17.6 milligrammes of previous moisture.
- (c) " 32.5 " " "
- (d) " 62.7 " " "

Table III.—Summary of Series IV.

0.53 gramme of cotton covering thermometer C. Saturated air immersion, with better arrangements than in Series III. Bath temperature 18°C . τ = about $5\frac{1}{2}$ minutes.

Order of experiment.	p .	ϕ .	t .	θ .	A.	m .	m (calcd.).
7	0	Not reached	3	7.93	14.8	12.2	11.6
5	0	8.85	6	8.85	40.2	19.9	18.9
6	0	8.75	15	6.42	109.7	33.3	33.8
2	0	8.87	16	6.12	117.5	35.7	35.5
1	0	8.78	30	3.30	180.6	48.7	48.4
4	0	8.95	35	2.70	197.0	51.3	51.9
8	0	8.90	50	1.82	226.4	57.5	58.4
3	0	8.90	65	1.39	252.4	65.0	64.5
7A	12.2	6.92	6	ϕ	—	16.4	—
5A	19.9	5.90	6	ϕ	—	13.5	—
6A	33.3	3.32	6	ϕ	—	9.2	—
4A	51.3	1.73	6	ϕ	—	5.3	—
3A	65.0	1.00	6	ϕ	—	3.6	—

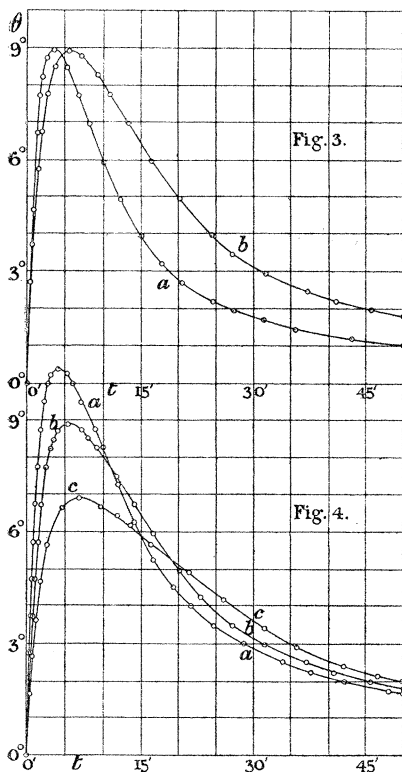


Fig. 3.—Immersion at 18°C of 0.53 gramme of dry cotton.

(a) In water.

(b) In saturated air.

Fig. 4.—Immersion of 0.53 gramme of dry cotton in saturated air.

(a) At 25°C .

(b) At 18°C .

(c) At 12°C .

The temperature curve of Experiment 8 is shown in fig. 3*b*, where the companion curve (*a*) represents a water immersion experiment under otherwise similar conditions.

In fig. 4, the temperature curves are shown as obtained by immersing the dry cotton in air saturated at (*a*) 25°, (*b*) 18°, (*c*) 12°, so as to test the effect of the greater vapour pressure. The following table summarises these additional tests.

Table IV.—Experiments Supplementary to Series IV, and with same Apparatus.

Experiment 3 of Series IV included for comparison. No previous moisture.

Immersion.	Bath temp.	τ .	ϕ .	t .	θ .	m .
Water	18°0	3·5	8·90	65	0·78	—
Saturated air	25°0	4·3	10·40	65	1·30	69·2
„	18°0	5·5	8·90	65	1·39	65·0
„	12°0	6·9	6·90	65	1·47	55·4

Table V.—Summary of Series V.

0·90 gramme of cotton covering thermometer D. Saturated air immersion with improved arrangements. Bath temperature 25°0. τ = about 5½ minutes. No previous moisture. For θ and m curves, see fig. 5.

Order of experiment.	ϕ .	t .	θ .	A.	m .	m (calcd.).
7	Not reached	2·35	10·07	12·8	15·7	14·5
10	12·8	5·35	12·8	48·8	28·5	26·8
2	12·8	5·5	12·8	51·0	27·4	27·3
3	12·62	10	10·95	104·5	39·3	39·3
16	12·62	10	11·25	103·6	39·4	39·3
4	12·50	18	7·60	177·4	53·0	54·5
5	12·68	18	7·57	178·9	53·8	54·8
12	13·00	18	7·77	183·4	55·7	56·2
1	12·68	30	4·73	253·0	72·6	71·0
6	12·58	30	4·44	245·5	68·5	68·7
15	12·68	30	4·70	252·4	68·8	70·8
8	12·63	45	2·95	300·0	80·9	81·3
9	12·58	60	2·18	339·4	90·2	90·6
11	12·80	80	1·74	382·5	103·3	101·4
13	12·80	80	1·68	382·0	103·7	101·2
14	12·80	80	1·82	393·1	101·7	104·2
17	12·54	120	1·12	425·8	114·7	112·0
18	12·80	180	0·85	508·8	130·8	133·2
19	13·00	360	0·40	608·8	159·8	158·7
20	12·72	720	0·22	723·3	187·9	183·3

The Temperature Curve.

In all the experiments this curve is obviously of such a form that, for any given value of θ , there are two t values, say t_1 on the ascending slope, and t_2 on the descending slope; and when θ has its maximum value ($= \phi$) $t_1 = t_2$ ($= \tau$).

Inspection of any of the curves representing experiments in which previously dry cotton was immersed, either in water or in saturated air, brings out two relations which hold good with approximate accuracy. The first is that the two times for any given θ vary inversely as one another, or

$$t_1 t_2 = a \quad \dots\dots\dots (I),$$

a being necessarily equal to τ^2 .

The second is that θ varies inversely as the sum of its two times, or

$$\theta (t_1 + t_2) = b \quad \dots\dots\dots (II),$$

and the value of b is necessarily $2\tau\phi$.

Selecting Experiment 20 of Series V to illustrate these rules, we find that a does not vary more than about 2 per cent. on either side of the value 30.8, and that b , which is 141.2 when θ is at its maximum, rises as θ falls to about 152 and then falls again towards its original value. Similar, and sometimes greater, deviations from constancy are shown in all the experiments.

Equations (I) and (II) can evidently be combined to give one which approximately characterises the whole curve, viz. :

$$\theta (t + a/t) = b \quad \dots\dots\dots (III),$$

where t is any time, θ has the corresponding value, and a and b must have the values already assigned to them, viz., $a = \tau^2$ and $b = 2\tau\phi$. It follows that the whole course of any such curve is definable in terms of the special values assumed by τ and ϕ . In other words, a "law of corresponding states" is arrived at, which may be most simply expressed by giving to Equation (III) the form $2\theta/\phi = t/\tau + \tau/t$, or may be put in words as follows :—

The temperature curves for all experiments, whatever the conditions, should be superimposable if in each case the θ values are expressed as fractions of ϕ and the t values as fractions of τ .

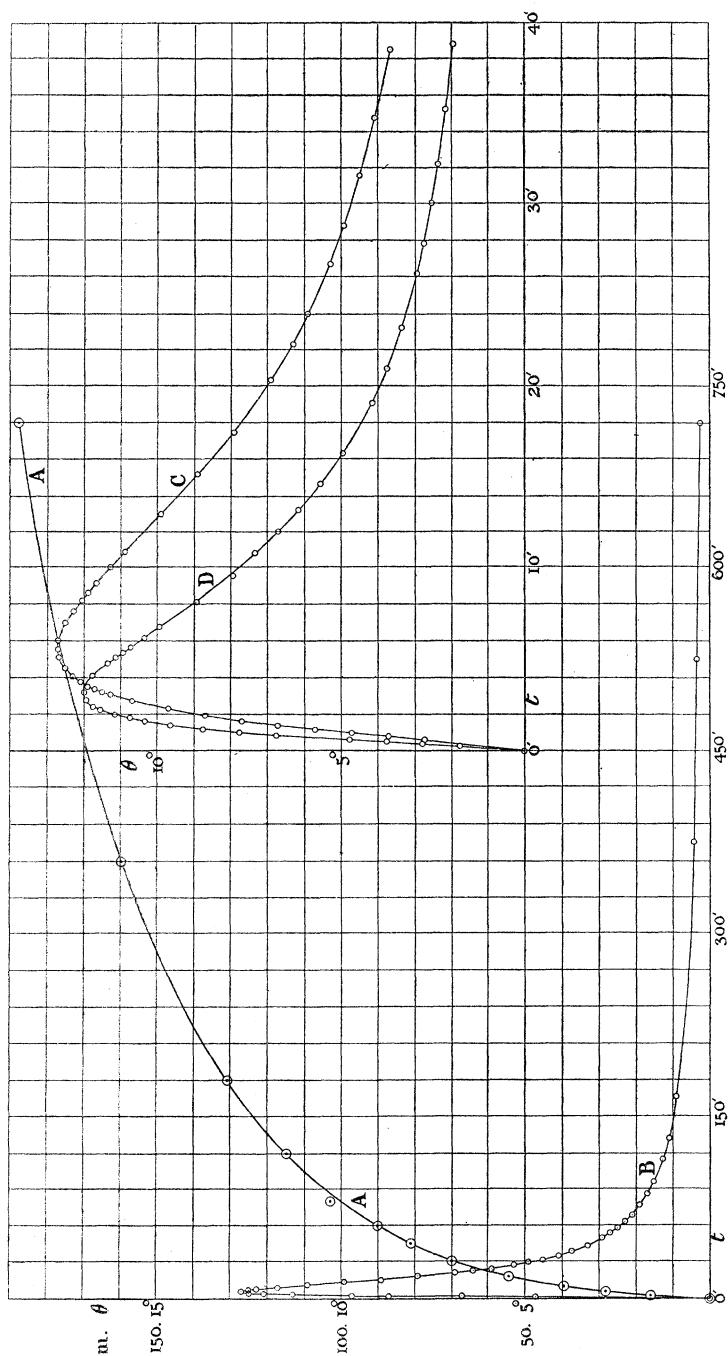
This suggests a method for comparing the curves for water immersion and saturated air immersion more exactly than can be done by mere inspection. The results are shown in Tables VI and VII. In each of these the fourth column contains the same selected values of θ/ϕ , and the first column contains the corresponding actual values of θ . The figures in the second and third columns respectively show the

times at which these θ values are obtained on the ascending and descending slopes of the curve, and the fifth and sixth columns show the corresponding values of t/τ . All the θ and t values may be taken as experimental numbers, having been found by careful interpolation from the recorded readings. ϕ is the result of actual observation; but τ is from its nature not sharply defined, for the temperature always remains sensibly constant at its highest point for a considerable fraction of a minute. The values of τ used in the tables, and shown at the head of the second and third columns, were therefore obtained by plotting the arithmetic means of t_1 and t_2 for θ values in the immediate neighbourhood of ϕ and then slightly extrapolating the curve so formed. No appreciable error is introduced by treating this short portion of the curve as a straight line, though in fact it is part of a rectangular hyperbola. Practically the same τ value is obtained by assuming that it is the geometric mean of the t_1 and t_2 of any closely contiguous θ value. The τ so found is of course well within the limits prescribed by actual observation.

For the comparison of saturated air immersion with water immersion, the figures in the fifth and sixth columns of Table VI should be read together with the corresponding figures of Table VII. The differences are such as would be accounted for by comparatively small experimental error, and are indeed not greater than might occur in a similar comparison of two saturated air tests. The results point therefore to the identity of the effects, and so of the causes at work, in the two cases.

For a comparison of either case with the results indicated by the Equation (III), the figures in the last four columns of Tables VI and VII may be read with the calculated values shown in Table VIII. It is evident that there are greater differences between the calculated and found values than between the found values of saturated air and of water immersion, and that the tendency in both cases is for the smaller t/τ to be in practice a little too small, and the larger t/τ to be a little too large for the theory, while their product still remains of practically unit value, as indicated by the equation. Such differences are somewhat more strongly marked when the experiments at the lower bath temperature (18°) are studied in the same way; but here, again, the close similarity between the water and saturated air tests is conspicuous. Whether the agreement between the equation values and those of the experiments would be improved by elimination of such errors as may arise from the short initial exposure of the cotton to outside air, from the lag of the thermometer, or from other causes (some of which may work in opposite directions), it is impossible to say without further data.

FIG. 5.



Description of Fig. 5.—Curves showing behaviour of 0.90 gramme of cotton originally dry. Bath temperature, 25°0 in all cases. (See Tables V, VI and VII.)

- A. Absorption curve in saturated air bath up to 12 hours. Moisture absorbed (m) in milligrammes.
 B. Temperature curve corresponding to A.
 C. The early part of curve B on an enlarged time scale.
 D. Temperature curve obtained by immersion in water; otherwise same as C.

Table VI.

Saturated air immersion at 25°. 0.90 gramme of cotton.

θ .	t_1 .	t_2 .	$\frac{\theta}{\phi}$.	$\frac{t_1}{\tau}$.	$\frac{t_2}{\tau}$.	$\frac{t_1 \times t_2}{\tau^2}$.	$\frac{\theta (t_1 + t_2)}{2\tau\phi}$.
12.72	5.55	5.55	1	1	1	1	1
12.08	3.78	8.27	0.95	0.68	1.49	1.01	1.03
11.45	3.22	9.70	0.9	0.58	1.75	1.01	1.05
10.18	2.50	12.37	0.8	0.45	2.23	1	1.07
8.90	2.07	15.17	0.7	0.37	2.72	1.01	1.08
7.63	1.65	18.25	0.6	0.30	3.29	0.98	1.08
6.36	1.37	22.10	0.5	0.25	3.95	0.98	1.05
5.09	1.08	27.85	0.4	0.19	5.02	0.98	1.04
3.82	0.85	37.3	0.3	0.15	6.72	1.03	1.03
2.54	(0.56)	56.6	0.2	(0.10)	10.2	—	1.03
1.27	(0.28)	117.2	0.1	(0.05)	21.1	—	1.06

Table VII.

Water immersion at 25°. 0.90 gramme of cotton.

θ .	t_1 .	t_2 .	$\frac{\theta}{\phi}$.	$\frac{t_1}{\tau}$.	$\frac{t_2}{\tau}$.	$\frac{t_1 \times t_2}{\tau^2}$.	$\frac{\theta (t_1 + t_2)}{2\tau\phi}$.
12	3.20	3.20	1	1	1	1	1
11.4	2.15	4.72	0.95	0.67	1.48	0.99	1.02
10.8	1.82	5.62	0.9	0.57	1.76	1	1.04
9.6	1.43	7.25	0.8	0.45	2.27	1.01	1.09
8.4	1.13	9.03	0.7	0.35	2.82	1	1.11
7.2	0.93	11.1	0.6	0.29	3.47	1.01	1.13
6	0.77	13.7	0.5	0.24	4.28	1.03	1.13
4.8	0.60	16.8	0.4	0.19	5.25	0.98	1.09
3.6	0.47	21.8	0.3	0.15	6.81	1	1.04
2.4	(0.32)	31.6	0.2	(0.10)	9.88	—	1
1.2	(0.16)	66	0.1	(0.05)	20.6	—	1.04

Table VIII.—Values Calculated from the Equation $\theta \left(t + \frac{a}{t} \right) = b$.

θ ϕ	$\frac{t_1}{\tau}$	$\frac{t_2}{\tau}$	$\frac{t_1 \times t_2}{\tau^2}$	$\frac{\theta (t_1 + t_2)}{2\tau\phi}$
1	1	1	1	1
0·95	0·72	1·38	1	1
0·9	0·63	1·60	1	1
0·8	0·50	2·00	1	1
0·7	0·41	2·45	1	1
0·6	0·33	3·00	1	1
0·5	0·27	3·73	1	1
0·4	0·21	4·79	1	1
0·3	0·15	6·51	1	1
0·2	0·10	9·90	1	1
0·1	0·05	19·95	1	1

One characteristic feature of the temperature curve in every case, and well shown in fig. 5, B, is the rapid approximation of the cooling portion to the form of a rectangular hyperbola. This is indeed indicated by Equation (III), since, when t is large enough a/t is practically negligible, and $\theta t = b$. The temperature of the cotton, therefore, cannot in any finite time return absolutely to that of its environment. This points, also, to there being no finite limit to the vapour absorption process which is the cause of the heat supply—a result which will be discussed later. Meantime, it may be noted that both the temperature effect and the progress of absorption are still distinctly manifest after 12 hours, and could certainly be followed for days if necessary.

The temperature curves showing the effects of previous moisture (figs. 1 and 2) may evidently be regarded, in respect to their down slopes, as representative of later portions of the dry curve, for they could take their origin from such times as would account for the absorption of so much previous moisture in the same environment. Thus the curves *b*, *c*, *d* (fig. 2) would start at 6, 15, and 64 minutes respectively. Even then, however, the new curve would at its highest point fall below the original one, and the two would never really coincide afterwards. Thus a permanent interference with the normal course of the temperature is caused by interrupting the absorption process, and again resuming it after the cotton has cooled in its closed tube, and this must naturally react to some extent on the subsequent absorption rate.

The Absorption Curve.

The best and most numerous m data are those for Series V (Table V), and the curve for these is shown in fig. 5, A. In plotting it, the mean m value has been used in cases where there

was more than one determination. The curves for earlier series are similar, as far as they go. The absorption occurs rapidly at first, and proceeds with diminishing velocity, but the evidence does not point to even practical finality being reached for many days, and there is no theoretical limit to the process. Like the θ curve, that for dm/dt would evidently show an asymptotic approach to the t axis. For comparison, the complete θ curve for the 12-hour experiment of the series is shown on the same plate (B) as the m curve (A). It is very evident that the moment of maximum temperature marks but a small advance in the progress of absorption, and that the heating effect of the latter must be continuous throughout, and would continuously raise the temperature if not counteracted.

Relation of the Temperature, Time, and Absorption Values.

The net rate of gain or loss of heat by the covered thermometer at any moment must depend upon both the rate at which it is receiving heat from the vapour condensation, and the rate at which it is losing heat by radiation, convection, and conduction. If it be assumed (1) that the heat received is directly proportional to the weight of moisture condensed, (2) that the rate of loss of heat due to the above causes is directly proportional to the difference of temperature between the thermometer and its environment (assumptions which the results will justify later), it follows that

$$dm/dt = c\theta + k d\theta/dt \dots\dots\dots (IV),$$

where m , t , and θ have the same significance as before; c is the normal heat loss by the covered thermometer, due to radiation, etc., per unit θ per minute; k is the heat capacity of the same, *i.e.*, of the cotton and that part of the thermometer which is directly affected; and the unit of heat adopted is that quantity which is rendered available by the absorption of 1 milligramme (unit m) of moisture by the cotton.

From Equation (IV) it follows by integration that $m = c \int_0^t \theta dt + k\theta$, or for brevity,

$$m = cA + k\theta \dots\dots\dots (V),$$

a result which is manifest when it is considered that the total heat received by absorption from the beginning of any experiment up to any stated time is represented in part by the total heat lost within that time, and in part by the amount still retained by the covered thermometer in excess of its original heat contents, and also that the total heat lost is proportional to the average θ and the whole time, the product of which is A .

It is evident that, while c is a constant (by hypothesis) throughout

any series of tests performed under similar conditions, k is from the very nature of the case a variable; for it must increase gradually in proportion to the vapour absorbed. As a fact, however, it will be shown that the error arising from a neglect of this increase of k in the application of Equation (V) is negligible, provided that its value near the beginning of the experiment be fairly correctly estimated; for it is only at this end that $k\theta$ is at all large in comparison with cA , and by the time that k has undergone any noteworthy increase $k\theta$ itself may be regarded as a mere correction.

The values of c and k may be deduced from the experiments themselves in the following manner:—In the first place, since at the turning point (when $\theta = \phi$ and $t = \tau$) $d\theta/dt = 0$, it follows from Equation (IV) that here $c\theta = dm/dt$. This value of dm/dt can easily be got with fair accuracy by measuring the slope of the m curve at the time τ : hence, c is approximately determined. But a more exact value can be obtained by measuring A for a long experiment in which θ has become a mere fraction of 1° and A is very large, so that $k\theta$ may be fairly neglected in Equation (V). The value of c being fixed, that of k (taken as constant) follows by applying this equation to experiments of short duration. The following case serves for illustration:—The m curve for Series V, in which $\tau = 5.55$ and $\phi = 12.72$, gave about 3.1 as the value of dm/dt at 5.55 minutes; hence,

$c = \frac{3.1}{12.7} = 0.25$ approximately. Experiment 20 of the series showed $m = 187.9$ in 720 minutes, when θ was only 0.22 and A was 723.3;

hence $c = \frac{187.9}{723.3} = 260$. This last value was found to give very consistent results in the other experiments if k were taken as having the value 1.1. The figures in the column headed m (calcd.) in Table V were got from these values of c and k . In the case of Series IV (Table III), where a different thermometer and less cotton were used, and where the atmosphere of the bath (saturated at 18° instead of 25°) was less moist, slightly different figures were required, viz., $c = 0.25$ and $k = 1.0$.

If the θ curve were rigorously defined by Equation (III), it would follow that $A = \frac{b}{2} \log_e \frac{t^2 + a}{a}$ and $\theta = \frac{bt}{t^2 + a}$, so that m could be calculated from the time by the equation

$$m = \frac{bc}{2} \log_e \frac{t^2 + a}{a} + kb \frac{t}{t^2 + a},$$

which involves the three constants, a ($= \tau^2$ of the θ curve), $\frac{1}{2}bc$, and kb . As a matter of fact, a very fair approximation to the actual m values may be got in this way, though the agreement is not quite so good as when the measured A and θ are used, in which latter

case also the calculation is independent of any purely empirical formula.

The Influence of the Bath Temperature.

The only experiments designed to test this question were those summarised in Table IV and illustrated in fig. 4. The θ curves are there seen to cross one another on the down slope in such a way as to suggest that the rates of absorption, originally higher at the higher bath temperature, reverse their order of magnitude not long after passing the maximum θ . This conclusion would necessarily follow from Equation (IV) if c were a constant for the three experiments at 12° , 18° , and 25° , for then $c\theta$ must be equal for any pair at the moment of crossing, and $k d\theta/dt$ is manifestly of larger negative value there for the curve belonging to the higher bath temperature. But c , though essentially a constant unaffected by temperature, is known to be susceptible to change if the amount of water vapour in the air be altered, as is the case in passing from an experiment at one bath temperature to one at another, and, as a matter of fact, measurement of the areas of the θ curves for 12° , 18° , and 25° , and comparison of them with the actual m values at 65 minutes, show that c must be given the approximate values 0.22, 0.25, and 0.27 respectively. And when this difference is allowed for, it appears that the rates of absorption in the three experiments originally different approach the same value, but do not reverse their order. For a proper investigation of this question complete series of experiments would be required at different bath temperatures, all other conditions being the same.

Magnitude of the Heat Development.

In the preceding tables there is sufficiently good agreement between the found and calculated values of m to justify the statement that the two assumptions on which the calculation is based are substantially correct. It is tolerably certain that neither of them is rigorously true, but it may be taken as proved that the heat liberated during the immersion of cotton is, for practical purposes, directly proportional to the weight of moisture absorbed. This does not necessarily mean that there is nothing else to be considered than the simple heat of liquefaction. It may be so, but the condensation of vapour may be supplemented by some other process, either exothermic or endothermic. The experimental method that has been employed cannot properly test the question thus raised, but the following rough calculation shows that there can be no very large difference between the heat of liquefaction and the heat of absorption by cotton:—

In Series V it was found that $k = 1.1$ in the neighbourhood of the maximum temperature. Therefore, from the definition of k the heat capacity of the instrument used $= 1.1x$, the heat liberated per milligramme of water absorbed. A measurement of the volume of the bulb and also of known lengths of the stem of the thermometer was made by weighing it suspended in water before it was covered with cotton, and the total volume of glass and mercury subsequently covered was calculated from these data to be 0.60 c.c. If the volume heats of glass and mercury be both taken as 0.45 cal. per c.c., which is not far from true, the heat capacity of that part of the thermometer which was directly affected was 0.27. The specific heat of cellulose is, according to Fleury,* 0.366, and as the cotton used weighed very nearly 0.900 gramme, the total heat capacity of the dry instrument may be taken as $0.27 + 0.33 = 0.60$ cal. The addition for moisture already absorbed at the maximum temperature is about 0.03 cal. Hence, the

heat evolved per milligramme of vapour absorbed is $\frac{0.63}{1.1} = 0.57$ cal.

This is practically equal to the heat liberated (0.576 cal.) when a milligramme of vapour at 25° condenses to form liquid water at $37^\circ.7$, which were the experimental conditions. But the uncertainties involved in the above calculation forbid any further conclusion than that already given, viz., that the heat of absorption by cotton is composed *mainly* of the heat of liquefaction of water.†

Summary and Discussion of Results.

In the preceding pages it has been shown (1) that the conspicuous rise of temperature which cotton undergoes when immersed in water and its subsequent slow fall follow the same course as the similar change which results from its exposure to air saturated with water vapour, and that both are affected in the same way by previous moisture and other conditions; (2) that in the latter case the heating is the direct result of the absorption of the vapour by the cotton, and that the two processes can be quantitatively connected; (3) that both absorption and heat production continue appreciably for many hours, though the rise of temperature is soon succeeded by a fall because the heating effect is counteracted by radiation, etc., and that the evidence points to no definite limit to the absorption process; (4) that the heat produced by the absorption is of about the same magnitude as the heat of liquefaction of the same quantity of water, but may be, in fact, either rather more or rather less; (5) that in the case of immersion in water, though the absorption of vapour cannot be

* 'Chem. Soc. Abstr.,' 1900, vol. 2, p. 188.

† The phenomena evidently have their origin in a difference of physical affinities, which implies *some* difference between their heats.

observed, it must certainly occur, and that the air which adheres to each fibre and fills all interstices maintains that separation of water and cotton surfaces which is necessary for distillation to occur from one to the other.

Two questions remain to be discussed, viz., the probable fate of the vapour after it has been condensed on the surface of the cotton, and the bearing of the conclusions here arrived at on the nature of the Pouillet effect in general.

As to the first question there seem to be three possible views. One of these—the view that it becomes chemically combined to form definite hydrates of cellulose—may be quickly dismissed, as there are no facts to support it and as the evidence points to the absence of any definite limit to the action. The ease with which the action is reversed (for the cotton parts with practically all its moisture if kept for a day at the ordinary temperature over sulphuric acid) is not by itself evidence against the chemical theory, but it may be mentioned here. At the opposite extreme is the view that the condensed moisture forms and remains as a liquid film on the surface of the solid. If it is so, the film must in time become a substantial one, as the following calculation shows.

The average diameter of cotton fibres varies, according to the quality, between 64×10^{-5} and 84×10^{-5} inch.* The mean of these may be taken as the most probable average diameter in the present case, viz., 74×10^{-5} inch, or 188×10^{-5} cm. Actual measurement of fibres under the microscope led to practically the same result but were not numerous enough to give a perfectly trustworthy average value. The density of cellulose may be taken as 1.525 (Clarke's Specific Gravity Table). The total surface of any given weight (w) of cotton may be calculated on the assumption that the fibres are uniform cylinders of such length that the ends are negligible, in which case the area is $4w/1.525 \times 188 \times 10^{-5} = 1395w$ sq. cm. If m grammes of water be deposited on this surface as a film, the thickness of the film is $m/1395w$ sq. cm. In Experiment 20 of Series V (Table V) w was 0.90 gramme and m was shown to have attained the value 0.188 gramme at the end of 12 hours. In this case, therefore, the thickness of the film would be about 15×10^{-5} cm. Now Dr. G. J. Parks† concluded from similar calculations that in all such cases “the thickness of the surface film varies from 10×10^{-6} to 80×10^{-6} cm. according to the substances used and the conditions of temperature and pressure, and for the water film on glass in saturated vapour at 15° C. the thickness is about 13.4×10^{-6} cm.” Hence the film on cotton in the above case was considerably outside Dr. Parks's superior limit, and it had by no

* Thorpe's 'Dict. of Techn. Chem.,' vol. 1, p. 613.

† “On the Thickness of the Liquid Film formed by Condensation at the Surface of a Solid,” 'Phil. Mag.,' May, 1903, p. 517.

means attained its full growth and, in fact, threatened to increase indefinitely.

It seems probable, therefore, that the deposited moisture does not all remain as a mechanically adherent film on the surface of the cotton; and the third hypothesis may be suggested. This is, that it undergoes continuous osmotic diffusion into the substance of the fibre and forms with it what may be regarded as a solid solution of cellulose and water. Such a solution would exercise a vapour pressure of its own which would, at anything less than infinite dilution, be smaller than that of pure water at the same temperature. In a saturated atmosphere therefore equilibrium would never be reached, though the velocity of the absorption process would decrease continuously as the solution became more dilute. The heat developed locally by the action, *i.e.*, the heat due to the deposition of the liquid plus or minus a small heat of solution, would go to raise the temperature of the cotton above that of the neighbouring water by which the vapour is supplied, and would thus tend to check the action by increasing the vapour tension of the solution; but the natural cooling by radiation, etc., would again act as a counter-check. If placed in an atmosphere containing water vapour at anything less than saturation pressure (*e.g.*, in the open air) the cotton would, in time, reach a state of equilibrium either by absorption or by evaporation, according to its initial condition, and it would part with all its water if the surrounding atmosphere were maintained in a perfectly dry state, slowly or quickly according to the temperature. This is all in accordance with the ascertained facts, and as it is also inherently probable that the cotton fibre is permeable by water, the hypothesis appears to be justified.

As solids in general have the power of condensing vapours on their surface, it was not surprising to find a marked heat development on immersing cotton wool in air saturated with the vapour of absolute alcohol, gun-cotton in air saturated with water vapour, and glass wool in the same; but the effect was considerably smaller than when cotton wool was immersed in water vapour under similar conditions. In the case of glass wool the temperature curve was taken and weighings were made so as to determine the amount of vapour absorbed. The thermometer was wrapped as closely as possible with the material, which was secured by a few turns of fine aluminium wire, and the other arrangements were the same as in Series V. The glass wool weighed, after drying, 1.22 gramme. The diameter of the fibres was measured under the microscope and was found to vary from about 0.001—0.003 cm. It would have been necessary to make a large number of measurements to determine an accurate mean value, but 0.0025 cm. may be taken as near the mark; and this, with a density of 2.7, would make the total area of surface about 720 sq. cm. or about 0.57 of the area exposed by the cotton wool of Series V. The maximum rise was 1°.94 and 2°.1 in

two experiments, and this was reached in 2 minutes, as nearly as possible. The first test was continued for 40 minutes, when about 17 milligrammes of vapour was found to have been condensed; the second was stopped at 5 minutes, when about 7 was the weight found. The temperature curve resembled that of cotton wool in a general way, for it rose steeply to the maximum and showed a slow descent; but its form was quite different in this, that it gave not even a rough approximation to those rules which have been found to govern the other case. This fact and the relatively small absorption (allowance being made for difference of surface area) are just what might be expected from the presumably impermeable character of glass, as here probably the condensed water remains as a mere surface film.

According to the views already put forward as to the cause of the temperature change when cotton is immersed in water itself, it seemed probable that little or no effect of the kind would be produced by immersing cotton in absolute alcohol or glass wool in water, though in both cases notable effects followed immersion in the bath of air saturated with vapour. As a fact, no change could be observed. In the case of glass wool and water, the test was very carefully carried out, and there was not the least sign of departure from the initial temperature, which was that of the thermostat surrounding the water. A change of $0\cdot02$ could hardly have escaped notice. Apparently, then, the effect does not occur when the liquid is capable of rapidly and completely wetting the solid, and thus destroys the air insulation. In confirmation, it was found here, as in the case of "absorbent" cotton wool already described, that the thermometer when lifted from the bath carries with it a much larger weight of mechanically adhering water than comes away with a wrapping of cotton of the ordinary variety.

There is not the least doubt that the thermal effect dealt with in this paper is radically different from that investigated by Dr. G. J. Parks by the use of precipitated silica and of glass wool* and attributed by him to a pressure at the surface of contact of solid and liquid. In the first place, the Parks effect is manifested as a general rise of temperature on mixing the solid and water, and he detected it and determined its value by employing the immersion vessel as a calorimeter; whereas the cotton wool effect is essentially local and would be altogether prevented by any mixing process efficient enough to make complete contact between the solid and liquid. In the next place, Parks took the maximum temperature, reached in about 3 minutes, as indicative of the completion of the action, while it has been proved in the other case that the action, though leading to a maximum temperature in about the same time, has then but started on an apparently endless career. Finally Parks estimates the

* 'Phil. Mag.,' August, 1902, p. 240, and May, 1903, p. 517.

value of his heat production as about 0.001 cal. per sq. cm. of surface of exposed glass or silica, whereas it can be shown from facts already given that even in the case of saturated air immersion, about twelve times this quantity of heat is not generated but transferred per square centimetre of cotton wool in the first few minutes when, as just stated, only a small fraction of the total action has occurred. As the Parks effect is so small it is easy to understand how it escaped observation in the author's experiment with glass wool, already described, where the conditions were altogether unfavourable, having been arranged with a different object; for Parks himself, using a larger quantity of material, which he gently stirred with about the same amount of water as was contained in the author's immersion vessel, obtained a rise of only $0^{\circ}01$.

It is difficult to say for certain whether the heating effects observed originally by Pouillet were due to the phenomenon investigated by Parks and styled by him "the Pouillet effect," or were the results of action similar to that described in this paper, or included both. But as he heaped his dry solid round the bulb of a delicate thermometer, and was careful not to disturb the heap by stirring it after adding the liquid, it is unlikely that true contact was established at once and completely, and it seems reasonable to suppose that he had to do with local heating by condensation of vapour. The still more striking, but similar observations of Martini* are probably to be explained in the same way and not, as he suggests, by the solidification of liquid water.

In conclusion, it may be pointed out that the hygroscopic behaviour of cellulose and the thermal changes associated with it have a practical importance of their own on the side of vegetable physiology, and perhaps also in other directions, apart from any interest they may have on purely physical grounds.

* 'Phil. Mag.' [5] vol. 47, p. 329; vol. 50, p. 618; [6] vol. 5, p. 595.