SMITHSONIAN

CONTRIBUTIONS TO KNOWLEDGE

VOL. XXIX

EVERY MAN IS A VALUABLE MEMBER OF SOCIETY WHO, BY HIS OBSERVATIONS, RESEARCHES, AND EXPERIMENTS, PROCURES
KNOWLEDGE FOR MEN.—SMITHSON.

CITY OF WASHINGTON
PUBLISHED BY THE SMITHSONIAN INSTITUTION
1903

ADVERTISEMENT

This volume forms the twenty-ninth of a series, composed of original memoirs on different branches of knowledge, published at the expense and under the direction of the Smithsonian Institution. The publication of this series forms part of a general plan adopted for carrying into effect the benevolent intentions of James Smithson, Esq., of England. This gentleman left his property in trust to the United States of America to found at Washington an institution which should bear his own name and have for its objects the "*increase* and *diffusion* of knowledge among men." This trust was accepted by the Government of the United States, and acts of Congress were passed August 10, 1846, and March 12, 1894, constituting the President, the Vice-President, the Chief Justice of the United States, and the heads of Executive Departments an establishment under the name of the "Smithsonian Institution, for the Increase and Diffusion of Knowledge among Men." The members of this establishment are to hold stated and special meetings for the supervision of the affairs of the Institution and for the advice and instruction of a Board of Regents to whom the financial and other affairs are intrusted.

The Board of Regents consists of two members ex officio of the establishment, namely, the Vice-President of the United States and the Chief Justice of the United States, together with twelve other members, three of whom are appointed from the Senate by its President, three from the House of Representatives by the Speaker, and six persons appointed by a joint resolution of both Houses. To this Board is given the power of electing a Secretary and other officers for conducting the active operations of the Institution.

To carry into effect the purposes of the testator, the plan of organization should evidently embrace two objects: one, the increase of knowledge by the addition of new truths to the existing stock; the other, the diffusion of knowledge, thus increased, among men. No restriction is made in favor of any kind of knowledge, and hence each branch is entitled to and should receive a share of attention.

The act of Congress establishing the Institution directs, as a part of the plan of organization, the formation of a library, a museum, and a gallery of art, together with provisions for physical research and popular lectures, while it leaves to the Regents the power of adopting such other parts of an organization as they may deem best suited to promote the objects of the bequest.

3. The results obtained from these appropriations to be published, with the memoirs before mentioned, in the volumes of the Smithsonian Contributions to Knowledge.

4. Examples of objects for which appropriations may be made:

(1) System of extended meteorological observations for solving the problem of American storms.

(2) Explorations in descriptive natural history, and geological, mathematical, and topographical surveys, to collect material for the formation of a physical atlas of the United States.

(3) Solution of experimental problems, such as a new determination of the weight of the earth, of the velocity of electricity, and of light; chemical analyses of soils and plants; collection and publication of scientific facts, accumulated in the offices of Government.

(4) Institution of statistical inquiries with reference to physical, moral, and political subjects.

(5) Historical researches and accurate surveys of places celebrated in American history.

(6) Ethnological researches, particularly with reference to the different races of men in North America; also explorations and accurate surveys of the mounds and other remains of the ancient people of our country.

I. TO DIFFUSE KNOWLEDGE.—*It is proposed to publish a series of reports, giving an account of the new discoveries in science, and of the changes made from year to year in all branches of knowledge not strictly professional.*

1. Some of these reports may be published annually, others at longer intervals, as the income of the Institution or the changes in the branches of knowledge may indicate.

2. The reports are to be prepared by collaborators eminent in the different branches of knowledge.

3. Each collaborator to be furnished with the journals and publications, domestic and foreign, necessary to the compilation of his report; to be paid a certain sum for his labors, and to be named on the title-page of the report.

4. The reports to be published in separate parts, so that persons interested in a particular branch can procure the parts relating to it without purchasing the whole.

5. These reports may be presented to Congress for partial distribution, the remaining copies to be given to literary and scientific institutions and sold to individuals for a moderate price.

[illegible]

[illegible]

[illegible]

[illegible] period, performer, etc.

[illegible] FINE ARTS

[illegible]

DETAILS OF THE SECOND PART OF THE PLAN OF ORGANIZATION.

This part contemplates the formation of a library, a museum, and a gallery of art.

1. To carry out the plan before described a library will be required consisting, first, of a complete collection of the transactions and proceedings of all the learned societies of the world; second, of the more important current periodical publications and other works necessary in preparing the periodical reports.

2. The Institution should make special collections particularly of objects to illustrate and verify its own publications; also a collection of instruments of research in all branches of experimental science.

3. With reference to the collection of books other than those mentioned above, catalogues of all the different libraries in the United States should be procured, in order that the valuable books first purchased may be such as are not to be found elsewhere in the United States.

4. Also catalogues of memoirs and of books in foreign libraries and other materials should be collected, for rendering the Institution a center of bibliographical knowledge, whence the student may be directed to any work which he may require.

5. It is believed that the collections in natural history will increase by donation as rapidly as the income of the Institution can make provision for their reception, and therefore it will seldom be necessary to purchase any article of this kind.

6. Attempts should be made to procure for the gallery of art, casts of the most celebrated articles of ancient and modern sculpture.

7. The arts may be encouraged by providing a room, free of expense, for the exhibition of the objects of the Art Union and other similar societies.

8. A small appropriation should annually be made for models of antiquities, such as those of the remains of ancient temples, etc.

9. The Secretary and his assistants, during the session of Congress, will be required to illustrate new discoveries in science and to exhibit new objects of art. Distinguished individuals should also be invited to give lectures on subjects of general interest.

In accordance with the rules adopted in the programme of organization, each memoir in this volume has been favorably reported on by a commission appointed for its examination. It is, however, impossible, in most cases, to verify the statements of an author, and therefore neither the commission nor the Institution can be responsible for more than the general character of a memoir.

OFFICERS

OF THE

SMITHSONIAN INSTITUTION

THEODORE ROOSEVELT,

PRESIDENT OF THE UNITED STATES,

EX OFFICIO PRESIDING OFFICER OF THE INSTITUTION.

MELVILLE W. FULLER,

CHIEF JUSTICE OF THE UNITED STATES,

CHANCELLOR OF THE INSTITUTION.

SAMUEL P. LANGLEY,

SECRETARY OF THE INSTITUTION.

RICHARD RATHBUN,

ASSISTANT SECRETARY.

MEMBERS EX OFFICIO OF THE INSTITUTION

Theodore Roosevelt	*President of the United States.*
(Vacancy)	*Vice-President of the United States.*
Melville W. Fuller	*Chief Justice of the United States.*
John Hay	*Secretary of State.*
Leslie M. Shaw	*Secretary of the Treasury.*
Elihu Root	*Secretary of War.*
Philander C. Knox	*Attorney-General.*
Henry C. Payne	*Postmaster-General.*
William H. Moody	*Secretary of the Navy.*
Ethan Allen Hitchcock	*Secretary of the Interior.*
James Wilson	*Secretary of Agriculture.*
George B. Cortelyou	*Secretary of Commerce and Labor.*

REGENTS

CONTENTS

SMITHSONIAN CONTRIBUTIONS TO KNOWLEDGE

842

ON THE APPLICATION OF
INTERFERENCE METHODS
TO
SPECTROSCOPIC MEASUREMENTS

With Five Plates

BY

ALBERT A. MICHELSON

CITY OF WASHINGTON
PUBLISHED BY THE SMITHSONIAN INSTITUTION
1892

SMITHSONIAN CONTRIBUTIONS TO KNOWLEDGE

842

ON THE APPLICATION OF
INTERFERENCE METHODS
TO
SPECTROSCOPIC MEASUREMENTS

With Five Plates

BY

ALBERT A. MICHELSON

* * *

CITY OF WASHINGTON
PUBLISHED BY THE SMITHSONIAN INSTITUTION
1892

ADVERTISEMENT.

The present research—an extension of a line of investigation pursued by the author, Mr. A. A. Michelson, for a year or two past—has in view an increased accuracy in the measurement of the wave-lengths of specific spectroscopic lines by means of new applications of the method of interference.

One ultimate object of such greater precision of determination is the employment of particular wave-lengths of light as standards of comparison of metrical units.

As a preliminary investigation of some importance, carried on under the auspices of the Smithsonian Institution, the memoir is adopted as one deserving a place in the Smithsonian "Contributions to Knowledge."

S. P. LANGLEY,
Secretary Smithsonian Institution.

WASHINGTON, July, 1892.

ON THE APPLICATION OF INTERFERENCE METHODS TO SPECTROSCOPIC MEASUREMENTS.

By Albert A. Michelson.*

The theoretical investigation of the relation between the distribution of light in a source, as a function of the wave-length, and the resulting "visibility curve" has been given in a paper bearing the same title as the present one in the *Philosophical Magazine* for April, 1891.

The physical definition of "visibility" there adopted is

$$V = \frac{I_1 - I_2}{I_1 + I_2}$$

in which I_1 is the intensity at the center of a bright interference band, and I_2 the intensity at the center of the adjoining dark band. In order to interpret the actual curves obtained by observation of interference fringes, it is first necessary to reduce the results of the eye-estimates of visibility, which may be designated by V_e, to their absolute values as above defined.

For this purpose, two quartz lenses, one concave and the other convex, and of equal curvatures, were mounted with their crystalline axes at right angles to each other between two Nicols. Under these conditions a series of concentric interference rings appeared. If α be the angle between the prin-

---

* I take this opportunity of presenting my acknowledgments and thanks to the Smithsonian Institution for the funds necessary to carry out this research; to Clark University for the facilities it has placed at my disposal; and especially to Mr. F. L. O. Wadsworth, Assistant in Physics of Clark University, for the valuable services he has rendered and his unflagging zeal in furthering this investigation.

cipal section of the polarizer and the axis of the first quartz, and ω the angle between the axis and the analyzer, the intensity of the light transmitted will be

$$I = \cos^2(\omega - \alpha) - \sin 2\alpha \sin 2\omega \sin^2 \pi \frac{k(t_1 - t_2)}{\lambda}.$$

where t_1 is the thickness through the first quartz, and t_2 that through the second. If the analyzer and polarizer are parallel,

$$\omega = \alpha, \quad \text{and} \quad I = 1 - \sin^2 2\alpha \sin^2 \pi \frac{k(t_1 - t_2)}{\lambda}.$$

whence $I_1 = 1$, and $I_2 = 1 - \sin^2 2\alpha$.

and $$V = \frac{I_1 - I_2}{I_1 + I_2} = \frac{1 - \cos^2 2\alpha}{1 + \cos^2 2\alpha}.$$

This curve, together with the mean of a number of eye-estimates, is given in Fig. 2, Plate I. From these the following table of corrections may be obtained:

V	Cor.	V	Cor.
0.00	0.00	0.55	0.12
.05	.03	.60	.14
.10	-.04	.65	-.15
.15	-.03	.70	.16
.20	-.02	.75	-.16
.25	.00	.80	-.14
.30	.03	.85	.13
.35	.05	.90	.11
.40	.07	.95	.08
.45	.08	1.00	.00
.50	.10		

The curves show a general tendency to estimate the visibility too high when the interference bands are clear, and too low when they are indistinct. This tendency may be modified by a number of circumstances; — thus, it increases with the refrangibility of the light used; it is greater when the field contains a large number of bands than when there are but few; it is greater while the visibility curve is falling than when it is rising; it does not seem to be greatly affected by the intensity of the light; finally, it varies on different occasions and with different observers. Notwithstanding these disturbing causes, the result, after applying the correction, will rarely be in error by more than one tenth of its value, and ordinarily the approximation is much closer than this.*

The observations necessary to construct the visibility curves, from which the distribution of light in any approximately homogeneous source is to be deduced, may be made with any form of interference apparatus, which allows a considerable alteration in the difference of path between the two interfering streams of light.

The apparatus actually employed for this purpose was designed for the comparison of wave-lengths, and while admirably adapted for the observation of visibility curves, it contains many parts not necessary for this use. Fig. 1, Plate I., presents the plan of an arrangement which, while showing all the essential parts, is much less complicated. Starting from V, a vacuum-tube containing the substance whose radiations are to be examined (and which is usually inclosed in a metal box in order that it may be raised to any required temperature), the light is analyzed by one or more prisms

---

* The formula for visibility deduced in the former paper (*Phil. Mag.*, vol. XXI; p. 340), is

$$V^2 = \frac{C^2 + S^2}{P^2}$$

in which $C = \int_0^\infty \varphi(x) \cos kx\, dx$,

$$S = \int_0^\infty \varphi(x) \sin kx\, dx,$$

$$P = \int_0^\infty \varphi(x)\, dx,$$

$$k = 2 \pi D,$$

$D =$ Difference in path,

and $\varphi(x)$ represents the distribution of light in the source.

In this expression, no account was taken of the effect of extraneous light, and it was assumed that the two interfering pencils were of equal intensities. It can be shown that the error due to both these causes tends to lower the visibility; but in either case the correct values may be obtained by multiplying by a constant factor.

In the first case, let e be the intensity of the extraneous light, and V' the resulting visibility; then, by definition,

$$V' = \frac{(I_1+e)-(I_2+e)}{(I_1+e)+(I_2+e)} = \frac{I_1 - I_2}{I_1 + I_2 + 2e}\ ; \quad \text{or if} \quad \frac{2e}{I_1 + I_2} = r, \quad V' = \frac{I_1 - I_2}{(I_1 + I_2)(1 + r)}$$

whence $V = (1 + r)\, V'$.

In the second case, let ρ be the ratio of intensities of the interfering pencils; then it can readily be shown that the resulting intensity is $I = (1 + \rho^2)\, P + 2\rho\, (C \cos \theta - S \sin \theta)$,

and hence the visibility is $V'' = \frac{2\rho}{1+\rho^2} \frac{\sqrt{C^2 + S^2}}{P}$, whence $V = \frac{1+\rho^2}{2\rho}\, V''$

If the interfering pencils differ by 25 per cent., the factor $\frac{1+\rho^2}{2\rho}$ differs from unity by about 4 per cent.; so that, in most cases, this cause of error may be neglected.

forming a spectrum from which any required radiation may be separated from the rest by passing through the slit S.[*]

The light from S is rendered nearly parallel by a collimating lens, and then falls on a transparent film of silver, on the surface of the plane parallel plate G_1.[†] Here it divides, part being transmitted to the fixed plane mirror M_1, and part reflected to the movable mirror M_2. These mirrors return the light to the silvered surface, where the first part is reflected, and the second transmitted; so that both pencils coincide on entering the observing telescope.[‡]

A little consideration will show that this arrangement is, in all respects, equivalent to a film or plate of air between two plane surfaces. The interference phenomena are therefore the same as for such an air-plate.

The theory of these interference bands has been given in an article entitled "Interference Phenomena in a New Form of Refractometer," *Philosophical Magazine* for April, 1882. As is there shown, the projections of the bands are, in general, conic sections, the position of maximum distinctness being given by the formula

$$P = \frac{t_0}{\tan \varphi} \tan i \cos^2 \theta$$

in which t_0 is the thickness of the equivalent air-plate, where it is cut by the axis of the telescope, φ, the inclination of the two surfaces, θ and i, the components of the angle of incidence parallel and perpendicular respectively to the intersection of the surfaces, and P, the distance of the plane of maximum distinctness from the surfaces. If θ be small, the variations of P with θ may be neglected, and we have then

$$P = \frac{t_0}{\tan \varphi} \tan i,$$

or with sufficient accuracy,

$$P = \frac{t_0}{\varphi} i.$$

---

[*] In the case of close groups of lines, the image of the source is first thrown on a slit; otherwise, the lines at S would overlap.

[†] The light entering the telescope is a maximum when the thickness of the silver film is such that the intensity of the transmitted light is equal to that of the reflected light. The silvering has another important advantage in diminishing the relative intensity of the light reflected from the other surface. Indeed, for this purpose, it is advisable to make the film heavier; even so thick that the reflected light is twice as bright as the transmitted. This does not affect the ultimate ratio of intensities of the interfering pencils; for what is lost by transmission on entering the plate G_1 is made up by reflection on leaving it, the effect being simply to diminish somewhat the whole intensity. Another advantage of the thicker film is that it can be made uniform with far less difficulty than the thin film. It may be mentioned that with this form of instrument the interference fringes in white light present a purity and gorgeousness of coloration that are surpassed only by the colors of the polariscope.

[‡] The second plane parallel plate G_2 is made of the same thickness as the first, and is required to equalize the optical paths of the two pencils.

From this it will be seen that the focal plane varies very rapidly with i, so that, unless $\varphi=0$, it is impossible to see all parts of the interference bands in focus with equal distinctness. If, however, $\varphi=0$, that is, if the two surfaces are strictly parallel, then $P=\infty$, and if the observing telescope is focused for parallel rays, all parts of the bands are equally distinct. Under these circumstances the interference fringes are concentric circles, whose angular diameter is given by

$$cos\ \vartheta = \frac{\triangle}{2\,t_o}.$$

If for $\triangle$ we put $2\,t_o - n\lambda$, and for $cos\ \vartheta$, its approximate value $1-\frac{\vartheta^2}{2}$, we have

$$\vartheta_n = \sqrt{\frac{n\lambda}{t_o}}.$$

In order to obtain an idea of the order of accuracy required in this adjustment, suppose the angle ϑ to be so small that its influence on the distinctness may be neglected. The intensity at the focus of the observing telescope will be

$$I=\int\int cos^2\ \tfrac{1}{2}\ \kappa\ \triangle\ dx\ dy, \text{ where } \kappa=\frac{2\pi}{\lambda}.$$

If the aperture be a rectangle whose height is $2b$, and width $2a$,

$$I=2b\int_{-a}^{+a} cos^2\ \tfrac{1}{2}\ \kappa\ \triangle\ dx.$$

But

$$\triangle = 2\,(t_o+\varphi\,x),$$

whence

$$I=2b\left[a+cos\ 2\kappa\,t_o\ \frac{sin\ 2\kappa\ \varphi\ a}{2\kappa\ \varphi}\right].$$

The maximum value of I is

$$2b\left[a+\frac{sin\ 2\kappa\ \varphi\ a}{2\kappa\ \varphi}\right]$$

and the minimum value is

$$2b\left[a-\frac{sin\ 2\kappa\ \varphi\ a}{2\kappa\ \varphi}\right],$$

whence

$$V=\frac{sin\ 2\kappa\ \varphi\ a}{2\kappa\ \varphi\ a}.$$

In attempting to verify this formula by actual observation, one is met by the difficulty that all parts of the bands are not in focus at the same time, the right and left bands being more distinct than the central one, to which attention ought to be directed. Notwithstanding the rather rough character of the observations, the results agree fairly well with theory. If φ_o is the ratio of the wave-length to the width of the rectangular aperture, the above formula becomes

$$V = \frac{\sin 2\pi\phi\phi_0}{2\pi\phi\phi_0},$$

from which the second column in the following table was calculated:

$\phi\phi_0$	V (calc.)	V (obs.)
0.0	1.00	1.00
.1	.94	.94
.2	.75	.73
.3	.50	.40
.4	.24	.13
.5	.00	.09
.6	.15	.10
.7	.22	.09
.8	.19	.07
.9	.15	.05
1.0	.00	.04

From this table it appears that if the visibility is to be estimated by observations with a telescope of 12 ^{mm} aperture (or with a circular aperture about one fourth greater), an error in the adjustment of the surfaces of a second of arc would produce a diminution of four or five per cent. in the visibility. Accordingly, if the ways on which the mirror-carriage moves are not true to this degree, it is necessary to make the adjustment for every observation.

This can be done with very great accuracy by moving the beam of light from side to side and adjusting the mirror until there is no perceptible alteration in the size of the rings. Since the admissible error in adjustment is inversely proportional to the aperture, the observations may be facilitated by making this as small as possible if there be light to spare. This is all the more necessary for the same reasons, if the surfaces be not true. However, the error due to this source may be easily corrected (since all the observations are affected alike) by multiplying by a constant factor.

In order that the visibility curve may extend as far as possible, it is necessary that the vapor should be very rare. Accordingly, in all but a few cases to be mentioned later, the substance to be investigated was inclosed in a vacuum-tube which was heated to drive off any moisture or occluded gases.

The vapor was rendered luminous by the discharge from the secondary of a large induction-coil, whose primary current was interrupted by a rotary break attached to the armature of an electric motor, making about 20 to 30 breaks per second. The steadiness of the light thus obtained was far greater than with the ordinary Foucault interrupter. Probably it would have been still more satisfactory to use an alternating dynamo properly wound to give a strong current with comparatively few alternations.

The box surrounding the vacuum-tube was heated just sufficiently to give a steady, bright light, and the temperature then kept as nearly uniform as possible. This temperature was usually taken to represent that of the vapor within the tube. This is of course only a rough approximation to the truth; and in some cases the estimate was much too low.

As it was not intended to include in the present work an elaborate study of the effect of temperature, this matter was not of great consequence. It may be suggested, however, that a very much closer approximation to the real temperature could be obtained by winding a platinum wire about the capillary portion of the tube, and deducing the temperature from the variation of its resistance. A preliminary experiment in which a platinum wire passing through the tube and heated by a current until the platinum spiral outside the tube was raised to fixed temperatures, would give a means of deducing, from the indications of the spiral, the true temperature within the tube.

These adjustments being effected, the screw of the "wave-comparer" was turned to zero; that is, till there was no difference of path between the interfering pencils. At this point the visibility should be as great as possible, and was accordingly marked 100. The screw (of 1 $^{\text{mm.}}$ pitch) was then turned through one turn, thus giving a difference of path of 2 $^{\text{mm.}}$, and the visibility again estimated, and so on. The curve was then drawn, giving the estimated visibility for each 2 $^{\text{mm.}}$ difference of path, and this was corrected for the personal equation, as before described.

Hydrogen. The full curve in Fig. 3*b*, Plate II., represents such a curve for the red hydrogen line* at a pressure of about 1 $^{\text{mm.}}$ and a temperature of about 50° C. The dotted curve represents $V = 2^{-X^{2}\ 19^{2}} \cos 0.7\ 30$.

---

* The hydrogen was prepared by dropping distilled water upon sodium amalgam, and allowing the gas to pass through sulphuric acid into the vacuum-tube, which was repeatedly exhausted until the spectrum of hydrogen was nearly pure.

It follows that the visibility curve is practically the same as that due to a double source, whose components have the intensity ratio 7:10, and in each of which the light is distributed according to the exponential law expressed by the first term.

The formula for a double source, where the components are similar, is

$$V^2 = \frac{1 + r^2 + 2r \cos 2\pi \frac{X}{D}}{1 + r^2 + 2r} V_1^2 \;*$$

in which D, the period of the curve, is inversely proportional to the distance between the components.

$$\text{But } D = N\lambda_1 = (N+1)\lambda_2, \text{ whence } \alpha = \lambda_1 - \lambda_2 = \frac{\lambda^2}{D}.$$

Hence, in the present instance we have for the distance between the components of the red hydrogen line, $1/30 \times (6.56 \times 10^{-4})^2 = 1.4 \times 10^{-8}$ mm., or 0.14 divisions of Rowland's scale.

Again, if δ be the "half-width" of the spectral line (the value of x when $\varphi(x) = \frac{1}{2}$), then

$$\varphi(x) = 2^{-\frac{x^2}{\delta^2}}, \text{ and } V = e^{-\frac{\pi^2 X^2 \delta^2}{l2}}.$$

If Δ be the value of X for $V = \frac{1}{2}$, then $\delta = \frac{l2}{\pi}\frac{1}{\Delta}$, or, with sufficient accuracy, $\delta = \frac{0.22}{\Delta}$.

Substituting the value of δ in the equation for V, we have

$$V = 2^{-\frac{X^2}{\Delta^2}}.$$

The value of Δ in the hydrogen curve is 19. Accordingly, after reducing to the same units as above, we have $\delta = 0.049$.

From these data, Fig. 3*a* was constructed, the full curve showing the distribution of light in the source.

Fig. 1*b*, Plate II., gives, in the full curve, the corrected values of the visibility of the blue hydrogen line at the same temperature and pressure as

---

* As frequent use is to be made of the function

$$\sqrt{\frac{1 + r^2 + 2r \cos 2\pi \frac{X}{D}}{1 + r^2 + 2r}}$$

it will be abbreviated to the form $\cos r/D$.

before. The dotted curve represents a double exponential, as before. The formula for this curve is

$$V = 2^{-X^2\ 24^2} \cos 0.7\ 28,$$

thus giving $\alpha = 0.08$ for the distance between the components, and $\delta = 0.057$ for the "half-width" of each. These values give for the distribution of light in the blue hydrogen line the full curve in Fig. 4*a*.

Oxygen. Fig. 5, Plate II., represents the results obtained from oxygen prepared by heating a tube containing mercuric oxide, drying the gas by sulphuric acid, and exhausting and filling repeatedly, till the spectrum was nearly pure. The lines are much less bright than those of hydrogen, and in order to obtain satisfactory results, the current had to be increased so far that the tube was frequently broken. Notwithstanding the somewhat uncertain character of the observations, it will be seen from Fig. 5*a* that the curve for the orange-red line corresponds very well with that given by the formula

$$V = 2^{-X^2\ 34^2}\left[0.36 + 0.32 \cos 2\pi X\ 2.69 + 0.16 \cos 2\pi X\ 4.85 + 0.16 \cos 2\pi X\ 1.73\right]^{\frac{1}{2}}.$$

The agreement between the coefficient $2^{-X^2\ 34^2}$, and the general curve drawn through the maxima, is also shown in Fig. 5*b*, Plate II.

The interpretation of these results is that the orange-red oxygen line is a triple, whose components have intensities in the ratios $1:1:{}^1{}_2$, and whose distances apart are 1.51 and 0.84 respectively, and whose "half-width" is 0.027. This is shown in Fig. 5*c*.

Sodium. The results obtained from metallic sodium in the vacuum-tube are so varied, the character of the lines being so considerably altered by temperature and pressure, that a complete study is at present impossible. This is especially true of the yellow lines, and the difficulty is considerably increased on account of the insufficiency of the dispersion used, which does not permit the separate examination of the lines. Some reference to the changes mentioned will be given at the close of this paper. At present it will suffice to take a particular case,—the pressure being very low, and the temperature about 250°.*

---

* The curve given above was obtained a year ago, and since then it has been impossible to reproduce it exactly.

The full curve in Fig. 6*b*, Plate II., gives the experimental result for the visibility at the maxima for yellow sodium, corrected for personal equation. The dotted curve corresponds to the formula

$$V = 2^{-x^2/c} \cos 0.7\ 50 \cos 0.1\ 140.$$

The complete equation, assuming that the two lines are alike, is

$$V = 2^{-x^2/c} \cos 0.8\ 0.58 \cos 0.7\ 50 \cos 0.1\ 140.$$

The interpretation of these results is that each of the sodium lines is a close double, as shown in Fig. 6*a*.

The yellow-green sodium line at $\lambda = 5687$ is a double whose components are about the same distance apart as the yellow pair. It was found to be far less variable than the yellow, and the full visibility curve, neglecting slight irregularities, gives the experimental results corrected for personal equation. Fig. 7*b*, Plate II., shows that its components are single and correspond in distribution of light fairly well with the exponential curve, Fig. 7*a*.

The same may be said of the orange-red double at 6156 also, except that this seems to have a companion of feeble intensity.

The doubles at 5150 and at 4982 were also examined, the curves showing nearly the same results as the red.

Zinc. The temperature at which the radiations from metallic zinc could be conveniently observed was in the neighborhood of the melting-point of the glass of which the vacuum-tubes were made. But few observations were recorded, though these were quite consistent. The results of the observations, corrected for personal equation, are given in Figs. 8 and 9, Plate II. The former is the record obtained from the red line near 6360, and shows that this line is single, the distribution of light agreeing very well with a simple exponential curve, the "half-width" being 0.013. The latter shows the results of observation on the blue line near 4811. The dotted curve is the visibility curve due to a distribution represented in Fig. 9*a*.

Cadmium. Metallic cadmium in the vacuum-tube at a temperature of about 280° gives a number of very bright lines, widely separated, and varying very slightly with temperature or pressure. Fig. 10*b*, Plate III., shows the experimental visibility curve of the red line near 6439, corrected for personal equation, together with the simple exponential curve

$$V = 2^{-X^2\ 138^2}.$$

The remarkably close agreement leaves no doubt that the distribution of light in the source follows very nearly the exponential law giving the curve in Fig. 10*a*, in which the "half-width" of the source is 0.0065.

The results of a single set of observations on the green line at 5086 is given in Fig. 11*b*, Plate III., the approximate agreement between the full line and the dotted curve, which corresponds to the equation

$$V = 2^{-X^2\ 120^2}\ \mathit{cos}\ 0.2\ 115,$$

showing that the source is a close double, the intensity of whose components is in the ratio 5:1, and whose distance apart is 0.022; the "half-width" of each component being 0.0048.

The curve for the blue radiation at 4800 is given in Fig. 12*b*, Plate III., and shows that the results may be approximately represented by

$$V = 2^{-X^2\ 64^2}\ \mathit{cos}\ 0.1\ 32,$$

which corresponds to the distribution of intensity given in Fig. 12*a*.

Thallium. The metal is not sufficiently volatile at the temperatures attainable, but the chloride answers admirably, giving a brilliant green light, the visibility curve varying but little with temperature. This curve is given in Fig. 13*b*, Plate III., together with the dotted curve representing the equation

$$V = \tfrac{1}{3}\ \mathit{cos}\ 0.2\ 160 \sqrt{4\ V_1{}^2 + V_2{}^2 + 4\ V_1\ V_2\ \mathit{cos}\ 2\ \pi X\ 25.3},$$

in which

$$V_1 = 2^{-X^2\ 246^2},$$

and

$$V_2 = 2^{-X^2\ 188^2}.$$

This is the visibility curve due to a double source, each of whose components is a close double, as shown in Fig. 13*a*.

Mercury. Mercury in a vacuum-tube gives two yellow lines 5790 and 5770, a very brilliant green line at 5461, and a violet line at 4358.

The yellow lines are not very bright, and are so close together that it is somewhat difficult with the dispersion employed to prevent the light from overlapping. Notwithstanding these difficulties, the close agreement of a number of observations shows that the curve for the lower line, given in Fig. 14*b*, Plate III., is a close approximation to the truth. Neglecting the effect of a line of feeble intensity at a distance of about 0.24 from the principal line, the distribution of light in the source is represented in Fig. 14, which gives for the visibility curve

$$V = \tfrac{1}{4}\sqrt{3\,V_1^2 + V_2^2 + 6\,V_1 V_2 \cos 2\pi X/28},$$

in which
$$V_1 = 2^{-X^2/200^2},$$

and
$$V_2 = 2^{-X^2/260^2} \cos 0.5/280.$$

Fig. 15*b*, Plate III., represents the results of observations on the upper yellow line, omitting some peculiarities due to the presence of one or more lines of feeble intensity. The curve agrees closely with the formula

$$V = \tfrac{1}{4}\sqrt{3\,V_1^2 + V_2^2 + 6\,V_1 V_2 \cos 2\pi X/70},$$

in which
$$V_1 = 2^{-X^2/183^2},$$

and
$$V_2 = 2^{-X^2/126^2},$$

which represents the visibility curve produced by two lines of intensities 1 : 3 and separated by 0.019 divisions as shown in Fig. 15*a*.

The green mercury line is one of the most complex yet examined. The constituent lines are nevertheless so fine that the interference bands are frequently visible when the difference of path is over four tenths of a meter!

The full curve in Fig. 16*b*, Plate III., gives the results of observations corrected for personal equation, while the dotted curve represents the equation

$$V = 2^{-X^2/230^2}\sqrt{0.69\,V_1^2 + 0.03\,V_2^2 + 0.28\,V_1 V_2 \cos 2\pi X/31.4},$$

in which
$$V_1 = 0.62 + 0.38 \cos 2\pi X/360,$$

and
$$V_2 = 0.77 + 0.23 \cos 2\pi X/110.$$

This is the visibility curve corresponding to the distribution represented in Fig. 16*a*. The components of the line for simplicity have been assumed to be symmetrical, as figured; but the observations are not sufficiently accurate to determine whether for instance each component is a double or a triple line. In this case also, as in the preceding ones, it is impossible from the data given to determine whether the smaller component is to the right or left of the principal line. A direct observation with the grating showed, however, that the smaller component is toward the red end of the spectrum.

The full curve shows that there is at least one other line—probably more than one—whose intensity is roughly one twentieth of the principal line, and whose distance from it is about three times that of the chief components.

The violet mercury line is much more difficult to observe than the others. The results obtained by observation, corrected for personal equation, are given by the full curve Fig. 17*b*, Plate III. The formula for the dotted curve is

$$V = \sqrt{0.88\ V_1^2 + 0.12\ V_1 V_2 \cos 2\pi X/23},$$

in which $$V_1 = 2^{-X^2/74^2}\left[0.62 + 0.38 \cos 2\pi X/200\right],$$

and $$V_2 = 2^{-X^2/120^2},$$

the resulting distribution of light shown in Fig. 17*a*.

The results of the preceding work are collected for comparison in Fig. 18, Plate IV., together with the D group in the solar spectrum. From these, as well as from the curves, it will be seen that it is easy by this method to separate lines whose distance apart is only a thousandth of that between D_1 and D_2, and even to determine the distribution of light in the separate components. The conditions most favorable to high values of the visibility are low density and low temperature, and these conditions were complied with as far as possible. Still, in many cases, the range of visibility due to slight variations of the conditions shows that the behavior of each substance must be carefully studied under all possible circumstances of temperature, pressure, strength of current, size and shape of the electrodes, diameter of the vacuum-tube, etc.

The effect of temperature and of pressure on the visibility may be readily accounted for on the kinetic theory. In fact, there is but little doubt that these are the chief if not the sole causes of the broadening of the spectral lines and the consequent diminution of visibility; the latter cause acting by altering the period of the source by frequent collisions, and the former by the change in the wave-length of the light due to the motion of the source in the line of sight.

If, now, the density of the vapor is very low, the second cause may be ignored, and it will be shown that in the case of hydrogen this is the case when the pressure is one or two millimeters.

In most of the cases investigated the pressure was so low that the discharge passed with difficulty. Supposing, then, the effect of collisions to be insignificant, let it be proposed to find the effect due to the motion of the molecule in the line of sight. If v be the mean velocity of the molecule and V that of light, then the formula for the resulting visibility curve, as given by Lord Rayleigh,* is $h = (1 - a^2) / (1 + a^2)$.

If the definition of visibility as given above be taken, however, this becomes

$$V = a'' = exp\left[-\pi\left(\frac{\pi X}{\lambda}\frac{v}{V}\right)^2\right].$$

If Δ be the difference of path at which the visibility is reduced to half its value at $X = 0$, then

$$\Delta = \frac{1}{\pi}\sqrt{\frac{l2}{\pi}}\frac{V}{v}\lambda,$$

or approximately

$$\frac{\Delta}{\lambda} = 0.15\frac{V}{v}.$$

If we take for hydrogen $v = 2000$ meters per second, then

$$\frac{\Delta}{\lambda} = 22500.$$

Again, if we ignore the difference in the temperature (about which there is considerable uncertainty) at which the other substances were examined, the velocities v would vary inversely as the square root of the atomic weight, and the number of waves in the difference of path at which the visibility is 0.5 is therefore $22500 \sqrt{m}$.

Considering the difficulties and uncertainties of the problem, the following table shows a remarkable agreement between the values actually found and the calculated results.†

---

* "On the Limit to Interference when Light is Radiated from Moving Molecules." *Philosophical Magazine*, April, 1889.

† It should be stated that the value of $\frac{\Delta}{\lambda}$ for the yellow sodium line, if taken from the curve, would be much larger than that given. The latter was the mean of a number of observations taken within the past month. As has been stated before, this particular curve has not been obtained since last year. A few other substances very difficult to examine, either because the lines are too feeble, or because the spectrum is so unstable, have given results not quite so consistent as the above, though all are of the same order of magnitude as that required by theory.

Subst.	At. Wt.	λ	Δ	$N = \frac{\Delta}{\lambda}$	N. (Calc.)
H_r	1	656	19.0	30000	22500
H_b	1	486	8.5	18000	22500
O	16	616	34.0	55000	80000
Na_r	23	616	66.0	107000	108000
Na_y	23	589	80.0	133000	108000
Na_{yy}	23	567	62.0	109000	108000
Na_g'	23	515	44.0	85000	108000
Na_g''	23	498	55.0	110000	108000
Zn_r	65.5	636	66.0	104000	182000
Zn_b	65.5	481	47.0	98000	182000
Cd_r	112.0	644	138.0	215000	238000
Cd_g	112.0	509	120.0	236000	238000
Cd_b	112.0	480	64.0	134000	238000
Hg_y'	200.0	579	230.0	400000	317000
Hg_y''	200.0	577	154.0	270000	317000
Hg_g	200.0	546	230.0	420000	317000
Hg_b	200.0	436	100.0	230000	317000
Tl	203.6	535	220.0	400000	322000

In order to show conclusively that the effect of density may be neglected in the foregoing observations, as well as to ascertain the law governing the broadening of spectral lines, by pressure or density, a series of observations was made on the red hydrogen line at varying pressures, with the results shown in Fig. 19*a*, Plate V.*

From these curves the following table was calculated:

Pressure in mm.	δ
90	0.128
71	0.116
47	0.095
23	0.071
13	0.056
9	0.053
3	0.050
5	0.048

---

* The numbers against the curves denote pressure in millimeters.

In Fig. 19*b* the curved line gives the relation between δ and $\frac{1}{p}$, and shows clearly that when p is less than 5^{mm} the effect of collisions has almost entirely ceased. If we take as variables δ and p, the results agree very closely with the straight line $\delta = \delta_0 + k\,p$, in which $\delta_0 = 0.047$ (the "half-width" of the line at zero pressure in the units adopted), $k = 0.00093$, and p is the pressure in millimeters.*

The same results were found for the blue hydrogen line, though, as might be expected, these were not so consistent.

It thus appears that in the case of hydrogen—and probably in all other cases—the width of the spectral lines diminishes toward a limit as the pressure diminishes, which depends upon the substance and its temperature; and that the excess of width over this limit is simply proportional to the pressure.

In general it may be said that under considerable ranges of temperature and pressure the character of the visibility curve remains the same; but it may be important to note that there are a number of exceptions to this rule, among which the green mercury line and the yellow sodium line may be especially mentioned.

Thus, Fig. 20*a*, Plate V., represents the visibility curve usually observed for the green mercury line, and Fig. 20*c* represents that obtained when the vacuum is so high that the discharge passes with difficulty, while Fig. 20*b* represents the intermediate stage. This last observation was obtained by placing the mercury in an atmosphere of hydrogen whose pressure could be measured by a McLeod gauge.

It might be objected that the presence of a foreign substance might of itself affect the distribution of light in the source, and therefore the form of the curve. In order to test this point, a series of observations of the red hydrogen was taken while the tube contained liquid mercury which was heated until the mercury spectrum was at least ten times as bright as that of the hydrogen. The character of the visibility curve was not perceptibly altered.

In the same series of experiments it was found that, provided the pressure of the hydrogen remained constant, the effect of a change in temperature from 75° to 140° had no appreciable effect on the result. In this connection it may be mentioned that the character of the curve for the green mercury line was not essentially altered when, in place of metallic

---

* In the figure the numbers representing values of the abscissæ for this line should be multiplied by 100.

mercury, the nitrate, iodide, or the chloride was substituted, the only important effect being a diminution in the visibility in the order named.

In the case of yellow sodium light, it has already been mentioned that the character of the curve is more variable than that of any other line thus far examined. This is illustrated by the curves in Fig. 21*a*, and Fig. 21*b*, Plate V. It has not been possible thus far to devote the attention which a systematic investigation demands. These changes are very puzzling to trace, but undoubtedly much of the difficulty is due to the fact that the dispersion employed was not sufficient to permit the separate examination of the components. Still there can be no doubt that the width of the lines, their distances apart, and their relative intensities vary rapidly with changes in temperature and pressure.

In addition to the preceding investigations of visibility curves for light emanating from a rare gas or vapor in a vacuum-tube, the curves for sodium, thallium, and lithium in the flame of a Bunsen burner have been observed, and the results are given in Fig. 22, Plate V. The thallium and lithium lines are clearly double, the distance between the components of the former agreeing very well with the results obtained with the vacuum-tube.

These substances were brought into the flame in the ordinary way, and the results obtained were at least as good as when a finely divided solution was used according to the method of Gouy. It appears from these curves that the width of the line is about ten times as great as when the vacuum-tube is used. But if the temperature of the flame be taken at 1500° C., and that in the vacuum-tubes at 350° C., the lines should be only twice as broad in the former case as in the latter. It appears then that notwithstanding the small quantity of substance present (barely enough to color the flame), the real density must be comparable to that of the vapor of the substance boiling under atmospheric pressure.

The principal object of the foregoing work is to illustrate the advantages which may be expected from a study of the variations of clearness of interference fringes with increase in difference of path. The fundamental principle by which the "structure" of a line or group of lines is determined by this method is not essentially different from that of spectrum analysis by the grating, both depending in fact on interference phenomena; but in consequence of the almost complete freedom from errors arising from defects in optical or mechanical parts, the method has extraordinary advantages for this special work. A glance at Fig. 18, Plate IV., will give a fair idea of the "resolving power" of the method as compared with that of the grating. In order that the comparison be quite fair, however, it would be necessary to take for a comparison spectrum that of the substances here used, and under the same conditions. With the best instrumental appliances now in use, it is difficult to "resolve" lines as close together as the components of either of the yellow sodium lines. It is evident, however, that by *Light-wave Analysis* —if I may venture so to call the foregoing method—a tenth of this distance is obviously within the limit; indeed, if the width of the lines themselves be less than their distance apart, there can be no limit.

SUPPLEMENT.

1. It has already been pointed out that in many cases it is difficult or impossible to decide between two or more distributions of lines which give very nearly the same visibility curve; and when there are many lines in the source, the combinations of intensities and arrangement of these, from which a type may be selected, are enormously great. Indeed, even when the number of lines is greater than three, excepting perhaps the cases where the lines may be in pairs (as in the case of yellow sodium light), the resulting visibility curve becomes so complex that it is very difficult to analyze. Doubtless in many cases where the components are not too close, the grating will give the information necessary for the investigator to select the proper combination.

It may readily be shown that the formula

$$V^2 = \frac{C^2 + S^2}{P^2},$$

for the *visibility* curve due to a distribution of light, $y = \varphi(x)$, is identical with that of the *intensity* curve at the focus of a telescope provided with apertures which produce this distribution in the light passing through. Accordingly, if a telescope be provided with apertures adjustable in width or length and distance apart, the diffraction image of a distant illuminated slit will give at once a representation of the whole visibility curve; and by adjustment of intensities and distances, any particular visibility curve may be more or less accurately copied; thus furnishing a means of studying the relations between V and $\varphi(x)$ which, while giving perhaps only a rough approximation to the truth, may prove more convenient than analytical or graphical methods.

II. One of the purposes which led to these investigations was the search for a radiation of sufficient homogeneity to serve as an ultimate standard of length. It will appear from the curves of cadmium that there are three lines which may be used for this purpose. The red cadmium line is almost ideally homogeneous, and will readily permit the estimation of a change of phase in the interference fringes of one hundredth of a fringe in a total distance of 200 millimeters or over 300,000 waves.

Both the green and the blue lines are fairly well adapted for the purpose, and will prove very valuable as checks. Each of these, however, has a small companion, and it is necessary to know the effect of this in altering the phase of the interference bands.

If φ be the fraction of a wave by which the position of a minimum is shifted on account of the presence of the companion, α the number of "periods" in the difference of path, and r the ratio of the intensities, then

$$tan\ 2\pi\varphi = -\frac{r\ sin\ 2\pi\alpha}{1 + r\ cos\ 2\pi\alpha}.$$

Thus, if $r = 1/4$, φ is a maximum when α is about $1/3$; and for this we have, approximately, $\varphi = -0.04$.

This is the largest correction to be applied, and is negative if the brighter line has the greater wave-length. It is theoretically possible, by this means, to determine, in case of an unequal double, or a line unsymmetrically broadened, whether the brighter side is toward the blue or the red end of the spectrum.

III. It has been argued that even if all practical difficulties in making large gratings could be removed, nothing further could be gained in resolution of groups of spectral lines, on account of the real width of the lines themselves, caused by the lack of homogeneity in the radiations which produce them. The results of the preceding investigations show that, while

---

* See *Philosophical Magazine*, April, 1891, page 345. (The value of r is the reciprocal of that here used.)

this is very far from being true with present gratings, such a limit undoubtedly exists. The accordance between the measured widths of 18 lines shows further that this broadening of lines in a rare gas can be fully accounted for by the application of Döppler's principle to the motion of the vibrating atoms in the line of sight, and indeed furnishes what may be considered one of the most direct proofs of the kinetic theory of gases.

The form of the ultimate components of all the groups of lines thus far examined is found to agree fairly well with an exponential curve,

$$\varphi(x) = e^{-a^2 x^2},$$

which shows that the distribution of velocities cannot vary widely from that demanded by Maxwell's theory.

If the limit above mentioned were due solely to the motion of the molecule, and the radiating substance could be rendered luminous while its temperature was very low, it might be possible to observe interference phenomena with difference of path of many meters. But it must be considered that, since every vibrating molecule is communicating its energy to the æther in the form of light-waves, its vibrations must diminish in amplitude; consequently the train of waves is no longer homogeneous even though the vibrations remain absolutely isochronous, and the result is a broadening of the line and limitation of the difference of path at which interference is visible.

Plate I.

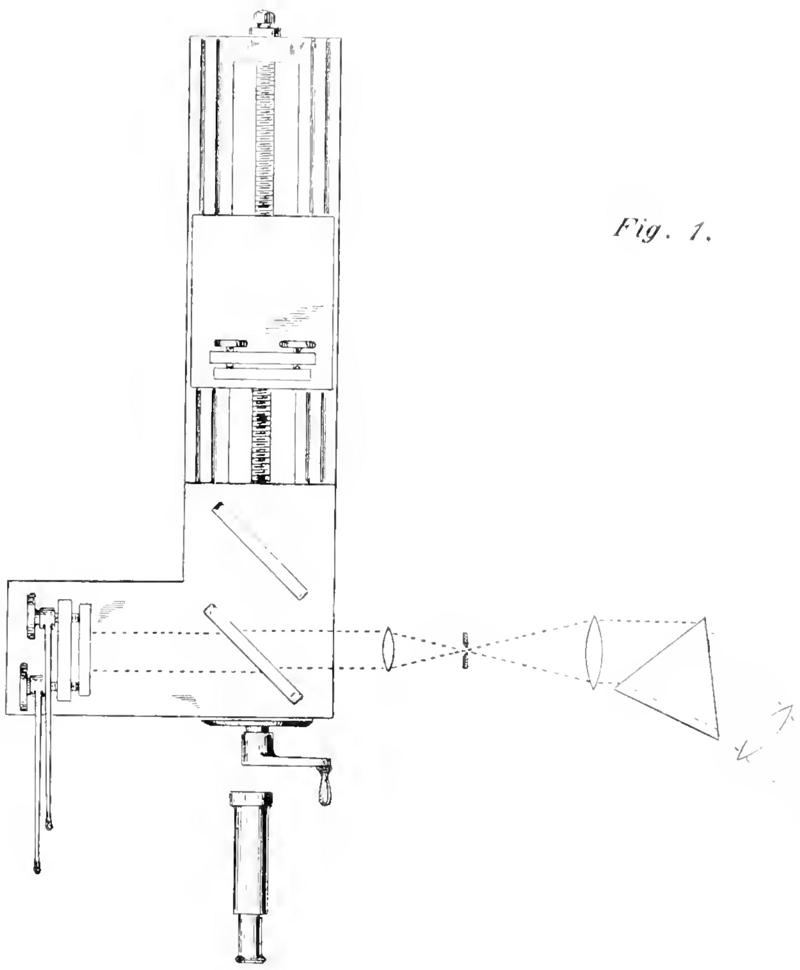


Fig. 1.

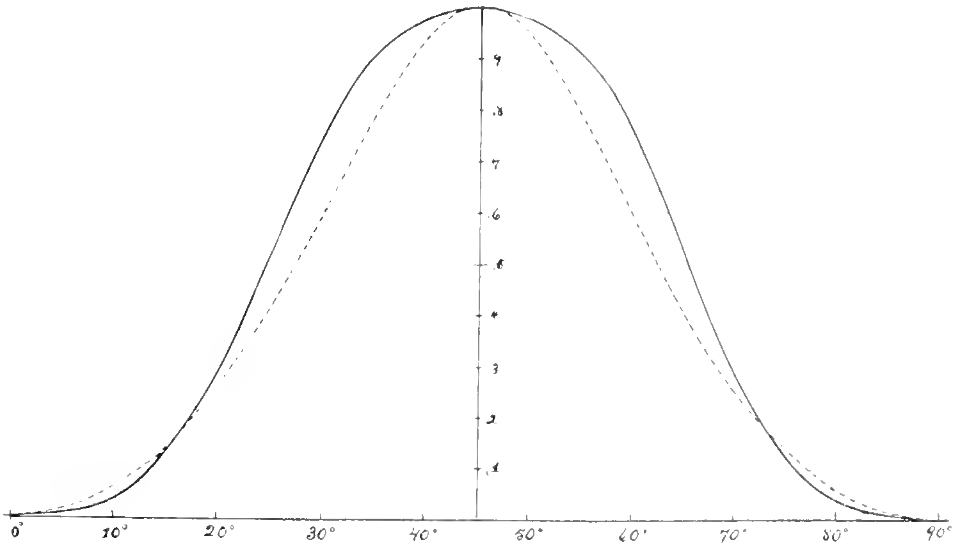


Fig. 2.

Equation Dot'd Curve.

$Y = \frac{1-\cos^2 2d.}{1+\cos^2 2d.}$

Full Curve.

Eye Estimates —Ye.

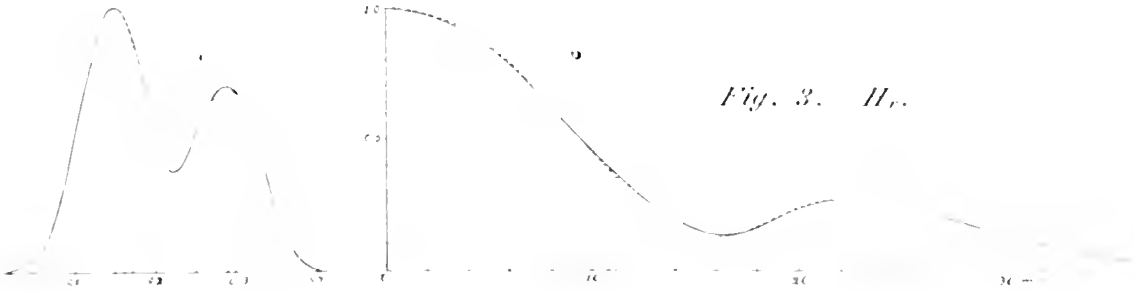


Fig. 3. H_r.

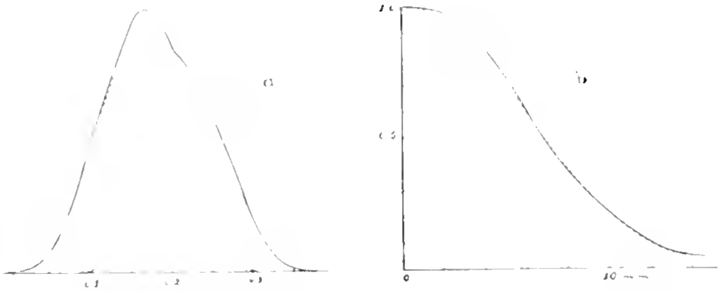


Fig. 4. H_s.

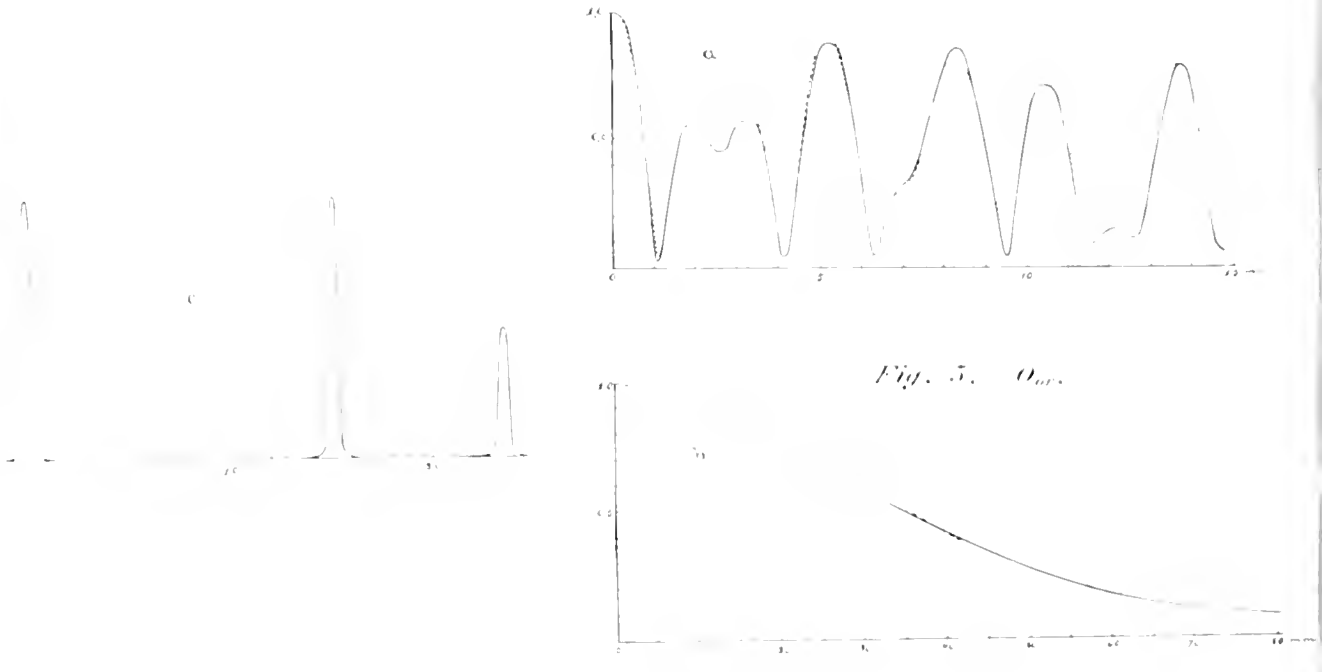


Fig. 5. O_{sr}.

Plate II.

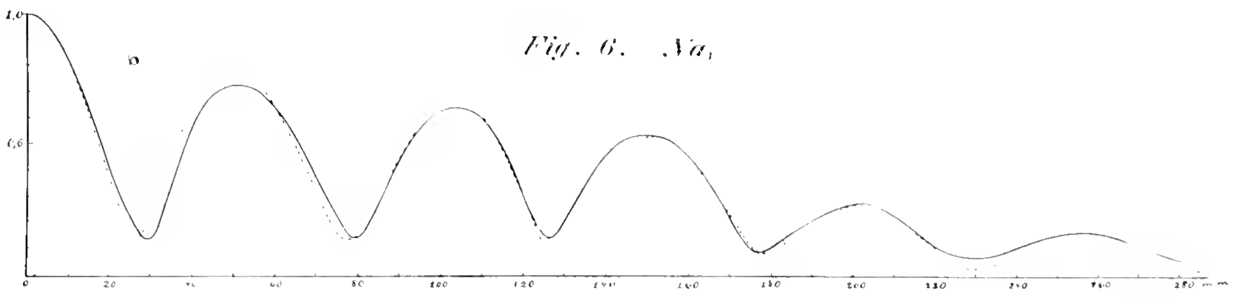


Fig. 6. Na_y

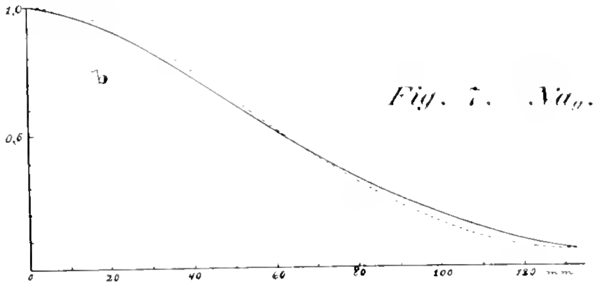


Fig. 7. Na_g.

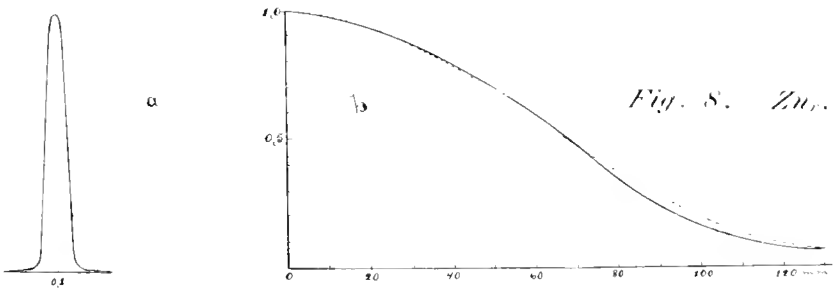


Fig. 8. Zn_r.

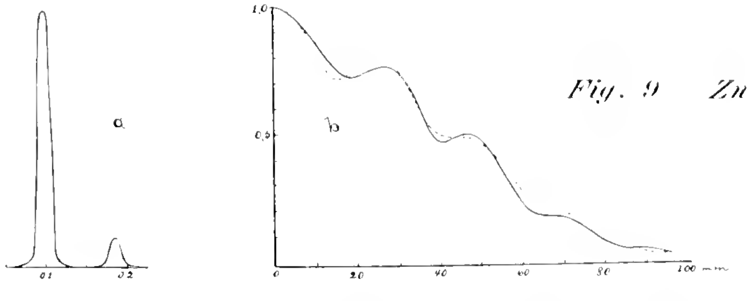


Fig. 9 Zn_b.

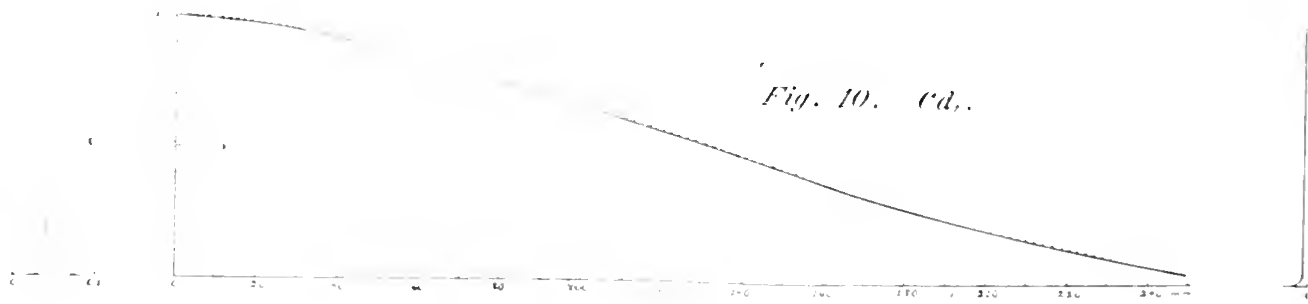


Fig. 10. Cd_r.

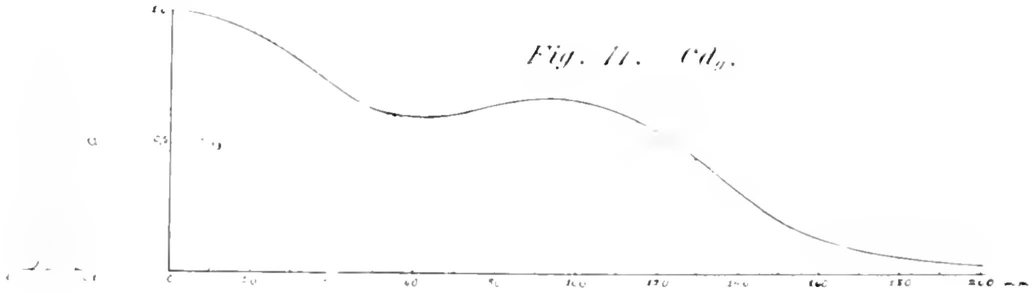


Fig. 11. Cd_g.

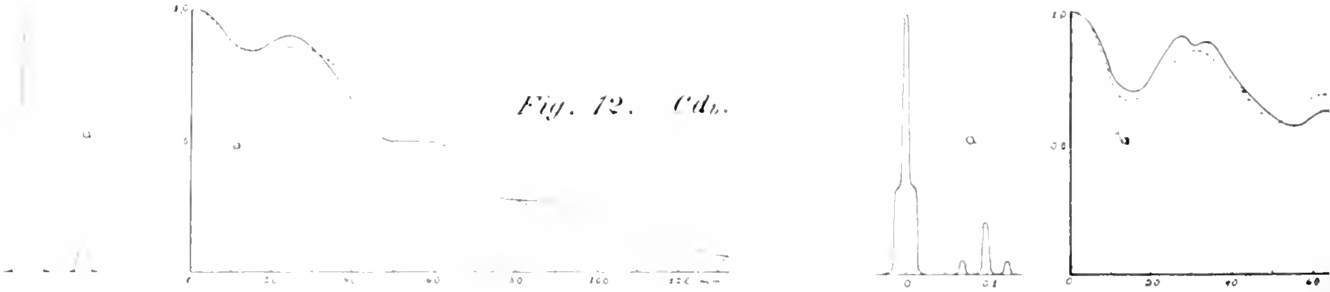


Fig. 12. Cd_b.

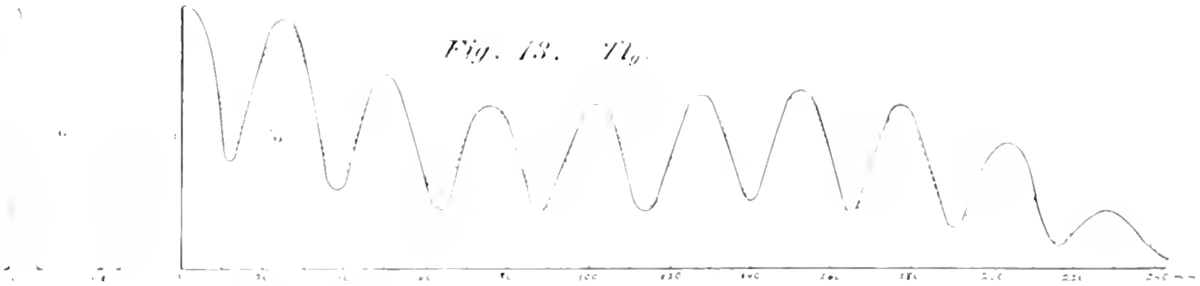


Fig. 13. Tl_g.

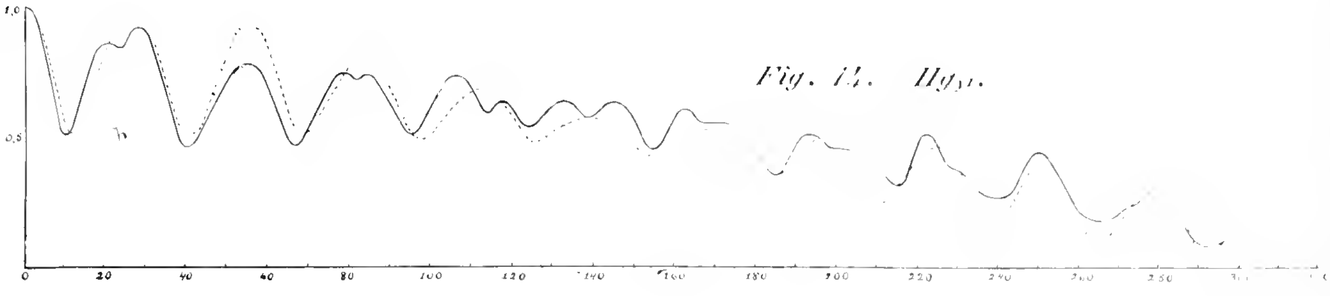


Fig. 14. $Hg_{\gamma 1}$.

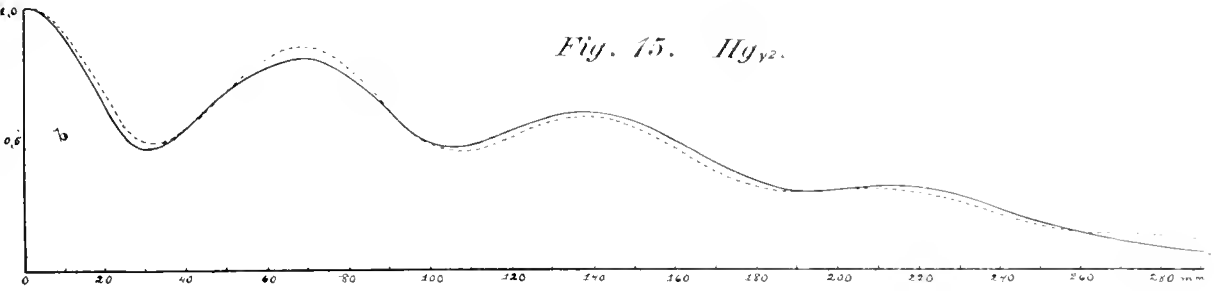
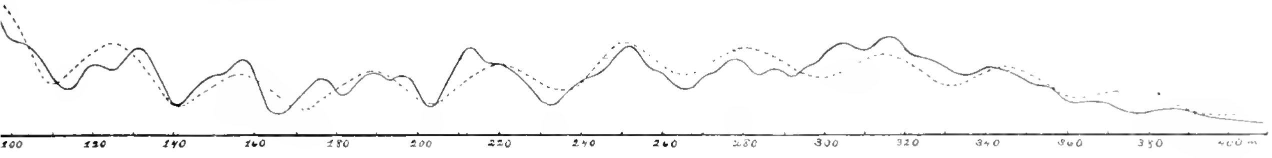
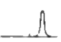


Fig. 15. $Hg_{\gamma 2}$.

Fig. 16. Hg_{g}.





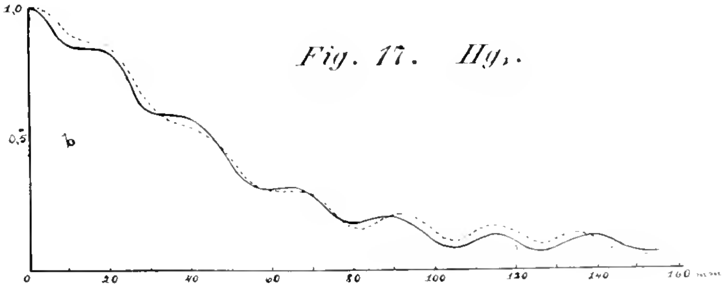


Fig. 17. Hg_{γ}.

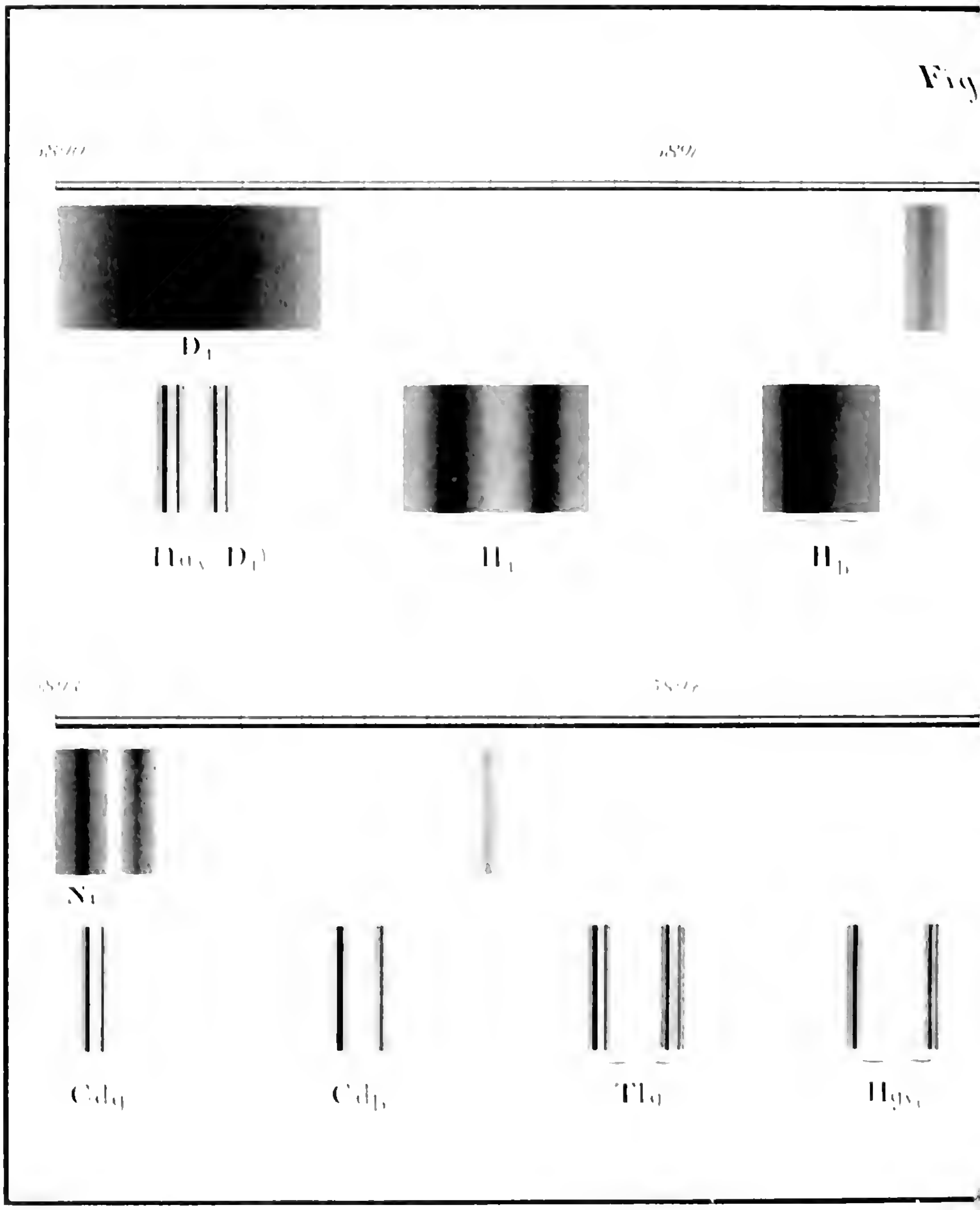


Fig
5890
5891
D₁
Na (D₁)
H₁
H_b
5897
5897
Ni
Cd_a
Cd_b
Tl_a
Hg_α

Plate VI

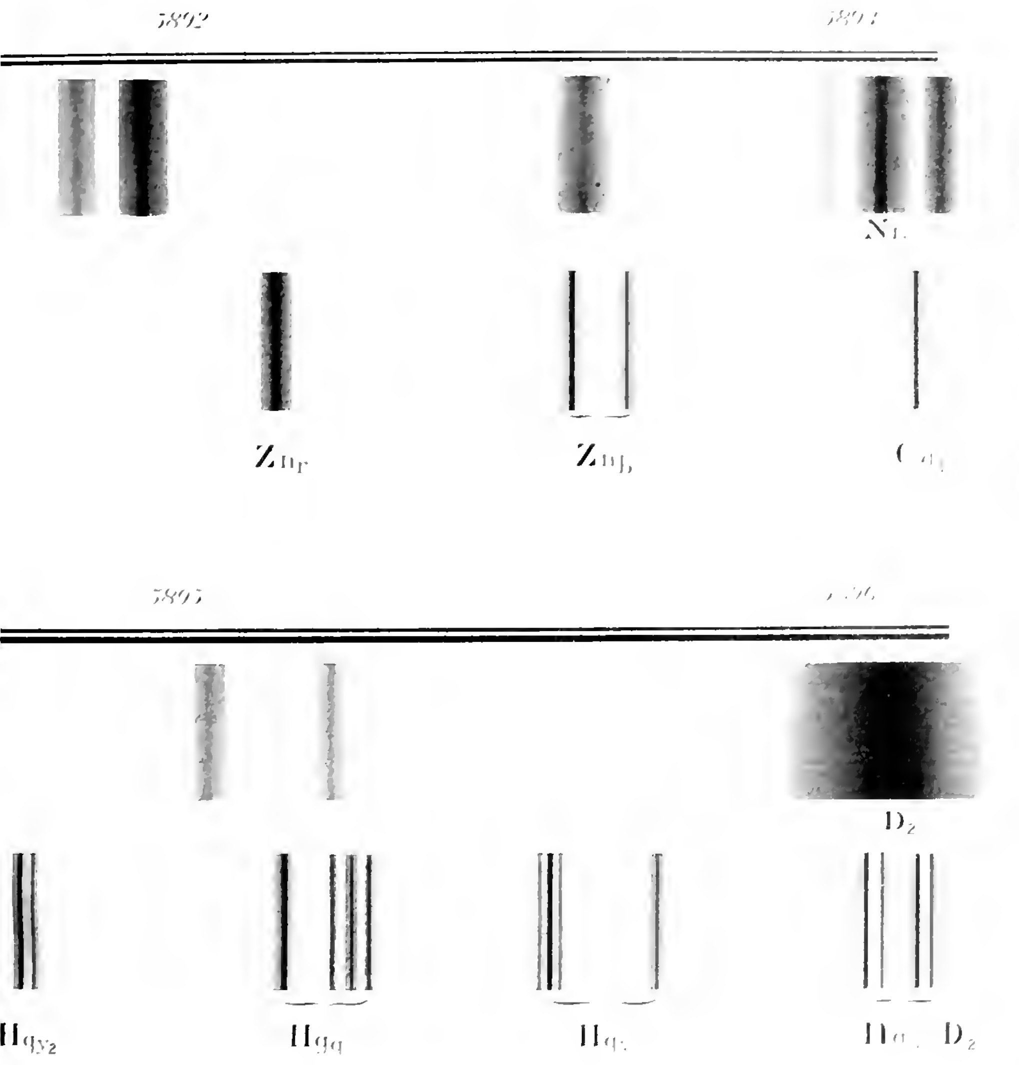


Fig. 19a. He.

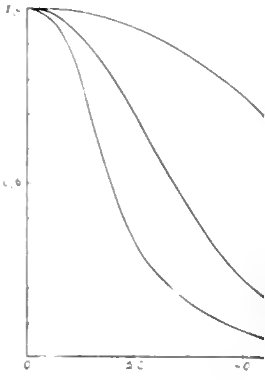
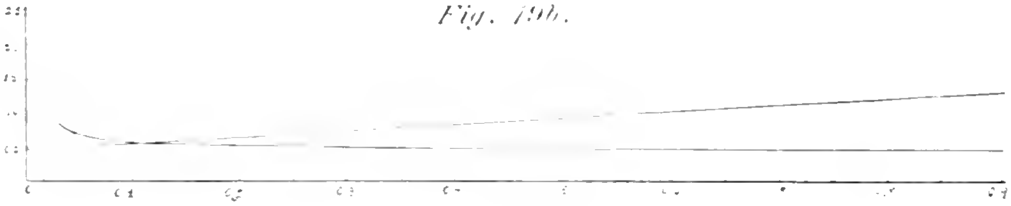
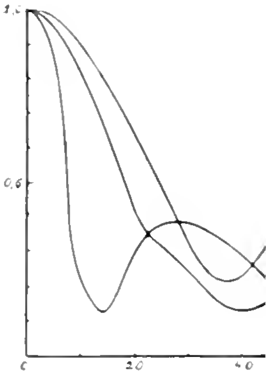
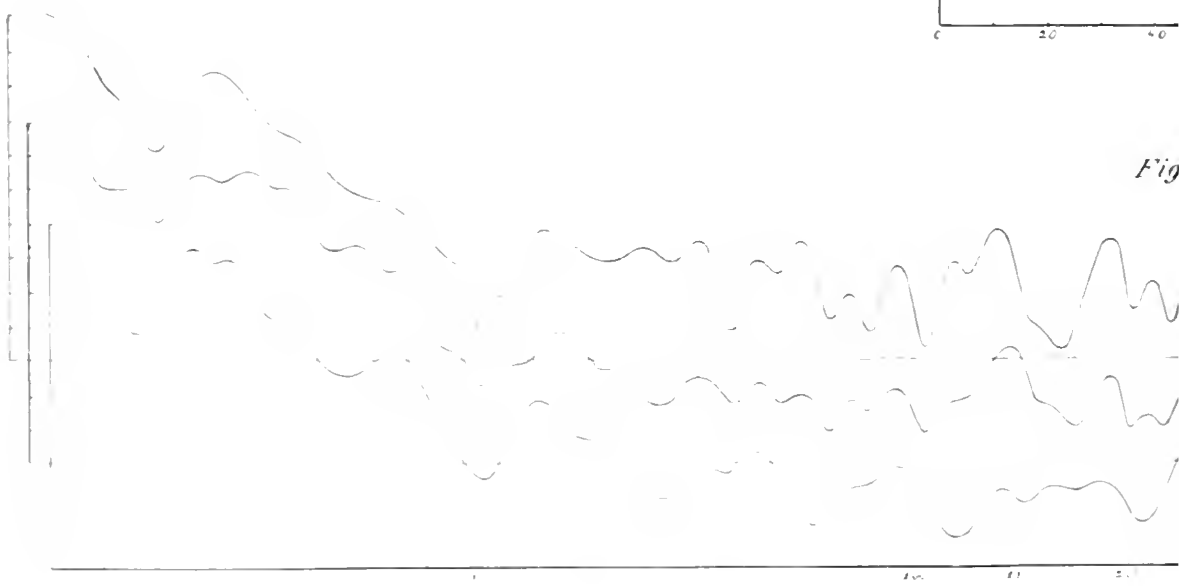


Fig. 19b.

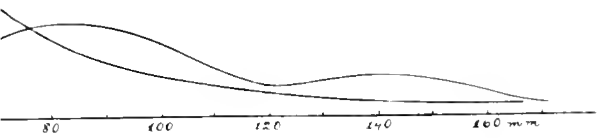






Fig

Fig. 21a. Na_γ.



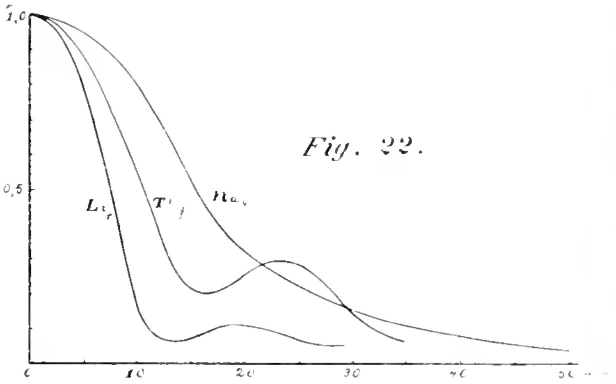
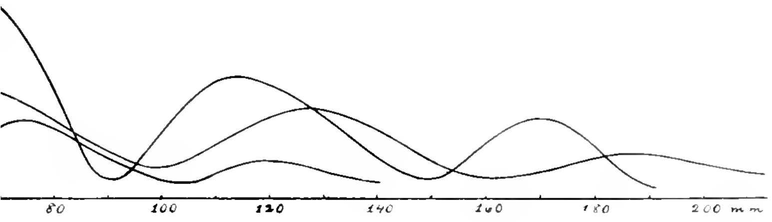
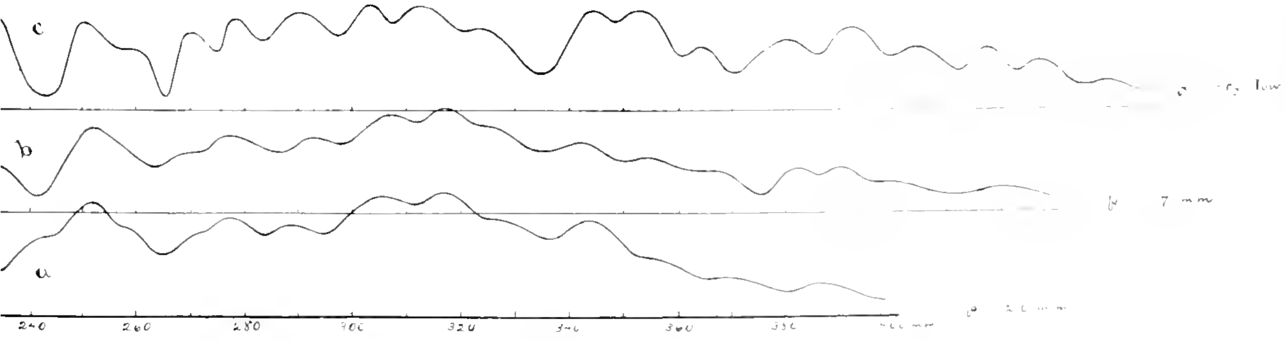


Fig. 22.

Fig. 21b. Na_1.



Hg.



SMITHSONIAN CONTRIBUTIONS TO KNOWLEDGE

980

ON THE DENSITIES
OF
OXYGEN AND HYDROGEN,
AND ON THE
RATIO OF THEIR ATOMIC WEIGHTS.

BY

EDWARD W. MORLEY, PH.D.

CITY OF WASHINGTON:
PUBLISHED BY THE SMITHSONIAN INSTITUTION
1895.

The Knickerbocker Press, New Rochelle, N. Y.

SMITHSONIAN CONTRIBUTIONS TO KNOWLEDGE.

980

ON THE DENSITIES
OF
OXYGEN AND HYDROGEN,
AND ON THE
RATIO OF THEIR ATOMIC WEIGHTS.

BY

EDWARD W. MORLEY, PH.D.

CITY OF WASHINGTON:
PUBLISHED BY THE SMITHSONIAN INSTITUTION
1895.

COMMISSION TO WHOM THIS MEMOIR
HAS BEEN REFERRED.

FRANK WIGGLESWORTH CLARKE.
CARL BARUS.

ADVERTISEMENT.

The present memoir is the result of a series of investigations by Professor Morley, which have been aided to some extent during the last two years by the Smithsonian Institution.

The atomic weight of oxygen may be called the base line upon which practically our entire system of atomic weights depends, and a small error in its measurement becomes large by multiplication in the higher parts of the atomic weight scale. Hence its accurate determination is of fundamental importance.

In his investigation, Professor Morley has studied the problem by two methods.

1st. By the synthesis of water, in which he, for the first time, has achieved completeness by actually weighing the hydrogen, the oxygen, and the water formed, whereas all his predecessors took one or another of these factors by difference.

2d. By the density ratio between oxygen and hydrogen. In this method he has weighed the gases of greater purity and in larger quantity than hitherto, and he has in some instances operated without the intervention of stopcocks, and therefore with no possibility of error due to leakage. He has also, as a correction to the density ratio, redetermined the composition of water by volume.

By both methods he reaches the same result:

$O = 15.879$, with variation in the *fourth* decimal place as between the two.

In accordance with the rule adopted by the Smithsonian Institution, the work has been submitted for examination to a committee consisting of Professor F. W. Clarke and Doctor Carl Barus, and having been recommended for publication it is herewith presented in the series of Contributions to Knowledge.

S. P. Langley,
Secretary.

Smithsonian Institution,
Washington, July, 1895.

PREFACE.

This paper consists of four parts, the first of which contains a determination of the weight of one litre of oxygen under standard conditions at the sea level in latitude 45°. The second part contains a similar determination for hydrogen; by the use of a method which is new in this application, although previously used by Buff in the case of some other gases, the accidental errors of observation have been made smaller than is usual with so light a gas, while it is hoped that a certain source of constant error also has been eliminated.

The third part contains an attempt to determine the volumetric composition of water. Both Scott and myself have made determinations of this ratio in which the gases were measured in eudiometric tubes. But the value thus found was smaller than when, afterwards, considerably larger volumes of the gases were measured in vessels of greater capacity. On account of this unexplained discrepancy, three determinations of the volumetric ratio by means of three different processes were thought to be desirable, and the apparatus required was made ready. Only the least helpful of the three methods, however, has been actually completed. When the other methods were to be used, a workman who had been taught to watch my apparatus when left in action during my absence from the room, had been assigned duties in another building, and the attempt to work without this assistance resulted in many accidents, and ended in completely disabling the apparatus; this part of the paper is therefore but fragmentary.

The fourth part of the paper contains a series of syntheses of weighed quantities of water from weighed quantities of hydrogen and of oxygen. A second series was begun, but the accidents just mentioned put an end to it. Perhaps, however, the series which is here described will have some value even without the confirmation which it was hoped to obtain from an independent series of observations of the same kind.

Excepting one combustion furnace belonging to Adelbert College, all the apparatus used was purchased or constructed expressly for this investigation, which has been carried on in a basement store-room in one of the college buildings

My hearty thanks are due to several friends at Cleveland who have given very substantial aid. Mr. C. F. Wason presented me with an electric motor which has been of great service. Messrs. Warner and Swasey have repeatedly sent at Christmas a receipted bill for the considerable amount of work which had been done for me at their shops. Mrs. Amasa Stone has generously given the means for purchasing many conveniences which have much facilitated the work. The East Cleveland Railroad Company kindly connected my private laboratory with their lines, and they, as well as the present corporation, The Cleveland Electric Railway Company, have supplied electricity for the uses needed in this work. And the Smithsonian Institution purchased and lent to me the admirable balance with which most of the work on the density of the gases has been done. To all these I desire to express my cordial thanks in connection with this account of the work to which they have so helpfully contributed.

Edward W. Morley.

CONTENTS.

PART I.—ON THE DENSITY OF OXYGEN.

FIRST SERIES OF DETERMINATIONS.

SECOND SERIES OF DETERMINATIONS.

THIRD SERIES OF DETERMINATIONS.

PART II. ON THE DENSITY OF HYDROGEN.

NEW METHOD OF DETERMINING THE DENSITY OF HYDROGEN.

NEW METHOD AND SECOND APPARATUS.

PART III.—ON THE VOLUMETRIC COMPOSITION OF WATER.

PART IV.—SYNTHESIS OF WATER FROM WEIGHED QUANTITIES OF HYDROGEN AND OXYGEN.

LIST OF ILLUSTRATIONS.

ON THE DENSITIES OF OXYGEN AND HYDROGEN, AND ON THE RATIO OF THEIR ATOMIC WEIGHTS.

BY EDWARD W. MORLEY.

PART I.—ON THE DENSITY OF OXYGEN.

I.—INTRODUCTION.

The first part of this paper describes three series of determinations of the density of oxygen. In the first series, the pressure and temperature of the gas to be weighed were determined with mercurial thermometers and a mano-barometer. In the second series, pressure and temperature were not determined for each experiment, but were made equal to the pressure and temperature of a standard volume of hydrogen, the comparison being made by means of a differential manometer. In the third series, the temperature was that of melting ice, so that the mano-barometer alone was observed.

In the first series, the surfaces of the globes in which the oxygen was weighed were hardly touched during the manipulation; and not touched at all in the second series. In the third series, the globes were in contact with cold water for a considerable time. The stopcocks were covered with rubber capsules during this exposure, but it seems that this protection did not much lessen the uncertainty usually noticed in the weight of glass so exposed.

In the reduction of each observation of the first series, account was taken of:

1. The expansion of the glass of the globes;
2. The errors of the two mercurial thermometers;
3. The deviation of the mercurial thermometer from the hydrogen air-thermometer;
4. The difference between the coefficients of expansion of hydrogen and of oxygen;

5. The elevation of the cistern of the mano-barometer above the centre of the globe while the latter was filling with oxygen;

6. The correction to the length of the scale of my mano-barometer; and

7. The force of gravity at my laboratory.

In the second series, the first three of these seven factors were eliminated, for thermometers were not used, and the expansion of the globe in which the oxygen had its pressure measured was compensated by the equal expansion of the similar globe containing the standard volume of hydrogen. In the third series, the cistern of the mano-barometer, which was then used as a syphon barometer, was at the level of the centre of the globe, so that the observations were reduced by taking account simply of the length of my scale and of the force of gravity at my laboratory.

In the forty-one determinations which are included in the three series, eight different globes were used, in order to eliminate the effect of accidental errors in the determinations of their capacity.

2. MEASUREMENT OF CAPACITIES OF GLOBES.

My measurements of the capacities of the globes used for weighing oxygen involved three processes, as follows:

1. The determination of the weight of the globe in air;

2. The determination of the weight required to be added to maintain the globe in equilibrium when immersed in water of known temperature; and

3. The determination of the loss of weight of the globe when full of water and immersed in water of the same temperature. Combining the first determination with the second, we get the external volume of the globe; from the third and first determinations we get the solid contents of the material of which the globe is composed. The difference between the external volume and the solid contents gives the capacity.

It is obvious that a determination of the weight of the water required to fill the globe at a known temperature would form a more direct and a more accurate determination of its capacity; but this would have required the use of a balance carrying twenty-five kilogrammes in each pan, which I should have had to purchase for the purpose. As the other expenses of the investigation were a heavy burden, the method just described was used; it is hoped that the results of the determinations will be found to have been sufficiently accurate. As the errors of the calibrations seem to have been made much less than the accidental errors of single experiments, as the number of calibrations of each globe was not too small, and as so many globes were calibrated and used in the determination of density, no error of sensible magnitude is likely to have been caused.

3.—PRELIMINARY WEIGHING OF GLOBES.

A balance carrying twelve hundred grammes in each pan was mounted on a case designed for the accurate weighing of globes containing oxygen or hydrogen. This case, with the balance, is seen in Fig. 1. Its walls are thirteen centimetres thick, as are also the top, the bottom, and the doors; all are filled with non-conducting material. Hooks attached to the pans of the balance pass through the top of the case. To one of these the globe, with its stopcock closed, was suspended, and a thermometer was placed at its side. After an hour, the weight of the globe was determined, the case was opened long enough to observe the thermometer, and the height of the barometer was noted. A second observation was made after

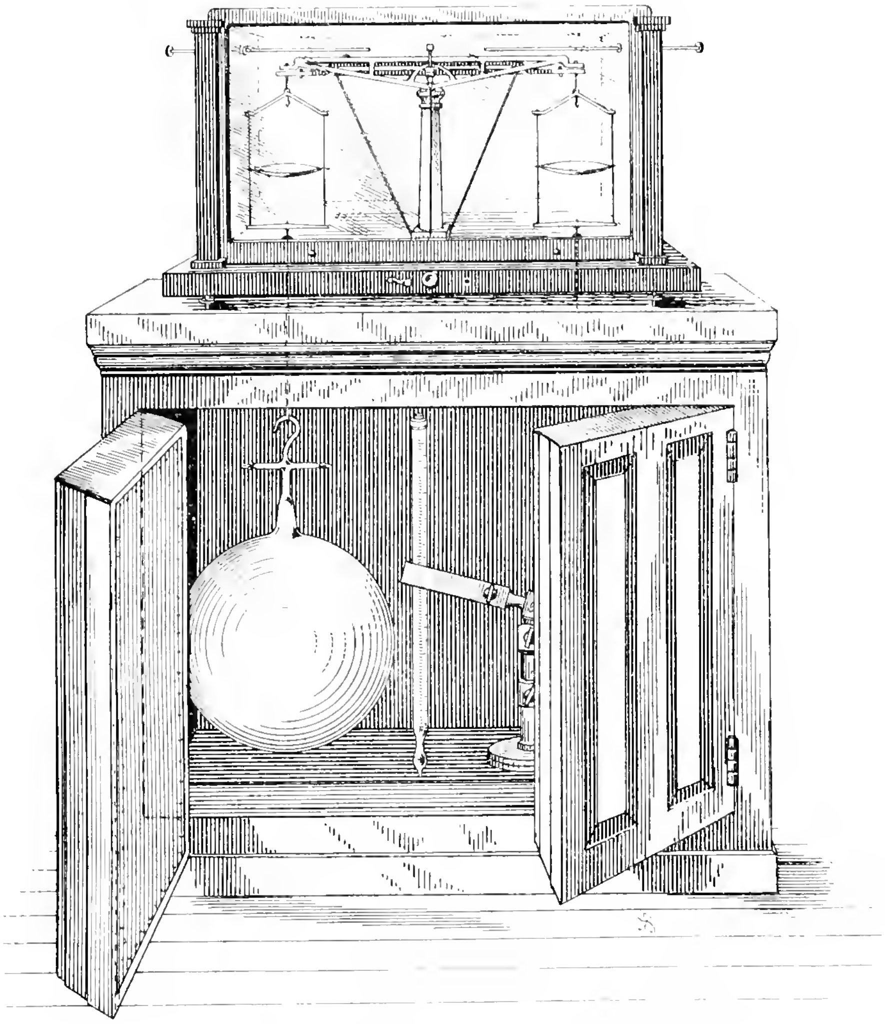


FIG. 1.—Preliminary weighing of a globe.

another hour; the weight corrected for the air displaced by the globe and by the brass weights could now be computed.

4. AUXILIARY WEIGHTS FOR HYDROSTATIC WEIGHINGS.

The additional weights required to sink in water my largest globes, amounted to more than twenty kilogrammes. This amount was made up of brass weights, each of which could be weighed on the balance just mentioned, while their sum was nearly twenty times its greatest admissible load. Each one of these weights was weighed while suspended in water of known temperature, so as to determine, not the absolute weight of the mass of brass, but its effective weight when used in the hydrostatic weighing of a globe. A scale pan with which to suspend the weights from the globe was also weighed in the same manner. The jar of distilled water, in which the weights were immersed, was placed in the case already mentioned, with a thermometer divided into tenths of degrees, and of known index error. Weighings could be made to single milligrammes, but weighings on different days differed by many times that amount.

The temperature of 18° C. was taken as a standard temperature to which the weights were reduced. If a brass weight is immersed in water of some lower temperature, its own contraction will add to its effective weight, while the contraction of the water will lessen the effective weight. The difference of these contractions, referred to the assumed standard temperature, will give the loss of weight of the unit volume of brass. The specific gravity of the weights was 8.4, so that the effective weight of the unit volume of brass when immersed was 7.4 units of weight. If, therefore, we divide the difference between the expansions of water and of brass, both counted from 18° C., by the factor 7.4, we shall obtain the change of the effective weight of the mass of brass which, when immersed in water at 18° C., has an effective weight of one kilogramme.

The following table gives the volumes of water and of brass at different temperatures referred to the volume at 18° taken as unity, the differences, and the differences after division by 7.4, expressed as grammes per kilogramme. The corrections taken with changed sign will reduce the weight observed at some other temperature to the weight at 18°.

Ten of these auxiliary weights were cylinders twenty-five millimetres in diameter; nine were disks about fifteen centimetres in diameter. The weight of each was determined by hydrostatic weighings on four different days; it was suspended by a fine brass wire in water whose temperature was noted, and the observed weight was reduced to the weight which would have been observed at 18° C. by applying the corrections given in the following table with their signs changed. Eight of them were also weighed in water at about 0° C. as a check on the accuracy of the corrections. These values obtained at 0° C. are given in column x of Table B.

Temperature.	Expansion of Water.	Expansion of Brass.	Difference.	Correction for one Kilogramme.
0°	.998 753	.998 996	.000 243	— .033
1	696	9 051	355	— .048
2	656	107	451	— .060
3	633	163	530	— .071
4	626	219	593	— .080
5	634	274	640	— .087
6	657	330	673	— .090
7	696	386	690	— .092
8	748	442	694	.092
9	814	498	684	.091
10	895	554	659	.089
11	.998 989	609	620	.084
12	.999 096	665	569	— .077
13	216	721	505	— .068
14	349	777	428	— .058
15	494	832	338	— .047
16	651	888	237	— .032
17	.999 810	.999 944	124	— .017
18	1.000 000	1.000 000	000	— .000
19	191	056	135	+ .018
20	394	112	282	+ .038
21	607	168	439	+ .060
22	830	223	607	+ .082
23	1.001 064	279	785	+ .106
24	307	335	972	+ .131

Since these reductions for temperature are so simple that they can scarcely need revision, I give only the reduced values. The weights marked with the letters A to L were, after using them for the globes numbered 1 and 2, so neglected that when they were used again it became necessary to polish them, after which their weights were again determined.

A.—EFFECTIVE WEIGHT IN WATER AT 18° C. NOT REDUCED TO WEIGHT IN VACUUM: GRAMMES.

	I	II	III	MEANS.
A	1001.698	1001.694	1001.698	1001.697
B	934.355	934.339	934.326	934.340
C	986.818	986.804	986.801	986.808
D	1010.032	1010.014	1010.007	1010.018
E	997.862	997.847	997.847	997.852
F	983.643	983.639	983.639	983.640
G	1009.041	1009.097	1009.104	1009.081
H	1003.117	1003.127	1003.124	1003.123
I	1002.324	1002.352	1002.365	1002.347
J	499.072	499.076	499.105	499.084
K		210.350	210.363	210.357
L	205.565	205.576	205.572	205.574

EFFECTIVE WEIGHTS IN WATER AT 15° C REDUCED TO WEIGHT IN VACUUM, GRAMMES.

	I	II	III	IV	V	MEANS.
A	1001.483	1001.488	1001.472	1001.483		1001.481
B	934.146	934.134	934.127	934.137	934.131	934.136
C	986.058	986.058	986.065	986.061	986.074	986.063
D	1009.662	1009.641	1009.641	1009.647	1009.645	1009.648
E	997.355	997.345	997.346	997.344	997.340	997.346
F	983.392	983.394	983.387	983.391	983.388	983.391
G	1008.826	1008.812	1008.797	1008.807	1008.805	1008.808
H	1002.280	1002.273	1002.264	1002.271	1002.270	1002.274
I	1002.052	1002.044	1002.034	1002.045	1002.047	1002.044
J				408.822		408.822
K	210.181					210.181
L	205.580					205.580
1	1144.511	1144.508	1144.502	1144.504		1144.506
2	1146.713	1146.712	1146.706	1146.720		1146.713
3	1153.838	1153.844	1153.835	1153.845		1153.840
4	1152.029	1152.03	1152.036	1152.037		1152.033
5	1145.013	1145.012	1145.026	1148.024		1145.019
6	1144.533					1144.533
6*		1004.47	1004.465	1004.467		1004.467
7	1149.305	1149.313	1149.310	1100.317		1149.311
8	1157.441		1157.455	1157.452		1157.450
9	1151.124		1151.127	1151.137		1151.129
10	1165.494		1165.500	1165.499		1165.498

The probable error of a single determination in Table A is 10, and in Table B is 1.6, milligrammes; that of a mean value in A is 6, and in B is 2.3, milligrammes; that of the sum of all the large weights in A is 20, and in B is 10, milligrammes. It is obvious that the values of the weights were sufficiently well determined.

5. HYDROSTATIC WEIGHING OF GLOBES.

The manipulation of the hydrostatic weighing of globes varied slightly with the size of the globes.

For the smaller globes numbered 1 and 2, the arrangement shown in Fig. 2 was used. The globe is in a copper cylinder having tubulatures for six thermometers. Around the neck of the globe is placed a brass collar, shown at *c* in Fig. 3. To this is suspended a pan *a* by means of copper ribbons *b b*. Distilled water is poured into the cylinder to a depth of perhaps twenty centimetres. The pan is laid in the bottom of the cylinder and loaded with the required weights, care being taken to remove air bubbles. The globe and its collar are adjusted in position, and the cylinder is filled with water without producing air bubbles. The cylinder is then set in the non-conducting case on which the balance stands, Fig. 2, and the globe is suspended from one of its pans by a small wire. The thermometers are thrust far enough through the tubulatures, and the case is shut. After a time, the weights needed to produce equilibrium are determined, when the case is opened and the thermometers are read.

The motion of the balance is slow, owing to the volume of water which has to be displaced for each vibration, but it is easy to determine within a centigramme the effective weight of the immersed system. The observations were repeated at intervals of an hour.

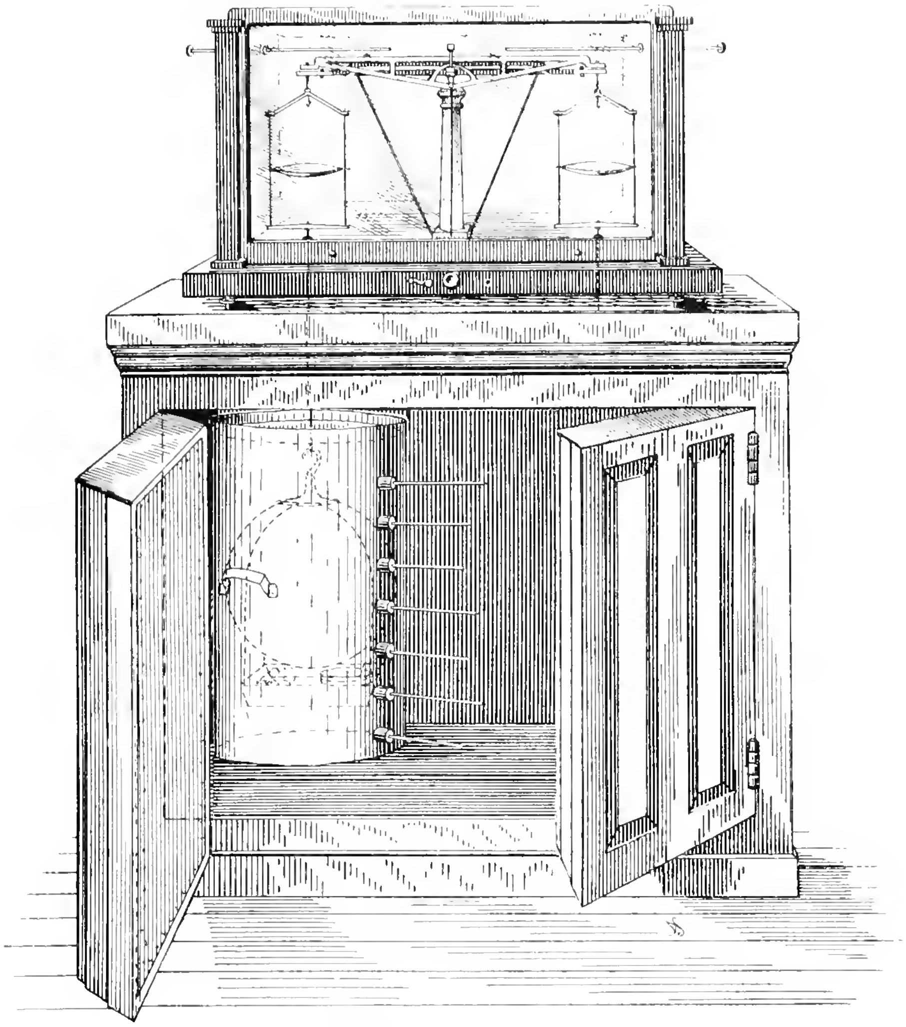


FIG. 2.—Hydrostatic weighing of small globes.

For the determination of the temperature I calibrated two thermometers whose scales were divided into tenths of degrees. That one marked G has a scale of equal parts; 741 had a scale intended to compensate for inequalities in the bore of the tube. Both were calibrated on the dividing engine, with no reference to the engraved scale, except in determining the proper length of the threads of mercury separated. One was calibrated by Bessel's method, the other, by the method of Hansen. After the calibration of the tube, the accidental errors and the intentional inequalities of the scale were determined. The results of the calibration were then reduced to suit the engraved scales. Thermometer number 741 was of the Jena normal glass; G was of the glass of which Geissler made his thermometers.

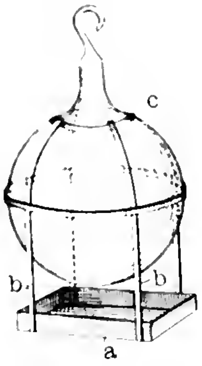


FIG. 3.—Collar and pan for submersion of globes.

The boiling point was determined after half an hour of exposure to steam. The freezing point was determined by noting the maximum depressed zero within two or three minutes after the last exposure to steam. The zero point was frequently redetermined.

Temperatures determined with the two thermometers agreed as closely as different readings of the same thermometer. To the scale of these two thermometers were reduced the readings of the other thermometers used for the temperatures of the water in the hydrostatic weighings.

DETAILS OF A HYDROSTATIC WEIGHING.

To give a clear idea of the details of the process, part of the determination of the volume of globe No. 1 is here given: first, the observations made on April 7th; secondly, the computation for this day; and, thirdly, the results for each of the other days on which this globe was weighed in water.

HYDROSTATIC WEIGHING, APRIL 7th.

On balance B, Globe 1, cage and pan, weights ABCDEFGHIJ, left.

HOUR.	TEMPERATURE BY SIX THERMOMETERS.						WEIGHTS, RIGHT.
	At bottom.					At top.	
12.30 P.M.	17.25	17.24	17.23	17.25	17.25	17.26	351.14 gr.
12.50 P.M.	17.25	17.22	17.22	17.22	17.22	17.24	351.11 gr.
2.15 P.M	17.20	17.19	17.19	17.19	17.20	17.19	351.05 gr.
3.15 P.M.	17.18	17.16	17.17	17.16	17.17	17.16	350.01 gr.
4.30 P.M.	17.14	17.14	17.14	17.17	17.17	17.16	350.99 gr.
6.00 P.M.	17.16	17.12	17.12	17.14	17.12	17.14	350.96 gr.

In the reduction, the indications of the thermometers at the top and bottom of the cylinder of water were not included in the mean. One of these was somewhat above the globe, and the other was somewhat below. They served to show the presence or absence of thermal inequalities producing currents; the other thermometers fairly showed the temperature of the water in which the globe was floating.

COMPUTATION OF THE OBSERVATION AT 12.30 P.M.

Weights ABCDEFGHJ	8425.64 gr.
Reduction to vacuum	− 1.17 gr.
Reduction of weights to temperature, 17.24° C.	− .11 gr.
Corrected weight of brass used as a sinker	8424.36 gr.
Cage and pan	178.32 gr.
Globe No. 1, corrected to vacuum	1015.22 gr.
Sum of weights, left pan of balance	9617.90 gr.
Weights on right pan, reduced to vacuum	351.09 gr.
Weight of water displaced	9266.81 gr.
Multiplying by 1.001237, we have volume at 17.24	9278.27 cc.
Reduction to 0° for expansion of glass	− 4.47 cc.
Volume at 0° C.	9273.80 cc.

In the same way, we get for the other weights and temperatures given above,

12.50 P.M.	9273.79 cc.
2.15 P.M.	9273.80 cc.
3.15 P.M.	9273.79 cc.
4.30 P.M.	9273.79 cc.
6.00 P.M.	9273.79 cc.

These determinations are recorded as one result: all the results for this globe are given in the table of data concerning the capacity of globes.

HYDROSTATIC WEIGHING OF THE LARGER GLOBES.

In the case of the larger globes, the manipulation in the hydrostatic weighings was slightly different; the cylinder filled with water in which the globe was immersed was too heavy to be conveniently moved into and out of the case on which the balance had been placed. The cylinder for the larger globes was accordingly placed permanently in a closet about three metres square which was built inside a basement room of tolerably constant temperature. It was surrounded with a non-conducting case. Over it was placed the balance with a clear space of three quarters of a metre beneath it. Further, the volume of water needed was now so much that the removal of it every time a globe was immersed became tedious. So a triangular platform was attached to three brass rods, and these to cords passing over pulleys in the ceiling, so that the platform with any load could be raised or lowered at will. The cords were arranged to pass before, behind, and to the left of, the balance without interfering with it. This platform being raised, the pan and its weights were arranged and the globe and its collar were attached to it. The platform was then lowered, and the globe sank to the bottom. The latter was then raised a little and suspended by a wire from the balance, and weighed as before.

In the other method, the water was stirred by pouring, which was tedious.

With the present apparatus, alternate raising and lowering of the globe by means of the movable platform soon made the temperature uniform.

When the thermometers were used for several weeks in the horizontal position, the column of mercury in two of them sometimes separated, so that they could no longer be read. For some determinations, therefore, I procured thermometers divided into fiftieths of a degree, having the graduations at the end of a long tube. With these the temperature could be read, even at the bottom of the cylinder, with the thermometer in the vertical position. By moving them, the temperature of the water at all depths could be determined.

Most determinations were made at the temperature of the room. But a few determinations were made with the temperature below 4° C., some by using ice in a large tank, and some by working in an attic room in winter.

6.—EXPANSION OF WATER AND OF GLASS.

The volume of one gramme of water at different temperatures which is required in reduction of the hydrostatic weighings was taken from the results of Marek, Thiesen, Scheel, and Kreitling, as given in the *Beiblätter zu den Annalen*, 18, 59. The following table gives the volume of one gramme of water for each tenth of a degree from 0° to 22°:

VOLUME OF ONE GRAMME OF WATER AT TEMPERATURE t.

t	0	1	2	3	4	5	6	7	8	9
0	1.000127	121	116	110	104	098	093	087	081	076
1	070	066	062	058	054	050	046	042	038	034
2	030	028	025	023	021	018	016	014	012	009
3	007	006	006	005	004	003	003	002	001	001
4	000	001	002	002	003	004	005	006	006	007
5	008	011	013	015	017	020	022	024	026	029
6	031	035	039	043	047	051	054	058	062	066
7	070	075	080	086	091	096	101	106	111	117
8	122	129	135	142	158	155	162	168	175	181
9	188	196	204	212	220	229	237	245	253	261
10	269	278	288	297	307	316	325	335	344	354
11	363	374	384	395	406	417	427	438	449	459
12	470	482	494	506	518	530	542	554	566	578
13	590	603	617	630	643	657	670	683	697	710
14	723	738	852	767	781	796	810	825	839	854
15	868	884	899	915	931	946	962	978	993	009
16	1025	042	059	076	093	109	126	143	160	177
17	1194	212	230	248	266	284	302	320	338	356
18	1374	393	412	431	450	470	489	508	527	546
19	1565	585	606	626	646	667	687	707	728	748
20	1768	789	810	832	853	875	896	917	939	960
21	1981	003	026	048	070	093	115	137	160	182
22	2204	227	250	274	298	321	344	368	391	415

The coefficient of expansion of the glass globes used for weighing oxygen was determined by making three weight thermometers of the necks of three globes, which were filled with mercury by boiling in a vacuum. These were transferred from ice to steam, and the expansion calculated from the amount of mercury expelled at the latter temperature. The height of the barometer during the exposure to steam, corrected for the force of gravity at my laboratory, was 744.1 millimetres. Hence the temperature of the steam, according to the table by Broch,* was 99.41°. The observations were as follows:

Tube, full at 99.41	410.22 gr.	308.56 gr.	433.53 gr
Weight of tube empty	41.03 "	28.34 "	28.40 "
Mercury	369.19 "	280.22 "	405.13 "
Mercury expelled on heating...	5.6759 "	4.3151 "	6.2197 "

If we assume for the density of mercury

At 0°, Log. 1 133 3888, at 99.41°, Log. 1.125 5573, the cubic expansion of the glass between 0° and 99.41° is found

A	.002 780
B	.002 755
C	.002 801
Mean,	.002 78
Hence the expansion for one degree is	.000 0280 †

7.—SOLID CONTENTS OF GLOBES.

Each globe was weighed in the air while open, and the apparent weight corrected for the weight of the air displaced by the glass and by the weights. It was then immersed in water, filled, and weighed, using the same cylinder and the same thermometers as in the previous hydrostatic weighings. The solid contents of the globes were then computed with the values of the expansions of water and glass just mentioned. As an example of the process, the determination of the solid contents of globe No. 1 is given.

Globe 1, open	1014.724	gr.
Reduction to vacuum	+ .39	"
True weight	1015.11	"
Globe 1, in water, at 16.58°	572.42	"
Reduction to vacuum	— .08	"
True weight in water	572.34	"
Loss in water	442.77	"
Loss multiplied by 1.001 123, solid contents	443.27	cc.
Reduction to 0°	— .20	"
Solid contents at 0°	443 07	"

8.—CAPACITY OF GLOBES.

If now we subtract the solid contents of each globe from the volume we shall have its capacity. For instance, we have

---

* *Travaux et Mémoires du Bureau International*, I *A*, 46.

† The glass was the ordinary soft German glass, obtained from C. Gerhardt, Marquart's Lager Chemischen Utensilien, Bonn.

Volume of globe No. 1	9275.1 cc.
Solid contents.	443.0 "
Capacity at 0°	8832.1 "

The capacities of the globes used in determining the density of oxygen are given in the following table:

Number of globe.	External volume.	Solid contents.	Capacity.
1	9275.1 cc.	443.0 cc.	8832.1 cc.
2	9229.6 "	435.7 "	8793.9 "
3	20569.5 "	511.9 "	20057.6 "
4	20286.9 "	474.2 "	19812.7 "
5	22029.2 "	471.4 "	21557.8 "
6	18340.3 "	444.7 "	17895.6 "
7	15881.5 "	498.1 "	15383.4 "
8	16949.7 "	432.5 "	16517.2 "
9	15561.2 "	479.5 "	15081.7 "

The following table gives all the hydrostatic weighings of these globes with the corresponding temperatures. All the weights are corrected for the weight of air displaced by them, and the weights which were used in water are corrected for the expansion of water and of brass to the temperature of the water in which they were immersed. These corrections are not very large, and may be assumed to be sufficiently well determined. If the other reductions need subsequent correction, the data given are sufficient.

It is, of course, obvious that my determinations of the capacity of a globe are not as accurate as they might have been made. By weighing the water contained in a globe at the temperature of melting ice, Regnault determined the capacities of the globes used by him in weighing known volumes of gases with a mean error of one fortieth of a cubic centimetre.* But it is thought that the accuracy attained is all that is necessary, especially since it is much more than that of other processes on which the knowledge of the density of a gas depends.

DATA CONCERNING THE CAPACITY OF GLOBES.

	LOSS ON IMMERSION. Grammes.	TEMPERATURE. Degrees.	VOLUME COMPUTED. Cubic Centimetres.
Globe	9266.21	17.87	9274.2
1	9267.49	16.84	9274.0
	9266.81	17.24	9273.8
	9266.97	17.12	9273.8
	9267.08	17.05	9273.8
	9267.07	17.06	9273.8
	9269.02	15.57	9273.8
	442.77	16.58	443.1
	442.64	16.60	443.0
	442.69	16.78	443.2
	442.65	16.83	443.0
	442.67	16.95	443.0

---

* Mendeleef, *Annals of the Bureau of Weights and Measures*, St. Petersburg, Part I., 59.

	LOSS ON IMMERSION. Grammes.	TEMPERATURE. Degrees.	VOLUME COMPUTED. Cubic Centimetres.
Globe 2	9220.02	18.18	9228.3
	9222.22	16.73	9228.5
	9221.11	17.24	9228.1
	9221.14	17.19	9228.0
	9222.65	16.06	9228.1
	435.40	17.02	435.7
	435.42	16.47	435.7
	435.39	16.48	435.7
Globe 3	20557.17	16.05	20569.2
	20557.83	16.08	20570.0
	20571.72	4.47	20569.3
	511.88	4.57	511.9
	511.98	3.7	511.9
	511.88	3.3	511.8
Globe 4	20275.26	15.98	20286.9
	By another method.		474.2
Globe 5	22016.71	16.04	22029.5
	22016.57	15.94	22029.1
	22021.00	14.26	22029.0
	22016.19	16.01	22028.9
	471.07	14.81	471.3
	471.30	13.36	471.4
Globe 6	18329.39	16.44	18340.0
	18329.08	15.92	18339.4
	18332.16	14.55	18339.4
	18342.18	4.58	18339.9
	18342.56	3.53	18340.8
	18343.59	6.55	18341.1
	444.99	15.92	445.2
	444.34	15.60	444.6
	444.14	14.6	444.3
	444.87	3.57	444.8
Globe 7	15872.24	16.27	15882.0
	15875.08	14.48	15881.1
	15882.91	3.51	15881.3
	15883.51	6.53	15881.4
	498.09	14.6	498.3
	498.02	3.3	498.0
Globe 8	16938.48	16.93	16950.4
	16950.96	3.43	16949.4
	16951.77	6.18	16949.5
	16951.66	6.60	16949.4
	432.51	3.30	432.5
	By another method.		432.4
Globe 9	15551.02	16.91	15562.0
	15562.60	4.32	15562.8
	15562.11	3.47	15560.7
	15563.47	6.55	15561.4
	15563.39	6.55	15561.4
	479.44	3.31	479.4
	By another method.		479.6

The other method used to obtain the solid contents of some globes, consisted in determining the specific gravity of the glass of the globe from the part cut off in fusing on its stopcock, from which the solid contents of the globe minus the key of its stopcock could be computed; to which was added the solid contents of this key.

9. COMPRESSION OF GLOBES WHEN EXHAUSTED.

The volume of a hollow globe varies with the variations of pressure to which it is subjected. The amount of variation due to a given difference of pressure depends on the radius and on the mean thickness of the walls of the globe, and on the variations of the thickness on different parts of the surface. For the globes used in these experiments, the difference of volume due to the exhaustion of the globe was from one six-thousandth to one twenty-five-hundredth of the capacity.

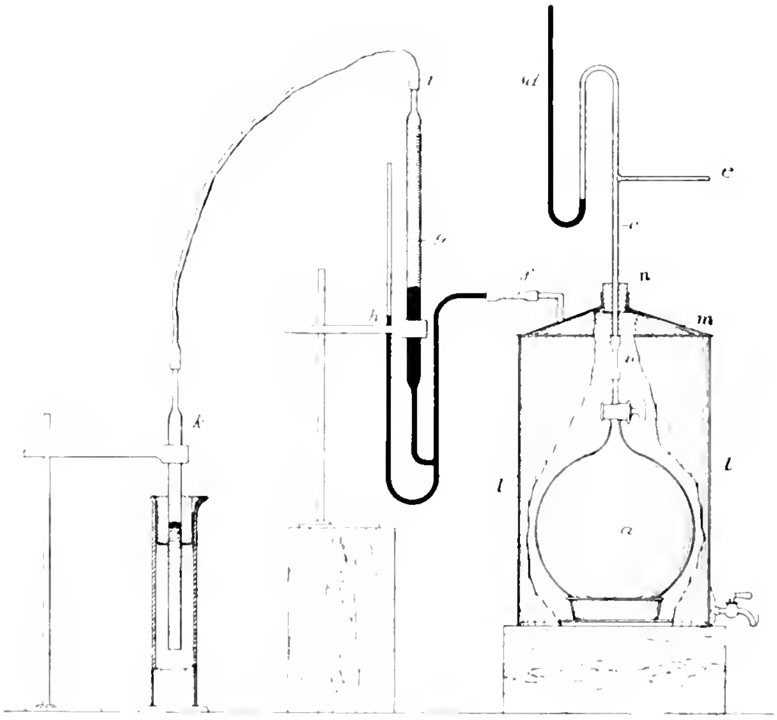


FIG. 4.—Apparatus for measuring compression of globes on exhaustion.

This change of volume must be determined with accuracy. A convenient method was employed. A copper cylinder, *l l*, Fig. 4, had a cover *m*, which could be soldered to the cylinder and easily removed again. In this the globe *a* was placed; sometimes it was nearly filled with water, sometimes it was held down by a sinker. The globe was connected by a thick rubber tube to the glass tube *c* leading to a syphon gauge and to an air-pump, and the cylinder was nearly filled with water.

The cover was then soldered in place, the cylinder was quite filled with water, and the rubber stopper *n* was inserted. To *f* were connected the tubes *g* and *h*. On the tube *h* was a mark: *g* was graduated in tenths of cubic centimetres. To the upper end of *i* was attached some simple device for varying the pressure of the air in it. These tubes were filled with water to the level of the mark *h*. The tube *h* is intended to act as a manometer showing the pressure on the water in the cylinder.

Let us suppose, for a moment, the temperature of the water in the cylinder to be constant; if we alter the volume of the globe, but keep the pressure on the water constant by watching the manometer, and introducing or removing water, we shall have a measure of the change of volume of the globe.

The manipulation is accordingly as follows: We bring the level of the water in the manometer tube *h* exactly to the mark, and note the reading on the graduated tube *g*. Then we exhaust the globe, and keep the pressure constant in the cylinder by introducing water into it from the graduated tube, which we read again. The difference of the two readings is the change of volume of the globe, provided the temperature of the water is constant. If now air is admitted, and the alternate readings are repeated at nearly equal intervals, we can eliminate the effect of slow changes of temperature and determine the change of volume of the globe with accuracy.

As to the convenience of the method it may be said that, when the globe was not filled with water, the whole operation of putting the globe in place, soldering the cover, making a sufficient number of determinations, and taking out the globe, could be finished in two hours. When the globe was filled with water, the intervals between readings were shorter, but the time required to fill the globe and to empty it again was considerable. Most of the determinations were made in this latter way; three determinations were the work of nearly a whole day. The method, as will be seen from the following example, gave concordant results; it also gave concordant results when applied to the same globe on different days.

DETERMINATION OF THE COMPRESSION OF GLOBE NO. 1.

Time.	Pressure.	Burette.	Differences.	
3 h. 48 m.	743 mm.	4.02 cc.		
3 " 53 "	30 "	2.77 "	713 mm.	1.22 cc
3 " 58 "	743 "	3.96 "	715 "	1.23 "
4 " 04 "	26 "	2.70 "	717 "	1.22 "
4 " 10 "	743 "	3.88 "	716 "	1.21 "
4 " 16 "	28 "	2.63 "	715 "	1.22 "
4 " 21 "	743 "	3.82 "		

The compression of each globe due to a difference of internal pressures measured by seventy-six centimetres of mercury is given in the following table:

COMPRESSION OF GLOBES DUE TO 76 CENTIMETRES' DIFFERENCE OF PRESSURE

Globe.	Compression
1	1.30 cc.
2	1.14 "
3	6.28 "
4	6.00 "
5	8.07 "
7	3.43 "
8	3.89 "
9	2.94 "

10. CORRECTION FOR COMPRESSION OF GLOBES WHEN EXHAUSTED.

The effect of the change of volume of a globe which is due to a change of internal pressure may be eliminated by suitable manipulation, or the amount of a correction to the weight of the globe may be computed from the amount of the change of volume, together with the density of the air at the time of weighing. There will doubtless be a difference of opinion as to which is the more convenient.

In the case of one of my globes, the change of volume was about eight cubic centimetres. In order, therefore, not to produce an error of one tenth of a milligramme in the value of the correction, it would be necessary to observe the pressure and temperature of the air at each weighing. But, with the balance which I procured for the present series of experiments, numerous weighings were required in order to determine a weight accurately enough, so that much labor would be involved in the observations and computations for the corrections. It was accordingly thought more convenient to make the needed correction a matter of manipulation consuming no time after the proper apparatus had been constructed. Each globe was therefore provided with a counterpoise equal in volume to the globe *when exhausted*. Then, for each globe, was made a pair of minute flasks whose volumes differed by the amount of the compression of the globe on exhaustion, and whose weights were exactly the same when they were weighed in a vacuum. For instance, the compression of globe No. 1, for the difference of pressure usual in my experiments, was 1.27 cubic centimetres. Two flasks were made whose volumes were 2.080 and 0.810 cubic centimetres, and whose difference of weight when weighed in air was equal to the weight of 1.27 cubic centimetres of air at the time, taking account of the true values of the weights employed.

Now, when the globe No. 1 was exhausted, it was weighed against its counterpoise, which had the same volume. When the globe was full of gas, the 0.81 cubic centimetres were placed with it on the balance, and the 2.08 cubic centimetres were likewise added to the counterpoise. The *true* weights of the globe and counterpoise suffered equal additions, for the *true* weights of the two additions were equal within a fiftieth of a milligramme. Therefore, the *apparent* difference of weight between the globe and its counterpoise would be the *true* difference of weight as expressed by brass weights in air.

The method was found so convenient that it was developed and improved for wider use.

II. AIR-PUMPS AND EXHAUSTION.

The exhaustions of globes and other apparatus required in this series of experiments were mostly effected with a mercurial air-pump of the form devised by Toepler. The tube by which it discharged itself was shaped as shown in Fig. 5. The recipient *a* could be itself exhausted with a piston pump when the discharge of the Toepler pump directly into the air began to be incomplete owing to the small volume to be discharged. The body of the pump had a capacity of 1.6 litres; during this series of experiments, it would exhaust a volume of twenty litres to two millionths of an atmosphere. But such a completeness of exhaustion was avoided. Since the tension of the vapor of mercury at ordinary temperatures is, if my experiments are sufficiently trustworthy, not much more than one millionth of an atmosphere, it was hoped that we could avoid the diffusion of mercury vapor into the globe which is exhausted, by opposing to the diffusion a rapid current of gas in the other direction. Now, if the tension of the residual gas in the globe is, let us say, ten millionths of an atmosphere, each stroke of the pump will draw a current of gas towards itself with considerable velocity. Unless, therefore, some vapor can pass from the pump to the globe during the up stroke of the pump, it will not reach it at all while the pump is in action. But if the tension of the residual air is made equal to that of the mercurial vapor in the pump, air will enter the pump by diffusion mainly, and then mercurial vapor will enter the globe. It was hoped that if the vacuum produced still contained gas at a tension ten or twenty times that of mercury vapor, its entrance into the globe would not take place while the pump was working; by making the connecting tube some two metres long, it was hoped that, even after the stopping the pump to measure the vacuum, not much mercury would diffuse into the globe.

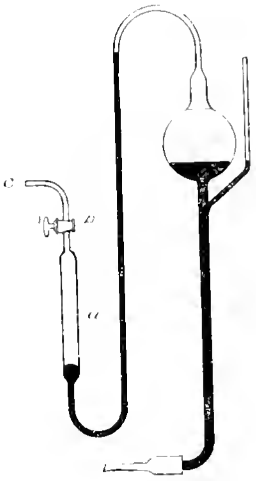


FIG. 5.—Discharge tube of Toepler pump for obtaining a better vacuum.

The exhaustion of globes, but not of other apparatus, was sometimes effected with a Geissler pump whose body has a capacity of 2.3 litres. When this is newly cleaned, it is possible to exhaust a volume of one litre to a ten-millionth of an atmosphere.

12. MEASUREMENT OF THE DEGREE OF EXHAUSTION EFFECTED.

The perfection of the vacuum produced in each experiment was measured with the gauge devised by McLeod. The capacity of the bulb of that one which was set up with the Toepler pump was about 300 cubic centimetres. On the tube were three marks, such that one millimetre of difference of level in the two tubes showed a vacuum of one millionth or five millionths of an atmosphere, or one measured by the two-hundreth of a millimetre of mercury in a syphon gauge.

The gauge used with the Geissler pump had a bulb whose capacity was 436 cubic centimetres. On the tube were six marks; the upper, third, and fifth indicate vacua of the ten-millionth, the millionth, or the hundred-thousandth of an atmosphere, by a difference of level of one millimetre; the second, fourth, and lower marks indicate in the same way, vacua expressed by one ten-thousandth, one thousandth, or one hundredth of a millimetre of mercury in a syphon gauge.

The tubes of the gauge belonging to the Toepler pump were of such size, and kept so clean, that difference of capillary action did not much interfere with the accuracy of its indications. This was often tested by exhausting the gauge to a ten-millionth of an atmosphere, when any irregularity in the level of the mercury in the part of the tube where the readings were commonly made could be detected. The error found has never been important in comparison with the quantities to be measured.

13. MANIPULATION OF GLOBE WHILE FILLING WITH OXYGEN.

In the present series of experiments, an elaborate apparatus was used to measure the amount of impurity in the oxygen. The method required that while a globe was filling with oxygen or hydrogen to be weighed, a second globe should also be filled with a quantity of the gas absolutely identical in quality for subsequent analysis, and that this sample should be absolutely safe from leakage. Now, when measurements were made in this way of the amount of impurity in the oxygen used for weighing, it was found to be negligible. But some experiments which proved this in another way are easier to describe, and are conclusive; so that perhaps it is not worth while to detail more at length the apparatus really used at the time the present series of determinations were made. I therefore describe only the manipulation required in filling the globe.

The globe *a*, Fig. 6, which had been previously exhausted, was placed in the case *m m*, in which *f f* is a non-conducting envelope, and *d d* is a mass of water contained in a vessel consisting of two concentric cylinders of iron. At *e e* is a stopper for the mouth of the inner iron cylinder; it consists of a cylinder filled with water. In this stopper are three tubulatures for the two thermometers and for the tube which is connected to the globe. The ground joint of the globe was placed in *n*, and made tight with melted wax or paraffin. The globe, tube, and stopper were put in place, and the tube *o* was connected by fusion to the tube *g h* leading to the air-pump, the mano-barometer, and the generator of oxygen. The stopcock *c* being open, the whole connected apparatus was exhausted, and the degree of exhaustion measured. The stopcock of the globe, *b*, could now be opened, and the degree of its exhaustion verified, if required, as, for instance, if the globe had just been weighed while exhausted, and it was desired to know if leakage had occurred. The globe was then closed during the further preparation of the apparatus for producing pure oxygen.

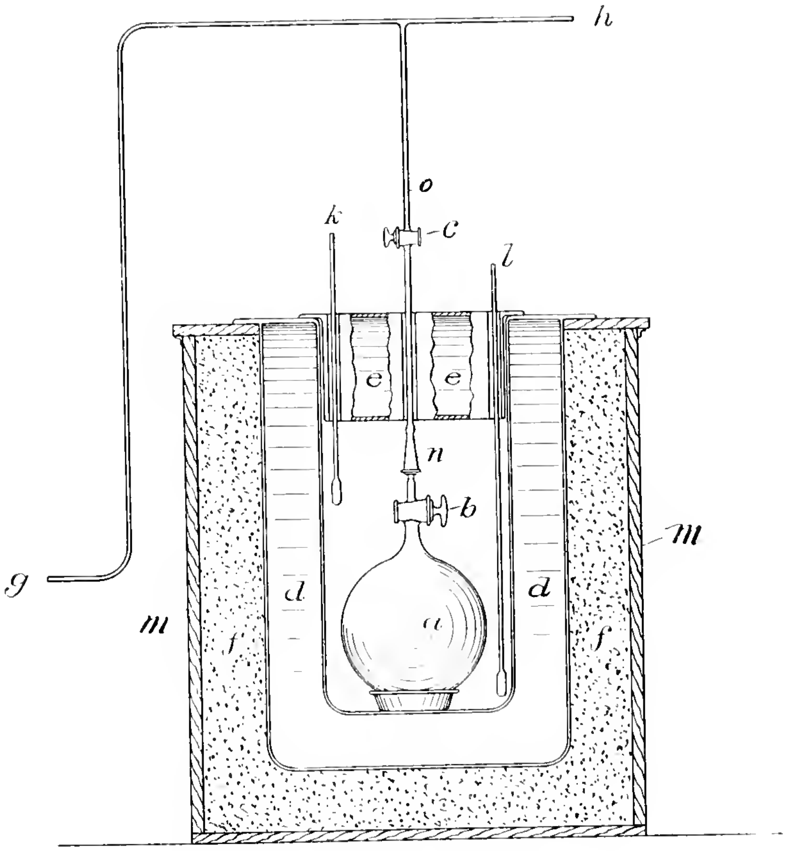


FIG. 6.—Calorimeter case for measuring temperature of oxygen.

14.—PREPARATION OF OXYGEN.

In all the experiments of this series, oxygen was obtained from potassium chlorate. A tube of infusible glass, *a a*, Fig. 7, was filled with the required quantity of the salt, the end *a d* was drawn out and fused to a ground joint made of the same glass. This was then cemented with wax to the joint *d*, made of soft glass, which was in turn fused to the rest of the apparatus.

It may be said that not a single connection of rubber was used, in any of my experiments, in contact with the gas on which I was working. It is of course true that with rubber joints the leakage may be so small as to be estimated and allowed for. But it was desirable to have no leakage at all, or, rather, to have no more than that which is inevitable between glass and mercury; and the manipulation which dispenses with rubber joints is by no means troublesome.

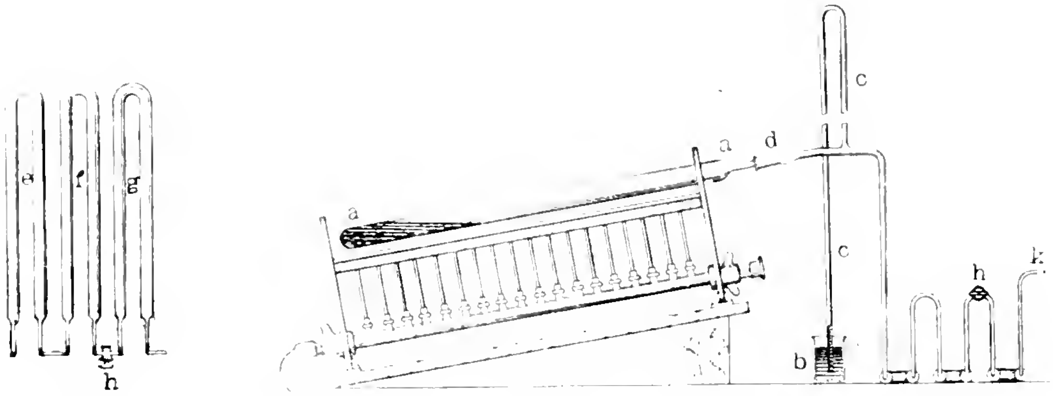


Fig. 7. — Apparatus for preparing oxygen; [illegible] shows in plan the tubes seen in elevation to the right of

At *c* is a gauge and overflow tube dipping in mercury. The oxygen coming from *d*, in some experiments, passed through a tube containing finely divided silver heated to redness, in order to absorb chlorine. When this was used it was connected to the tube *a* by fusion, and the joint *d* was at the end of the tube containing silver. The gas next passed through a tube 1 metre long, and 2.5 centimetres in diameter, which was filled with glass beads moistened with a strong solution of potassium hydroxide; then through a similar tube with sulphuric acid. At this point was placed a stopcock, whose office was to keep the pressure of the oxygen filling the part of the apparatus so far described at about the pressure of the atmosphere, so as to allow sufficient time for the action of the reagents. The tubes lay horizontally, so that the reagents might be advantageously distributed. After the stopcock, the gas passed through a tube of the same dimensions, filled with phosphorus pentoxide between layers of glass wool. From this, it was led to the apparatus which was to be filled with it.

In preparing oxygen, the apparatus was exhausted, and the degree of exhaustion measured; it was commonly the thirty-thousandth or fifty-thousandth of an atmosphere. Then the stopcock *h* was shut, and the chlorate was heated till it was thought safe to assume that any organic matter present had been oxidized. The chlorate was then cooled, the stopcock *h* was opened, and the apparatus was again exhausted. Then the stopcock *h* was again closed, the tube containing the chlorate was heated till the pressure of the oxygen in it was nearly that of the atmosphere. The stopcock *h* was then opened so as to permit a slow passage of oxygen into the globe, the rate being determined according to the indication of the gauge *e*.

15.—PURITY OF THE OXYGEN PREPARED FROM POTASSIUM CHLORATE.

Oxygen prepared from chlorate might contain chlorine; it might contain nitrogen which had not been removed from the apparatus, or which entered it during the experiment; or carbon dioxide produced by the combustion of organic matter; or finely divided chlorate or chloride; or the vapor of water.

The vapor of water can be so completely removed that the remainder is negligible. If the current is properly related to the dimensions of the drying tube, sulphuric acid does not leave more than one milligramme in four hundred litres of the gas.* The drying power of phosphorus pentoxide is yet greater, so that the amount of water vapor left unabsorbed is perhaps not more than one hundredth part as much as in the case of sulphuric acid.† If, as seems to be proved, a current of three litres an hour is dried completely by a drying tube whose capacity is twenty-five cubic centimetres, it may be safely assumed that a current at five times this rate will be dried by a tube five times as large.

Cooke has observed that the desiccating power of phosphoric anhydride may be lessened by the formation of a sort of glaze over the surface. The difficulty will be overcome if the gas to be dried does not simply pass *over* the pentoxide, but passes *through* a long column of it. If the pentoxide be so filled into the drying tube that a channel can form, the difficulty would no doubt exist. But if the pentoxide is alternated with plugs or diaphragms of glass wool, between which it fills the tube completely, the difficulty is removed. The initial deliquescence which forms the glaze is long limited to the compartment first reached by the gas to be dried; then at each diaphragm the current of gas spreads itself throughout the whole area of the tube, and if the tube be properly filled, it also spreads itself throughout the whole area of the part filled with pentoxide except in the first compartment. But if no plugs of glass wool are interposed, the channel which has formed in this compartment gradually extends throughout the tube, and the gas is no longer properly exposed to the action of the anhydride.

Nitrogen was sought for by eudiometric analysis, as well as in other ways. The maximum amount found was one twelve-thousandth, the minimum was about five millionths; the mean was one thirty-thousandth. Since the densities of

---

* *American Journal of Science*, 30, 140.

† *American Journal of Science*, 34, 199.

oxygen and nitrogen differ but by an eighth part, even the maximum found was negligible in its effect on the density of oxygen.

In some experiments, about half of the oxygen contained in a globe was combined with hydrogen, and chlorine sought in the water thus produced. Sometimes it could not be detected; it never amounted to the twentieth of a milligramme. It was in the same experiments that the presence of nitrogen was investigated; after twenty litres of oxygen had been combined with hydrogen, the residue was analyzed, and the amount of nitrogen measured, with the result given above.

If the absorption of chlorine was so complete, it may be hoped that the absorption of carbon dioxide was also complete. The experiments to detect chlorine also served to detect carbon dioxide, and the amount found was negligible.

Whether any vapor of mercury interfered with the trustworthiness of the determinations cannot be affirmed; the evidence is too indirect. But the evidence is perhaps sufficient that the error, if any, is negligible. If the density of oxygen is in error for this cause, the error in the determination of the density of hydrogen by the same method, in the same conditions, would be some sixteen times as much. But I have succeeded in determining the density of hydrogen, not only in exactly the way used for oxygen, but also in a way in which the error from the presence of vapor of mercury is entirely avoided; and this error is found to be not above some such quantity as one thousandth of the density of hydrogen; therefore in the case of oxygen it is not likely to be more than the ten or twenty-thousandth part.

16. MEASUREMENTS OF TEMPERATURE AND PRESSURE.

The temperature of the gas in the globe *a* Fig. 6, while resting in the case *m m*, was observed by means of two thermometers made of Jena normal glass and divided into fiftieths. Their bulbs were diametrically opposite, one near the top and the other near the bottom of the globe.

The pressure of the gas in *a* was measured with the mano-barometer shown in Fig. 8. The tubes *a* and *b* together constitute a syphon barometer; *c* is the tube which was used to measure the pressure of the oxygen in this set of experiments; a fourth being used for the experiments on hydrogen which were made at the same time. The tubes all stood in a box containing water, two of the faces of which were made of selected plate glass. In front of each tube and in contact with it was a glass scale graduated into millimetres. The lines of the scale are about three thousandths of a millimetre in width, so that the uncertainty in setting a division of the eye-piece micrometer for coincidence is negligible. The three scales were of the same kind of glass, graduated at the same time, and agreed well with each other. They were adjusted so that their three zeros were on the same level, as shown by comparison with the level of the mercury in the tubes behind them when all were open to the atmosphere. The tubes were of nineteen millimetres in internal diameter, so that differences of capillary depression could not be great, but the scales were adjusted so as to eliminate any difference which may have existed.

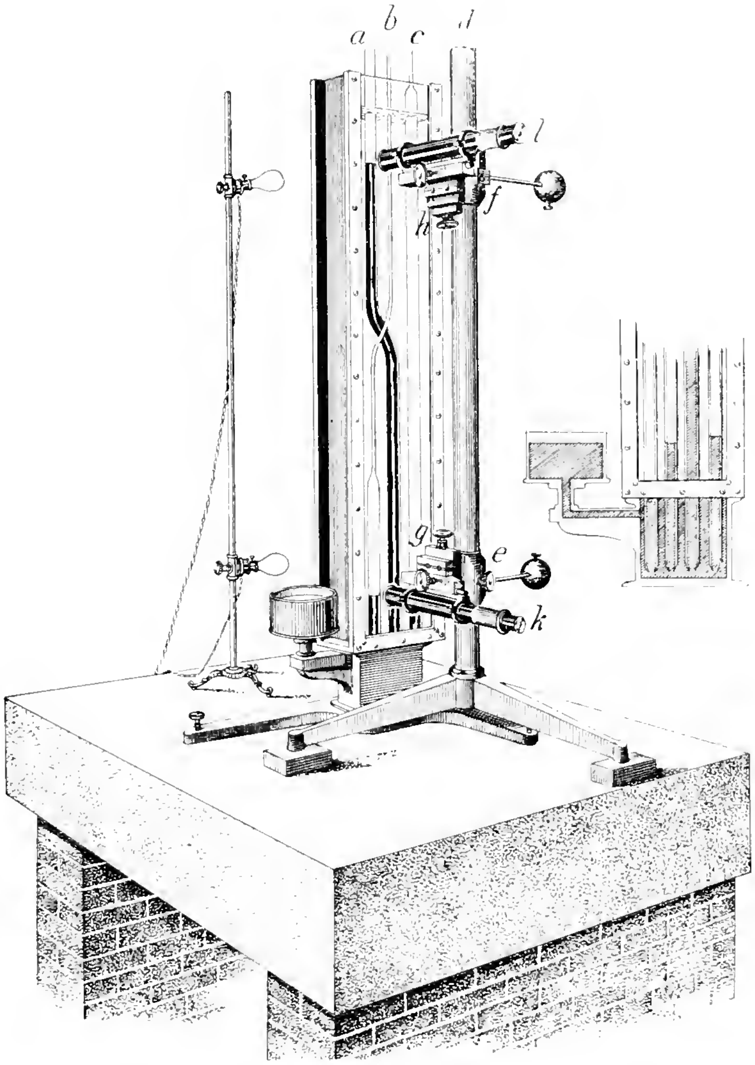


FIG. 8.—Barometer and reading microscopes.

These four tubes all stood in a cast-iron box filled with mercury; connected to this was an iron cylinder open to the air and filled with mercury so that the mercury in the tubes stood a few centimetres above the bottom of the casing full of water which surrounded them.

Before the mano-barometer stood an iron column carrying the reading microscopes. As is well known, a cathetometer with a scale somewhat removed from the length to be measured cannot be trusted like one in which the scale is near this length; my scale and the length to be measured were as near as they could be on any plan except that lately used by Lord Rayleigh, in which the scale was *in* the barometer. Further, the adjustment of the level of the telescope of a cathetometer of the first mentioned type demands care and time; but when the scale and barometer are in contact, the error due to lack of horizontality in the line of collimation of the telescope is lessened in the same ratio as that in which the distance of the scale from the object measured is lessened. To reach a given degree of precision requires much less care in adjustment and time is saved.

It is obvious that if a case containing water is used so as to make certain of the temperature of the column of mercury and of the scale, it is necessary to place the barometer and its scale in contact to avoid errors due to refraction at curved parts of the plates of glass enclosing the water.

To the column *d* can be clamped two pieces *e* and *f*, which carry two slides moving vertically by means of the screws *g* and *h*. To these slides are fixed ways on which the microscopes *k*, *l*, move horizontally by means of a rack and pinion.

The method of observation was as follows: The microscopes were made to give distinct vision of the scales, and were then adjusted vertically till the terminal divisions of the eyepiece micrometers coincided with certain divisions of the scale. The microscopes were then moved by the focussing movement so as to give distinct vision of the meniscus of the mercury in the two tubes. The divisions of the eyepiece micrometer were then virtually the divisions of the long scale carried forward into the centre of the tube. The divisions of the micrometer corresponded to twentieths of a millimetre; by proper manipulation of the illumination, it was not difficult to read the level of the mercury with a mean error less than one hundredth of a millimetre, which is of course much more than the precision attained in other parts of the manipulation.

It will be seen that in this method of observation it is assumed that the two slides on which the two microscopes move horizontally, are not horizontal, but *parallel*; or, rather, that the deviation from parallelism is negligible in the distance between the scale and the axis of the barometric tube. The accuracy of this assumption is easily tested by exchanging the positions of the microscopes, or by setting a scale perpendicularly before the microscopes, adjusting the micrometers to coincide with certain divisions of the scale, and then moving the scale farther from the column, and seeing whether the divisions of the micrometer are again at the same distance apart. In this way, it was found safe to trust the mechanism of my reading microscopes to the hundredth of a millimetre.

The mercury used in filling the tube of this barometer was purified by treatment with nitric acid, and subsequent distillation in a vacuum; and these operations were repeated several times, the distillation each time being made from a clean apparatus. The tube was filled by boiling under reduced pressure, and the ebullition after each addition of mercury was maintained for twenty or thirty minutes. The perfection of the vacuum was examined in the usual way by varying the volume of the space left vacuous above the mercury, and measuring the corresponding barometric height. It was proved that the residual air or vapor in the vacuum had a tension less than the hundredth of a millimetre, which had not increased measurably at the close of the experiments to be described in this paper.

Since the globe *a*, Fig. 6, was not maintained at constant temperature, the pressure of the gas was not constant. It was therefore impossible to make several readings of pressure and temperature and take their mean. Pressure and temperature were therefore read simultaneously at intervals till it was thought that they had attained a regular march; then they were read finally, and the stopcock *c* was closed. This pair of readings was adopted in the reduction. The cover *e e* was then raised till the stopcock *b* of the globe could be closed. Any slight change of temperature could do no harm for the stopcock *c* had been closed at the time of the final readings of temperature and pressure. The globe was now separated from the ground joint *n*, when it was ready for weighing.

The determination of temperature depended on a thermometer numbered 2053. It is of Jena normal glass, and is divided into fiftieths of a degree. Its principal scale is from 12° to 26°; but it has also short scales from − 0.3° to + 0.3°, from 49.5° to 50.5°, and from 97.5° to 100.5°.

This thermometer I have twice calibrated. The fundamental interval was obtained by the following observations:

Time.	Barometer, reduced to 0°.	Water pressure.	Thermometer 2053.	Water pressure.
h. m.				
10 30	737.64 mm.	2.8 mm.	98.880°	2.8 mm.
10 33	.51 mm.	3.5 mm.	.880°	4.0 mm.
10 35	.70 mm.	3.0 mm.	.882°	3.6 mm.
10 37	.70 mm.	3.6 mm.	.883°	4.0 mm.
10 38	.70 mm.	4.4 mm.	.884°	5.4 mm.
10 40	.77 mm.	2.4 mm.	.878°	1.7 mm.
10 42	.76 mm.	2.8 mm.	.877	2.7 mm
10 43	.84 mm.	2.6 mm.	.877	2.6 mm.

At 10.44, the thermometer was nearly at the temperature of melting ice, and the following observations were obtained:

Time.	Thermometer 2053.
h. m.	
10 45	− 0.292°
10 45 30	.300
10 46	.300
10 46 30	.298
10 47	.294
10 48	.292
10 49	.292

Hence we have

Mean barometric pressure	737.70 mm.
Water pressure in boiling-point apparatus reduced to equivalent column of mercury	.23 mm
Pressure of steam in boiling-point apparatus	737.93 mm
Pressure reduced to sea level in latitude 45	737.67 mm
Boiling point corresponding	99.170
Mean reading of maximum depressed zero	0.300
Correction for internal pressure	+ .014
Correction for inequalities of bore	.003
Corrected reading for freezing point	− 0.289
Mean reading for boiling-point	98.880
Correction for internal pressure	+ .098
Correction for inequalities of bore	— .002
Corrected reading for boiling-point	98.976
Observed interval	99.265
True interval	99.170
Correction to observed interval	.095

The following table shows the corrections found for a reading between 12° and 26°.

Degree.	Calibration.	Interval.	Compression.	Total.
12	+ .042	— .011	+ .017	+ .048
13	+ .035	.012	+ .021	+ .044
14	+ .029	— .013	+ .026	+ .042
15	+ .021	— .014	+ .030	+ .037
16	+ .013	.015	+ .035	+ .033
17	+ .006	.016	+ .039	+ .029
18	.001	.017	+ .044	+ .026
19	.004	.018	+ .048	+ .026
20	— .008	.019	+ .053	+ .026
21	— .011	— .020	+ .057	+ .026
22	.013	— .021	+ .062	+ .028
23	.016	— .022	+ .066	+ .028
24	.021	.023	+ .071	+ .027
25	.024	.024	+ .075	+ .027
26	.027	.025	+ .080	+ .028

With this thermometer were compared two thermometers of Jena normal glass numbered 826 and 1353, each having a scale in fiftieths of a degree enclosed in its tube. This pair was used for the actual determination of the temperature of the oxygen; their indications are given, as well as the indications of the hydrogen air thermometer computed from them.

During the present series of determinations, the cistern of my barometer was 3.9 metres higher than the centre of the globe while it was filling with oxygen. The temperature of the tube connecting them was assumed to be the same as the temperature of the room. The indications of the mano-barometer, reduced for the expansion of the mercury and of the scale, were therefore still further corrected by adding the term $3.9 \times \frac{D}{13596}$, where D is the weight of a litre of oxygen at the temperature of the room and at the pressure shown in that experiment.

The elevation of the cistern of my barometer above mean tide level at New York was during these experiments 216.1 metres, and the latitude of my laboratory is 41° 30′ 15″. The force of gravity there, computed by the formula

$$G = G_{45} (1 - .00259 \cos 2L) (1 - .000000196 H), \text{ is}$$
$$G = .9996423 G_{45}$$

By the formula of Helmert, which is used in recent publications of the United States Coast and Geodetic survey,

$$G = 980.5934 - 2.5967 \cos 2L \text{ (with the same correction for altitude), we get}$$
$$G = 980.235.$$

The Coast and Geodetic survey has made my laboratory one of their stations for determining the force of gravity, and its superintendent has furnished me with the result

$$G = 1.000132 \; G \text{ (Washington)}.$$

The value which has been provisionally adopted for Washington is

$$G \text{ (Washington)} = 980.098.$$

Hence

$$G = 980.227.$$

Dividing this value by the constant term of the formula of Helmert, we have

$$\frac{G}{G_{45}} = .999627.$$

All the observations contained in this paper have been reduced to the values which would be obtained at the sea level in latitude 45° by dividing by the factor

$$.999627.$$

Further, the value of gravity at my laboratory, according to the same determination, is

$$G = .999311 \; G \text{ (Paris Observatory)}.$$

In order, therefore, to reduce the values which will be given in this paper to the values which would be obtained at Paris, we must multiply them by

$$\frac{999627}{999311} = 1.000316.$$

The scale of my mano-barometer is of glass; its coefficient of expansion has not been determined. But the length of the bar at ordinary temperature has been determined by comparison with a bar whose coefficient of expansion is regarded as well known. This is one of two bars made by the Société Génevoise, which have been obtained at different times by the Case School of Applied Science, at

Cleveland. Since the bars, taken with the correction certified by the Société Génevoise, give the same value for the metre within the limits of the precision of the observations, the length of my bar is perhaps well enough known. At 20.9°, by observations with two thermometers on each bar, in a room whose temperature varied half a degree during the six hours of the observations, my bar was found to be 1.000114 metres in length. If we assume for my bar the coefficient of expansion of glass used in computing the table for reducing the height of the barometer given in the compilation of Landolt and Boernstein, and with this compute the length at 0°, the value obtained will be uncertain to some extent, but it will reproduce the true value at 20.9°, and will enable us to use these tables for the necessary reductions. We then have

Length of my bar at 20.9°	1.000114
Expansion for 20.9°, = 20.9 × 0.00085	.000178
Length of bar at 0°	.999936

The errors of the graduation were found to be insignificant for our purpose. The observations were therefore reduced by multiplying the observed pressure by the factor

.999936.*

17.—THE BALANCE USED IN THE FIRST SERIES OF EXPERIMENTS.

The balance used in the present series of experiments was made by Becker of Rotterdam, and will carry 1200 grammes in each pan. It was procured for this investigation, and has been used for nothing else. During these experiments, it was mounted on a case of non-conducting materials, thirteen centimetres thick, with doors of the same thickness. It was placed in a small room containing no source of heat, but surrounded on all sides with rooms kept as nearly at constant temperature as is usual in large buildings.

Much difficulty was experienced at first in determining the difference of weight between the globe and its counterpoise with sufficient accuracy and within a reasonable time. This difficulty is mostly due to currents of air affecting unequally the two globes, or, possibly, the two pans of the balance. The balance itself was enclosed in a case which had doors for manipulating the weights, and had also two openings in front, each some three centimetres in diameter. The lower of these contained a lens by which light could be condensed on the scale over which

---

* Since this paper was written, Professor Dayton C. Miller has had these two metres compared by the United States Coast and Geodetic Survey with the national prototype metre, which is in its custody; with the result that they are a thirty-thousandth part too short. It is too late to correct the reduction of each observation on density which is mentioned in this paper, but the means of each series, and the final values, have been corrected by increasing each by a thirty-thousandth part.

the pointer of the balance moves. Through the other, the observer could watch the vibrations of the balance with very little possibility of disturbance of its indications by his presence. The arrangement is shown in Figure 9, which is in part a section from the front to the rear of the balance through its centre. With this arrangement, it became certain that most disturbances were due to causes affecting the globes.

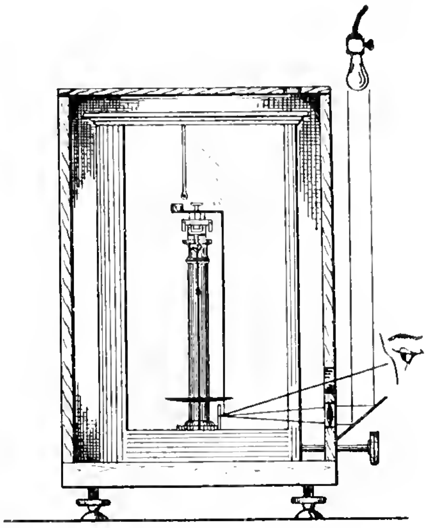


Fig. 9.—Balance surrounded with non-conducting case illumination of scale and pointer.

The inside of the case, seen in Fig. 10, was, therefore, lined with sheet metal, so as to lessen the entrance of air currents through the joints of the woodwork. But the opening for an instant of the room in which the balance stood, so as to admit warmer or colder air, would in a few minutes disturb the indications of the balance, not of course by changing the temperature within the case, but by producing currents of air in the room which penetrated the case and affected the globes unequally. Then the remaining joints in the woodwork around the doors were closed during a weighing by pasting paper over them; this lessened the disturbances, but not sufficiently. A metal box was then made, seen in Fig. 10, which had a cover with two openings for the suspension of the globes, but had no opening except at the top. The globes being put in this box, it was covered, and placed in the non-conducting case mentioned before, and the globes were hung on the balance. Since the only openings of this box were at the same level, and were small and symmetrically placed, it was hoped that the entrance into it of the air currents due to the motion of the air in the room would be mostly prevented, so that there would remain only the disturbing influence of the convection currents produced within the box itself by differences of temperature. This hope seemed to be justified, for weighings of the globes placed within the box had a mean error not larger than in the case of objects of the same mass, but far less bulk. The box contained calcium chloride for drying somewhat the air which surrounded the globes. It was not till the art of quickly weighing a globe had been learned by some months of trial that experiments on oxygen or hydrogen were made.

The globe containing the gas to be weighed was always suspended, in this series of experiments, from the left pan of the balance, and the weights required to produce equilibrium were also placed on the same pan. After an hour, three successive excursions were noted, the balance was arrested, and the observation repeated a few times. Riders were not used. The globe remained on the balance at least twenty-four hours, and the observations were repeated at intervals. The position of equilibrium of the unloaded balance and the value of a scale division were observed sufficiently often.

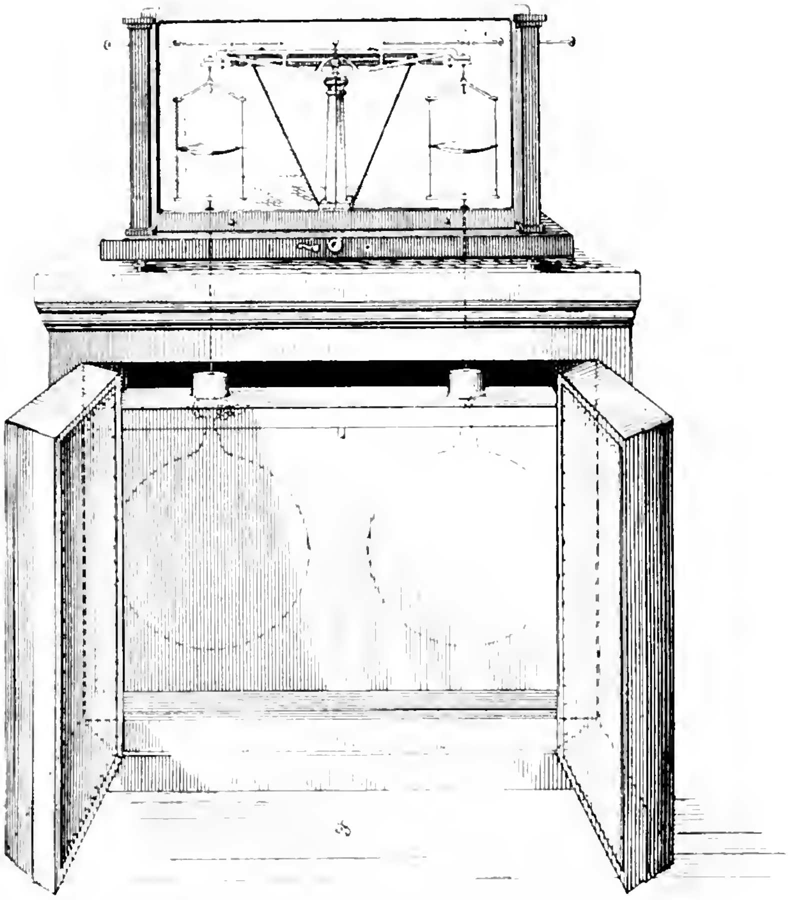


FIG. 10. Balance, case, and metal box for accurate weighing of globe.

The exhaustion of the globes for the purpose of determining the tare, hardly needs mention. The weight of the gas remaining in the globe was always computed from the indications of the McLeod gauge. All weights were corrected for the weight of the air displaced by them.

18. VERIFICATION OF THE WEIGHTS EMPLOYED.

The weights employed were, first, a brass kilogramme and its subdivisions to one milligramme, and, secondly, a platinum gramme and its subdivisions to one tenth of a milligramme. The relation of these to each other has been determined on three occasions. The chief object of determining the relation between the small weights and the kilogramme is of course to make the unit of weight and the unit of volume concordant. The true value of the weights is a matter of indifference.

The values of all the weights of the two sets, assuming the kilogramme as the standard of reference, are given below. The table shows the values of the brass weights at the two dates at which they were compared, as it may be of interest to know the amount of the change to which lacquered brass weights are liable, even when used but little and with extreme care.

VALUES OF WEIGHTS OF SET MARKED K IN 1887 AND IN 1892.

1000 000.00 mg.	1000 000.00 mg
499 999.95 "	499 999.83 "
200 000.07 "	199 999.88 "
99 999.62 "	99 999.55 "
99 999.34 "	99 999.51 "
49 999.97 "	50 000.36 "
19 999.97 "	19 999.96 "
9 999.62 "	9 999.92 "
4 999.90 "	4 999.94 "
1 999.97 "	1 999.99 "
1 999.79 "	1 999.98 "
999.91 "	999.94 "

VALUES OF THE FRACTIONS OF THE GRAMME IN SETS MARKED K AND B.

Set K.		Set B.	
1887	1892	1887	1892
500.02 mg.	500.01 mg.	1000.04 mg.	1000.05 mg.
199.96 "	199.96 "	500.02 "	500.02 "
100.00 "	100.02 "	200.01 "	200.04 "
99.94 "	99.94 "	100.01 "	100.00 "
49.97 "	49.96 "	100.05 "	100.06 "
20.04 "	20.05 "	50.01 "	50.02 "
10.07 "	10.09 "	19.95 "	19.97 "
10.01 "	10.02 "	9.98 "	9.98 "
5.00 "	5.01 "	10.01 "	10.02 "
2.01 "	2.01 "	5.06 "	5.05 "
2.01 "	2.01 "	1.97 "	1.96 "
.98 "	1.02 "	1.97 "	1.96 "
		.99 "	1.00 "

19.—RESULTS AND REDUCTION.

The following table gives the results obtained by this method, together with the values of the density of oxygen computed by the formula

$$D = \frac{W}{V} \cdot \frac{760}{P} \cdot \frac{L}{l} (1 + .003674\, t) \frac{G_4}{g}$$

No. of experiment	Volume cubic centimetres	Temperature mercurial thermometer	Temperature air thermometer	Pressure at barometer	Correction for difference of level.	Pressure at centre of globe	Weight of oxygen grammes.	Density of oxygen grammes.
1	8797.8	15.78	15.71	734.21 mm	.37 mm.	734.58 mm.	11.4805	1.42864
2	8798.4	17.89 "	17.81 "	752.97 "	.38 "	753.35 "	11.6882	1.42849
3	8830.7	18.58 "	18.40 "	757.92 "	.39 "	758.31 "	11.7879	1.42838
4	21569.6	19.54 "	19.45 "	770.22 "	.39 "	770.61 "	29.1560	1.42900
5	21569.3	19.03 "	18.94 "	774.74 "	.39 "	775.13 "	29.3791	1.42907
6	21569.3	19.02 "	18.93 "	747.26 "	.38 "	747.64 "	28.3346	1.42887
7	21569.4	19.17 "	19.08 "	744.00 "	.38 "	744.38 "	28.1935	1.42871
8	21568.4	17.47 "	17.39 "	752.90 "	.38 "	753.28 "	28.6958	1.42872
9	21568.4	17.48 "	17.40 "	745.91 "	.38 "	746.29 "	28.4308	1.42883

If we increase the mean by one thirty-thousandth,* we get

$$D = 1.42879 \text{ gr.} \pm 0.000034.$$

20.—SECOND METHOD OF DETERMINING DENSITY.

In the second series of determinations of the weight of one litre of oxygen, the barometer and thermometer were not used to measure the temperature and pressure of the gas at each observation. A globe like those used for the weighings was connected to a delicate differential manometer and filled with pure dry hydrogen. It was surrounded with melting ice, the open branch of the differential manometer was connected to the syphon barometer mentioned before, and the pressure required to bring the differential manometer to equilibrium was elaborately determined.

When afterwards a globe was filled with oxygen, it was connected with the open branch of the differential manometer, the temperature of the two globes was made the same, and the pressure of the oxygen was made such as to produce equilibrium in the manometer. It is obvious, assuming for a moment that oxygen and hydrogen have the same coefficient of expansion, that if the gases in the two globes had the same pressure at some unknown but uniform temperature, they would also have the same pressure at the temperature of melting ice, which pressure has been determined for the hydrogen. For the actual difference in the coefficients of expansion we can make a numerical correction.

One advantage of the method is that we may observe the equilibrium of pressure and temperature as long as we please, whereas, when we measure pressure and temperature, we are limited to the reading at the instant of closing the globe. This advantage can also be obtained by surrounding the globe with melting ice. A second advantage is that the globe in which the gas was weighed by this method was kept untouched, contained in a desiccator and surrounded by dry air, during the two determinations of the weight of the globe empty and of the globe filled with oxygen.

---

* See note, page 28.

21.—OXYGEN BY SECOND METHOD. STANDARD OF PRESSURE AND TEMPERATURE.

The globe *a*, Fig. 11, whose capacity was about sixteen litres, contained the hydrogen which was used to reduce to the standard temperature and pressure the

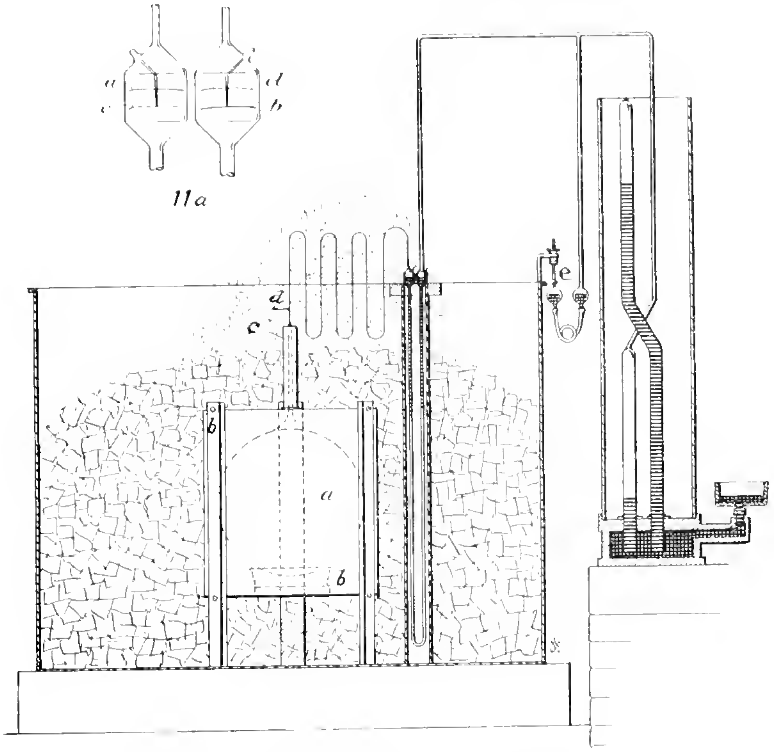
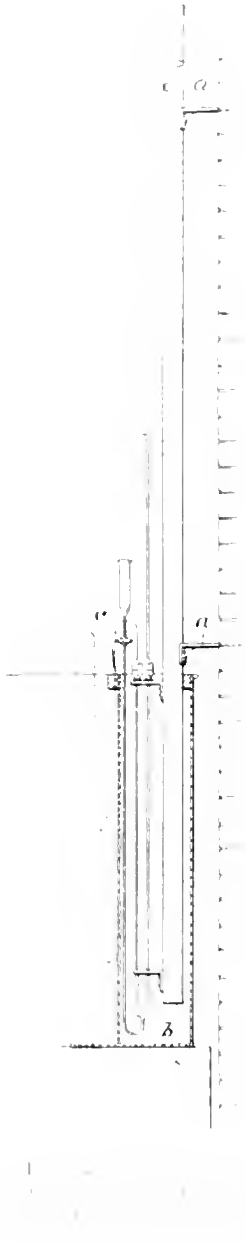


FIG. 11.—Globe containing hydrogen for a standard of comparison.

oxygen which was to be weighed. It was supported in the copper cylinder *b b*, having a water-tight cover provided with a tube *c*. This globe was connected by a somewhat flexible glass tube *d* to a differential manometer, of which part is shown in more detail in Fig. 11*a*. The tubes, of 24 millimetres internal diameter, contain platinum points which are in nearly the same horizontal plane. It is not necessary that they be at exactly the same level, but it is important that they preserve an invariable relation to each other. The gauge was therefore firmly secured by brass brackets, *a*, Fig. 12, to a brass tube which was solidly attached to a brick wall. The tube and the gauge touched nothing else during the whole series of experiments, except that they were partly immersed in water. The branches of the manometer were some eighty-five centimetres long; a tube *b* was fused into the bend and provided with a stopcock *c*, by which the volume of the mercury in the manometer could be regulated. At *d*, Fig. 11, was a tube leading to the Toepler pump and to a supply of pure dry hydrogen. When the globe had been exhausted



to a pressure of a few millionths of an atmosphere, hydrogen was admitted to about the atmospheric pressure, and this connecting tube was fused off, so that the hydrogen was now of unalterable mass. The cylinder containing the globe was then deeply covered with melting ice, from which the tube carrying the manometer was protected, so that it should not be disturbed. The manometer was also covered with powdered ice, and examined through an opening. The open branch of the manometer was connected to the syphon barometer and also to a contrivance for micrometrically regulating the pressure of the air in this connecting tube, seen at *c*, Fig. 11. The two levels of the mercury in the syphon barometer were in the same vertical, and were surrounded with water kept well stirred by a current of air; temperature was determined with the thermometer numbered 2053.

While the differential manometer was covered with ice, it was not easy to adjust the volume of mercury in it so that the two surfaces should be tangent to the two platinum points at once. Accordingly, two pressures were alternately measured which should bring the surface *b* to the right-hand point, and then the surface *c* to the corresponding point. The mean would be the pressure which would make both surfaces tangent to the two points at the same time, provided the volume of mercury were properly adjusted.

The following determinations of the pressure required to produce equilibrium of the gauge were made; all the readings are corrected for expansion of the mercury and of the scale of the barometer, but not for error in the length of the scale.

DETERMINATION OF PRESSURE OF HYDROGEN FOR COMPARISON WITH PRESSURE OF OXYGEN

[illegible] 1, 3 [illegible] M.	736.48 mm
3 [illegible] M.	736.52 mm
3 [illegible] M.	736.51 mm
4 [illegible]	736.51 mm
[illegible] M.	736.49 mm
[illegible] M.	736.45 mm
[illegible] 2, [illegible] M.	736.47 mm
Mean	736.49 mm

During the determination of the pressure of the gas in the globe *a*, Fig. 11, the cylinder containing it stood at the centre of the tank *f f*, so that a sufficient thickness of ice could be placed on every side of the globe. But for the subsequent use of the apparatus this globe had to be near the side of the tank. The cylinder *b b* was therefore held free from the tank while the latter was moved into its new position, when the globe full of hydrogen was again supported by resting the containing cylinder on the bottom of the tank. The differential manometer was not disturbed.

22.—OXYGEN BY SECOND METHOD. DESICCATORS FOR HOLDING GLOBES.

The globes used for weighing oxygen in this series of determinations were kept, during the whole course of an experiment, in desiccators, one of which is shown in Fig. 13. A copper vessel has a flange and cover at *a*, and a glass plate secured to a flange at *b*. At the centre of this plate is a fitting into which may be screwed a socket carrying the glass tube *c*. The whole is water-tight.

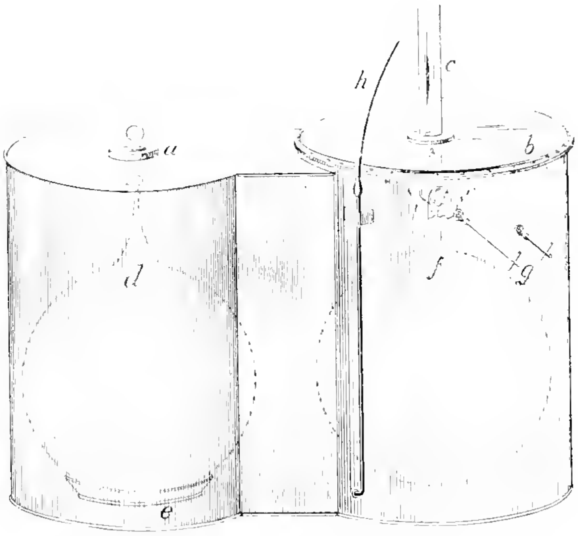


FIG. 13.—Desiccator for containing and manipulating globes during filling, weighing, and exhaustion.

The counterpoise *d* simply rests on a pan *e*, except when the cover is removed and the counterpoise suspended to the balance. The globe *f*, however, must be firmly held in order that the key of its stopcock may be manipulated. It is accordingly grasped by the clamp shown in Fig. 14. The jaws *a a* are moved in opposite directions by the right-hand and left-hand screws on the shaft *b*. A key which turns this shaft can be removed and the opening stopped with a cork. When the globe is held by this clamp, a handle *g*, Fig. 13, can be pushed forward so as to turn the key of the stopcock. When this handle is withdrawn and the globe is suspended from the balance, the jaws are made to release the globe which then hangs perfectly free. The glass tube *c*, Fig. 13, is removed during the weighing.

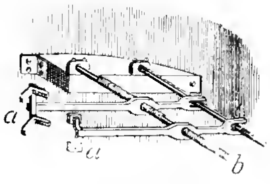


FIG. 14.—Clamp for holding globe while in the desiccator.

When it is desired to exhaust a globe in its desiccator, it is secured by the clamp, a ground joint is fitted in place, as in Fig. 6, and the desiccator is set near the Toepler air pump. Connection is made by fusion, as in the previous series of experiments. The stopcock is opened by the handle *g*, Fig. 13, and when the exhaustion has been completed, the stopcock is closed in the same way, the handle is withdrawn, the ground joint is removed, and the desiccator is put in place under the balance. The counterpoise is hung on one pan of the balance and the globe on the other and then released from the clamp, when it is ready to be weighed.

23. OXYGEN BY SECOND METHOD. DRYING THE AIR IN THE DESICCATORS.

It would be difficult to keep dry the air in desiccators as large as these, especially when open to the air during the weighings, unless the air is dried in some other apparatus and introduced into them. A current of dry air was accordingly brought into the desiccator through a tube for the purpose, *h*, Fig. 13, which delivered it at the bottom of the desiccator in a fanlike horizontal current. The air was forced by a hydraulic blower through two carboys containing pure sulphuric acid. While the globe was at the balance, this current passed through the axis of the mechanism for weighing the globes by reversal, which was used in the second series of determinations, and is described at page 42. The current was stopped a few minutes before each weighing, but suffered little other interruption. When the globes were filling or exhausting, one opening of the desiccator was closed and the other was loosely stopped with cotton-wool; an occasional introduction of dry air was then thought sufficient.

24. OXYGEN BY SECOND METHOD. FILLING GLOBES WITH OXYGEN.

When it was desired to fill a globe with oxygen, the desiccator containing it had the cover *a*, Fig. 13, put in place. The ground joint of the globe was cemented into its corresponding piece, and to the latter was fused a tube long enough to project above the tube *c*, Fig. 15, which was then screwed into position. The desiccator was then placed in the tank *a a*, near the globe of hydrogen and the differential manometer. The tube *b* was then fused to the tubes leading to the air pump, the manometer, and the apparatus for producing oxygen. The filling with oxygen was conducted in all respects as in the first series of determinations, the only difference being that the key of the stopcock of the globe could not be reached by the hand but by the handle *g*, Fig. 13.

While the globe was filling, beams *d d*, Fig. 15, were secured in position to hold down the desiccator containing the globe and also the cylinder containing the globe serving as a standard of pressure and temperature. The tank was then filled with water, which was well stirred by a current of air. When the pressure of the oxygen in the globe in the desiccator was very nearly the same as that of the hydrogen in the standard globe, the tube *e* was fused off. The pressure of the oxygen was then reduced by drawing off mercury from the stopcock *g*, till equilibrium was produced at the differential manometer. The water was well stirred, and the equilibrium was maintained for a sufficient time, sometimes for four hours, commonly for one hour. When the equilibrium was regarded as satisfactory, the stopcock of the globe was closed, the water was drawn off from the tank, the connections of the globe to the other part of the apparatus were severed, the desiccator was lifted out of the tank, dried, and taken to the balance. The cover *a*, Fig. 13, was removed, the tube *e* was unscrewed, the ground joint of the globe was cleaned, and the globe and its counterpoise were suspended from the pans of the balance as before.

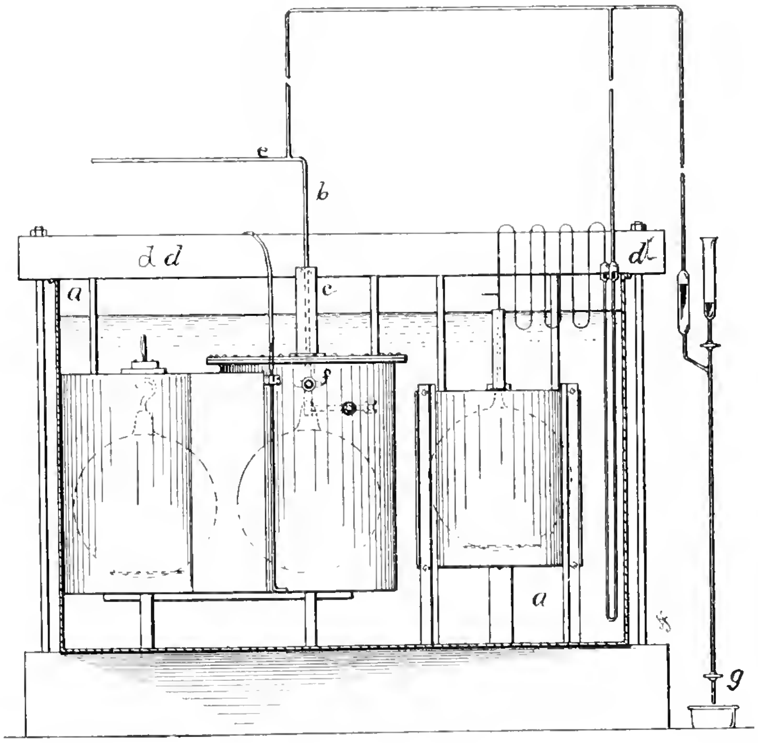


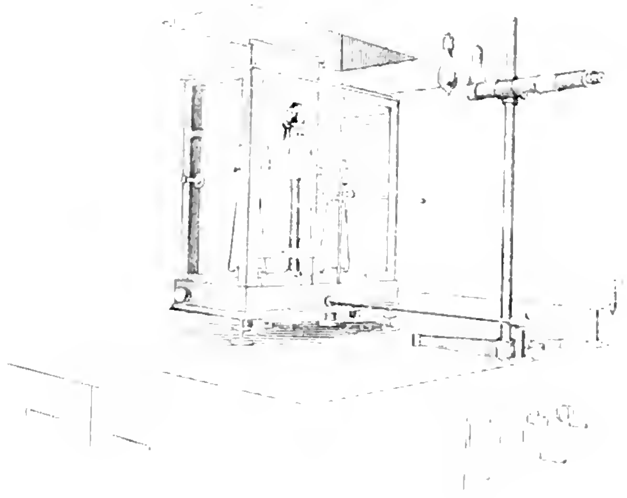
FIG. 15.—Filling globe with oxygen; use of desiccator; hydrogen used for comparison.

25.—OXYGEN BY SECOND METHOD. THE BALANCE WHICH WAS EMPLOYED.

The balance used in the weighings of this series of determinations was made by Rueprecht, of Vienna, and was lent to me by the Smithsonian Institution. It will carry twelve hundred grammes in each pan. The excursions of the beam are read by the telescopic observation of the image of a scale of equal parts which is seen reflected by a mirror carried by the beam. Of the many merits which this balance possesses in the highest degree yet attained, that one which made it desirable for my work was the great constancy of its indications. As was proposed in the preliminary discussion with Rueprecht, its sensitiveness has been reduced as far as is permitted by the range of the adjustment for this purpose.

MECHANISM FOR WEIGHING BY REVERSAL.

Fig. 16 gives a perspective view of the balance standing over the closet in which all objects to be weighed by reversal are contained. The shafts and handles by which the balance is manipulated are seen a few centimetres above the stone cover of the closet. The oscillations of the balance are observed by means of the telescope, in which are seen two images of a scale (not shown) placed over the telescope, one reflected from a mirror carried on the beam of the balance, and the other from a fixed mirror placed just over the first. The latter image serves to verify the stability of the scale and telescope.



F[illegible] 16.—Balance standing [illegible] closet [illegible] contains mechanism for reversing [illegible] objects to be compared [illegible]

Just below the stone cover of the closet are seen the handles for manipulating the reversal mechanism within the closet. The larger crank rotates the apparatus in transferring an object from one pan of the balance to the other; the smaller crank lifts and lowers the objects, and the milled head seen between the two cranks moves latches for accurately centering and for keeping unmoved the apparatus. A dial indicates the position of the reversal mechanism and of the several objects with reference to the pans of the balance.

The closet is of brick, 13 decimetres high and 12 decimetres square inside. At one side are two pairs of doors; the space between them could be filled with sacks of non-conducting material if desired, but this has not been found necessary. The whole inner surface of the closet is lined with sheet zinc, soldered so as to leave no openings but those which are required.

Attached to the stone cover of this closet, directly under the middle knife edge of the balance, is the axis of the reversal mechanism, on which rotates an object carrier, which is provided with six arms. All the rest of the mechanism serves to manipulate this carrier.

The hooks which are supported on this carrier need to pass in continuous rotation *through* the hooks which are attached to the pans of the balance. The details of these hooks are shown in Figs. 17 and 18; one is seen at *a*. It consists of two hollow cones, about 2.5 centimetres in diameter, joined by a cylinder about 1.5 centimetres long. The lower hollow cone has a slot four millimetres wide cut through it perpendicular to the plane of the paper, and the cylinder is cut away as shown. The lower hook *b* is a smaller cone, fixed to a short rod, *b g*, on which is also fixed the larger cone *c*; *d* is a hollow cone, borne on the object carrier, on which the system *b c g* is supported when not suspended from the hook *a*.

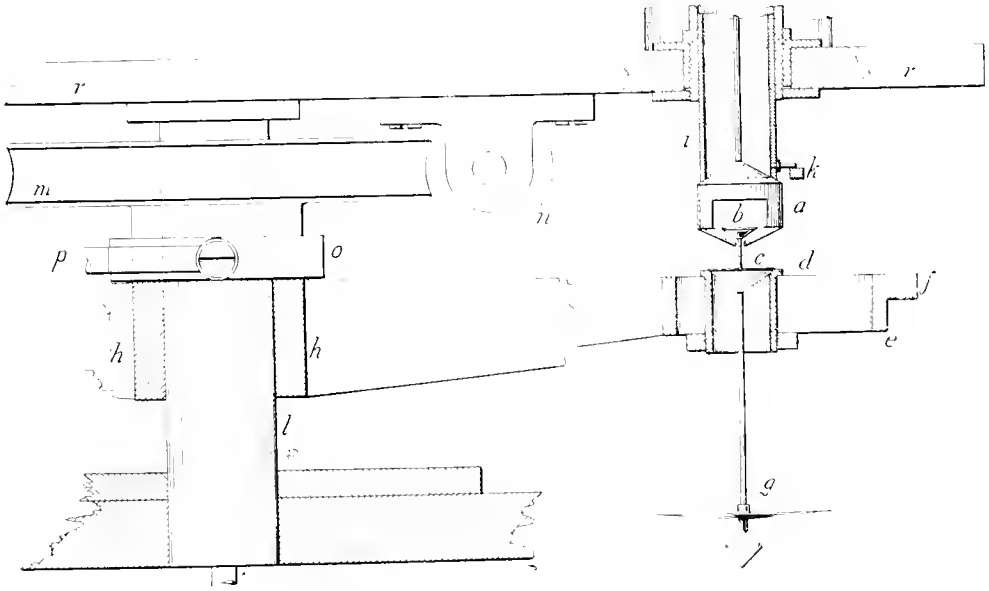


FIG. 17.—One arm of revolving carrier, raised, hooks disengaged.

If the object carrier, of which the centre and one arm are shown at *e h h*, is raised, as in Fig. 17, the hook *b* is quite free from *a*, so that *e h* may be rotated. If *e h* is lowered when it is in a proper position, *b* will engage with *a*, and *d* will descend some 2.5 centimetres, leaving *a b c g* quite free. In order that *a* and

b may properly engage with each other, it is necessary that a should be held in a definite position whenever it does not support b; accordingly, a tube i, ending below in a hollow cone, is placed as shown. Whenever $c\ h$ is lowered, k, and therefore i, are raised, taking the position shown in Fig. 18; a and c are therefore both supported or both freed by a single motion of the handles seen in Fig. 16.

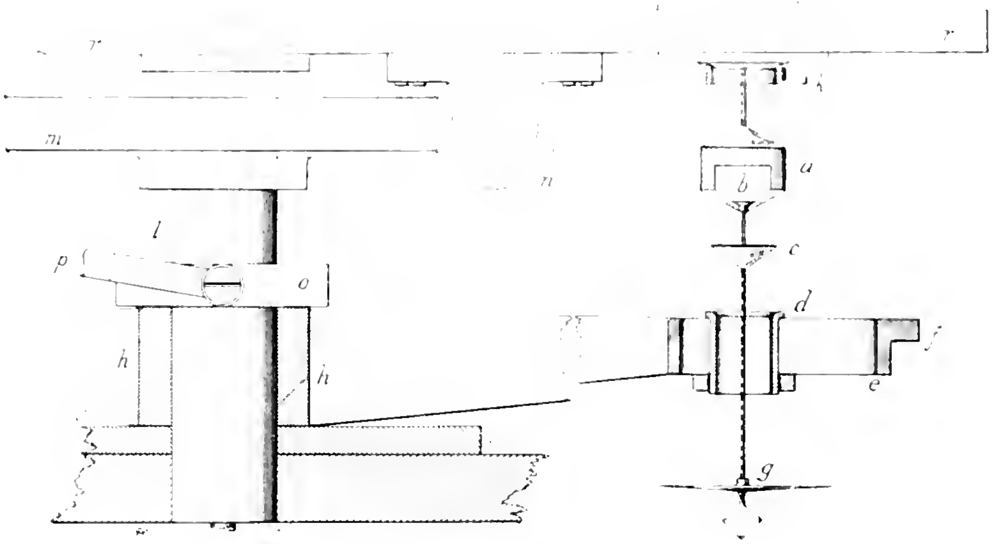


FIG. 18. One arm of revolving carrier, lowered, hooks engaged.

The object carrier $c\ h$ slides vertically upon a sleeve l. A collar o is attached to $c\ h$ so as not to turn with it, and is moved vertically by the lever p. But $c\ h$ also rotates with the sleeve l, and the motion of both is produced by the worm n and the worm gear m which is fixed to l. By the rotation of m and the motion of p, any one of the six hooks b can be put in any desired position. The sleeve l turns on a stud which is screwed into the plate $r\ r$.

Fig. 19 is a plan of the reversal mechanism seen from above, the stone cover being supposed removed, and the plate $r\ r$, by which the apparatus is attached to the stone cover, being indicated only in dotted outline. The worm gear, also, is broken away to show parts beneath it. At the centre of the plan is seen the hollow stud which is screwed to the plate $r\ r$. The worm and gear are shown at $m\ n$. The lower end of the sleeve is fixed in the disk s; to this is attached the radial arm t which carries at its end a stud u which compels the object carrier to turn with the sleeve and the worm gear; p is the lever by which $c\ h$ is raised or lowered; it receives motion from a crank on the shaft w, which also moves the arm y, by which in turn are moved the arms $k\ k$.

When the carrier has brought two opposite hooks exactly into position, two projections $c\ c$ are ready to enter two notches in the latches $x\ x$, which, being released by the motion of z, secure the correct centering of the lower hooks b, Fig. 17. When these latches are closed by turning z, the arm A locks the shaft B, and another arm at the end of the shaft z unlocks w. While $f\,f$ is lowered, and the hooks a and b are engaged, B and n cannot be turned, for the arm A is also locked by turning w; when w has lifted $f\,f$, z is unlocked, and can then in turn unlock B and the latches $x\,x$, after which B and $m\,n$ can be turned.

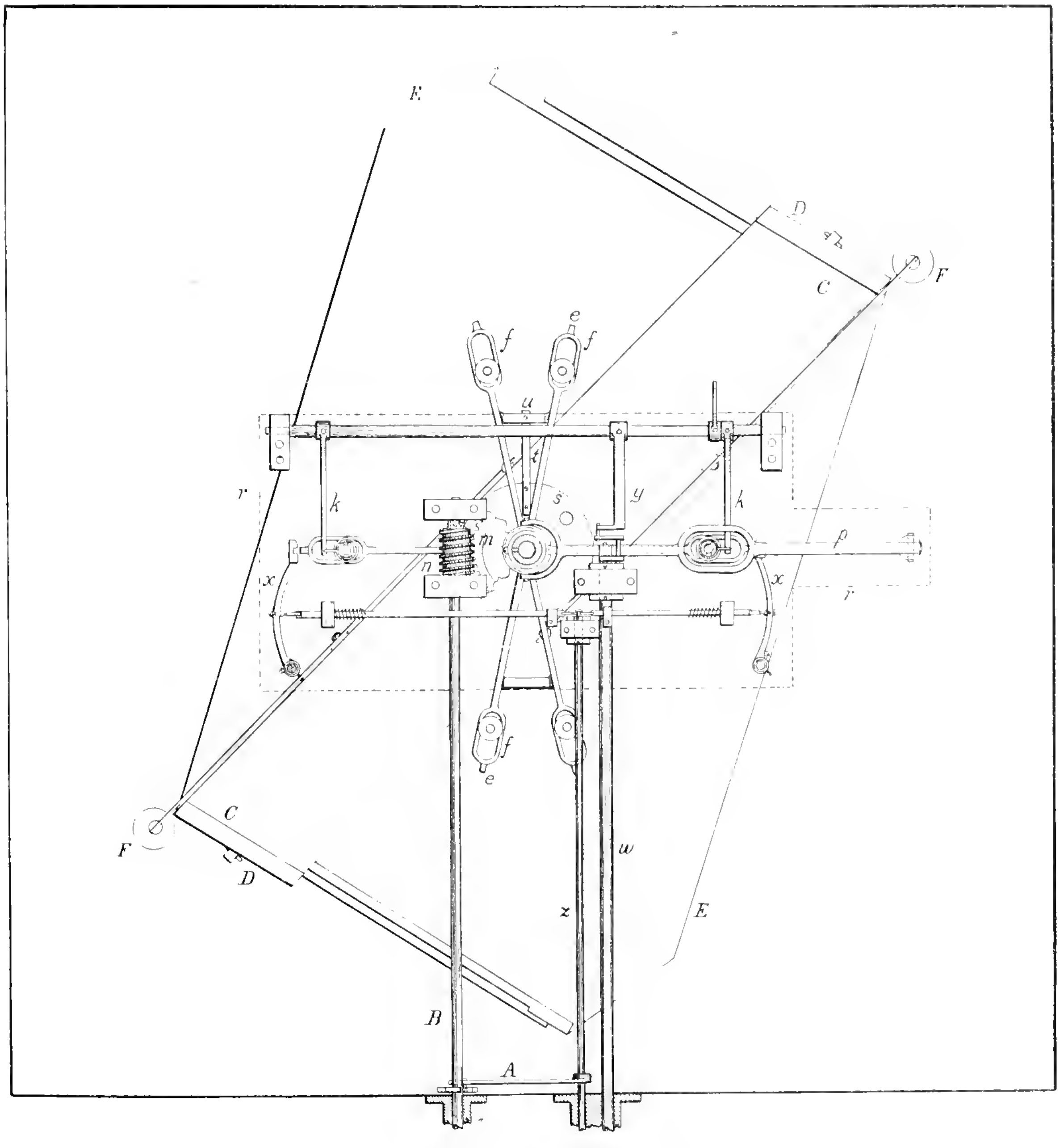


Fig. 19. Plan of reversing mechanism

Most of the objects weighed with this apparatus have to be contained in desiccators during the weighing. In order to carry these desiccators around with the objects which they contain, it is required to let the platform *E E*, which is placed eleven decimetres below *f f*, rotate with the latter. *E E* is supported on a pivot fixed in the floor of the closet, directly under the centre of *f f*. To the underside of the disk *s* is fastened the plank *C C*, and the latter is joined to *E E* by two boards seen in section at *D D*.

When it is convenient to place two pairs of globes on the apparatus at once, a desiccator containing the first pair stands on this platform *E E*, and the globes are suspended by long wires to the hooks near *e e* in Fig. 19 (this arm should have been shown parallel to the longer sides of *E E*). Across this desiccator, is then placed another, whose globes are suspended from the hooks seen near the latches *r r*. The central part of this upper desiccator has to be somewhat contracted so as to leave free the wires suspending the lower globes. There is then still room for a third pair of objects of no great bulk, like the tube containing palladium which is to be mentioned in describing the experiments on hydrogen. Since it was commonly thought proper to leave objects on the balance as much as twenty-four hours, these facilities for weighing three objects within the interval required for one were a very great convenience.

The desiccators for containing the globes needed to have dry air brought to them from without. In order to maintain this current while the globes were in the balance closet, it was convenient to introduce it through the axis of the reversal apparatus. For this purpose, the stud on which the apparatus rotates was made hollow, as seen at the centre of the plan, and the hose bringing dry air was attached to the upper end of this tube. It ended beneath in a little chamber, turning with the revolving object carrier, to which could be connected rubber tubes leading to the desiccators. The air was forced by a hydraulic blower through two carboys each half full of pure sulphuric acid. After bubbling through the acid, the air was filtered through a long column of cotton-wool.

Even when the mechanism was turned slowly, it was not easy to avoid some oscillation of the objects carried on the reversal apparatus. A mechanism for stopping this oscillation was therefore devised. The hooks *a a* are suspended from the pans of the balance by rods which are enclosed in the brass tubes on which the pans of the Rueprecht balance are supported when the balance is arrested. On these rods, two brass disks slide freely down to two pins which limit the motion. In the tubes are placed perforated disks covered with velvet. When the tubes carrying the disks and the pan arrests are let down six millimetres, the sliding disks still rest on the velvet. The pans have at this moment been freed from their arrests; the oscillations of the pans and the suspended weights are soon stopped by the friction between the disks and the velvet. But when the pan arrests are further moved down 3.5 centimetres, the disks are left perfectly free.

This apparatus for weighing by reversal was first used with the balance made by Becker, but the apparatus for damping oscillations was then different. When the Rueprecht balance was put in place of the Becker balance, the difference in the arrest for the pans made it necessary to modify the apparatus previously used for this purpose, and to readjust the distance of the hooks *a* and *b* from the axis of the mechanism, to suit the shorter length of the beam of the new balance. *F F* are counterpoises which support the weight of the object carrier, and of the objects placed on it.

26.—OXYGEN BY SECOND METHOD. WEIGHING BY REVERSAL.

All the weighings of this series of determinations were made by Gauss' method of reversals. The globe containing the oxygen was suspended from one of the auxiliary pans of the reversal apparatus just described, and its counterpoise from the opposite hook. Weights were placed on the auxiliary pan, on the side from which the globes were suspended (not on the pan of the balance itself), nearly sufficient to produce equilibrium. Except in two cases, weights smaller than ten milligrammes were not used here; as the weights were removed from observation till the end of the operation of weighing, the falling off of a small weight in closing the doors of the closet might not be noticed at the time, and it was then a question whether it fell off at the closing of the door at the beginning of the weighing, or at the end. But if a weight of ten milligrammes or more fell off, there was no ambiguity.

The globe with its weights, being at the left of the observer, was suspended from the pan of the balance itself by manipulation of the handles shown in Fig. 16. The beam of the balance was then released, and the weights smaller than ten milligrammes which were needed were added to one side or the other as indicated. The balance was then arrested, and the current of dry air introduced into the desiccator, passing through the axis of the reversing mechanism. After a proper interval, the balance was released and three excursions were noted; then the reversing mechanism was used to transfer the globe to the right of the observer, to suspend it to the pan, and to stop its vibrations. The small weights placed on the pan of the balance itself were by hand transferred to the opposite pan, and three excursions were noted. The mean of the apparent weights required in the two positions gives the difference between the weights of the globe and its counterpoise as well as it can be given by a single observation. But in general it will not be the true difference.

It will be observed that currents of air produced outside of the closet of the weighing apparatus have but little effect in disturbing the balance. The openings in the desiccator are small, and are at the same level. It is therefore impossible for a current of air to enter the desiccator near the top, and leave it near the bottom, striking against one of the globes during the passage. If the whole body of air in the small room surrounding the closet becomes less dense, the whole body of air within the closet will ooze out at some opening near the bottom; but this movement will not take place in part through the desiccator.

But if convection currents are produced within the closet itself, they are very likely to enter the desiccator, unless this has a certain symmetrical exposure to them; and if convection currents are produced within the desiccator itself, they are still more likely to disturb the balance to which the globes are suspended.

Suppose, for instance, that the distribution of temperature in the closet is such as to produce currents; a downward current may well enter the desiccator and strike upon one of the globes. Currents in the same direction will also be produced within the desiccator, since its inequalities in temperature will be in the same direction as those of the walls of the closet. The globe on the left hand, let us say, will appear too heavy. If now the positions of the globes be reversed, the currents which enter the desiccator from without are reversed in their effect on the globes, but those which are produced within the desiccator itself will continue for some time, making the right hand globe appear too heavy. These currents, therefore, make the globe appear too heavy in both positions.

As a matter of observation, the convection currents produced within the desiccator are so much the more important that the effect actually noticed in conditions when weighing is possible is attributable entirely to them. When the effect of the currents entering the desiccator from without is noticed, the equilibrium of the balance is so inconstant that weighings have to be postponed. This has occurred but seldom.

Fortunately the effect of the currents set up within the desiccator is easily eliminated. If we wait for, say, half an hour, until we may assume that a new constant condition of temperature has been attained, and again weigh by reversal, the convection currents produced within the desiccator will produce an effect on the apparent difference of weight of the two globes which is opposite to the effect produced in the first weighing. If the conditions of temperature have not materially changed, and if the time used in the manipulation is about the same, the two opposite effects will have about the same magnitude, and will nearly disappear from the mean. The mean of two successive weighings by reversal with an interval of half an hour or an hour ought, therefore, to give very nearly the true difference of weight of the globe and its counterpoise.

That this is the case may be seen from many illustrations in my note-books. I give one in which the globes counterpoised against each other were both closed by fusion, so that their true difference of weight was constant. The volumes were equal on the two sides of the balance, and were 15.77 litres.

TABLE SHOWING THE ELIMINATION OF THE EFFECT OF AIR CURRENTS:

Date.	Hour.	Apparent Weight, gr.	Means.
April 29	11.45 A.M.	41.81888	
			41.81902
	12.45 P.M.	41.81916	
			41.81905
	1.45 P.M.	41.81894	
			41.81904
	5 P.M.	41.81913	
			41.81903
April 30	9.40 A.M.	41.81892	
			41.81903
	10.05 A.M.	41.81913	
			41.81903
	12.45 P.M.	41.81893	

It will be observed that, although successive weighings differ two or three tenths of a milligramme, the means of pairs of successive weighings agree as well as could be desired.

27.—OXYGEN BY SECOND METHOD. CHANGE OF SURFACES OF GLOBES.

In this series of experiments, the surfaces of the globes were not touched during the determination of the weight of the globe when empty and that of its weight when filled with oxygen. In one case, seven successive experiments were finished without touching the globe. Commonly, some trifling accident or the necessity of renewing the lubrication of the stopcock changed the weight of the globe or of its counterpoise; in the series of seven determinations just mentioned, the difference between the weight of the globe and of its counterpoise was determined three times, and the agreement was good.

Although changes in the surface of the globe or of its counterpoise were not to be feared in this series of experiments, it was thought worth while to determine the amount of the changes which might be expected if cleaning were necessary. To eliminate errors which might be caused by changes in the lubrication or by leakage, two globes were used which had been closed by fusion. To one of them was added a flask, also closed by fusion, so as to make the volumes of the masses on the two pans of the balance equal; each measured 15.7667 litres.

The globes had been standing in the balance room for a year. For the first experiment, both were moistened by breathing on them and wiped with a dry cloth. Their difference of weight was then determined as they hung in the desiccator; it was found to be, as just given, 41.8190 gr.

One of the globes was now washed with distilled water and at once wiped dry and replaced in the desiccator; this was at 12.40 P.M. on April 30. The following observations were then made:

Date.	Hour	Weight, gr.
April 30	5.30 P.M.	41.8167
May 1	12.15 P.M.	41.8167
May 2	8.30 A.M.	41.8168
May 3	11.00 A.M.	41.8167
May 4	8.40 A.M.	41.8167
May 7	5.00 P.M.	41.8173

The mean is 41.8168; so that the washed globe had lost 2.2 milligrammes.

On May 11, the same globe was washed again, its counterpoise being simply wiped as before; both were replaced in dry air at 9.30 A.M. The following observations were made:

Date.	Hour.	Weight, gr.
May 11	2.30 P.M.	41.8176
May 11	6.00 P.M.	41.8172
May 12	11.45 A.M.	41.8172
May 12	2.15 P.M.	41.8171
May 12	6.00 P.M.	41.8169
May 13	9.00 A.M.	41.8171
May 13	10.00 A.M.	41.8171
May 13	2.40 P.M.	41.8172
May 14	12.00 M.	41.8173

The mean is 41.8172; so that the globe had lost no more in weight by the second washing soon after the first.

On May 14, the same globe was washed by scouring gently with powdered pumice-stone and distilled water. It was then wiped, passed through the flame of a Bunsen lamp, and replaced in the desiccator at 5 P.M. The following observations were made:

Date.	Hour.	Weight, gr.
May 15	5.30 P.M.	41.8175
May 16	8.30 A.M.	41.8175
May 16	11.45 A.M.	41.8174
May 16	5.50 P.M.	41.8175
May 17	9.00 A.M.	41.8173
May 17	11.15 A.M.	41.8175
May 17	7.20 P.M.	41.8175
The mean is		41.8175

On May 18, at 9 A.M., the same globe was washed with pumice-stone, using hard friction; it was then wiped and put in the desiccator at 12.30 P.M. Weighings were made as follows:

Date.	Hour.	Weight, gr.
May 18	4.30 P.M.	41.8173
May 18	5.40 P.M.	41.8155
May 19	2.30 P.M.	41.8159
May 19	7.30 P.M.	41.8159
May 20	11.00 A.M.	41.8159

Obviously the first weighing was made too soon. The mean of the other weighings is 41.8158 gr.

The weighing after the first washing shows the well-known loss of material produced by the solvent action of water after glass has been exposed for a long time to the decomposing effect of the air. The next weighing shows that a second washing soon after the first may have a much less solvent action; that of May 15 shows that gentle friction with powdered pumice may not remove anything from a surface already well washed.

If it were safe to argue from the increase from 41.8168 to 41.8175 gr. we might perhaps infer that repeatedly wiping the second globe was gradually producing a loss such as the first suffered from the first washing; but the inference is too insecure.

28.—OXYGEN BY SECOND METHOD. PREVENTING LEAKAGE OF GLOBES WHEN EXHAUSTED.

Since, with a balance of such gratifying constancy, but a few repetitions of a weighing were necessary, it would have perhaps been safe to trust the stopcocks which had been fused to the globes. But since the manipulation which entirely prevents the leakage of the stopcocks when the globe is exhausted is by no means difficult, it was always used in this series of determinations.

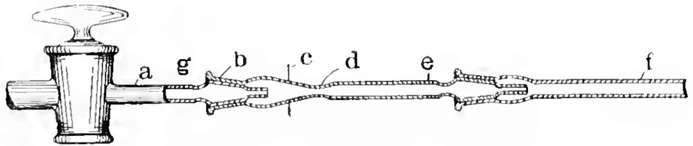


FIG. 20.—Method of preventing leakage of globes when exhausted.

At *g*, Fig. 20, is the ground joint of the stopcock by which the globe is always connected to other apparatus. The piece *b d*, which fits on *g* was reduced to a small diameter at *c* (the tube at *c* should have been drawn as at *d*) and a mark was etched here; the piece was then put in position on the stopcock, and the volume contained between this mark and the key of the stopcock was determined by filling from a burette. This was done once for all. When the globe was to be exhausted, this joint was fused to the joint *d e*, and drawn to a small diameter at *d*, ready to be closed by fusion when exhausted, and the volume between the mark *c* and the point *d* was determined by filling it with water and weighing. The two joints having been thus made ready, *b* was warmed and coated internally with wax ready for cementing on *g*. Then the two joints with this wax were carefully weighed by reversal, after which *b* was warmed and fitted to the stopcock of the globe. On *e* was now fitted the corresponding ground joint *f*, and this was fused to the air pump. When the exhaustion was completed, *d* was closed by fusion, the part fused off was removed from *f*, cleaned, and put on the balance with the globe. From the weight of the glass attached to the globe, together with the volume between the key of the stopcock and the point *d*, is computed the volume added to the globe. The weight of the glass added is known from the preliminary weighing; it of course simply replaces a certain amount of brass and platinum weights which otherwise would have been needed. The manner in which the addition of this volume was cared for is to be described in the next paragraph.

29.—OXYGEN BY SECOND METHOD. CORRECTION FOR DIFFERENCE OF VOLUMES.

In all the experiments of this series, the volumes suspended from the opposite pans of the balance were made equal at every weighing. For this purpose, some sixty minute flasks were made, of sizes ranging from one cubic centimetre to ten. They were all made nearly equal in weight by loading with mercury, closed by fusion, and provided with platinum hooks. The appearance of one is shown in Fig. 21. Their volumes were then determined by hydrostatic weighings and marked on them by etching, after which they were made rigorously equal in weight when weighed in a vacuum. This was accomplished on an assay balance whose needle moved fifty divisions for a difference of one milligramme, taking account of the density of the air and of the errors of the weights employed.

FIG. 21. Small flask for equalizing volumes.

When the difference of volume of two masses to be counterpoised against each other had been determined, two of these minute flasks were selected, such that the difference of their volumes was equal to the difference of volumes of the masses to be weighed; adding the small flask to the large volume and conversely, the volumes to be weighed became equal. These flasks had been so accurately adjusted to equality of weight in vacuo by repeated determinations that it was not necessary to take account of their weight or of the minute differences of their weights.

As an example of the simplest application of the equating flasks, a joint, *b c*, Fig. 20, weighed approximately 7.77 grammes, and had therefore a volume of 3.11 cubic centimetres. The weights to balance it had a volume of 0.85 cubic centimetres. Adding to these two volumes two flasks having volumes of 1.41 and 3.65 cubic centimetres, we have the two volumes on the opposite pans of the balance 3.11 cc + 1.41 cc = 4.52 cc, and 0.85 cc + 3.65 cc = 4.50 cc.

In the case of an exhausted globe, the number of volumes to be added together is greater, but the principle is the same. For instance, in weighing globe No. 5 when exhausted and closed as described on page 47, we have the following volumes on the two sides of the balance:

	Globe 5	Counterpoise 5
Joint	3.11 cc	
Space below mark *c*, Fig. 20	1.08 "	
Space above mark *c*	0.10 "	
Brass weights	2.62 "	
Platinum weights	0.03 "	
Small equating flasks	1.41 "	8.35 cc.
Sums	$G_5 + 8.35$ "	$C_5 + 8.35$ cc.

Since the volume of globe 5 is equal to that of its counterpoise when the globe is exhausted, $G_5 = C_5$, hence the volumes on the opposite sides of the balance are equal, so that the immediate result of the weighings, with no observation of temperature and pressure, and with no computation of correction, gives the true difference of weight between the globe and its counterpoise.

30. OXYGEN BY SECOND METHOD. OBSERVATIONS.

The following table gives the weights obtained of globes filled with oxygen at the same temperature and pressure as that of the hydrogen which was used as a standard of comparison.

OBSERVATIONS WITH GLOBE 5.

Date.			Weight, gr.
May	25	Filled	4.3827
"	28	Exhausted	34.2284
Renewed lubrication:			
June	10	Filled	4.7165
"	21	Exhausted	34.5512
Renewed joint:			
June	24	Exhausted	30.3731
"	25	Filled	0.5466
"	27	"	0.5482
"	29	"	0.5473
July	1	"	0.5441
"	1	Exhausted	30.3735
October	31	"	30.3734
November	7	Filled	0.5358
"	19	"	0.5376
December	4	"	0.5394

OBSERVATIONS WITH GLOBE 3.

May	20	Filled	0.0190
"	26	Exhausted	27.7736

Renewed joint :			
June	27	Exhausted	29.8270
"	28	Filled	2.0727
"	30	"	2.0720
July	4	Exhausted	29.8253
Renewed lubrication :			
November	11	Exhausted	29.7385
"	12	Filled	1.0855
"	22	"	1.0778
Counterpoise changed :			
December	1	Filled	1.0434
"	12	Exhausted	29.3024

31. OXYGEN BY SECOND METHOD. REDUCTION OF OBSERVATIONS.

The weights of the oxygen found to have the same pressure as the standard volume of hydrogen when at the same temperature need a correction for the difference between the coefficients of expansion of hydrogen and of oxygen. If these coefficients were the same, the equality of pressure observed at ordinary temperatures would also be preserved at the temperature of melting ice. Since the expansion of oxygen is greater than that of hydrogen, the mass of the oxygen required at 0° will be greater than that at ordinary temperatures. If we assume for the coefficients of expansion at constant volume the values .003661 and .003674, we may apply the correction for the mean temperature of the whole series of experiments, which was 13.5° C. The formula for reduction therefore becomes :

$$D = \frac{W \cdot 760 \cdot L \cdot (1 + 13.5 \times .003674) \cdot G_{12}}{V \cdot 736.40 \cdot L \cdot (1 + 13.5 \times .003661) \cdot g};$$

by which are obtained the values given in the following table.

32. OXYGEN BY SECOND METHOD. RESULTS.

The following table gives the weights of oxygen contained in the globes in the given conditions, with the weights deduced for one litre of oxygen at normal temperature and pressure at the sea level in latitude 45°.

OBSERVATIONS WITH GLOBE 5.

Number.	Weight of oxygen grammes.	Density of oxygen grammes.
1	29.8457	1.42952
2	29.8347	1.429[illegible]
3	29.8267	1.42863
4	29.8251	1.42853
5	29.8260	1.42858
6	29.8292	1.42873
7	29.8376	1.42913
8	29.8358	1.42905
9	29.834[illegible]	1.42866

OBSERVATIONS WITH GLOBE 3

Number.	Weight of oxygen grammes.	Density of oxygen, grammes.
1	27·7546	1.42880
2	27·7535	1.42874
3	27·7542	1.42878
4	27·7530	1.42872
5	27·7507	1.42859
6	27·7490	1.42851

If we increase the mean by one thirty-thousandth,* we get

$$D = 1.42887 \text{ gr.} \pm 0.000048.$$

33. OXYGEN BY THIRD METHOD.

In a third series of determinations of the density of oxygen, the globes were surrounded with melting ice while filling with the gas, and the pressure was measured by connecting the globe to the syphon barometer. The surface of the globe was therefore exposed to contact with water; as it was convenient to put the globe in position in the ice before the operation of exhausting the connecting tubes and filling it with oxygen, the contact was somewhat prolonged. Change of weight of the globes during the exposure was therefore inevitable: it was accordingly thought proper to determine the weight of the globe filled with oxygen, and then to exhaust it and determine its weight when empty, and to consider the difference of the two weighings as expressing the weight of the gas removed by the exhaustion. An attempt was made to protect the stopcocks and their lubrication from the action of water by surrounding them with rubber capsules while they lay in the ice.

The cistern of the barometer was at the level of the centre of the globes during this series of determinations. The reduction of the observations took account of the force of gravity at my laboratory, and of the correction to the length of the scale of my barometer.

34.—OXYGEN BY THIRD METHOD. FILLING THE GLOBES WITH OXYGEN.

The globe *a*, Fig. 22, was placed in a cylinder, *i*, and surrounded with finely crushed ice. This cylinder stood in a large tank, *k*, also filled with ice, so that the globe was surrounded on all sides with a layer of more than thirty centimetres of ice. To the joint *c* was fitted the tube which led to a self-acting Toepler pump, to the apparatus for producing oxygen, and to the syphon barometer. The globe and

---

* See note, page 28.

its connections having been exhausted and the vacuum having been measured, the pump was shut off by means of a stopcock, and oxygen was then admitted till the desired pressure was obtained, when a second stopcock near *d* was closed. The pressure of the oxygen was then measured. The globe was left in the ice for this purpose for from one to four hours. The stopcock near *d* was not required to be tight against any material difference of pressure on the two opposite sides of its key: its only office was to shut off from the globe, during the measurement of pressure, the part of the apparatus whose temperature was somewhat variable. The use of a fusible metal plug at a convenient part of the tube prevented leakage during the exhaustion of the globe and connecting tubes.

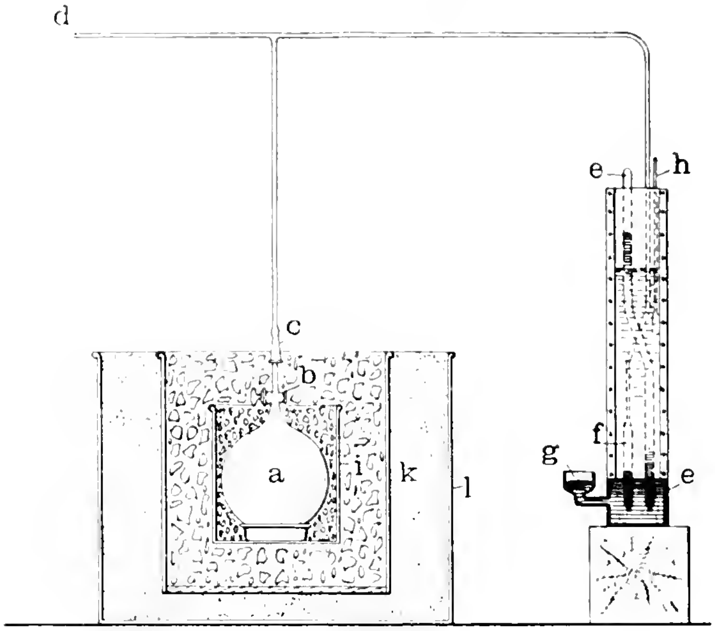


Fig. 22. Filling a globe with oxygen; use of ice.

35. OXYGEN BY THIRD METHOD. SOURCES OF OXYGEN.

In seven of the experiments of this series, oxygen was obtained from potassium chlorate; the process was in all respects exactly like that in the previous series. In the other experiments, oxygen was produced by the electrolysis of pure dilute sulphuric acid. The gas issuing from the voltameter passed through a strong solution of potassium hydroxide, where the time of contact was over fifty seconds; then over heated copper oxide, and through drying tubes filled with calcium chloride, powdered potassium hydroxide, and phosphorus pentoxide, each of which was one metre long and two and a half centimetres in diameter. All were connected by fusion, except that the tube of infusible glass containing the copper oxide was joined to the soft glass of the rest of the apparatus by means of ground joints made gas-tight with paraffin. The pure dry oxygen issuing from the last drying tube passed to a manometer indicating its pressure, and to a stopcock separating the apparatus up to this point from that on the other side of the stopcock, where the pressure was less until the completion of the process of filling the globe with oxygen. Beyond the stopcock, a fusible metal plug closed the tube leading to the globe until the exhaustion was finished. The tube between this stopcock and the fusible metal plug was freed from air by exhaustion with another pump, after which the tube leading to this pump was closed by fusion. When the required exhaustion had been obtained, this plug was removed, and the passage of the oxygen to the globe was regulated by a stopcock. The manometer which showed the pressure of the gas in the voltameter was connected by so long a tube, and oxygen was so often blown out at it, that it was thought impossible for mercurial vapor to mingle with the current of the gas on its way to the globe.

36.—OXYGEN BY THIRD METHOD. MEASUREMENT OF PRESSURE.

The measurement of pressure in this series was like that in the first series, except in one particular. In the first series I used what Regnault called a mano-barometer, the relation of the tubes in which is well known. But in the present case I used a syphon barometer, as shown diagrammatically in Fig. 22. In a box stand two tubes, *e* and *f*, one connected to the globe, and the other filled with mercury by boiling in a vacuum. The upper part of *e* and the tube *f* are in the same perpendicular. The difference of level which measures the pressure of the oxygen in the globe can be accurately and conveniently measured by means of a scale standing in contact with the two tubes and viewed with proper optical apparatus.

37.—OXYGEN BY THIRD METHOD. WEIGHING THE GLOBES.

The globes, after washing and wiping, were hung with their counterpoises in desiccators in the closet under the balance. But the desiccators now used were not required to hold the globes permanently, and were therefore simple boxes of sheet metal, with a cover having holes for the suspension of the globes from the balance. The globes were placed in one of these desiccators, the cover was put on, the box was put in position on the rotating platform of the reversal mechanism of the balance, and the wires attached to the globes were hung to the auxiliary pans of the reversal apparatus. Dry air was then admitted at the bottom of the desiccator and there spread horizontally in all directions. This current was introduced

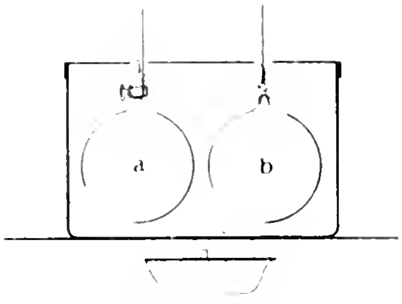


Fig. 22.—Desiccator.

through the axis of the reversal apparatus, and could therefore be continued without interruption except for the purpose of weighing.

The volumes suspended from the opposite pans of the balance were always made equal, as in the previous series of determinations, and the weighings were made by reversal in precisely the same way.

38. OXYGEN BY THIRD METHOD. WEIGHT OF GLOBES WHEN EXHAUSTED.

As already observed, it was thought proper to determine the amount of oxygen in the globe by determining the difference of weight between the filled globe and the globe exhausted immediately afterwards. In this exhaustion and the subsequent weighing, leakage through the stopcock of the globe was prevented by the manipulation described on page 47. Now, since the tare of the globe thus obtained was only for the one experiment immediately preceding, the weight of the joint shown in Fig. 20, and used to prevent leakage, did not need to be known. The joint was therefore made ready for application to the globe when the latter was to be weighed with its contents of oxygen, and was, during that weighing, put on the balance with the globe. After the weighing was completed, the joint was put on the globe, a vacuum was produced, the joint was closed by fusion, and the globe with the joint was weighed again. The difference of these two weighings (in which the volumes on the opposite pans were made equal as usual) gave the weight of the oxygen contained in the globe.

Since there was no room for any exercise of judgment in the combination of observations made in this way, it is sufficient to give simply the number of the globe employed, the pressure, the weight of oxygen, and the density of oxygen found. The capacities of the globes have already been given.

39. OXYGEN BY THIRD METHOD. OBSERVATIONS AND RESULTS.

The results obtained by the method in which the globes were filled with oxygen at the temperature of melting ice were as follows. It may be said that three observations were made with the globe numbered 6. But it was found that an error had been made in the computation of the volume of its counterpoise, so that all the observations made with it were subject to an uncertain and variable correction for the difference of the volume of the globe and its counterpoises. These three results were therefore rejected.

OXYGEN FROM POTASSIUM CHLORATE.

Number of experiment.	Globe used.	Pressure, millimetres.	Weight of oxygen, grammes.	Density of oxygen, gramme.
1	2	727.04	12.0179	1.42920
2	1	746.93	12.3954	1.42860
3	2	769.76	12.7227	1.42906
4	1	773.22	12.8400	1.42957
5	1	772.22	12.8192	1.42910
6	2	778.68	12.8745	1.42930
7	2	778.04	12.8628	1.42945

OXYGEN BY ELECTROLYSIS.

Number of experiment.	Globe used.	Pressure, millimetres.	Weight of oxygen, grammes.	Density of oxygen, gramme.
8	1	774.39	12.8572	1.42932
9	2	750.12	12.3983	1.42908
10	1	769.83	12.7796	1.42910
11	8	765.35	23.7671	1.42951
12	3	761.52	28.7134	1.42933
13	9	774.98	21.9675	1.42905
14	5	772.55	31.3039	1.42914
15	7	747.88	21.6150	1.42849
16	7	754.99	21.8274	1.42804
17	7	763.80	22.0808	1.42886

If we increase the mean by one thirty-thousandth,* we get

$$D = 1.42917 \text{ gr.} \pm 0.000018.$$

40. — OXYGEN. FINAL RESULT FOR THE DENSITY.

The values found by the different methods used are as follows:

By use of thermometer and manometer......D = 1.42879 ± .00003 4
By compensation..........................D = 1.42887 ± .00004 8
By use of ice and barometer...............D = 1.42917 ± .00004 8

The combination of these results into a final mean must be left mostly to the judgment of those interested in the matter. The probable errors of the three means would indicate that the first method should have double weight, which would be very improper, in my judgment. This method involves more easy manipulation, but gives less security against constant error. So also with the second method. The manipulation of the third involves more accidental errors, but involves no constant errors which are not common to the other methods, while it avoids some. I shall therefore compute a mean in which the third result is given double weight; from which we get

$$D_0 = 1.42900 \pm 0.000034.$$

---

* See note, page 28.

PART II. ON THE DENSITY OF HYDROGEN.

I. INTRODUCTION.

The density of hydrogen has been determined in five series of experiments of very unequal value. In the first series, temperature and pressure were measured with mercurial thermometers and the mano-barometer. The reduction took account of the same factors as the reduction of the first series in the case of oxygen. This series consisted of fifteen separate determinations.

In a second series, the globes were surrounded with melting ice while the pressure was measured with the syphon barometer. The reduction was the same as in the third series of experiments on oxygen. This series consisted of nineteen experiments.

In a third series the hydrogen was weighed, not in the globes where its volume, temperature, and pressure were observed, but before it was introduced into them. Globes making jointly a capacity of forty-two litres were connected together, and to a self-acting air pump, to a syphon barometer, and to a tube for admitting hydrogen. A tube containing six hundred grammes of palladium foil was charged with hydrogen, and was weighed. Its hydrogen was transferred to the globes, previously exhausted and shut off from the air-pump. Here its volume and pressure were determined at the temperature of melting ice. The tube of palladium was again weighed, and so the weight of hydrogen was determined. This series consisted of eight experiments, together with five experiments which were made before the apparatus and its manipulation were satisfactory, and which were regarded as only preliminary. The reduction of these observations takes account of the elevation of the cistern of the barometer above the centre of the globes and of the force of gravity at my laboratory.

The fourth series was simply a continuation of the third after a summer vacation. Several accidents occurred. The series was therefore abandoned, and a new apparatus was constructed. The fifth series was a repetition of the third and fourth with a different apparatus; these two series consisted of six and eleven experiments respectively, but accidents occurred in two experiments of the fourth series.

2.—DETERMINATION OF DENSITY BY FIRST METHOD.

In the first series of determinations of the density of hydrogen, nearly all the manipulation was almost precisely the same as that used in the first series of determinations of the density of oxygen. The two were carried on at the same time, with the same apparatus in the same condition; it was hoped that in this manner of working the ratio of the two densities might be subject to fewer systematic errors. Only a brief account is therefore required.

3.—FIRST METHOD. PREPARATION OF HYDROGEN.

In all the experiments of this series, hydrogen was prepared by the electrolysis of pure dilute sulphuric acid. The gas was passed through a strong solution of potassium hydroxide, over incandescent copper, and through three drying tubes one metre long and two and a half centimetres in diameter, the last filled with phosphorus pentoxide and the preceding one with powdered potassium hydroxide. In the apparatus up to this point, the pressure was always kept equal to that of the atmosphere by a stopcock and a manometer.

In some experiments of this series the gas was admitted at once to the globe as it issued from the regulating stopcock. In the remaining experiments, the gas was first absorbed in metallic palladium. When this was to be filled with hydrogen, it was first heated in a vacuum. Then hydrogen was passed through it while it was still too hot to absorb the gas, and the current was continued for some time, after which the source of heat was removed. After the absorption was complete, a current of gas was passed for a long time to expel any gas other than hydrogen which might have accompanied the latter. When this end was thought to have been attained, the connection between the palladium and the voltameter was cut off, and the connection opened to deliver the hydrogen into the globe. Heat being applied to the palladium, the globe was filled.

In all the experiments in which palladium was used, the tubes for conducting the gas were closed, either by fusion or by fusible metal plugs, so that leakage from the atmosphere into the apparatus was absolutely excluded.

4.—FIRST METHOD. PROOF OF THE PURITY OF THE HYDROGEN.

The voltameter in which hydrogen was produced contained about five litres of dilute sulphuric acid, and the drying tubes and other parts of the apparatus had a capacity of one or two litres more. To remove the air from this apparatus took of course a considerable time. It was thought proper to meet any objections by actually determining the amount of nitrogen remaining in the gas which was weighed.

This might have been done by taking hydrogen from the globe in which it had been weighed, and analyzing in some suitable apparatus. Circumstances made it convenient to adopt a slightly different method. Instead of filling one globe with hydrogen which was to be first weighed and then analyzed, two globes were filled at the same time. They had been exhausted to the same degree. The current of gas divided and went to the two globes in quantities proportional to their capacities; so that the two contained gas of identical quality. One globe was afterwards detached and weighed. The other globe remained permanently connected with the apparatus for determining the impurities in the gas, and was somewhat elaborately guarded against possibility of leakage.*

With this apparatus, the method of determining the amount of nitrogen in the hydrogen was as follows: A vacuous tube containing copper oxide was heated till no more gas was given off. This tube was connected to the globe containing the hydrogen reserved for analysis, and the copper oxide was heated. By noting the change of pressure in the globe the amount of hydrogen withdrawn from it was determined. Then the connection with the globe was closed, the copper oxide was cooled, and the gas remaining was extracted with a Sprengel pump, and transferred to the eudiometer. The structure of the pump made impossible any admixture of air with the gas transferred with it, for the mercury which actuated it all passed through a vacuum trap which was kept exhausted by an auxiliary pump.

When in this way, let us say, one litre of hydrogen had been withdrawn from the part reserved for analysis, and had been reduced to, say, ten cubic centimetres, it was measured in the eudiometer, mixed with oxygen and exploded, and so the amount of hydrogen in the residue was determined. Since cupric oxide is at best but a treacherous material, examination was also made for gas absorbable by alkali, and when absorption occurred, the experiment had to be resumed with a better sample of copper oxide. If the experiment showed no absorption, the gas not hydrogen was considered as nitrogen. Since qualitative examination showed that sulphur and carbon were not present, this supposition was probably justified. It will be noted that it is a matter of indifference whether the oxygen used in the explosion contained nitrogen, but it did not.

In several experiments of this series, nitrogen was found in the hydrogen. But after a considerable volume of hydrogen had been produced, the apparatus was practically free from nitrogen except after breakage. Soon after the use of

* *American Journal of Science*, II, 220

palladium for purifying the hydrogen in the way described, nitrogen could no longer be detected, though sought for repeatedly in a volume as large as two litres. The search for it was then discontinued.

AMOUNTS OF NITROGEN FOUND IN HYDROGEN WHICH WAS WEIGHED:

Experiment.	Date.	Volume taken.	Nitrogen found.	Correction to density.
3	April 28,	828 cc.	.030 cc.	.000045
4	May 6,	1734 "	.035 "	.000025
5	May 8,	640 "	.010 "	.000020
6	May 28,	798 "	.036 "	.000057
7	June 9,	838 "	.005 "	.000008
8	June 20,	1083 "	.005 "	.000006

5. FIRST METHOD. OBSERVATIONS AND RESULTS.

The weights of hydrogen observed in this series of experiments are given in the following table, which shows also the number of different observations of the equilibrium of the balance, counting all the different releases and arrests made at one time as but one observation.

OBSERVATIONS WITH GLOBE 2.

Date.					Weight, gr.
October	23–24	Exhausted	12	observations	14.2025
November	4– 7	Filled	21	"	13.4905
March	27–29	Exhausted	9	"	14.1195
April	6–11	Filled	20	"	13.3579

Renewed lubrication.

April	23–25	Exhausted	16	observations	14.1132
April	28 – May 1	Filled	17	"	13.3711
May	6– 7	Filled	8	"	13.3490

Renewed joint.

May	8– 9	Filled	10	observations	13.3760
May	10–12	Exhausted	8	"	14.1237

OBSERVATIONS WITH GLOBE 4.

May	28–29	Filled	6	observations	18.4361
May	29–30	Exhausted	7	"	20.0546
June	5– 6	Exhausted	10	"	20.0542
June	9–11	Filled	8	"	18.3942
June	11–13	Exhausted	3	"	20.0555
June	20–21	Filled	10	"	18.3835
June	24–26	Filled	7	"	18.3897
July	1– 2	Exhausted	5	"	20.0577
July	3– 5	Filled	8	"	18.4092
July	9–11	Exhausted	6	"	20.0579
July	13–14	Filled	9	"	18.3738

OBSERVATIONS WITH GLOBE 3.

July	15–16	Exhausted	7	observations	29.9430
July	17–18	Filled	7	"	28.2648
July	19	Filled	3	"	28.2404

OBSERVATIONS WITH GLOBE 5.

July	12–13	Exhausted	6	observations	30.7055
July	14–15	Filled	4	"	28.8641
July	16–17	Exhausted	5	"	30.7042
July	18–19	Filled	5	"	28.9660

Combining the observations in the way which was thought proper at the time of the experiments, we get the following determinations of the weight of the hydrogen in the globes. The table gives the pressures reduced to 0°, the readings of the thermometers reduced to the scale of 2058, the computed reading of the hydrogen air thermometer, the gross weight and the tare of the globes, their capacities at the temperature of the experiment, and the density computed; the latter includes the correction for nitrogen given on page 59, and is computed for the sea level in latitude 45°, by the formula $D = \frac{W}{V} \cdot \frac{760}{P} \cdot \frac{L}{l} (1 + .003661\, t) \frac{G_{45}}{g}$

Experiment.	Pressure. mm.	Temperatures. Mercury.	Air	Weight Filled, gr.	Weight Empty, gr.	Volume, cc.	Density, gr.
1	730.96	18.68	18.59	13.4005	14.2025	8798.5	.089904
2	783.33	19.33	19.24	13.3579	14.1195	8798.7	.089936
3	754.09	15.95	15.87	13.3711	14.1132	8797.9	.089945
4	770.13	13.6[illegible]	13.55	13.3490	14.1132	8797.3	.089993
5	762.80	17.12	17.04	13.3760	14.1237	8798.1	.089974
6	736.30	18.47	18.38	18.4361	20.0548	19822.9	.089941
7	759.77	20.15	20.06	18.3942	20.0548	19823.9	.089979
8	764.87	19.94	19.85	18.3835	20.0555	19823.8	.089936
9	765.30	20.71	20.62	18.3807	20.0577	19824.2	.089904
10	760.02	22.00	21.90	18.4092	20.0578	18824.9	.089846
11	772.09	20.41	20.32	18.3738	20.0578	19824.0	.089878
12	775.88	20.65	20.55	28.8641	30.7048	21570.3	.089920
13	761.70	21.43	21.33	28.2648	29.9430	20069.2	.089990
14	734.99	21.51	21.41	28.9660	30.7048	21570.8	.089926
15	768.63	21.21	21.11	28.2404	29.9430	20069.5	.089928

If we increase the mean by one thirty-thousandth,* we get

$$D = 0.089938 \text{ gr.} \pm 0.000007.$$

6. HYDROGEN, SECOND METHOD.

In a second series of experiments, the manipulation was precisely like that in the third series of experiments on the density of oxygen, except in the preparation of the hydrogen. No examination of the hydrogen for impurities was made, since

---

* See note, page 28.

the result of many previous examinations had shown how to obtain the gas with no measurable amount of impurity.

It may be not without interest to consider how small an amount of nitrogen might be detected when mixed with hydrogen. If the hydrogen should be removed from the mixture by absorption, as carbon dioxide may be removed, it would be possible to detect a very small quantity. My measuring apparatus, for instance, would measure a considerably smaller quantity than the thousandth of a cubic centimetre. If, then, two litres of hydrogen were absorbed by some supposable reagent for the purpose, a two-millionth of nitrogen would be detected. But the case is different when the amount of hydrogen in a mixture must be determined by explosion with oxygen. In my experiments, two litres of hydrogen were reduced to ten cubic centimetres by absorption by means of copper oxide, but the remaining ten centimetres had to be measured, and the hydrogen determined by explosion, and the nitrogen determined by difference. With sufficient care, one ought to be able to answer for a hundredth of a cubic centimetre; for how much less, I have no means of knowing.

But to detect a hundredth of a cubic centimetre, in the case supposed (and realized), means to detect a two-hundred-thousandth; to this approximation, the examination was carried, in duplicate analyses, with the result that hydrogen containing less than this could be obtained in the usual working of the apparatus, except after fracture. The removal of nitrogen from the apparatus was then tedious, but the result was certain, and hydrogen of such purity is thought to have been used in all the experiments of this series.

7.—SECOND METHOD. PREPARATION OF HYDROGEN.

Hydrogen was prepared in this series of experiments in very nearly the same way as in the preceding; but some details were different. The hydrogen from the voltameter passed through an almost saturated solution of potassium hydroxide, over incandescent copper, through a tube one metre long and two and a half centimetres in diameter, which was filled with glass beads moistened with a strong solution of lead oxide in potassium hydroxide, then through three tubes of the same dimensions, filled with calcium chloride, with powdered potassium hydroxide, and with phosphorus pentoxide. Here was placed a manometer and a regulating stopcock; all parts were connected by fusion, except where infusible glass had to be connected to the soft glass of the rest of the apparatus.

When the tube containing palladium was to be filled, it was connected by fusion to the tube delivering pure hydrogen, and was heated. When it was so hot that no absorption would take place, a current was passed through it, and this was continued for half an hour; care was taken to make this current pass through every branch of the connecting tubes so as to expel all air. When the exit of the hydrogen had been closed by fusion, the palladium was cooled, and hydrogen was admitted till its tension was equal to that of the atmosphere. Hydrogen was then again passed through the tube of palladium, escaping into the air for three hours, so as to remove any nitrogen which should have accumulated. When this had been accomplished the exit of the gas and the connection with the voltameter were then closed by fusion. The tube containing palladium had been from the first connected with the globe, but the passage had been stopped by a plug of fusible metal.

8. SECOND METHOD. FILLING GLOBES WITH HYDROGEN.

When the globe and its connections had been exhausted to the desired degree, one of the fusible metal plugs which obstructed the connection with the supply of hydrogen was fused, and hydrogen admitted. When the pressure had become some few centimetres, the connection with the palladium was closed by fusion, and the globe was again exhausted. When the exhaustion was sufficient, a second fusible metal plug was removed, and hydrogen admitted till the atmospheric pressure was reached. The preliminary exhaustion of the globes was always such that less than a hundred-thousandth of air remained. For the second exhaustion, a vacuum of a thousandth was thought sufficient.

9. SECOND METHOD. MEASUREMENT OF PRESSURE.

When the globe had been filled with hydrogen, the ice in which it stood was well heaped around it, and the cover replaced over the tank. Readings of the syphon barometer were made as in the case of oxygen. In all cases, the two levels of the mercury to be read were in the same perpendicular, and the scale used stood in contact with the glass tubes of the barometer, so as to minimize the effect of any want of parallelism in the directions of the motions of the reading microscopes.

It will be seen that in all my experiments on the density of gases, their pressure has been determined without any communication between the gas and the atmosphere; contamination was therefore impossible. It was necessary that my work should be so arranged that it could be left at almost any point with little danger of the loss of an experiment in consequence of the interruption.

In the first series of experiments with oxygen and hydrogen, a mano-barometer was used, owing to the conditions of the experiment; but in all other experiments the two central tubes of the manometer, which together constituted a syphon barometer, were used. In this case, the two readings of level were made on the same scale, because the two levels of the mercury were in the same perpendicular.

The time during which occasional readings of pressure were made varied from an hour to three or four hours.

10.—SECOND METHOD. OBSERVATIONS AND RESULTS.

As in the case of the third series of determinations of the density of oxygen, there was no room for the exercise of judgment in combining the observations. The experiments are also affected with a source of constant error, as will be mentioned in more detail; so that there is the less reason for giving more than the pressures and weights observed, together with the density reduced to the sea level at latitude 45°, by the formula

$$D_h = \frac{W}{V} \cdot \frac{760}{P} \cdot \frac{L}{l} \cdot \frac{G_{45}}{g}$$

Experiment.	Volume. cc.	Pressure. mm.	Weight. gr.	Density. gr.
1	8793.9	781.43	.8132	.089977
2	"	769.84	.8004	.089894
3	"	764 72	.7959	.089987
4	"	756.59	.7871	.989949
5	8832.1	770.52	.8051	.089951
6	"	779.44	.8145	.089960
7	"	768.23	.8033	.090018
8	20057.6	766.34	1.8176	.089909
9	"	746.50	1.7714	.089953
10	15383.4	756.60	1.3773	.089974
11	16517.2	711.57	1.3900	.089922
12	"	759.94	1.4873	.090093
13	"	768.44	1.5025	.090007
14	"	756.25	1.4769	.089899
15	"	757.87	1.4813	.089974
16	15081.7	761.32	1.3576	.089900
17	"	760.24	1.3552	.089869
18	"	762.34	1.3631	.090144
19	"	760.44	1.3573	.089984

If we increase the mean by one thirty-thousandth,* we get

$$D = 0.089970 \text{ gr.} \pm 0.000011.$$

11.—REMARK ON THE RESULTS OF THE FIRST AND SECOND SERIES.

The degree of precision attained in weighing so light a gas as hydrogen in either series of experiments was of course not very great, and the two mean values obtained agree more closely than would be expected. Perhaps they are sufficient to show that the method of weighing hydrogen in globes exhausted with

---

* See note, page 28.

mercurial pumps will give results not far from the value obtained. But they by no means show that this value is the truth. If we can trust to a method which seems free from objection, and which has been carried out with as much care as can well be used, the value here obtained is not far from one thousandth part too large.

12. HYDROGEN BY NEW METHOD. INTRODUCTION.

The accidental errors of the measurement of the density of hydrogen by weighing a given volume are considerable. A globe containing 1.8 grammes of hydrogen under standard conditions, and itself weighing not more than twelve hundred grammes, can be obtained, though with difficulty. The gross weight of the globe is then six hundred times the weight of the hydrogen to be determined by its use. It is true that the weight of the globe at any given stage of the experiment can be determined with an error of not much more than one tenth of a milligramme, and that in no long time, provided a pretty elaborate plant be employed. But it has not yet been found easy, I believe, by any one, to secure constancy of the weight of the globe and of the lubrication of its stopcock during the exposure to contact with water, which is necessary if a constant temperature is maintained in the usual way.

It is possible to avoid the use of a stopcock on the globe in which a gas is weighed, and the manipulation for this purpose is not troublesome. I had expected to make use of this method; but a severe explosion broke nearly all my calibrated globes. It is probable that some increase in precision could be obtained by this method. For the globe, after filling with the gas, and after thorough cleansing, could be put in a desiccator, and kept on the balance till it was certain that all effects of contact with water had disappeared. It could then be exhausted without removal from the desiccator, closed by fusion, and again weighed. During both weighings, the globe would have a surface of continuous glass. Still, it is doubtful whether the labor of making a sufficient number of determinations would be well bestowed.

For, unless elaborate precautions are taken, the efficiency of which remains to be proved, mercurial vapor may diffuse into the globe in which the gas is to be weighed. Until, therefore, we can dispense with the use of mercurial pumps and yet produce a vacuum of a few millionths, it seems necessary to devise some method of measuring the density of hydrogen in which the contamination of the gas with the vapor of mercury shall occasion no error.

The weighing of the hydrogen while it is absorbed in palladium, and measuring its volume and pressure in another vessel after expelling it from the palladium seemed likely to give a more accurate value for the density than could be obtained in any other way now possible. My palladium would absorb about 3.8 grammes, and would give off as much as 3.7 grammes at atmospheric pressure, this quantity measuring over 40 litres. From the increase in net weight alone could be hoped some increase in precision; some from the decrease in gross weight, for the palladium tube with its contents weighed eight hundred grammes, while the larger globes weighed half as much more; some from the small surface of glass exposed; some from the disuse of stopcocks and their lubrication, exposed as it is to so many accidents. But the principal gain hoped for was the fact that mercurial vapor would have no effect on the *weight* of the hydrogen used in the determination; and its effect on the *pressure* and volume of the gas is negligible.

Whether the improvement hoped for has actually been secured is now to be submitted to the judgment of those interested.

The use of palladium for the purpose of obtaining pure hydrogen was, so far as I know, first suggested by Chirikoff. Its use for the purpose of accurately weighing hydrogen first suggested itself to me in 1882, so that I discussed the method with other chemists in 1883, and began preparations for the present work. The same method of weighing hydrogen suggested itself independently to Keiser, to whom belongs the credit of first publishing results obtained by it; questions of priority are of slight consequence, but it seems that to me belongs the credit of first inventing the method and beginning to work with it.

13.—HYDROGEN BY NEW METHOD. APPARATUS FOR MEASUREMENT OF VOLUME.

My stock of palladium foil would absorb about 3.8 grammes of hydrogen, and would give off about 3.7 grammes at atmospheric pressure. A volume sufficient to contain this amount was made up of three globes. They were placed so as to be used like one, while their individual capacities fell within the range of my plant for determination. These three globes were the globes numbered 1, 6, and 7, in the list of globes prepared for weighing gases by Regnault's method mentioned on page 12. Of these, globe No. 6 had not been used before, for the reason mentioned on page 54.

These three globes were placed in three cylinders, *a*, *b*, *c*, Fig. 23, surrounded with finely crushed ice, and these again placed in a larger cylinder, *r r*, 1.2 metres in diameter, and .9 metre high. This tank was surrounded with a non-conducting layer. The globes were now connected to a common inlet tube whose branches led, one to the syphon barometer, one to the self-acting Toepler pump, and one to the place for admitting hydrogen. The latter tube was closed by a fusible metal plug till the proper time.

The tube leading to the pump had to be closed during the introduction of the hydrogen and the measurement of its pressure in such a way that no leakage could occur. A glass stopcock can often be lubricated so that when closed it will not leak, but if opened and closed repeatedly it is liable to leak. In fact a stopcock, in all accurate work, ought to be considered as an instrument for *reducing* the flow of a current of gas.

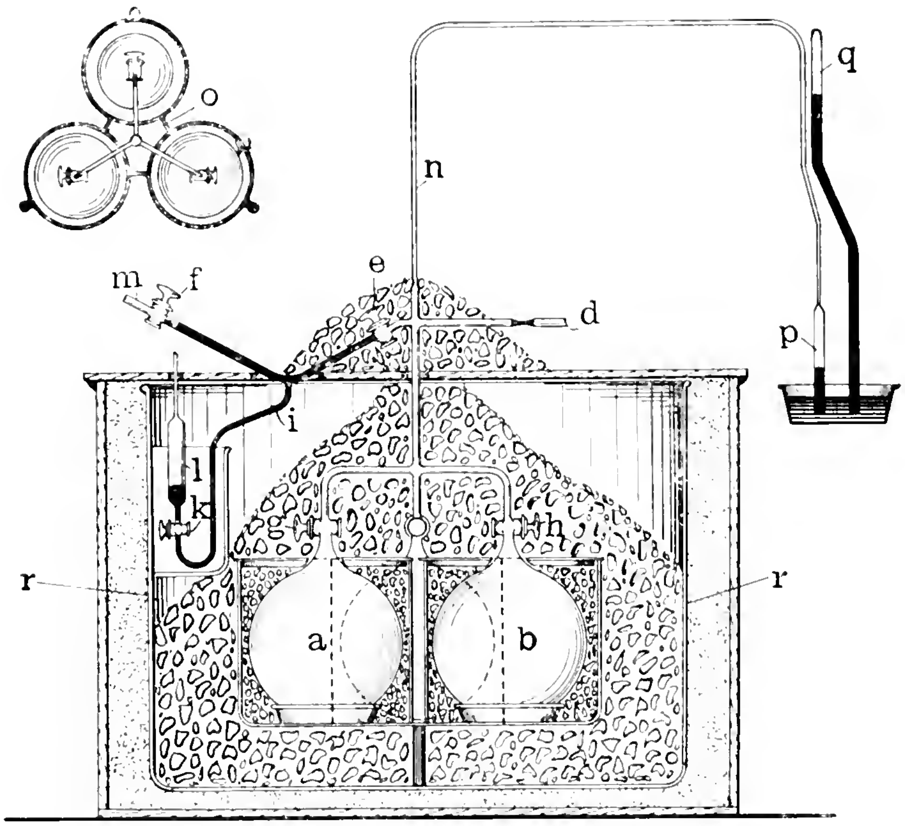


FIG. 23.—Apparatus for receiving hydrogen and measuring its volume and pressure at constant temperature.

The connection between the measuring globes and the air pump was therefore made proof against leakage by using two stopcocks, and filling the space between them with mercury at the atmospheric pressure whenever it was desired to close the passage. The two stopcocks are shown at *e*, *f*; a tube inserted at the lowest point between them led to the stopcock *k* and the funnel *l*, which was full of mercury. If the stopcocks *e* and *f* were open and the tube between them free from mercury, a clear passage existed between the air-pump and the globes. When a sufficient vacuum had been obtained by the action of the pump, the stopcocks *e* and *f* were closed and *k* was opened. The pressure of the atmosphere then forced mercury from the funnel to fill the space between *e* and *f*; when *k* was closed. It is obvious that leakage from the globes towards the air-pump could take place only as mercury was forced out from this closed space through the keys of the stopcocks; which would easily be detected by inspection.

The apparatus met all reasonable expectations until a time when, as was afterwards found, the key of the stopcock *c* formed an incipient crack, producing capricious and intermittent leakage.

14. —HYDROGEN BY NEW METHOD. CAPACITY OF CONNECTING TUBES.

It is obvious that when a weighed quantity of hydrogen was admitted to these globes, the connecting tubes and one branch of the syphon barometer had to be filled; so that the capacity thus added to the globes had to be determined. Part of these tubes was always at the temperature of the globes themselves, being covered with melting ice, while part was at the temperature of the room, or at the temperature of the water with which the barometer was surrounded. These two parts had to be determined separately.

The tube leading to the barometer being closed by fusion, *c*, Fig. 24, a three-way stopcock, *e*, was fused to the tube for admitting hydrogen shown at *d*. One branch of this was connected to an air-pump, and the other to a gas burette standing in sulphuric acid. Water could not be used, for condensation of its vapor on the cold parts of the connecting tubes would cause error. First, the blank space between the key of the stopcock and the fusible metal at *d* was determined. This was done by exhausting this space by turning the stopcock into the proper position, during which time the level of the acid outside and inside the burette was made the same, and the level read off. Then the degree of exhaustion was noted, and the key of the stopcock was turned so that the vacuous space was filled with air from the burette, the volume and temperature of which were also noted, after making the adjustment of level again. The volume of the air thus drawn from the burette was obviously equal to the volume of the exhausted space, after applying a correction for the imperfection of the vacuum.

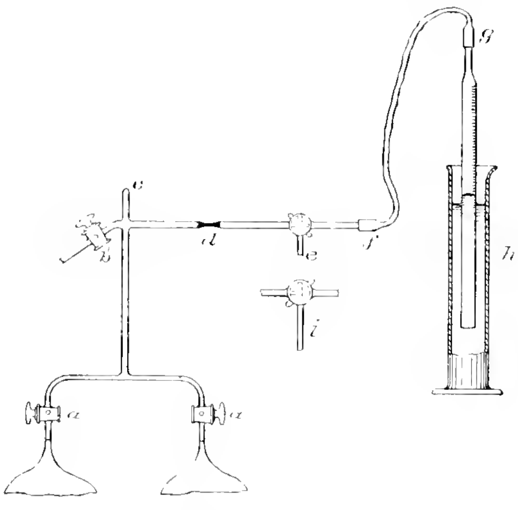


FIG. 24.—Apparatus for determining volume of connecting tubes.

When a few concordant determinations of the blank space had been made, the fusible metal was removed by fusion, and the same determination made of the volume of the tubes between the three-way stopcock *c*, and the stopcocks of the globes, *a a*. But here the volume of the air drawn from the burette to fill the vacuous tubes had to be corrected for difference of temperature as well as for degree of exhaustion; the determination was made with these tubes covered with ice, just as they were to be covered with ice in the measurement of the pressure of hydrogen in the globes. Afterwards, the three-way stopcock was connected in the same way to the tube leading to the barometer and its capacity determined. The level of the mercury was noted, and determinations of volumes made at different levels. Taking account of the degree of exhaustion and of the differences of temperature at the burette and at the barometer, if any, the volumes contained to different levels in the barometer were computed, and a table made showing them. The tube leading to the barometer, which had been separated, was now fused in place, and a few determinations made of the united volumes.

As an example of the process is given the first determination made.

Blank space, 0.3 cc.

Connecting tubes which are kept covered with ice; vacuum, 6 mm., burette, 19.0. Air drawn in on opening stopcock, 18.4 cc., 18.4 cc., 18.5 cc., 18.5 cc.; mean, 18.4 cc.; reduced to 0° and corrected for 6 mm., 15.6 cc., the capacity of the ice-covered tubes.

Fused three-way stopcock to tube leading to barometer; blank space same as before. Air left in vacuum, negligible.

	Readings at Barometer.		Readings at Burette.	
Exhausted			144.2 cc.	at 21.0
Filled to	218.2 mm.	at 19.2	32.0 "	"
Filled to	342.0 "	" "	69.6 "	21.3
Exhausted			149.3 "	21.5
Filled to	342.1 "	" 19.8	75.6 "	"
Filled to	218.2 "	" 19.9	37.9 "	"
Exhausted			148.1 "	21.8
Filled to	218.7 "	" 20.0	36.8 "	"
Filled to	340.6 "	" "	70.5 "	"

The details of the computation are unimportant. The tubes were renewed several times; the table following gives their capacities at different dates:

CAPACITY OF CONNECTING TUBES AT DIFFERENT DATES.

Tubes kept in ice.	
May 17	45.6 cc.
May 19	41.6 "
October 31	40.1 "
November 6	36.5 "
January 18	41.1 "

Barometer and tubes leading to it.		
Mark.	May Oct.	Nov. April
210 mm.	66.0 cc	66.3 cc
220 "	63.0 "	63.3 "
230 "	59.9 "	60.2 "
240 "	56.9 "	57.2 "
250 "	53.8 "	54.2 "
260 "	50.8 "	51.1 "
270 "	47.7 "	48.1 "
280 "	44.7 "	45.0 "
290 "	41.6 "	42.0 "
300 "	38.6 "	38.9 "
310 "	35.5 "	35.9 "
320 "	32.5 "	32.8 "
330 "	29.4 "	29.8 "
340 "	26.4 "	26.7 "

15.—HYDROGEN BY NEW METHOD. EXHAUSTION OF GLOBES.

When the capacity of the connecting tubes had been determined, the stopcocks of the globes were opened, the pump was set in action, and a sufficient exhaustion obtained and measured with the McLeod gauge which was mentioned on page 18. The measurement was not made till about half an hour after the pump had been stopped. The automatic pump by acting during one night would produce a vacuum of ten, twenty, or forty millionths, according to circumstances; when acting through one day and two nights, it would leave from two millionths to three ten-millionths of an atmosphere. But such a degree of exhaustion was unnecessary in experiments in which simply the increase in pressure due to the admission of a known weight of hydrogen was to be determined.

16.—HYDROGEN BY NEW METHOD. MANIPULATION OF TUBE CONTAINING PALLADIUM.

It was thought to be of prime importance to use on the tube containing palladium no stopcock requiring lubrication or admitting the possibility of leakage. It is necessary to determine the volume of this tube before and after each experiment. If the lubrication of the stopcock is exposed to water during the hydrostatic weighings, a source of uncertain error is introduced. It would be possible to wait till the effect of this exposure should be thought to have passed off, or to immerse the palladium tube only to a certain mark in the hydrostatic weighing. But the manipulation without any stopcock is easy and more accurate, and was always used in the experiments of this series, and in all the following experiments by this method.

A strong argument in favor of dispensing with the stopcock is the difficulty of knowing that, in a given case, the stopcock did not leak. A stopcock is often found, after an experiment, not to have leaked. I have repeatedly exhausted a globe, weighed it, connected it again to the pump, exhausted the connecting tubes to the same degree as before, and then have opened the globe and again measured the vacuum. When the lubrication was freshly applied, not infrequently the amount of leakage in one, two, or even four days has been found to be negligible. But these stopcocks were of very special dimensions ordered for the purpose, and even these often leaked, causing great annoyance and loss of labor. If some such measurement, or other proof that leakage has not taken place, cannot be applied, it would be necessary to use some method which should entirely eliminate leakage.

The tube holding the palladium was therefore arranged as shown in Fig. 25. At *d* is the tube by which hydrogen is admitted; at *e* is a drying tube, filled with phosphorus pentoxide; at *g* is a plug of fusible metal, at *h* is a small bulb filled with asbestos, to prevent loss of fusible metal by projection when melted. *i* is a ground joint by which the tube can be connected with other apparatus. The tube between *g* and the point *k* is exhausted and then closed at *k* by fusion, and a notch made between *i* and *k*.

FIG. 28.—Palladium tube with no stopcock.

When the palladium is to be charged with hydrogen, *d* is fused to the source of the gas, and the palladium is heated. When the temperature is such that no absorption would take place, hydrogen is passed through the tube from *d* to *a*, the tube having been broken off at this point. The heat is raised, and the current continued for half an hour, when *a* is closed by fusion, and the heat withdrawn. Hydrogen is admitted from an apparatus in which it is produced by electrolysis of sulphuric acid in voltameters, and then freed from oxygen, and compounds containing oxygen, by passing over heated copper, potassium hydroxide, and phosphorus pentoxide. When the pressure of the gas in the palladium tube becomes equal to that of the atmosphere, the point *a* is again broken off, and the current continued for three or four hours; during part of this time, the gas is allowed to escape at *f*. By this long-continued passage of the gas escaping at *a* and *f*, it was hoped to remove very nearly all the nitrogen which, if once present in the gas, would not be removed by the purifying train. Since the tension of the gas in the palladium, especially when it is saturated, is considerable, the removal of the nitrogen with the air-pump cannot be effected.

When the charging with hydrogen is completed, the ends *a* and *f* are closed by fusion, and the connection with the source of hydrogen at *d* is closed in the same way, when the palladium is ready for weighing.

17. HYDROGEN BY NEW METHOD. HYDROSTATIC WEIGHING OF TUBE CONTAINING PALLADIUM.

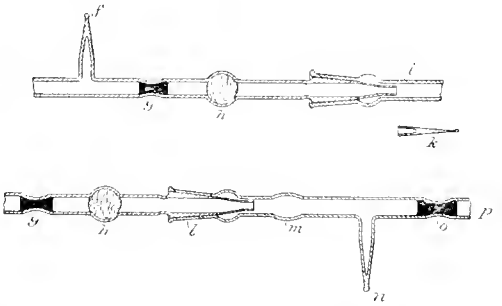
When the tube was charged with hydrogen, and closed by fusion, its volume was determined by hydrostatic weighing in a way which calls for no remark. The tube exposed nothing to the water but a continuous surface of glass. It was therefore not likely to suffer much change of weight by immersion. The tube was of the common German glass; it would now be possible to construct it of one of the new sorts of glass which resist the action of water in a much greater degree. But the exposure to water lasted less than two minutes, and solubility of the glass was thought to be negligible.

18. HYDROGEN BY NEW METHOD. WEIGHING THE TUBE CONTAINING PALLADIUM.

The tube containing palladium was weighed against a counterpoise of nearly equal volume and weight. The volumes on the two pans of the balance were then made equal within the twentieth of a cubic centimetre by means of the small equating flasks of various volumes but of weights made equal if weighed in a vacuum, which were mentioned on page 18. The tube of palladium was hung on one of the auxiliary pans of the reversing mechanism shown in Figs. 16 to 19, on pages 38 to 41, and its counterpoise on the opposite pan, the equalizing flasks were added, and the weights were laid on the pan which carried the palladium. After the closet had been shut for an hour, weighings were made by reversals just as in the second and third series of determinations of the density of oxygen. Weights smaller than ten milligrammes were not put on the auxiliary pans, but were put on the pans of the balance itself; the fractions of a milligramme were determined by observation of the value of a scale division and computation from the position of equilibrium in the two weighings by reversal. Four weighings at suitable intervals were thought sufficient; but sometimes time was allowed for more.

19.—HYDROGEN BY NEW METHOD. INTRODUCTION OF HYDROGEN INTO THE GLOBES.

The palladium tube was put in an iron trough containing magnesia, and laid on the furnace where it was to be heated. The point *k*, Figs. 25 and 26, was broken off at the notch previously made, and scrutinized to see if some minute fragment were detached. Air was in this way admitted as far as the plug *g*. To the ground joint *i*, was then cemented the corresponding joint *l*, and this was then fused to the tube *m n o p*, Fig. 27, by which hydrogen was to be admitted to the globes; *o* in Fig. 27 is the same as *d* in Fig. 23. The air-pump was then connected to *n*, Fig. 27, the space between *g* and *o* was exhausted, and the connection with the pump was closed by fusion. After some few minutes, the fusible metal valve at *o*, Fig 27, *d*, Fig. 23, was opened by fusion; if the joint at *l*, Fig. 27, and the fusible valve at *g* were tight, the fused metal would not be forcibly projected. Before this time the vacuum in the globes had been measured, and the



FIGS. 26 and 27.—Palladium tube, ready to connect to apparatus. Palladium tube, connected to apparatus, connection exhausted.

connection with the pump had been closed. The fusible metal plug *g* was now removed, and the palladium was heated.

When the delivery of gas ceased, *d*, Fig. 23, was closed by fusion. As the palladium cooled off, most of the hydrogen remaining between *g* and *o*, Fig. 27, was absorbed. If the vacuum obtained originally in this space was equal to the vacuum produced by this reabsorption, this blank space had absolutely no effect on the experiment. When the palladium was cold, the tube was closed by fusion at *g*, Fig. 25. *i* was separated from the joint *k*, Fig. 26, and cleaned, and the whole was made ready for weighing.

20.—HYDROGEN BY NEW METHOD. MEASUREMENT OF PRESSURE.

When *d*, Fig. 23, had been closed by fusion, the pressure of the gas in the globes was determined by observations of the syphon barometer, just as in series second. Ice was heaped around the connecting tubes as shown above *e*, and the ice around the globes was renewed. Then readings were taken, as has already been sufficiently described.

The readings were continued at intervals for one hour; sometimes, in test cases, for a day, but there never seems to have been reason for suspecting the accuracy of a reading taken after fifteen minutes from the end of the filling, when the ice had been renewed an hour previously.

21. HYDROGEN BY NEW METHOD. SECOND WEIGHING OF THE PALLADIUM.

The tube containing the palladium now consisted of three parts: the large part, closed again by fusion, the short tube containing the asbestos, and the point which had been broken off at *k*, Fig. 26. The small parts were commonly united by fusion. The large part again presented a continuous surface of glass; its volume was determined by hydrostatic weighing. The volume of the smaller parts was computed from their weight and specific gravity. In some earlier experiments for a different purpose, the volume of the palladium tube was changed a little by the heat which expelled the gas; but this did not occur in any experiment of this series. If any change had occurred, the second hydrostatic weighing would have shown its amount.

The tube was now weighed against the same counterpoise as before, with the exception that the flasks for equalizing volumes were not the same as before. A larger volume of weights was now required, and the palladium tube was smaller by the capacity of the part between *g* and *k*, Fig. 25, which was closed when first weighed, but was now open to the air. These effects nearly counterbalanced each other.

22.—HYDROGEN BY NEW METHOD. VERIFICATION OF ACCURACY OF WEIGHTS.

The accuracy of the weights used for determining the weights of hydrogen received careful attention. I determined the relation of each weight of two additional sets of small weights to the kilogramme of the set marked K, on which all my determinations of volume depend. Then determinations of weights of hydrogen were made with all these four sets of weights; so that it is improbable that any serious error is due to the uncertainty of the values of the weights employed. I moreover determined the relation to the same kilogramme of two other sets of small weights which were kept simply for the purpose of comparing them with the weights which were used in weighings, so as to detect any accident to any of these.

23.—HYDROGEN BY NEW METHOD. REDUCTION OF OBSERVATIONS.

The readings of the barometer were corrected by means of the table given by Landolt and Boernstein. The corrected numbers are called observed values. To the capacities of the globes at 0° was added the capacity of that part of the connecting tubes which was always covered with ice. The volume contained by the syphon barometer down to the mark noted was taken from the table on page 68, and reduced to the volume which that amount of gas would have at 0°. The three or four cubic centimetres which were not below the water level of the case surrounding the barometer were assumed to be at the temperature of the barometer; which was near enough to the truth. The sum of these three volumes made up the observed volume. The observed temperature is that of melting ice; the elevation of the cistern of the barometer introduces a correction of less than five thousandths of a millimetre of mercury. We have therefore

$$\begin{array}{c}\text{Weight of one litre of hydrogen}\\ \text{at sea level, latitude } 45^\circ\end{array} = \frac{W}{V + v + v'} \cdot \frac{760}{P} \cdot \frac{G_{45}}{g} \cdot \frac{L}{l}$$

24.—HYDROGEN BY NEW METHOD. OBSERVATIONS AND RESULTS.

The table gives the observations of the third and fourth series, together with some observations which were unsuccessful on account of various slight accidents or unforeseen circumstances. Five columns define the volumes which are to be added to the calibrated capacities of the globes; these show the mark at which the mercury stood in the barometer, the temperature here, the volume corresponding this volume reduced to 0°, and the volume of the tubes which were covered with ice. Next is shown the volume of the globes, the total volume, the pressure reduced to 0°, but uncorrected for the length of my bar, the observed weight of hydrogen, and the density computed for the sea level in latitude 45°.

Number of experiment.	Date.		Height of mercury in manometer, mm.	Temperature.	Volume of gas in manometer, c.c.	Volume reduced to 0°, c.c.	Volume of gas in connecting tubes, c.c.	Volume of globes, litres.	Total volume, litres.	Pressure, mm.	Weight of gas, grammes.	Density of hydrogen, grammes.
PRELIMINARY.												
	May	13	345.8	17.3	24.7	23.3	45.6	42.1111	42.1860	603.07	3.0092	.089946
		17	236.1	18.3	58.1	54.4	45.6	42.1111	42.2111	750.64	3.7470	.089915
		19	239.7	20.1	57.9	53.9	41.6	42.1111	42.2066	744.97	3.7169	.089881
		20	236.7	18.9	57.9	54.2	41.6	42.1111	42.2069	747.46	3.7302	.089901
		22	240.8	18.7	54.4	51.4	41.6	42.1111	42.2041	736.59	3.6775	.089945
SERIES THIRD.												
1	May	23	249.1	18.6	54.1	50.6	41.6	42.1111	42.2033	738.55	3.6843	.089874
2		25	250.7	18.2	53.6	50.2	41.6	42.1111	42.2029	737.86	3.6815	.089891
3		26	243.2	17.3	55.9	52.6	41.6	42.1111	42.2053	747.72	3.7307	.089886
4		27	277.5	15.0	45.4	42.9	41.6	42.1111	42.1956	705.41	3.5180	.089866
5		29	262.1	16.1	50.2	47.4	41.6	42.1111	42.2001	724.88	3.6173	.089911
6		31	250.2	17.2	53.8	50.6	41.6	42.1111	42.2033	743.45	3.7080	.089856
7	June	1	264.5	18.4	49.4	46.3	41.6	42.1111	42.1990	721.94	3.6026	.089912
8		2	252.8	18.8	53.0	49.6	41.6	42.1111	42.2023	739.53	3.6890	.089872
SERIES FOURTH.												
1	Oct'r	19	282.7	21.6	43.9	40.7	41.6	42.1111	42.1934	704.43	3.5171	[.089972]
2		23	249.9	21.0	53.8	50.0	41.6	42.1111	42.2027	742.83	3.7057	.089877
3		25	253.0	22.3	52.9	48.9	41.6	42.1111	42.2016	740.66	3.6944	.089867
4		31	254.8	19.6	52.4	48.9	41.6	42.1111	42.2016	740.84	3.6973	.089916
5	Nov'r	2	251.2	21.5	53.4	49.5	41.6	42.1111	42.2007	738.33	3.6790	[.089777]
6		4	236.5	22.5	57.8	53.4	41.6	42.1111	42.2046	743.51	3.7080	.089846

If we increase the means by one thirty-thousandth,* we have

$$\text{Series III., } D_h = 0.089886 \text{ gr.} \pm 0.000004\ 9$$
$$\text{Series IV., } D_h = 0.089880 \text{ gr.} \pm 0.000008\ 8$$

25.—HYDROGEN BY NEW METHOD. SOURCES OF ERROR.

If, after measuring the vacuum in the globes, leakage occurred, the pressure of the hydrogen in the manometer would appear too great, and the density, therefore, too small. Now it is believed that in experiment 5 of series iv. this accident occurred. The key of stopcock *c*, Fig. 23, was found, afterwards, to have formed an incipient crack at some previous and unknown time, and leakage from this cause had become so troublesome that, unable to detect the real source, and ascribing it to the wrong source, I broke up the apparatus and made a new one in which leakage was impossible, and in which it never took place. This crack was in such a position on the key that the leak was likely to be developed only when the stopcock

---

* See note, page 28.

was closed, and only when, in closing, the crack was turned towards the globes. This determination ought fairly to be rejected, although there was no means of knowing, at the time, that leakage was actually taking place.

There were some accidents which might make the weight of a litre of hydrogen appear too high. In breaking off the point *k*, Fig. 25, an unnoticed fragment might be lost. The asbestos in *h*, if not properly adjusted, might permit the escape of a globule of the melted metal. If the moisture absorbed by the asbestos during the construction of the tube was not removed during the first exhaustion of the space *g k*, Fig. 25, it would be given off with the hydrogen. Either of these would make the weight of the hydrogen expelled from the tube appear too great. It was thought that the first experiment of series iv. was in error from the first of these causes, though the evidence was not so conclusive as to lead to the instant abandonment of the experiment.

Five experiments were made before the proper conduct of the experiment was mastered. The mishaps were various, and perhaps do not need to be detailed. The observations are given, though they are not used in obtaining the final mean.

26.—HYDROGEN BY NEW METHOD. SECOND APPARATUS.

The determinations of series iii. were made as soon as the apparatus was put together and the preliminary experiments finished, and while the apparatus was in perfect order. The stopcocks showed no leakage even in a somewhat protracted test. But after an absence during the summer, much trouble was experienced, of which the true cause was not easily learned. Leakage appeared, sometimes slow, but sometimes rapid or capricious, so that many experiments were abandoned at different stages. Fresh lubrication of the stopcocks not helping much, they were surrounded with rubber capsules holding glycerine. This stopped the leakage long enough to get the results of series iv., but the leakage then became so capricious that sometimes an action of the pump which ought to have given a vacuum of one millionth left one or two thousandths instead. The apparatus was broken up and replaced with one which should be proof against leakage; some time afterwards the nature of the difficulty was learned. The crack in the key of the stopcock caused the small leak. The rubber capsules holding glycerine, by continued pressure, gradually loosened the key of one stopcock, admitting glycerine, then water, and finally air; hence the larger and capricious leakage.

27.—HYDROGEN BY NEW METHOD. SECOND APPARATUS. CAPACITY OF GLOBES.

It will have been noticed that the stopcocks of the three globes, Fig. 23, were useful only during the measurement of the capacity of the connecting tubes.

The stopcocks leading to the pump could be easily replaced by a U-shaped tube filled with mercury when the passage was to be interrupted, and the stopcocks of the globes could be replaced with plugs of fusible metal.

Three globes were therefore arranged as shown in Fig. 28. At *m*, *n*, were plugs of fusible metal closing the tubes which connect the globes to the other apparatus. Each globe was weighed in air and then in water before these tubes were applied, and before the necks of the globes were drawn out; from which could be computed the solid contents of the globe, or rather the specific gravity of the glass of that globe. The globes were then brought to the form shown in the figure, but with the horizontal tube only a few centimetres long, and were again weighed in air and in water so as to determine their external volume, just as in case of the globes used for oxygen. The weighing being repeated at a different temperature the capacities of the globes were thought to be sufficiently well determined.

The table gives the data of the experiments together with the capacities inferred. Weights are corrected for air displaced by objects weighed and by weights used; temperatures are made to correspond with the true scale of a thermometer of mercury in Jena normal glass.

GLOBE	WEIGHT IN AIR. Grammes.	LOSS IN WATER. Grammes.	TEMPERATURE. Degrees.	CAPACITY. Cubic Centimetres.
A		9169.2	0.32	9170.2
		9164.9	16.10	9170.3
		9165.2	15.50	9169.9
B		18575.4	0.31	18577.3
		18566.4	16.05	18577.2
C		16968.9	0.26	16970.7
		16961.1	16.00	16970.9
A	922.70	372.24	19.0	372.6
	923.23	372.36	17.3	372.6
	Closed 933.20	Computed volume		376.9
B	1295.93	522.80	19.0	523.3
	1295.93	522.90	17.3	523.3
	Closed 1303.95	Computed volume		526.5
C	1368.41	551.92	19.1	552.5
	1368.41	552.02	17.4	552.4
	Closed 1377.11	Computed volume		556.0

From the foregoing determinations of the external volume and solid contents of each globe, we get the capacities as follows:

	Cubic Centimetres.
Capacity of A	8793.2
Capacity of B	18050.7
Capacity of C	16414.8
Sum	43258.7

This is the value to be used for the experiments (on another matter) after January 18th. But during the experiments of this series, there were 18 grammes of mercury in globe A, introduced by slight accident. The volume to be subtracted from the capacity of the globes is therefore 1.3 cubic centimetres, and the effective capacity during the experiments of this series was therefore 13257.4 cubic centimetres.

28.—HYDROGEN BY NEW METHOD. SECOND APPARATUS. CONNECTION OF GLOBES TO PUMP AND BAROMETER.

The globes called A, B, and C were now placed in the cylinders which were to protect them from the contact of large fragments of ice, and were packed in finely crushed ice, and connected as shown in Fig. 28. The tube *e* led to the upper edge of the tank where it joined the mercurial valve shown at *f g h*, which was interposed between the globes and the pump. At *i* was a mark. In measurements of the pressure of hydrogen in the globes, the level of the mercury in the mercurial valve was always brought to this mark. All the tubes between this

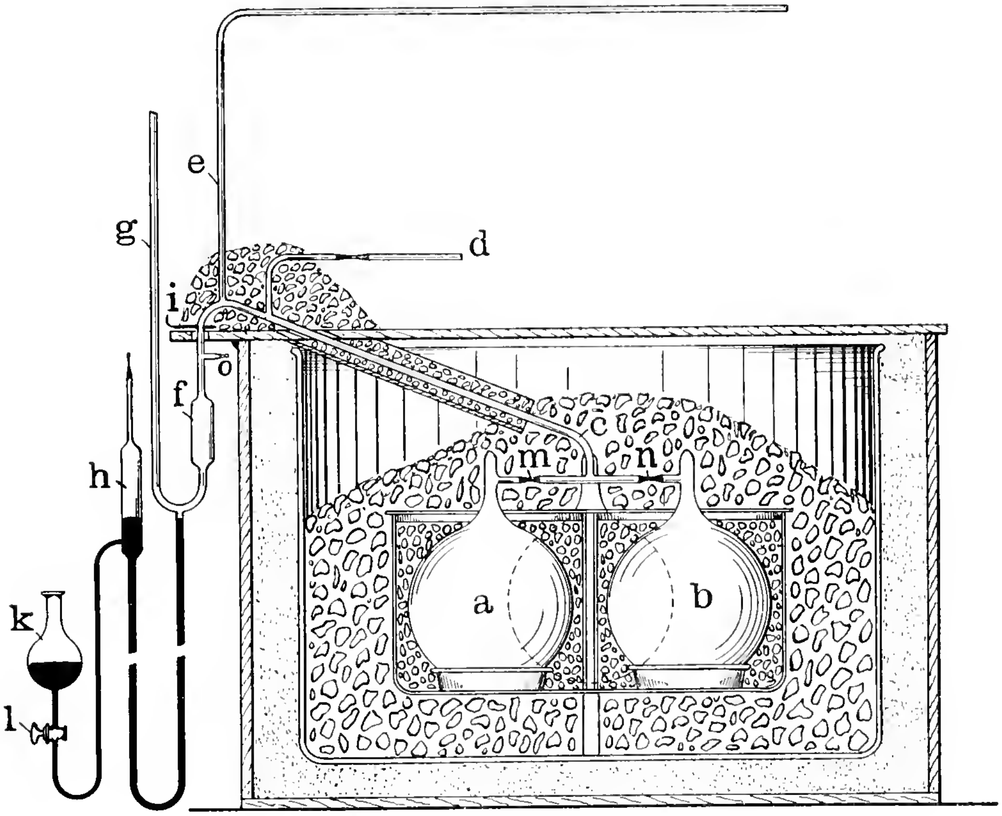


FIG. 28.—Second apparatus for receiving hydrogen and measuring its volume and pressure at constant temperature globes without stopcocks.

mark and the globes were covered with ice during the measurement. The tube *e* led to the barometer, and *d* was for the admission of hydrogen.

The valve between the globes and the pump consisted of a U-shaped tube, *f g*, which could be filled with, or emptied of, mercury by means of the tubes and stopcock shown in connection with it. Suppose the globes to have been exhausted and the pump to be ready to shut off, the stopcock *l* was opened, when mercury in *k* was raised by atmospheric pressure, passing first into the vacuum in *h*, where any air accompanying the mercury would be stopped. From here, the mercury passed into the U tube, *f g*, and filled it to near the top of the enlargement *f*. If now the globes are filled with gas, its pressure will force the mercury up the tube *g* leading to the pump, but leaving the U tube filled above the bend. When pressure was to be measured, the stopcock *l* was opened, and pressure applied to the surface of the mercury in the flask *k* so as to force mercury up to the mark at *i*.

When it was desired to exhaust the globes again, the mercury was brought to stand in the lower part of the enlargement, and the point *o* was cut off and replaced with a tube prepared to be closed by fusion. A Bianchi pump was connected to this and the globes were exhausted to three or four millimetres, when the connection was closed by fusion, leaving the glass as shown in the figure. The air-pump was then applied to the flask and the stopcock *l* opened, when the mercury left the bend of the U-shaped tube free. The Toepler pump then continued the exhaustion of the globes.

29. HYDROGEN BY NEW METHOD. SECOND APPARATUS. CAPACITY OF CONNECTING TUBES.

Before the valve *f g*, Fig. 28, was fused to the tube *e i*, it was sealed off a little below the mark *i*, and filled with mercury to this mark. Then the capacity of the tubes between this mercury and the fusible metal plugs near the globes was determined just as in the previous case; the values obtained have already been given on page 68. After the determination was completed, the fusible valves were opened, and *f g* connected by fusion, when the apparatus was ready for use.

30. HYDROGEN BY NEW METHOD. SECOND APPARATUS. REMAINDER OF THE PROCESS.

The rest of the process was in every respect like that in the preceding series of experiments. The only differences have been noted; the pleasure of working with an apparatus which could leak only by fracture was great. Several verifications were made of the fact that there was no appreciable leakage; it will suffice to give one. The apparatus was exhausted, and the vacuum measured with the

McLeod gauge. Then it was left at rest for twenty-four hours, and the vacuum measured again, with the following result:

December 11. Exhausted apparatus; at 9 A.M., vacuum three ten-millionths. Left at rest.

December 12. Measured vacuum left undisturbed since yesterday. Vacuum at 10.30 A.M., three ten-millionths.

It is obvious, therefore, that leakage had been eliminated.

31.—HYDROGEN BY NEW METHOD. SECOND APPARATUS. REMARKS.

With this apparatus eleven determinations were made, none being lost by reason of accident to the apparatus, in which the probable error of the determination of the density of a gas so light as hydrogen was only one part in eight thousand for a single experiment. The agreement of the results with those of series third and fourth, depending as they do on entirely different calibrations of different apparatus at an interval of months, leads me to hope that they are not seriously in error.

It is a misfortune that it was not possible to make one or two more series of determinations, with new apparatus, or with new determinations of the capacity already involved, so setting at rest any remaining doubt. But to the patience and courage and endurance and powers of recuperation of a single person laboring without assistance at a matter confessedly so difficult, there are limits already too nearly reached.

The nature of the reduction in this series is precisely the same as in the preceding, using only the altered values for capacity of the globes and of the tubes connected with them. The sources of error are the same, except that leakage could take place only by carelessness in constructing the fusible metal plug which closed the apparatus during the exhaustion, or of the connection by which hydrogen was admitted to the globe; which was easy to detect, and did not occur. The other sources of error, also, it is thought, were avoided throughout this series of determinations.

32.—HYDROGEN BY NEW METHOD. SECOND APPARATUS. OBSERVATIONS AND RESULTS.

The observations and results of the fifth series of determinations are given in the following table, which is in all respects like that at page 74, which may be consulted for explanations. The values computed for the density of hydrogen are for the sea level in latitude 45°.

1	November	2[illegible]	231.9	[illegible].9	[illegible]9.6	[illegible]	36.5	13.2571	13.3489	725.1[illegible]	3.7161	.089861
2	"	26	30.7	18.[illegible]	6[illegible]	6.3	36.5	13.2571	13.3502	728.13	3.7314	.089877
3	"	29	228.5	[illegible]	6[illegible].7	5.9	36.9	13.3498	13.3498	723.05	3.7048	.089870
4	December	[illegible]	240.7	19.[illegible]	[illegible]7.[illegible]	3.3	36.9	13.2571	13.3472	726.41	3.7217	.089867
5	"	7	241.6	19.5	[illegible]	3.1	36.5	13.2571	13.3470	728.05	3.7289	.089839
6	"	9	231.3	2[illegible].7	59.8	53.6	36.5	13.2571	13.3495	726.36	3.7219	.089874
7	"	1[illegible]	239.[illegible]	19.[illegible]	57.1	53.6	36.5	13.2571	13.3475	725.30	3.7158	.089864
8	"	14	237.3	22.7	59.[illegible]	53.5	36.5	13.2571	13.3474	727.71	3.7290	.089883
9	"	18	231.7	22.9	55.8	54.3	36.5	13.2571	13.3482	722.54	3.7004	.089830
10	"	21	261.7	22.1	50.7	46.9	36.5	13.2571	13.3478	722.93	3.7037	.089877
11	"	27	240.6	19.3	57.0	53.2	36.5	13.2571	13.3471	721.90	3.6979	.089854

If we increase the mean by one thirty thousandth,* we shall have

$$D_h = .089866 \pm 0.0000034.$$

33. HYDROGEN. FINAL RESULT FOR ITS DENSITY.

The results of five series of determinations of the density of hydrogen at normal temperature and pressure at the sea level in latitude 45° are:

Series I., D = .089938 gr.
Series II., D = .089970 gr.
Series III., D = .089886 ± .0000049 gr.
Series IV., D = .089880 ± .0000088 gr.
Series V., D = .089866 ± .0000034 gr.

It is believed that the results of series first and second are affected with some source of constant error. It is supposed that this is due to the entrance of mercurial vapor into the globes in which the hydrogen is weighed. The remaining series of determinations are free from at least this source of error; until further light on the matter is secured, they give the best value of the density of hydrogen which I can obtain. No ground for preference of one result over the others is known except what is to be inferred from the magnitude of the deviations from the mean value in each series, so that they may be given weights as indicated by the probable errors. We then have as a final value:

$$D_h = .089873 \text{ gr.} \pm .0000027.$$

---

* See note, page 28.

PART III.—ON THE VOLUMETRIC COMPOSITION OF WATER.

I.—INTRODUCTION.

A knowledge of the density of oxygen and hydrogen is important, even without reference to the further question of atomic weight. But my principal object was to use these determinations to determine the latter. For this purpose, it is necessary to know also the ratio of the volumes in which the two gases combine to form water, the measurement to be effected in conditions nearly the same as those in which the volume and pressure were measured in the determination of density. This ratio I have attempted to measure by eudiometric methods. My apparatus for the purpose was made about fourteen years ago, but it was never used with oxygen and hydrogen till the measurements which were published in 1891.* Before this, the manipulation of the apparatus had been mastered in a long series of analyses of air. The errors of measurement of a volume of gas with this apparatus depend on the errors of determining temperature, and on the error in reading the level of the mercury in the eudiometer; for the error at the top of the manometric column of mercury is, by the use of suitable means of exact setting, made evanescent in comparison with the other two errors. These two sources of error cannot be well separated. But a discussion of all the analyses made up to a certain date showed that if the probable error of volume in measuring a gas be attributed to either one of these sources, supposing for the moment that the other error did not exist, then the probable error of level was less than the hundredth of a millimetre, or the probable error of temperature was less than the hundredth of a degree. Why therefore any one should call it an objection to my measurements that I read the level to the two-hundredth of a millimetre is incomprehensible.

The reason why my measurements do not agree with those of Scott is not yet explained. He says that the reason is to be found in the presence of ethane in my hydrogen, due to the electrolysis of impure hydroxide; but I never used potassium or sodium hydroxides; as my paper states, I abandoned their use during my preliminary experiments. Carbon dioxide was always sought for, and all which I found

---

* *American Journal of Science*, 41, 220.

is set down in the table of results in my paper. Nor were my measuring tubes too wide for accurate measurement. The fact that my results were consistent shows that the probable error of a measurement was small, as is computed in the paper.

At the time when the paper was published it was thought, with what still appears to be good reason, that the atomic weight of oxygen is very nearly 15.88. There was also fairly good reason for supposing that the ratio of the densities of the two gases was but very little greater than 15.88; Lord Rayleigh had obtained the value 15.882, and I had obtained the value, 15.879. My value for the volumetric ratio therefore seemed consistent with other data, except with what is known of the divergence of hydrogen and oxygen from Boyle's law.

But the case is now altered. Scott's excellent work* yields the value at 0, 2.00285. Leduc by two experiments obtains the value, 2.0037. For the ratio of the densities, Lord Rayleigh's discussion of the published data give the densities of the two gases, at Paris, as 1.42961 gr. and .08991 gr., the ratio of which is 15.900. Further, the best result to which I could come from my own experiments, a year ago, is, that the densities at sea level in latitude 45 are 1.4289 gr. and .08987 gr., whose ratio is 15.900. Now if the atomic weight is 15.88 and the ratio of densities is 15.90, the ratio of the volumes is not far from 2.0025.

It is therefore obvious that whatever physical constant is involved in my former determination, the value obtained in the eudiometer by measurement of gases saturated with aqueous vapor cannot be applied to pure oxygen and hydrogen collected in globes whose dimensions are so different from those of the measuring tubes.

Now, it seems probable that, if sources of constant error can be eliminated, an accurate knowledge of the volumetric ratio, combined with the ratio of the densities, would give a value of the atomic ratio which might not be very far behind the methods hitherto employed, either in trustworthiness or even in precision. It was accordingly adjudged worth while to prepare apparatus for three new determinations by three different processes. The apparatus for two of these new processes has been constructed, and the other could be put together for use in a week.

In the first proposed method, the volumes of oxygen and hydrogen which are to be combined, in order to determine the excess of either, were to be measured in the same globes which were used for weighing the gases. Two globes were to be filled with hydrogen while they were surrounded with ice, and the pressure was to be measured. A globe was to be filled in the same way with oxygen. The three globes were to be of such capacities and the pressures were to be so adjusted, that very nearly thirty litres of hydrogen and fifteen litres of oxygen were to be

---

Philosophical Transactions, 184. A, 543 (1893) used. After the measurement had been made, they were to meet in a vacuous apparatus at two platinum jets and be mostly combined. The residue, when the pressure was too small for combustion to continue, was to be transferred by a self-acting leakage-proof Toepler air pump to a eudiometer, where eight hundred cubic centimetres of electrolytic gas have been safely exploded. After all but ten cubic centimetres had been exploded in this way, the residue was to be transferred from this eudiometer to a common Bunsen eudiometer, and analyzed. The apparatus is set up, ready for use, and it has been used, though no experiment has been finished, and there is no difficulty in its use, and since so much is self-acting it is not very laborious. But, as I have not had time uninterrupted enough, nor nerves steady enough, to finish, without assistance as I am, even a single experiment, the apparatus had to be broken up, unused, for lack of room.

The apparatus which is nearly ready is designed to measure in the same vessel three nearly equal volumes of hydrogen and oxygen, each of about 2.6 litres, and to combine them by combustion from platinum jets in a space containing a part of the measured volume, and afterwards to transfer the remainder to a eudiometer for analysis. It is completed, except building a pier and putting together the apparatus; whether it will be used is doubtful.

The third method, which, with the apparatus already set up for other purposes, was easiest to carry out, has been successfully employed in a series of ten determinations. Unfortunately, it is that one of the three which, on account of the uncertainty in some of the constants needed in the reduction of observations, is the least helpful. The experiments by this method will now be described.

2.—METHOD EMPLOYED.

It will be recalled that Leduc made two experiments, in which he decomposed an alkaline hydroxide by electrolysis, and measured the density of the mixed gases. From this could be computed the ratio of the volumes of the components. No determination seems to have been made whether the electrolytic mixture would recombine without residue; which very much needs proof in any experiment claiming precision. If the numbers given in *Comptes Rendus*, August, 1892, page 313, are correctly printed, the reduction fails to take into account the physical conditions involved.

Having the apparatus with which the fifth series of determinations of the density of hydrogen was made, I resolved to make a determination by means of the process used by Leduc, but with material modifications. One consisted in avoiding the contamination of the gas with mercurial vapor, by weighing, not a globe full of gas, but a voltameter from which the gas was delivered. Secondly, the composition of the gas, after weighing and measuring pressure, was determined by adequate eudiometric analysis. Lastly, in the computations of the composition of the mixture from the density, the deviations of the two gases from Boyle's law have been taken into account.

The observations attained a precision which it is hoped will be thought satisfactory. But the constants required in the computation may not be thought sufficiently well determined. The uncertainty, however, does not much affect the computed result. The remaining uncertainty will doubtless be removed in time, when the results here obtained will admit of re-computation, which will make them more useful. I therefore venture to give the details of the experiments.

3. DENSITY OF ELECTROLYTIC GAS. VOLUME, TEMPERATURE, AND PRESSURE.

The apparatus for the measurement of pressure, temperature, and volume was the same as that used in the last preceding determinations, with some trifling modifications.

Fig. 29. Method of connecting voltameter, and regulating the current.

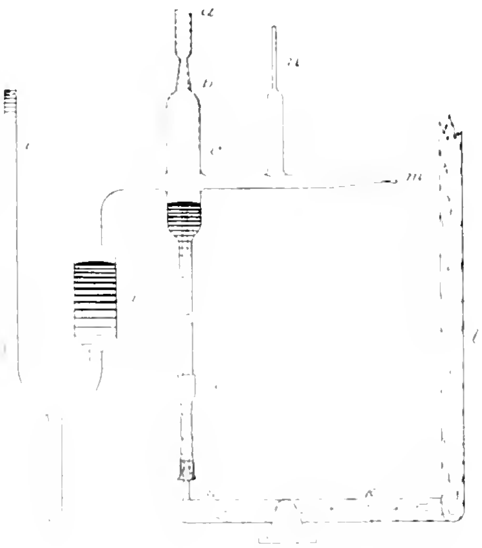


Fig. 30. Connection of globes to pump, serving to regulate admission of gas to the eudiometer.

For the admission of the gas from the voltameter a stopcock had to be interposed, so as to keep the pressure in the voltameter equal to that of the atmosphere. In Fig. 29, *h* is the fusible metal valve by which hydrogen is to be admitted to the globes; to this is fused the stopcock *g*, which, during the operation of filling, was immersed in sulphuric acid.

The connection of the globes to the pump was modified so as to serve two purposes. In order to admit to an exhausted eudiometer an appropriate quantity of the gas, some stopcock was necessary; but one which could possibly leak was objectionable. The apparatus was therefore constructed as shown in Fig. 30. At *a* is the tube leading to the three globes in the ice. But the connection of this tube with the Toepler pump was modified so as to contain the glass stopper *h*, ground so as to fit into its seat, and attached to a long glass rod which continued downwards about 90 centimetres within the glass tube *e g*. The end of this tube was prolonged in the rubber tube *g*, which was attached also to the rod, so that the space between them could be filled with mercury. The elasticity of the rubber tube permitted the stopper to be raised and lowered; the mercury prevented leakage. It is obvious that when this stopper is forced into its seat, and the vacuum below it is filled with mercury, gas cannot pass from the globes into the space below the plug, provided the pressure of the mercury upwards is kept greater than that of the gas downwards.

4.—DENSITY OF ELECTROLYTIC GAS. VOLTAMETER FOR PRODUCING AND WEIGHING.

A voltameter to produce electrolytic gas, and to make it perfectly dry, and to do it at the rate desired, without being too heavy or too bulky, took some pains in constructing. Using five voltameters combined in one and connected electrically in series, it was deemed best to use a current of four amperes. The platinum wires to conduct this current without undue heating I found it somewhat difficult to introduce into the glass of my apparatus without having them afterwards crack. Several experiments were lost in this way; after the passage of the current for four hours, some minute crack around a wire would leak at the rate of half a milligramme an hour. Gradually the faulty joints were made good, and the apparatus worked without failure till a heedless plumber knocked a brick through the wall, without even looking to see what damage might be caused, and crushed it into a hundred fragments.

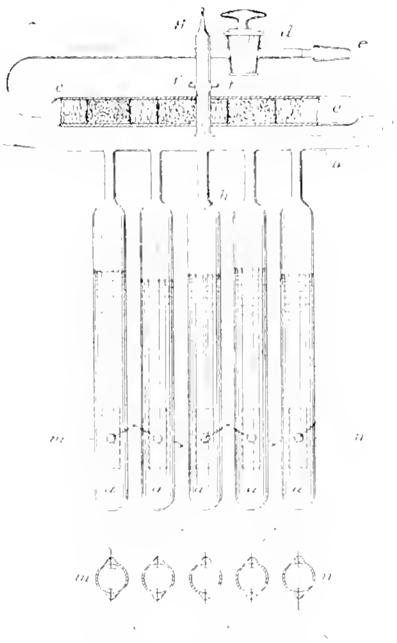


FIG. 31.—Voltameter for producing and weighing mixed gases.

In Fig. 31 are shown five tubes 2.5 centimetres in diameter, having platinum wires as seen in section at *m n*. To these was connected a tube filled with phosphorus pentoxide, and also a stopcock ending in a ground joint. Into the central tube was introduced a gauge to show the pressure of the gas in the voltameter; the gauge was filled with gas to the desired point (having being filled with liquid when constructed) by electrolysis at the wires *f f*, while the stopcock *d* was open to the atmosphere.

The voltameter was filled with sodium hydroxide which had been made from clean sodium; it was freed from carbon dioxide with barium hydroxide. The stopcock *d* was never turned except once to open and once to close for each experiment, and was lubricated often; it is thought that it did not leak, as the pressure on the two sides of the key was always nearly the same during the times when leakage might cause error. The regulation of the current required to maintain a pressure equal to that of the atmosphere was obtained, not from this stopcock on the voltameter, but from the one mentioned before, which was immersed in sulphuric acid.

For some experiments the stopcock of the voltameter was replaced by a fusible metal valve. The opening it by fusion is simple; but when it is to be closed, the metal has to be pushed into its place in the constricted part of the glass tube. When this has to be done without opening the tube to the atmosphere, the manipulation is accomplished by introducing into the tube an iron instrument which is moved by a current in a helix enclosing the tube.

5. DENSITY OF ELECTROLYTIC GAS. FILLING GLOBES WITH THE MIXED GASES.

When a current had been passed through the voltameter for a few days, it was closed, wiped, and weighed against a counterpoise of equal volume and nearly equal weight. When the weights required had been learned, the two volumes on the opposite pans of the balance were made very nearly equal, exactly as described at page 48.

After the weighing, the voltameter was set in a tank of water and ice. A ground joint was fitted to that of the voltameter, shown in Fig. 31 at *e*, and then fused to the stopcock which was attached to the globes, as shown at *e*, Fig. 29. The tube *f* was now connected to the air-pump and a three-way stopcock, and the volume included between *h*, Fig. 29, and *d*, Fig. 31, was determined, exactly as the volume of the tubes connecting the globes to the barometer had been determined (page 67). This space was finally exhausted and sealed off. The stopcock *d*, Fig. 31, was then opened, and *g*, Fig. 29, was closed. The passage through *h*, Fig. 29, was now opened by fusion, a current was passed through the voltameter, and the passage of the gas into the globes was regulated by the stopcock till the globes were filled. The pressure in the voltameter was kept very nearly constant. The filling the globes took about three hours and three quarters.

6. DENSITY OF ELECTROLYTIC GAS. MEASUREMENT OF PRESSURE.

The measurement of pressure of the gas was made exactly as in the case of hydrogen, except that the tube for admitting the gas was not now closed by fusion, and that therefore a different method of being safe against leakage was needed.

7.—DENSITY OF ELECTROLYTIC GAS. CLOSING THE GLOBES DURING THE ANALYSIS OF THE GAS.

It was necessary to close the globes in such a way as to prevent the introduction of air, not only during the measurement of pressure, but also during the withdrawal of the gas used for analysis. During the measurement of pressure, the voltameter was left connected as during the filling. Both stopcocks were shut, and the pressure was the same in the globes and the voltameter. Leakage, therefore, could not take place.

In order to prevent leakage for a day or two, and against an inequality of pressure, the stopcock *g*, Fig. 29, could not be trusted. Of course it was impossible to fuse the tube. I therefore bent the tube by which the gas was admitted, as shown at *r q*. At the bottom of the short U tube was a branch through which mercury could be admitted to fill the bend. A mark at *s* defined the volume whose capacity was determined in the calibration. To this point the mercury was brought during the measurement of pressure. When the voltameter was to be disconnected, the mercury was made to fill the bend. If now slight leakage should take place through the key of the stopcock, it could be detected by the change of level of the mercury in time to admit of remedy before the gas in the apparatus was contaminated.

8.—DENSITY OF ELECTROLYTIC GAS. CLOSING THE VOLTAMETER.

The stopcock of the voltameter was closed, or the fusible metal plug was replaced, and the apparatus was wiped and again weighed, as before. The volumes on the two sides were made equal, and the weighings were by reversal.

9.—DENSITY OF ELECTROLYTIC GAS. PREPARING THE VOLTAMETER FOR A FOLLOWING EXPERIMENT.

The weight of the gas delivered by the voltameter was about twenty-three grammes in each experiment. Instead of adding successive increments of twenty-three grammes, to make up this loss of weight, the counterpoise was made lighter by this amount. The counterpoise consisted of a number of the tubes of the same glass as the voltameter, closed by fusion, one of which was loaded with mercury. A duplicate of this loaded tube was adjusted by removing mercury to the amount indicated by the weighing just made, so that when the weighing of the voltameter after an experiment was finished, the duplicate counterpoise was ready, with its weight about the same as that of the voltameter. A current was passed through it for a few minutes and its stopcock was opened to secure that the pressure in it should be that of the atmosphere, and the indications of the gauge were verified or adjusted. Then a current was passed long enough to expel any air which might have entered, when it was again closed and weighed for the next experiment.

10. DENSITY OF ELECTROLYTIC GAS. EUDIOMETRIC ANALYSIS.

In the earlier experiments, a Toepler pump was connected to the globes as shown in Fig. 32. At *a* is the inclined tube leading to the globes, seen in its connection with them in Fig. 28, page 77. The U tube filled with mercury to shut off the pump is also shown. To this was connected the tube *c*, leading to the Toepler pump *d*. While the pressure of the gas in the globes was measuring, the tubes leading to the pump were filled with mercury to the plug, and the mercury in *c* rose thirty inches or more. After the pressure had been determined, the mercury was lowered till the bottom of the tube *c* was uncovered. Gas from the globes then passed through the tube to the Toepler pump, driving over the mercury in the tube *c*, but without doing damage. The pump body having been filled with gas, the volume withdrawn was determined by a second reading of the pressure of the remaining gas. The mercury in the pump was then raised so as to separate this fraction from that left in the globes.

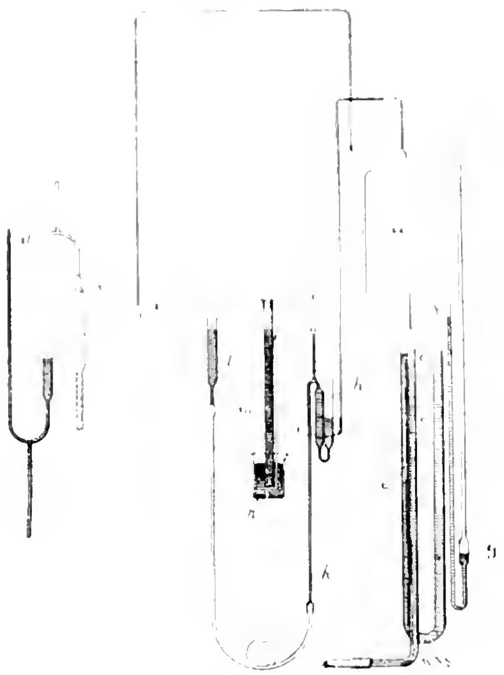


FIG. 32.—Toepler pump used to measure sample for analysis; small Toepler pump for transferring convenient quantity to eudiometer.

A Bunsen eudiometer was filled with mercury and set at *m*, Fig. 32. A small Toepler pump, having a capacity of, say, twenty cubic centimetres, had been connected as shown at *h*, and was provided with a trap against the entrance of air with the mercury which actuated it. With this, the gas was transferred in suitable volumes to the eudiometer and exploded. Four explosions a minute was the usual working rate, so that the 1.6 litres which the pump held were exploded in forty or fifty minutes.

11. DENSITY OF ELECTROLYTIC GAS. DIFFICULTY OF PREVENTING ENTRANCE OF AIR INTO THE EUDIOMETER.

The eudiometer stood in mercury to the depth of about ten centimetres, but at first nitrogen was always found in the residue after explosion. Increased care did not accomplish anything till the mercury in which the eudiometer stood was covered with a layer of sulphuric acid, after which no more nitrogen was found. It was therefore fair to assume that all the nitrogen found had been due to the entrance of air at the last operation; the volume of oxygen accompanying it was therefore computed and double this volume of hydrogen was assumed to have disappeared by combination with this oxygen derived from the air.

12.—DENSITY OF ELECTROLYTIC GAS. LEAKAGE OF AIR BETWEEN MERCURY AND GLASS.

It may be said that the contact of mercury with glass is proof against leakage only when it is nearly as perfect as in a barometric tube. A joint which leaks a little may not be perceptibly improved by immersion in mercury. I have seen a joint between a rubber and a glass tube, which leaked into a vacuum at the rate of a bubble a minute, keep on at apparently the same rate when immersed ten centimetres in mercury, because the contact between the glass and the mercury was not sufficiently perfect. Since a clean surface is hard to maintain on the outside of a tube, the only way in which mercury can be safely assumed really to stop a leak is, by using it to carry a layer of sulphuric acid, as was indicated by Crookes in his experiments with high vacua.

13.—DENSITY OF ELECTROLYTIC GAS. OXIDATION OF MERCURY. LARGE EUDIOMETER.

In some of the eudiometric analyses, some oxidation of mercury was noticed, as might be expected. The amount of oxygen thus consumed was obviously negligible, but it was thought well to avoid possible objection by making it less. A measured volume of hydrogen was therefore introduced into the eudiometer before the admission of the electrolytic mixture. The results thus obtained were the same as before within the errors of observation.

I then constructed a large eudiometer in which all but a hundredth or a thousandth of the gas taken for analysis could be exploded out of contact with mercury. It has a capacity of 3.2 litres. A stopper ground into its place and extending down through ninety centimetres of mercury is so arranged that it can be raised or lowered at will, without danger of leakage. When an explosion was to be made, the passage was stopped by this contrivance, so that the explosion did not reach to the mercury. This eudiometer will safely bear the explosion of eight hundred cubic centimetres of the mixed gases as measured at atmospheric pressure.

The admission of gas to the eudiometer was controlled by the stopper *b*, Fig. 30. When the desired pressure was reached, *b* was closed and then the similar stopper of the large eudiometer, after which the spark was passed. The two stoppers were then again opened, and the process repeated from four to twenty times. At the end of the process the pressure in the globes was observed, thus determining the volume withdrawn for analysis. The globes were kept surrounded with ice during the whole course of the experiments.

It is obvious that the measurement and analysis of the residue could not be effected in the large eudiometer. This was therefore connected by a leakage-proof mercurial valve, with a self-acting Toepler pump. When the last explosion had been made, this valve was opened, and the pump set in action. The large quantity of water formed during the explosion had to be absorbed between the eudiometer and the pump. A special form of drying tube was constructed, but it is hardly worth while to describe it. It may suffice to say that the drying agent was pure sulphuric acid boiled in a vacuum till it did not give off a harmful quantity of absorbed gas, and that this acid could be flowed over the glass beads filling the drying chamber. Even after absorbing fifty grammes of water, it was so effective that a vacuum of two or three millionths could be attained.

From the Toepler pump, the gas was transferred to a Bunsen eudiometer. Owing to the fact that the explosion in the large eudiometer did not extend to the surface of the mercury, there was always enough uncombined oxygen and hydrogen in the residue to admit of satisfactory explosion, after which the residue was analyzed.

11. DENSITY OF MIXED GASES. CAN ELECTROLYTIC GAS BE OBTAINED IN ATOMIC PROPORTIONS?

In all my experiments, I found an excess of hydrogen. This is due to secondary reactions in the electrolytic cell, attended with consumption of oxygen. Now it is one of the innumerable possible cases that there should be an equilibrium between the production and destruction of the oxide formed, so that for a time the two gases should be delivered in atomic proportions. But all the precautions which occurred to me were used in vain. The voltameter was treated in a manner perfectly uniform, and used only at the temperature of melting ice, but there was always an excess of hydrogen.

Once, to learn a little about the stability of any supposed equilibrium, I connected the voltameter directly to the delivery tube leading to a Bunsen eudiometer containing a measured quantity of hydrogen, designed to prevent oxidation of mercury. The eudiometer stood deeply in mercury covered with sulphuric acid. Electrolytic gas was introduced and exploded for many times; the amount of hydrogen gradually increased. The current was now increased so as to warm the endiometer about twenty degrees. The hydrogen in the endiometer soon began to decrease as the explosions were repeated, showing that now oxygen was in excess.

The equilibrium was so easily disturbed that some doubt cannot but be felt whether Leduc obtained the equilibrium which he hoped for.

15.—DENSITY OF ELECTROLYTIC GAS. OBSERVATIONS ON THE EXCESS OF HYDROGEN.

The determinations of the excess of hydrogen above the atomic ratio in the mixtures whose density was determined, are given in the following table. In the first four experiments, the Bunsen eudiometer was used; in the others, the large eudiometer containing 3.2 litres. The first column gives the pressure originally noted; the second, the diminution of pressure caused by taking out a part for analysis, the third the excess of hydrogen found in this part; and the last, the ratio of this hydrogen to the whole volume analyzed.

Experiment.	Pressure.	Diminution of pressure.	Hydrogen found.	Ratio.
1	749 mm.	23.7 mm.	.39 cc	.00029
2	758 "	23.8 "	.34 "	.00025
3	758 "	23.4 "	.25 "	.00019
4	756 "	24.1 "	.45 "	.00033
5	751 "	313 "	6.42 "	.00036
6	755 "	142 "	1.70 "	.00021
7	756 "	341 "	4.32 "	.00022
8	774 "	133 "	2.13 "	.00029
9	755 "	134 "	2.83 "	.00037
10	756 "	126 "	3.05 "	.00042

The mean is .000293. This is the ratio of the excess of hydrogen to the whole combined volumes of oxygen and of hydrogen. Multiplying by the factor 3, we have .00088, a correction to be applied to the ratio of the hydrogen to the oxygen of the mixture in order to obtain the ratio of the volumes of hydrogen and oxygen which would combine without residue.

16.—DENSITY OF ELECTROLYTIC GAS. OBSERVATIONS.

The following table gives the particulars of the determinations of the density of the mixture of oxygen and hydrogen obtained by the electrolysis of sodium hydroxide. Seven columns give the mark at which the mercury stood in the barometer, the temperature here, the volume corresponding, this volume reduced to 0°, the volume of the ice-covered connecting tubes, the volume of the small connecting tube near the voltameter, and the volumes of the globes. Following these are the columns which give the total volume, the pressure, the weight of the mixed gases, and the density computed for the sea level in latitude 45°, according to the formula

$$D_m = \frac{W}{V+v+v'+v''} \cdot \frac{760}{P} \cdot \frac{L}{l} \cdot \frac{G_{45}}{g}.$$

Exp.	Mark, mm	Temperature.	Volume, cc.	v_1 cc.	v_2 cc.	v_3 cc.	V, litres.	Volume, litres.	Pressure mm.	Weight, gr.	Density, gr.
1	212.8	20.0	65.5	60.8	41.1	3.1	43.2587	43.3637	746.16	22.7858	.535441
2	211.0	19.5	66.0	61.7	41.1	3.4	43.2587	43.3640	754.95	23.0541	.535459
3	210.9	19.5	66.0	61.6	41.1	3.2	43.2587	43.3646	748.03	22.8770	.535584
4	210.9	19.6	66.0	61.6	41.1	3.0	43.2587	43.3644	753.20	23.0027	.535477
5	212.2	22.1	66.3	61.3	41.1	2.9	43.2587	43.3640	748.20	22.8521	.535531
6	209.0	20.9	66.6	61.8	41.1	2.9	43.2587	43.3645	752.15	22.9723	.535514
7	212.6	19.9	65.5	61.0	41.1	3.1	43.2587	43.3639	753.36	23.0064	.535456
8	244.3	16.8	55.9	52.7	41.1	3.2	43.2587	43.3557	772.17	23.5798	.535434
9	214.6	17.8	64.9	60.9	41.1	3.4	43.2587	43.3638	753.39	23.0098	.535515
10	215.0	21.7	64.8	60.0	41.1	3.0	43.2587	43.3628	753.97	23.0269	.535513

If we increase the mean by one thirty-thousandth,* we have

$$D = 0{,}535510 \text{ gr.} \pm 0{,}000010.$$

17. DENSITY OF ELECTROLYTIC GAS. REDUCTION OF RESULTS.

If, now, Boyle's law applied to this mixture of gases, we should have, putting H, O, M for the three densities involved, and $\frac{1}{2+x}$ for the ratio of the volumes of oxygen and hydrogen which combine, measured at standard temperature and pressure,

$$\frac{O+(2+x)H}{3+x}=M, \text{ whence } x=\frac{O+2H-3M}{M-H}.$$

If we may judge by the brief account of Leduc's experiments given in the *Comptes Rendus*, this reduction was adopted by him. But the reduction takes no account of the deviations of the gases from Boyle's law. We require to know what would be the pressure of one volume of oxygen and two volumes of hydrogen when mixed and made to occupy three volumes. Until direct observations are made, we must compute from observations of the volume and pressure of the separate gases at different pressures. Since such observations are represented by the equation of Van der Waals with little precision, we may only hope that a reduction founded on it may temporarily serve as an approximation. Writing capitals for oxygen and small letters for hydrogen, we have

$$\left(P+\frac{A}{V^2}\right)(V-B)=C,$$

$$\text{and} \quad \left(p+\frac{a}{v^2}\right)(v-b)=c.$$

Putting the original volume and pressure equal to unity, we get

$$1+A-B-AB=C,$$

$$\text{and} \quad 1+a-b-ab=c.$$

---

* See note page 28.

When the gases are mingled, it is obvious that the constants B and b will each enter into both equations; whether the same is true of A, and how, are perhaps uncertain. First supposing that it should not: when

$$V = 3, \text{ and}$$
$$v = \frac{3}{2}, \text{ we have approximately}$$
$$P = \frac{1}{3}, \text{ and}$$
$$p = \frac{2}{3}.$$

We may therefore write

$$\left(P + \frac{A}{9}\right)(3 - B - 2b) = C, \text{ and}$$
$$\left(p + \frac{4a}{9}\right)\left(\frac{3}{2} - b - \frac{B}{2}\right) = c.$$

Neglecting products of the constants, we get

$$P = \frac{1}{3} + \frac{2}{9}(A - B + b), \text{ and}$$
$$p = \frac{2}{3} + \frac{2}{9}(a - b + B).$$

The sum of these gives the pressure of the mixture, supposing that the oxygen and hydrogen were originally measured at unit pressure and then mixed without change of their joint volume; therefore

$$P + p = 1 + \frac{2}{9}(A + a).$$

This is on the supposition that no mutual attraction acts between the unlike molecules. If such attractions exist, and if they follow the law $f = \frac{Mm}{d^2}$, we can take notice of them by writing

$$\left(P + \frac{A}{8}\right)(3 - B - 2b) = C, \text{ and}$$
$$\left(p + \frac{4a}{9} + \frac{A}{72}\right)\left(\frac{3}{2} - b - \frac{B}{2}\right) = c.$$

Reducing as before, we get

$$P + p = 1 + \frac{7}{36} A + \frac{2}{9} a.$$

The value of A seems to depend on the temperature, so that it must be determined from observations of pressure and volume at 0°. The experiments of Amagat* serve to determine A and *a*. Sarrau† has discussed the first series, but with some modification of Van der Waals' formula. If we reduce the constants

---

* *Annales de Chimie et de Physique* (5), 22, 353.

† *Comptes Rendus*, 94, 844.

computed by Sarrau to those which would obtain in the unmodified equation, we have

$$A = 0.0020$$
$$a = 0.0002$$

But, as Sarrau remarks, the proof that a has a sensible magnitude is insufficient.

From Amagat's later series of observations,* no value of A can be computed which will satisfy the determinations at all pressures, as Professor William Harkness has assured me. That Van der Waals' equation needs modification is attested by the more or less successful attempts of Clausius, Sarrau, and Amagat. But it will answer our purpose, provided that we compute its constants from observations at pressures not far from those to which we desire to apply it. If we compute A and a from various combinations of observations at three different pressures, we get the following values:

VALUES OF A AND a FROM AMAGAT'S EXPERIMENTS.

Pressures used in computation in Atmospheres.			Values of A.
1	100	150	0.002284
1	100	200	0.002174
1	100	250	0.002127
1	150	250	0.002022
1	150	300	0.002006
			Values of a.
1	100	200	0.000035
1	100	300	−0.000016
1	200	400	0.000167

Only the positive, or the numerically smaller negative, root is given. It is plain that constant values of A and a will not satisfy the observations; we can scarcely do better than to assume, with Sarrau,

$$A = 0.0020$$
$$a = 0.0000$$

Substituting these values in the expression for the pressure of the mixture of two volumes of hydrogen and one volume of oxygen when occupying three volumes we have

$$P + p = 1.000389$$

We may therefore correct for the deviation of the mixed gases from the density computed by Boyle's law, by multiplying the observed density by the factor 1.000389; we thus find

$$X = \frac{O + 2H - 3.001167M}{1.000389M - H.}$$

---

* *Annales de Chimie et de Physique* (5), 29, 68.

If we use the values

O = 1.42900 gr.,
H = .089873 gr.,
M = .535510 gr.,

we find the ratio of the volumes of hydrogen and oxygen in the mixture whose density was determined:

Ratio of Mixture
2.00357.

Subtracting from this the excess of hydrogen found by analysis, we get the ratio of the combining volumes:

Ratio of Combining Volumes.
2.00269.

PART IV. SYNTHESIS OF WATER FROM WEIGHED QUANTITIES OF HYDROGEN AND OXYGEN.

1. INTRODUCTION.

In the following pages are described some experiments in which a quantity of hydrogen was weighed while absorbed in palladium, a quantity of oxygen was weighed in a globe, the two were combined, and the water produced was weighed.

The two gases were brought together at two platinum jets enclosed in a small glass apparatus, which was weighed while exhausted, where they were made to combine. When the combustion was ended, the gas remaining in this combustion apparatus and the connecting tubes was extracted with a Toepler air pump, measured, and analyzed. The combustion tube, the globe which had contained oxygen, and the palladium tube were weighed again. From the amounts of oxygen and hydrogen extracted were subtracted the amounts of the gases found in the analysis; the remainders were the quantities combined in the combustion apparatus, from which the atomic weight of oxygen was found. The amount of water produced was measured by the gain in weight of the combustion apparatus; dividing this by the amount of hydrogen used, the molecular weight of water was known, and so a second value for the atomic weight of oxygen was obtained.

The volume of hydrogen used in most of the experiments was forty-two or forty-three litres; the amount of water produced was about thirty-four grammes in each experiment; twelve successful experiments were made. The amount of gas left unburned and therefore measured in the eudiometer varied from a six-hundredth to a ten-thousandth of the quantity concerned.

2. PRODUCTION AND WEIGHING OF OXYGEN.

The oxygen used in all the experiments of this series was produced by heating potassium chlorate; the apparatus used is shown in Fig. 7, page 20; the manipulation here was precisely the same as in the other experiments. In fact, often the same quantity of oxygen served for a determination of density and for a synthesis of water. After the tube containing the chlorate and the whole apparatus and its connecting tubes had been exhausted, the chlorate was heated till oxygen came off freely, when it was cooled, and the apparatus again exhausted. The gas passed through three tubes each a metre long and two and a half centimetres in diameter; the first was filled with beads moistened with a strong solution of potassium hydroxide, the second with beads and sulphuric acid, the third with phosphorus pentoxide and glass wool so that no channel could form above the oxide. A regulating stopcock kept the pressure in the first part of the apparatus at about that of the atmosphere.

It was convenient to use in the combustion the oxygen contained in two globes; they were commonly filled at the same time.

3.—SYNTHESIS OF WATER. BALANCE AND WEIGHING ON REVERSAL APPARATUS.

All the weighings of this series were made on the Becker balance carrying twelve hundred grammes, which was mentioned at page 28, and shown in Fig. 10, page 30. It was mounted on the closet shown in Fig. 16, page 38. It was provided with the apparatus for weighing by reversal which is shown in Figs. 16 to 19. But at that time, some trifling details were not quite as shown by the drawings: the operation of weighing was, however, effected exactly as by the apparatus in its present condition.

4.—SYNTHESIS OF WATER. MANIPULATION OF TUBE CONTAINING PALLADIUM.

These experiments were the first in which large quantities of hydrogen were weighed while absorbed in palladium; so some changes were by degrees introduced into the apparatus. As far as I see, these trifling modifications simply made the manipulation shorter and more convenient, without affecting the accuracy of the results. But opinions may differ on this matter, so that it is proper to describe the three forms which the tube containing palladium successively assumed.

In experiments 1 and 2, the palladium was contained in two separate hard glass tubes, Fig. 33. To each was fitted a stopcock of common glass by means of a ground joint and paraffin. A stopcock of hard glass cannot be made. The manipulation of this tube would have been very simple if a stopcock were anything more than a contrivance for *lessening* the flow of a gas through a tube. But for any precision, together with freedom from large constant error, in manipulation with a gas so light as hydrogen, it was necessary that leakage should be rendered excessively improba-

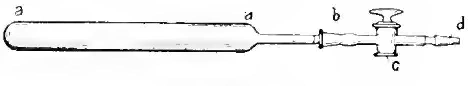


Fig. 33.—Palladium tube, first form.

ble. The sole use of these stopcocks was to prevent the admission of any considerable quantity of air during the preparation of the tube for filling it again with hydrogen.

To the tube of infusible glass *a, a*, therefore, was fitted by a ground joint the stopcock *c*, ending in another ground joint. When the tube was to be filled with hydrogen, a connecting tube with a ground joint was fitted to the second joint, *d*, with paraffin, and connected by fusion to the source of hydrogen. The connecting tubes were then freed from air by repeated exhaustion. The stopcock *c* was then opened, the palladium was heated, and the exhaustion continued. After cooling the palladium, hydrogen was admitted to saturation. In these two experiments, any nitrogen which might possibly have accompanied the hydrogen was removed, or, rather, an attempt was made to remove it, by repeated exhaustions of the tube at the end of the admission of hydrogen.

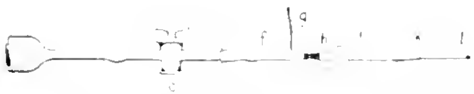


Fig. 34. [illegible]

When the tube was charged with hydrogen, the pressure in the tube was a little greater than that of the atmosphere. No leakage was therefore to be feared during the moment required to remove the ground joint which connected the palladium tube with the source of hydrogen, its stopcock being closed, and to replace it with the joint *f, l*, Fig. 34, which had been prepared beforehand. The tube *g* was then connected with the air pump, and the space between the stopcock and the plug of fusible metal *h* was repeatedly exhausted and filled with hydrogen. When it was exhausted for the last time, the connection with the pump was closed by fusion at *g*.

The space between the fusible metal plug *h*, and the point *l*, had been exhausted before the point *l* was sealed. The apparatus, therefore, contained no gas but hydrogen.

The volume of the two tubes was now determined by a hydrostatic weighing of both at once. A counterpoise was made of the same two kinds of glass, and of nearly the same volume and weight.

When the hard glass tubes containing the palladium were used, they were heated so gently that it was obvious that no change of volume was to be feared; it was therefore unnecessary to determine their volume after the expulsion of the gas by a second hydrostatic weighing.

Fig. 35. Palladium tube, second form.

Procuring some tubes large enough to contain the whole of the palladium, it was concluded to use them, although they were of soft glass.

This tube took the form shown in Fig. 35. It was now not safe to assume that there would be no change of volume on heating to expel hydrogen. Accordingly, a mark was etched at *c*. After determining the volume of the whole tube by hydrostatic weighing, the volume below this mark was also determined. After the expulsion of the gas, any change of volume was determined by immersion to this mark. The stopcock was therefore not wet during the progress of the experiment. The effect of the immersion of the stopcock during the preliminary work of reconstructing the tube before the charging with hydrogen was eliminated by waiting a sufficient time before the weighing.

One important advantage was gained by the use of soft glass. It was now possible, when the absorption was ended, to continue the current of hydrogen, by breaking off the point *m* of the tube, so as to expel any nitrogen which might have accompanied the hydrogen and accumulated in the tube. After this was accomplished by a current lasting three or four hours, the point was closed by fusion, and the tube prepared for weighing in the same way as before.

But a certain difficulty remained. The stopcock had to be immersed for at least one hydrostatic weighing for each experiment, and this involved waiting a day or two in order to be sure that the lubrication had come again to a constant state. A third apparatus was therefore constructed, in which no stopcock was used. This is the form always used afterwards. It has been shown in Figs. 25, 26, and 27, and its manipulation has been sufficiently described.

5.—SYNTHESIS OF WATER. APPARATUS FOR PRODUCING AND WEIGHING WATER.

The apparatus in which the gases were combined and in which the water produced was weighed is shown in Fig. 36. At *a* are two platinum jets from which the gases issue into the combustion chamber. Two tubes filled with phosphorus pentoxide, kept in place by rolls of asbestos, are shown at *b*, *b*. At *c*, *c*, are joints ground to fit corresponding joints by which the apparatus may be connected to the sources of hydrogen and of oxygen. These tubes are closed by fusion at *d* and *e*, and notches are made where they are afterwards to be broken off. Wires *f*, *f*, provide for the inflammation of the jet of hydrogen, or of oxygen, as the case might be. The ends of the apparatus have hooks facilitating the hydrostatic weighing which determines its volume. The whole apparatus was exhausted to a ten-thousandth of an atmosphere and sealed off from the pump at *g*.

A counterpoise of suitable weight and volume was then made. Since the apparatus had to be reconstructed for each experiment by providing it with new drying tubes, a new counterpoise had also to be made. To facilitate this, a series of volumes of 50, 20, 20, 10, 5, 2, 2, and 1 cubic centimetres were prepared and the volume of each determined. Then a series of tubes having all nearly the same volume, and weights of 55, 60, 65, 70, 75, and 80, grammes were made, and their volumes determined. By the aid of these a counterpoise of a given volume and nearly a given weight could be made up in a moment.

The combustion apparatus was then weighed by reversal, as in the case of the palladium and of the globes containing oxygen. But few weighings were required for a small and light object like this.

Fig. 36.—Ap[illegible] [illegible]

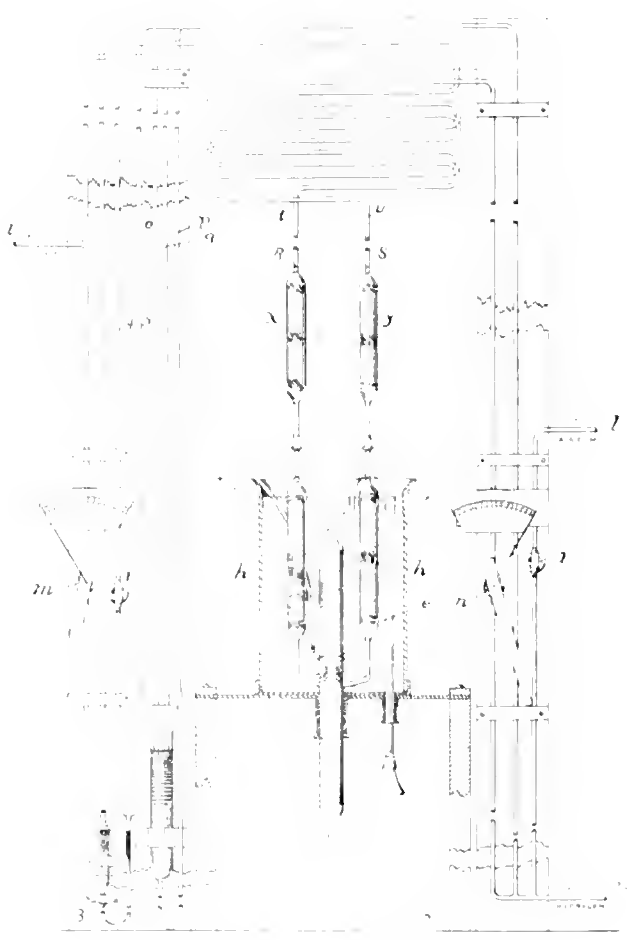


Fig. 37.—[illegible] oxygen [illegible]

6. SYNTHESIS OF WATER. MANIPULATION IN SETTING TOGETHER THE APPARATUS FOR COMBUSTION.

When the weights of the globes, of the tube containing palladium, and of the combustion apparatus, had been determined, the apparatus was put together for a synthesis. First, the combustion apparatus had one of the points *d*, Fig. 36, broken off while it was enclosed in a tube which delivered dry air. The ground joints which fitted *c*, *c*, formed the ends of two drying tubes filled with phosphorus pentoxide. One of these tubes was now put on *c*. The other point *c* was broken off and the other drying tube also put in place; both joints were of course made tight with paraffin. The object of these tubes was, to prevent the admission to the weighed tube of any moisture produced in the glass-blowing operations required in putting the apparatus together. It is now seen that the manipulation might have been made simpler; but not more accurate.

The combustion apparatus with the addition of the phosphorus pentoxide tubes was now placed in the condenser *h*, *h*, Fig. 37. This consisted of a cylinder of glass, having a brass bottom with two tubulatures; into one of them the combustion apparatus was placed, and made tight with a rubber tube.

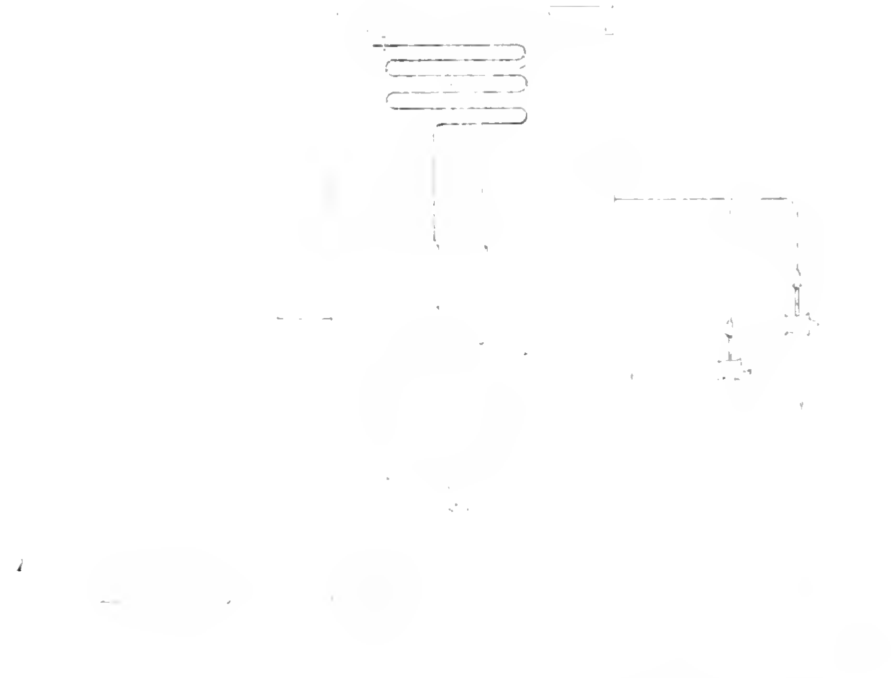
7.—SYNTHESIS OF WATER. MANIPULATOR FOR REGULATING THE PROGRESS OF THE COMBUSTION.

The condenser with its contents is next placed in the manipulator shown in Fig. 37. At *i* and *k* are the tubes by which oxygen and hydrogen are to be introduced; *l* leads to the Toepler air pump. The stopcocks *m* and *n* serve to control the admission of the gases into the combustion chamber. The tubes *o* and *p*, which are connected directly to the tubes *i* and *k*, show the pressure of the oxygen and hydrogen at their sources. The tube *q*, interposed between the stopcock *m* and the combustion chamber, shows the pressure of the gas therein. The ends *r* and *s* are now fused to the somewhat flexible connections *t* and *u*. As said before, the drying tubes *x* and *y* prevent the entrance into the weighed drying tubes of the water formed in this process.

The globes containing oxygen are now fitted into the corresponding ground joints, and these are fused to the branches leading from the tube *i*, as shown in Fig. 38. The point of the palladium tube is broken off and a joint is fitted on and connected by fusion to the tube *k*.

The five stopcocks *m*, *n*, *1*, *2*, *3*, being open, the apparatus is exhausted to one part in ten thousand, and the pump is shut off by closing the stopcock *2*. The stopcock *3* is opened, when mercury fills the tubes *4*, *5*, closing all connection between the hydrogen and the oxygen sides of the apparatus. The stopcocks *1* and *3* are now closed, preventing disturbance of the level of the mercury in these tubes. The stopcocks *m* and *n* are next closed, and the stopcock of one of the globes of oxygen is opened, when the gauge *o* shows the pressure of the oxygen in it; the other globe is also opened. The fusible metal plug is then fused, when the gauge *p* shows the pressure of the hydrogen from the palladium.

The stopcock m is opened so as to admit say half an atmosphere of oxygen to the apparatus, after which it is closed. Sparks are passed between the points t, t, and stopcock n is cautiously opened. Hydrogen enters and mixes with the oxygen which already fills the apparatus, and the mixture soon comes to the jets; it takes fire, and for a moment burns within the asbestos at G. Soon the gas burns quietly at one of the jets; heat is applied to the palladium, and the pressure of the gas from the palladium is watched by means of the gauge. The stopcocks m and n are regulated by the indications of the other gauges and the appearance of the flame. The combustion chamber is kept cool by renewing the water surrounding it.



[illegible]

The combustion of pure hydrogen in pure oxygen is a very interesting phenomenon. Since it was convenient to have a visible indication by which to regulate the admission of gas, I commonly adjusted so as to produce vivid incandescence of one or the other of the platinum jets. In this case, nothing else could be seen unless for a moment the heat was sufficient to volatilize something from one of the wires used to ignite the gases. But often, when the current was made more rapid, the incandescence of the jet ceased, and then there was a small pointed flame, invisible except on careful exclusion of other light. But the risk and consequent anxiety attending the appearance of this flame prevented minute and trustworthy observation. The risk was due to the fact that if the flame were extinguished by slight error in adjustment of the stopcocks for admitting the gases, the pressure of the hydrogen would, before it was possible to make readjustment, so increase as to blow off through the mercury, as once happened even when the safe pressure was two atmospheres, and the working pressure only half an atmosphere.

8. SYNTHESIS OF WATER. THE COMBUSTION.

The combination of forty-two litres of hydrogen with twenty-one litres of oxygen took about an hour and a half. When the pressure of the oxygen became very small, extreme care was required to continue the combustion. I have once carried it till the pressure of oxygen and water vapor together was only eight centimetres of mercury. The attempt to do the same again was unsuccessful.

When the combustion was ended, the stopcocks *m* and *n* were closed, the palladium tube was closed by fusion at the point *h*, Fig. 34, and the globes containing oxygen were closed at their stopcocks. In experiments numbered 10, 11, and 12, the globes were also closed in the same way as the palladium tubes.

The lower part of the combustion chamber was now immersed in a freezing mixture. When the water produced had been frozen and cooled as much as possible, the stopcocks of the apparatus were opened, the mercury was withdrawn from the tubes *4* and *5*, and the Toepler pump was used to transfer the gas remaining in the apparatus and its connecting tubes to an eudiometer. The tension of the vapor of the water at — 18° C. being only 1.1 *mm.*, the exhaustion could be made sufficiently complete. The phosphorus pentoxide tubes showed no signs of harmful deliquescence during the half hour they had to serve.

When the exhaustion was complete, the combustion apparatus was closed by fusion at *h* and *h*, Fig. 36. The parts fused off from the different parts of the apparatus were now cleaned from adhering wax or paraffin, and the points which had been broken off were put with those to which they belonged. The four parts of the apparatus were then weighed.

9.—SYNTHESIS OF WATER. WEIGHING THE OXYGEN AFTER A COMBUSTION.

It is obvious that the volumes of the globes when full and when partly empty would differ by the amount of the corresponding elastic compression. In the first and second experiments, the oxygen was withdrawn from the globe as completely as possible; the globe after the experiment was therefore weighed against the counterpoise proper for the empty globe, and a correction computed for the difference of volume. In the experiments from the third to the seventh, the oxygen was nearly half withdrawn; the globes were therefore weighed, one against the counterpoise for the empty globe and the other against the counterpoise for the full globe, and a correction computed for the difference of volumes; the two corrections nearly balanced each other. In the eighth and ninth experiments, the globes, both full and half empty, were weighed against the counterpoise of the empty globe, and corrections computed; the counterpoises for the filled globes had suffered injury. In the last three experiments, the globes were closed by fusion; they were weighed when half empty against the counterpoises of the full globes, and corrections computed for the difference in volumes.

10. SYNTHESIS OF WATER. WEIGHING THE PALLADIUM AFTER A COMBUSTION.

The volume of the tube containing palladium was determined by hydrostatic weighings. In the cases where the tube was provided with a stopcock, it was immersed only to a certain mark at this second hydrostatic weighing. When no stopcock was used, the tube was submerged. In all cases, the volume of the part which had been fused off was determined from its weight and specific gravity.

From the change in the volume of the tube a correction to the observed weight was computed. These experiments were made before the construction of the system of flasks for making equal the volumes of the masses placed on the opposite pans of the balance.

11. SYNTHESIS OF WATER. EUDIOMETRIC ANALYSIS OF THE RESIDUE LEFT UNCOMBINED.

The gas extracted from the apparatus after the combustion was ended, was measured and analyzed. Only one point needs mention.

In some experiments some carbon dioxide was found. The amount was not large, but the question as to its origin was an important one. If it came from carbon weighed with the hydrogen, the experiment was valueless. The probability was that it came from the asbestos, where the combustion was carried on for a few seconds. This asbestos had to be handled in the construction of the tubes, and it was not easy to free it from dust by ignition, as, after ignition, my sample was not well suited for its use. To settle the question, some two or three hundred grammes of water were formed in a combustion apparatus of the same kind, but without weighing the gases introduced. The water produced was allowed to flow out, as formed, by a tube fused to the bottom of the apparatus; it was kept from contact with the atmosphere. In this case there was no asbestos, but the hydrogen was the same as that used in all the experiments.

To the water produced in this experiment, barium hydroxide was added, and the whole showed no trace of turbidity. It was then evaporated to the bulk of five cubic centimetres; of course carbon dioxide was not admitted. Even when reduced to this bulk, there was no turbidity. It is obvious, therefore, that the hydrogen used in these experiments did not contain carbon compounds. It is precisely the same in quality, obtained from the same apparatus, with the same solution, as that used in all my experiments so far; the only change ever made has been the introduction of fresh distilled water to take the place of that removed by electrolysis.

If now this carbon dioxide was formed by the oxidation of organic matter adhering to the asbestos, it was supposed that each cubic centimetre of carbon dioxide formed represented a cubic centimetre of oxygen withdrawn from the globes but not used in forming water.

In some experiments, nitrogen was also found. The quantity was small. When the globes for oxygen contained air, and were exhausted and filled with oxygen, a certain amount of nitrogen remained in the globes. If the globes were exhausted again when partly filled with oxygen, the nitrogen was mostly eliminated. As the amount of nitrogen found agreed fairly in amount with what might be expected from the previous contents of the globes and the degree of the last exhaustion, no hesitation was felt in counting this nitrogen as having come from the globes of oxygen.

12.—SYNTHESIS OF WATER. SOURCES OF ERROR.

In the weighing of the hydrogen, no source of appreciable constant error has yet been thought of. The magnitude of the accidental errors must be learned from the concordance of the experiments.

In the weighing of the oxygen, leakage might act in two opposite directions. If leakage occurred before the combustion began, the amount so lost would be extracted by the Toepler pump in the exhaustion preliminary to the combustion, and so would seem to have been used in the combustion. If the leakage occurred in the contrary direction, when the half-exhausted globe was hung on the balance for the final weighing, the amount of oxygen taken from the globe would appear less than the truth. Now the leakage during exhaustion, if noticeable in amount, would be readily detected by the behavior of the pump during the preliminary exhaustion. A very slight leak can be detected when the vacuum obtained is something like a ten-thousandth of an atmosphere. Such a leak would be the more certainly detected, since the pump was always left at rest for fifteen minutes after exhaustion and before the measurement of the vacuum, so as to make sure of an equilibrium of pressure. Once such a leak was detected; when the apparatus was dismounted, and the globes weighed again. A leakage during the second weighing ought to be detected by the slow change of weight which it produces. It was not detected during any of the experiments of the present series. It may be said that the stopcocks of five of my globes were of large size so as to make the distance which air must travel around the key, from the entrance to the exit, as much as four centimetres. These were often found to be tight for some days when freshly lubricated and turned but a few times.

It was to avoid both these errors that, in the last three experiments, the globes holding oxygen were closed in the same way as the tube containing the palladium

Two sources of error in the determination of the weight of water produced were known to exist. The platinum wires for the passage of the spark might become loosened by the heat, so as to admit some water or air. On the other hand, the exhaustion by means of a Toepler pump, unless regulated by opening the stopcock but partly, may sometimes draw the gas through the drying tubes faster than it can be dried. Probably this happened, to a slight extent, in some of the experiments, but the amount was not very large. The manipulation which might have easily and completely prevented this was not thought of till the second (unfinished) series of experiments was begun.

13.—SYNTHESIS OF WATER. COMPLETENESS OF DRYING OF GASES WITH PHOSPHORUS PENTOXIDE.

In a paper describing some of the earliest of my experiments relating to oxygen and hydrogen, it is shown that the amount of moisture left by phosphorus pentoxide in even a thousand litres of a gas is negligible. My experiments proved that a current at the rate of three litres an hour was made absolutely dry by a rightly filled tube whose capacity was twenty-five cubic centimetres; it was therefore thought safe to pass a current of twelve litres an hour through a tube containing one hundred cubic centimetres.

14.—SYNTHESIS OF WATER. IS HYDROGEN GIVEN OFF BY PALLADIUM FREE FROM WATER?

A source of error would exist if, as has been thought, water should accompany the hydrogen delivered from palladium. This would imply that oxygen in some way found access to the palladium, and that the water produced was not removed with any nitrogen which might have accompanied the hydrogen. Keiser considered his experiments as proving that water is given off from palladium together with hydrogen. I made five experiments, which show that a tube containing palladium and filled with hydrogen as in all my use of it, gives off no water. The tube containing six hundred grammes of palladium was charged in the usual way, and then connected with a U tube containing phosphorus pentoxide, which had been carefully weighed against a tube similar in shape and equal in volume. The hydrogen was expelled through the drying tube at the rate of not more than six litres an hour, it being collected over water to control the rate. This was repeated five times. The drying tube showed the usual slight variations of weight from day to day, but the weight did not increase. When two hundred litres had been passed through it, the weight was the same as at first, and the algebraic sum of all the slight variations during the course of the experiment was zero. It is obvious therefore that if palladium is charged with hydrogen as in my experiments, it will give off no water.

15.—SYNTHESIS OF WATER. IS OXYGEN ABSORBED BY THE PHOSPHORUS PENTOXIDE USED?

A source of error in the present series of experiments would exist, if the drying tubes used were capable of absorbing oxygen in their ordinary use. If this were the case, the drying tubes *b*, *b*, Fig. 36, would absorb oxygen, which would seem to have been combined with hydrogen. But all the pentoxide used in these experiments had been examined to determine whether it were suitable for the purpose.

A drying tube filled with the pentoxide, *a b*, Fig. 39, was fused to the short arm of a syphon barometer lying on its side as seen. Pure dry oxygen was passed into *c*, escaping at *d*, and these two tubes were closed by fusion while the current was passing. The barometer was then set upright, and securely fixed to a wall, so as to remain undisturbed for months. A tank of water was put so as to cover the drying tube, giving the means of knowing the temperature of the gas. A thermometer divided into fiftieths of a degree was placed in the water, and two other thermometers gave the temperature of the column of mercury. The apparatus was set up in a basement room of tolerably constant temperature. As soon as it was set up, readings were taken till equilibrium was attained, when a split tube was fixed with its lower edge tangent to the upper meniscus of the mercury, at *c*, Fig. 40. The reading having been verified several times, by warming or cooling the water till the mercury was again tangent to the mark, the pressure of the enclosed oxygen was known.

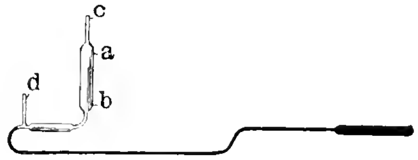


FIG. 39.—Apparatus for detecting absorption of oxygen by phosphorus pentoxide; filling with oxygen.

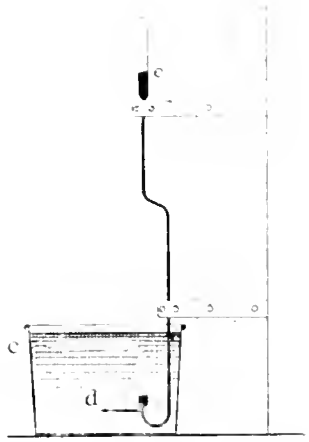


Fig. 4.—Apparatus for testing absorption of oxygen by lower oxides of phosphorus [illegible] experiment.

The same observations were then repeated after say ten days; if no diminution of pressure was noticed, the experiment was continued say fifty or a hundred days, when the final readings were made. In order to reduce the indications of pressure to weight, in one of these experiments, we need to know the approximate volume of the oxygen and the approximate height of the column of mercury. The first was estimated from the capacity of the tube; which suffices for a differential observation. The height of the mercury was measured with a wooden metre. Correcting the observed pressures for the temperature of the mercurial column, we have the results given below.

	Temperature of Oxygen	Pressure	Weight
October 17	18.06	842.[illegible] mm	1485 gr.
" 27	18.2	841.07 "	.1484 "
December 25	17.15	842.22 "	.1484 "
" 27	18.16	842.23 "	1484 "

In this sample, therefore, no appreciable absorption of oxygen by lower oxides of phosphorus was to be feared in the conditions in which the tubes were used.

The precaution is by no means unnecessary, as a somewhat troublesome mishap showed.

The result is of interest as confirming Regnault's opinion that oxygen does not act on mercury at ordinary temperatures.[*] The contrary opinion is sometimes attributed to him. My observations, extending over some months, agree perfectly with his opinion.

16. SYNTHESIS OF WATER. DATA OF EXPERIMENTS.

The two following tables give the results of the experiments. In Table I. are given the volume of the gas extracted after the combustion, with its composition; the weight of the hydrogen; and the weights of the oxygen found, of the

---

[*] *Mémoires de l'Académie*, 26, 237.

nitrogen, and of the oxygen equivalent to the carbon dioxide, all collected in a single value in the last column.

Table II. gives the weights of the hydrogen and oxygen apparently taken from the sources of the two, by simple difference of the means of all the observations with the balance in each case. Then follow the corrections for difference of volumes in the two weighings, and for the residues found in the eudiometric analysis; after which are given the amounts actually combined, with their ratio, and the weight of the water formed, with the ratio of this quantity to the hydrogen used in forming it.

TABLE I.

	Residue.	Hydrogen.	Nitrogen.	Oxygen.	Carbon Dioxide.	Weight of Hydrogen.	Weight of Oxygen.
1	28.71 cc.	20.3 cc.	0.3 cc.	8.1 cc.	0.0 cc.	1.8 mg	12.3 mg.
2	10.69 "	4.2 "	0.0 "	6.5 "	0.0 "	0.4 "	9.2 "
3	12.68 "	6.7 "	0.0 "	6.0 "	0.0 "	0.6 "	8.4 "
4	32.10 "	23.7 "	0.2 "	7.0 "	1.2 "	2.1 "	11.8 "
5	13.65 "	10.7 "	0.0 "	2.2 "	0.8 "	1.0 "	4.1 "
6	107.93 "	75.2 "	1.7 "	30.9 "	0.1 "	6.7 "	46.3 "
7	3.40 "	2.0 "	0.0 "	1.2 "	0.2 "	0.2 "	2.0 "
8	14.80 "	6.4 "	0.0 "	8.3 "	0.1 "	0.6 "	11.9 "
9	73.75 "	59.7 "	0.3 "	13.4 "	0.3 "	5.3 "	19.5 "
10	119.94 "	57.1 "	0.9 "	61.7 "	0.2 "	5.1 "	88.9 "
11	12.79 "	5.1 "	0.5 "	7.0 "	0.2 "	0.5 "	10.9 "
12	37.78 "	13.3 "	0.8 "	23.7 "	0.0 "	1.2 "	34.6 "

TABLE II.

	Hydrogen Taken.	Air Correction.	Residue.	Hydrogen Used.	Oxygen Taken.	Air Correction.	Residue.	Oxygen Used.	Ratio.	Water Formed.	Ratio.
1	3.2661	+.0002	−.0018	3.2645	25.9307	−.0008	−.0123	25.9176	15.878	29.1788	17.877
2	3.2562	+.0001	−.0004	3.2559	25.8631	−.0008	−.0092	25.8531	15.881	29.1052	17.878
3	3.8199	.0000	−.0006	3.8193	30.3276	+.0018	−.0084	30.3210	15.878	34.1389	17.873
4	3.8471	.0000	−.0021	3.8450	30.5414	−.0002	−.0118	30.5294	15.880	Apparatus broken.	
5	3.8392	.0000	−.0010	3.8382	30.4723	+.0018	−.0041	30.4700	15.877	34.3151	17.881
6	3.8538	+.0052	−.0067	3.8523	30.0262	+.0019	−.0463	30.5818	15.877	34.4327	17.876
7	3.8294	+.0005	−.0002	3.8297	30.4036	−.0003	−.0020	30.4013	15.877	34.2284	17.875
8	3.8291	+.0001	−.0006	3.8286	30.4161	−.0076	−.0119	30.3966	15.878	34.2261	17.879
9	3.8271	+.0007	−.0053	3.8225	30.3769	−.0077	−.0195	30.3497	15.879	34.1742	17.881
10	3.8246	+.0025	−.0051	3.8220	30.4225	+.0093	−.0889	30.3479	15.881	34.1743	17.883
11	3.7622	+.0020	−.0005	3.7637	29.8884	+.0090	−.0109	29.8865	15.881	33.6540	17.883
12	3.8207	+.0016	−.0012	3.8211	30.3683	+.0092	−.0346	30.3429	15.882	34.1559	17.878

The mean values for the atomic weight of oxygen are:

From ratio of hydrogen and oxygen.. .... 15.8792, and
From ratio of hydrogen and water..................... 15.8785.

If, then, no important source of error is detected in the processes employed, the atomic weight of oxygen referred to hydrogen as unity is very nearly

$$O = 15.879.$$

17. ATOMIC WEIGHT COMPUTED FROM DENSITY AND VOLUMETRIC RATIOS.

The atomic weight of oxygen may also be computed from the ratio of the densities of hydrogen and oxygen, together with the ratio of the volumes in which the gases combine. The value of the density of oxygen obtained in the forty-one experiments described in this paper is:

Density of oxygen . . . . 1.42900 gr.

For hydrogen, by the mean of twenty-three successful experiments in the third, fourth, and fifth series, the value is:

Density of hydrogen . . . . .089873 gr.

These values are for the sea level in latitude 45°. In order to compare them with the results of others, we may reduce to the values corresponding to the force of gravity at Paris by multiplying by 1.000316. We then have

Density of oxygen at Paris. . . . . 1.42945 gr.
Density of hydrogen at Paris . . . . .089901 gr.

Lord Rayleigh has lately published a table showing the values found by various experimenters, as follows:

	Oxygen.	Hydrogen.
Regnault, 1847.	1.42980 gr.	.08958 gr.
Corrected by Crafts.	1.43011	.08988
Von Jolly, 1880.	1.42939	
Ditto, corrected.	1.42971	
Leduc, 1891.	1.42910	.08985
Rayleigh, 1893.	1.42952	.09001

In taking the mean, he omits the uncorrected numbers and obtains:

Density of oxygen, at Paris. . . . . 1.42961 gr.
Density of hydrogen, at Paris . . . . .08991 gr.

Hence we obtain for the ratio:

Ratio of densities, mean of all previous experiments. 15.9005
Ratio of densities, my own experiments. 15.9002

As to the volumetric ratio, the value obtained in this paper is:

Ratio of volumes of oxygen and hydrogen which combine . . . 2.00269
Scott has found the value 2.00285
Leduc found, from two experiments, the value 2.0037

But the reduction seems to have omitted to take into account the deviation of the gases from the law of Boyle. If we suppose that the gas which he weighed contained no excess of hydrogen, this value would become something like 2.0024.

Why the earlier experiments of Scott and myself gave values so much less than these need not be discussed now. Since our later experiments, as well as those of Leduc when properly reduced, give concordant results, we may have some confidence in them.

If we combine the ratios of the densities and of the combining volumes obtained in this paper, we get the

Atomic weight of oxygen 15.879

The results of my experiments are then as follows:

Weight of one litre of oxygen, latitude 45°	1.42900 gr.
Weight of one litre of hydrogen, latitude 45	.089873 gr.
Atomic weight of oxygen, chemical method	15.879
Molecular weight of water, chemical method	17.879
Atomic weight of oxygen, physical methods	15.879

The last value is subject to correction by further determinations of the volumetric ratio.

SUMMARY OF ALL PUBLISHED RESULTS.

It may be useful to compare the values of the atomic ratio of oxygen and hydrogen, which have been obtained in this paper, with the results of other experimenters. One such value may be computed by combining the ratio of the densities of the two gases, derived from all experiments hitherto published, with the ratio, determined by Scott, of the volumes in which the gases unite. Determinations of the ratio of the densities have been made by Regnault,[*] Rayleigh,[†] Cooke,[‡] and by Leduc.[§] Regnault and Leduc measured volume and pressure at the temperature of melting ice; the others at the temperature of the laboratory. Cooke weighed hydrogen and air, and compared the ratio of their densities with the ratio of the densities of air and oxygen, determined by Regnault. The results

---

[*] *Mémoires de l'Académie*, 21, 143; with *Comptes Rendus*, 106, 1662.

[†] *Proceedings of the Royal Society*, 43, 356; 50, 448.

[‡] *American Chemical Journal*, 11, 537.

[§] *Comptes Rendus*, 113, 186.

of the experiments are given, with some facts which may assist in forming an opinion of the merits of the experiments, in the following table:

RATIO OF DENSITIES OF OXYGEN AND HYDROGEN

Observer	Gas	Number of Experiments	Average Weight	Mean Ratio	Probable Error	Weight of Result
Regnault.	H	3	0.88 gr.			
	O	3	14.1 "	15.9615	0.0147	0.02
Rayleigh,	H	2	0.15 "			
1887.	O	2	2.5 "	15.884	0.0047	0.20
Rayleigh,	H	[illegible]	0.15 "			
1892	O	11	2.5 "	15.882	0.0021	1.00
Cooke	H	3	0.41 "			
	Air	3	5.95 "	15.869	0.0067	0.10
Leduc	H	3	0.2 "			
	O	3	3.18 "	15.905	0.0103	0.04

The last column gives weights assigned according to the probable errors, which are given in the previous column. The mean, with these weights, is

$$D = 15.887 \pm 0.0017.$$

Since the weights assigned to the observations at common temperatures are five times as much as those assigned the observations at 0° C., we may consider this mean as holding for common temperatures; we therefore combine with it the value, given by Scott[*] from forty seven selected observations, of the ratio of the volumes in which the gases combine when measured at common temperatures,

$$R = 2.00245 \pm 0.00015.$$

From these ratios we obtain the atomic ratio,

$$O = 15.868 \pm 0.0017.$$

The atomic ratio has been determined directly by Berzelius and Dulong,[†] Dumas,[‡] Erdmann and Marchand,[§] Cooke and Richards,[‖] Keiser,[¶] Noyes,[**]

---

[*] *Philosophical Transactions of the Royal Society*, 184, A, 543 (1893).

[†] *Annales de Chimie et de Physique*, [2] 15, 386.

[‡] *Annales de Chimie et de Physique*, [3] 8, [illegible]

[§] *Journal für praktische Chemie*, 26, 468.

[‖] *American Chemical Journal*, 10, 81, and 191.

[¶] *American Chemical Journal*, 10, 249.

[**] *American Chemical Journal*, 12, 441.

Dittmar and Henderson,* Rayleigh,† and by Leduc.‡ The values which they found are given in the following table, together with the value computed above from the ratio of the densities; they are arranged in the order of their magnitude.

SUMMARY OF DETERMINATIONS OF THE ATOMIC WEIGHT OF OXYGEN.

Observer.	Quantities Weighed Directly.	Values Found.	Probable Errors.
Dittmar and Henderson.	Oxygen and water	15.866	0.0062
See First Table	Ratios	15.863	0.0017
Cooke and Richards.	Hydrogen and water	15.869	0.0017
Leduc.	Oxygen and water	15.881	0.012 §
Rayleigh.	Hydrogen and oxygen	15.89	0.0088
Berzelius and Dulong.	Oxygen and water	15.894	0.031
Noyes.	Hydrogen and oxygen	15.897	0.0017
Keiser.	Hydrogen and water	15.950	0.0010
Dumas.	Oxygen and water	15.961	0.0070
Erdmann and Marchand.	Oxygen and water	15.975	0.011

The result of Berzelius and Dulong has so large a probable error that it may be disregarded. Those of Dumas and of Erdmann and Marchand may be safely dismissed from consideration, on account of the error detected by Dumas at the end of his work. There remain only the results which have been published within the last ten years. Six of these results differ but little from their mean, which has the value 15.88: one result differs from this mean by 0.07; it is difficult to resist the suspicion that some source of constant error vitiated this discordant value. The results which remain are those upon which our present knowledge of the atomic weight of oxygen will doubtless be considered to rest. They are repeated, with some details which may serve to assist in judging of the trustworthiness of the several series of determinations, for the convenience of any who may not care to refer to the original papers.

VALUES ON WHICH OUR KNOWLEDGE OF THE ATOMIC WEIGHT OF OXYGEN DEPENDS.

Observer.	Quantities Weighed Directly.	Number of Experiments.	Amount of Hydrogen Weighed.	Amount of Oxygen Weighed.	Amount of Water Weighed.	Value Found.	Probable Error.
Dittmar and Henderson.	Oxygen and water	7 (of 11)		21.4 gr.	24.1 gr.	15.866	0.0062
See First Table.	Ratios	32 and 47	See First	Table.	—	15.868	0.0017
Cooke and Richards	Hydrogen and water	16	0.42 gr.	—	3.8 "	15.869	0.0017
Morley, I.	Hydrogen and water	11	3.75 "	—	34 "	15.879	0.00066
II.	Ratios	23 and 10	To 3.75 gr.	To 31 gr.	—	15.879	0.0014
III.	Hydrogen and oxygen	12	3.75 gr.	30 gr.	—	15.879	0.00032
Leduc.	Oxygen and water	2	—	18.7 "	21 "	15.881	0.012
Rayleigh.	Hydrogen and oxygen	5	0.11 "	0.9 "	—	15.89	0.0088
Noyes.	Hydrogen and oxygen	24	0.77 "	6.1 "	—	15.897	0.0017

---

* *Proceedings of the Philosophical Society* (Glasgow), 22, 33 (1891).

† *Proceedings of the Royal Society*, 45, 425.

‡ *Comptes Rendus*, 115, 43. § The probable error of Leduc's result is arbitrarily assigned on the assumption that one of his experiments was equal in accuracy to one of Dittmar and Henderson's.

I have entered my three results separately in the table, in order to indicate the probable errors of the several values. It is obvious, from a comparison of the nine results, that we may compute a mean in almost any way which even caprice may suggest, without materially altering the value deduced. We may assign equal weights to all the values, or weights proportional to the numbers of observations in each series, or according to our judgment of the merits of the processes employed, or inversely as the probable errors, or inversely as the squares of the probable errors; in each case, our mean differs from the value obtained in the last case,

$$O = 15.879,$$

by less than a ten-thousandth of this quantity. Until further light is obtained concerning the sources of error which, doubtless, affect all these experiments, this value is the most probable which can be derived from the existing data.

INDEX.

SMITHSONIAN CONTRIBUTIONS TO KNOWLEDGE.

989

Hodgkins Fund.

THE
COMPOSITION OF EXPIRED AIR
AND ITS
EFFECTS UPON ANIMAL LIFE.

BY

J. S. BILLINGS, M.D., S. WEIR MITCHELL, M.D.
AND D. H. BERGEY, M.D.

CITY OF WASHINGTON:
PUBLISHED BY THE SMITHSONIAN INSTITUTION.
1895.

The Knickerbocker Press, New Rochelle, N. Y.

SMITHSONIAN CONTRIBUTIONS TO KNOWLEDGE.
989

Hodgkins Fund.

THE
COMPOSITION OF EXPIRED AIR
AND ITS
EFFECTS UPON ANIMAL LIFE.

BY

J. S. BILLINGS, M.D., S. WEIR MITCHELL, M.D.
AND D. H. BERGEY, M.D.

CITY OF WASHINGTON:
PUBLISHED BY THE SMITHSONIAN INSTITUTION.
1895.

COMMITTEE TO WHOM THIS MEMOIR
HAS BEEN REFERRED.

HORATIO C. WOOD.
WILLIAM HENRY WELCH.
CHARLES SEDGWICK MINOT.

ADVERTISEMENT.

The present memoir is the result of a series of investigations made by Doctors J. S. Billings and S. Weir Mitchell, assisted by Doctor D. H. Bergey, under a grant from the Hodgkins Fund of the Smithsonian Institution, for the purpose of determining the nature of the peculiar substances of organic origin contained in the air expired by human beings, with special reference to the practical application of the results obtained to problems of ventilation for inhabited rooms.

In accordance with the rule adopted by the Smithsonian Institution the work has been submitted to a committee, in the present instance consisting of Doctor H. C. Wood, Professor William H. Welch, and Professor Charles S. Minot, and having been recommended by them for publication, it is herewith presented in the series of Contributions to Knowledge.

S. P. LANGLEY,

SECRETARY.

WASHINGTON, *November, 1895.*

THE COMPOSITION OF EXPIRED AIR, AND ITS EFFECTS UPON ANIMAL LIFE.

REPORT ON THE RESULTS OF AN INVESTIGATION MADE FOR THE SMITHSONIAN INSTITUTION UNDER THE PROVISIONS OF THE HODGKINS FUND.

By J. S. BILLINGS, M.D., S. WEIR MITCHELL, M.D., AND D. H. BERGEY, M.D.

In May, 1893, a grant was made from the Hodgkins Fund to Drs. John S. Billings and S. Weir Mitchell, "for the purpose of conducting an investigation into the nature of the peculiar substances of organic origin contained in the air expired by human beings, with special reference to the practical application of the results obtained to problems of ventilation for inhabited rooms."

For a number of years prior to 1888 the prevailing view among physicians and sanitarians had been that the discomfort and dangers to health and life which had been known to exist, sometimes at least, in unventilated rooms occupied by a number of human beings, were largely or entirely due to peculiar organic matters contained in the air expired by these persons, and that the increase in carbonic acid due to respiration had but little effect in producing these results, its chief importance being that it furnished a convenient means of determining the amount of vitiation of the air. Recently, however, several experimenters have concluded that the organic matters in the exhaled breath are not harmful, at all events to animals, and the main object of the proposed investigation was to determine the correctness of these conclusions. For this purpose a scheme of experimentation was prepared by Drs. Billings and Mitchell, which scheme has been carried out in the Laboratory of Hygiene of the University of Pennsylvania, by Dr. D. H. Bergey, assisted at times in the chemical work by Dr. Hill S. Warwick, and in some of the pathological investigations by Dr. Ingersoll Olmsted, and under the general supervision of Dr. A. C. Abbott, First Assistant in the Laboratory, to whom thanks are due for many valuable suggestions during the progress of the work. From time to time Dr.

Bergey's notes on the results of his experiments have been submitted to Drs. Billings and Mitchell, who have suggested modifications or new experiments as the work progressed. This report is based on these notes, and accompanying tables and charts, given in the Appendix.

The effects produced on animals and men by an atmosphere contaminated with their exhalations, and with particulate matters derived from their bodies or their immediate surroundings, may be divided into acute and chronic. The acute effect may be death in a few minutes or hours, as shown by the results observed in the Black Hole of Calcutta, in the steamer *Londonderry*, and in many of the experiments referred to in this report, or it may be simply great discomfort, especially in those unaccustomed to such conditions.

The chronic effects include the favoring of the action of certain specific causes of disease commonly known as contagious, if these are present, and perhaps also a general lowering of vitality.

The statistical evidence collected by the English Barrack and Hospital Commission (1)* as to the effects of insufficient ventilation upon the health of soldiers in barracks, published in 1861, showed that men who live for a considerable portion of their time in badly ventilated rooms have higher sickness and death-rates than have those who occupy well ventilated rooms, other conditions being the same; and this has also been found to be true with regard to monkeys and other animals. It is evident, however, that in a room occupied by animals or men there are many sources of impurity besides the exhaled breath, and it is still a question whether the expired air contains substances injurious to life, excluding carbonic acid.

The widely divergent results obtained and conclusions reached by different investigators during the last ten years as to whether the exhaled breath of men and animals contains a peculiar volatile organic poison, have made it desirable to repeat and vary such experiments in order, if possible, to settle this important point. The chemical analyses of the air of overcrowded rooms, and the experiments upon animals with various proportions of carbonic acid, made by many investigators, indicate that the evil effects observed are probably not due to the comparatively small proportions of carbonic acid usually found under such circumstances.

It was shown by Leblanc (2), in 1842–43, that an animal can breathe an atmosphere containing as much as 30 per cent. of carbonic acid for three-quarters of an hour, provided that the percentage of oxygen was 70, and then quickly recover from the depression induced by this mixture after removal to the normal atmosphere. He also demonstrated that under the conditions in which the quantity of

---

* The numbers in parentheses refer to the bibliographical list appended to this report.

carbonic acid rises perceptibly in theatres, etc., the reduction of oxygen is quite insignificant, and that the proportion rarely falls below 20 per cent.

Regnault and Reiset, (3), in 1849, also found that when sufficient oxygen is supplied to an atmosphere quite rich in carbonic acid, an animal can still live in it. Friedländer and Herter (4) found that the breathing of an atmosphere containing 20 per cent. of carbonic acid for an hour produced no symptoms of depression, but caused stimulation of the respiratory centres and an increased activity of the heart.

Claude Bernard (5), in 1857, experimented with animals confined in atmospheric air and in mixtures both richer and poorer in oxygen than atmospheric air. A small bird placed in a bell glass of a little more than two litres' capacity, containing a mixture of 13 per cent. carbonic acid, 39 per cent. oxygen, and 48 per cent. of nitrogen, died in two and one-half hours. He demonstrated that carbonic acid is not poisonous when injected under the skin of animals—as much as one litre injected under the skin of a rabbit producing no ill effects. No ill effects followed the injection of the gas into the jugular vein and into the carotid artery. An atmosphere of equal parts of oxygen and nitrogen had no effect upon an animal confined in it, while an atmosphere composed of equal parts of carbonic acid and of oxygen produced immediate death in the animal placed in it. He explains the poisonous effects of carbonic acid when respired to be due to the fact that it deprives the animal of oxygen. Similar results were reported by Valentin (6) and by Paul Bert (7).

Richardson, in 1860–61, (8), found that a temperature much higher or lower than 20° C. had the effect of shortening very considerably the lives of animals confined in an unventilated jar, and that these effects were more marked when the animals were confined in an atmosphere richer in oxygen than air, in which case he found that by passing electric sparks from a frictional machine through the fatal air (having previously deprived it of its carbonic acid) it was again made capable of supporting life, from which he concluded that the oxygen is "devitalized" during respiration, and that the electric spark has the faculty of revitalizing it.

Von Pettenkofer, in 1860–63, (9), showed that the symptoms observed in crowded ill-ventilated places were not produced by the excess of carbonic acid, nor by a decrease in the proportion of oxygen in the air: neither of these being sufficient in our dwellings, theatres, etc., to produce toxic effects. He did not believe that the impure air of dwellings was directly capable of originating specific diseases, or that it was really a poison in the ordinary sense of the term, but that it diminished the capability of withstanding the influence of disease-producing agencies on the part of those continually breathing such air, and laid down the rule, which has been accepted and taught by sanitarians for thirty-five years, that the proportion of carbonic acid in the atmosphere of inhabited places affords a safe indication as to the amount of the other impurities resulting from respiration and other exhalations from the bodies of the occupants.

Hammond, in 1863, (10), reported experiments in which he sought to remove the carbonic acid and moisture, and to supply fresh air as fast as it is needed to take the place of the carbonic acid removed, thus leaving the "organic matter" to accumulate in the vessel. For this purpose he confined a mouse in a large jar, in which were several sponges saturated with baryta-water, by which the carbonic acid was removed as fast as formed. Fresh air was supplied as fast as required by means of a tube communicating with the bell jar and closed by water in the bend of the tube, which acted as a valve. As the air in the bell glass was rarefied by respiration and absorption of the carbonic acid, fresh air flowed in from without, while the arrangement of the tube prevented the air of the bell glass from passing out. The watery vapor exhaled by the animal was absorbed by two or three small pieces of chloride of calcium. The mouse died in forty minutes. The observation was repeated many times, and death ensued invariably in less than an hour. On causing the vitiated air to pass through a solution of permanganate of potash the presence of organic matters in large quantity was demonstrated.

Ransome, in 1870, (11), reported a series of very interesting investigations upon "Organic Matter of Human Breath in Health and Disease." By condensing the aqueous vapor of the human breath and analyzing it by the Wanklyn and Chapman method, he found that "in ordinary respiration about 0.2 g. of organic matter is given off from a healthy man's lungs in 24 hours," while in the air expired by persons affected with certain diseases, he found great variations in the amount of organic matter, the amount being greatest in a case of phthisis complicated with Bright's disease.

Smith (12) employed a lead chamber in his investigations upon the question whether human lungs give off any poisonous agent other than carbonic acid. He found the pulse to fall from 73 to 57 beats per minute, and the number of respirations to rise from 15.5 to 24, as the carbonic acid in the atmosphere increased from .04 to 1.73 per cent. during four hours. When the proportion of carbonic acid rose to 3 per cent. there appeared great weakness of the circulation with slowing of the heart's action, and great difficulty in respiration. He believed that these results should be attributed to other conditions rather than to the excess of carbonic acid, because he found later that it was only when lamps became dim in an atmosphere

—indicating a proportion of about 10 per cent. of carbonic acid present that the respiration became difficult.

Seegen and Nowak, in 1879, (13), believed they had demonstrated the presence of poisonous organic matter in the expired breath, but the quantity found was so small that they failed to determine its exact nature and properties.

Hermans, in 1883, (14), was unable to detect any organic matter in the atmosphere of a tin cage in which several persons had been confined for a number of hours, and found that an atmosphere containing from 2 to 4 per cent. of carbonic acid and 15 per cent. of oxygen was not toxic.

Brown-Séquard and d'Arsonval, in 1887, (15), reported that the air expired by men and dogs in a state of health has the power of producing toxic phenomena; citing three series of experiments on rabbits where such phenomena were observed. In the first series they injected into the vascular system of a rabbit 4 to 6 c. c. of fluid obtained by injecting from 15 to 25 c. c. of pure filtered water into the trachea of a dog. In a second series, from 6 to 7 c. c. of a liquid obtained by condensing the moisture in the exhaled breath of a man, were injected into the aorta, or into a vein, of a rabbit. In the third series from 4 to 6 c. c. of a liquid, obtained by condensing the moisture in the exhaled breath of a tracheotomized dog, were used. The condensed liquid thus obtained was filtered and then injected either into the jugular vein or the carotid artery.

The symptoms observed were dilatation of the pupils and increase of the heart-beat to 240, 280, or even 320 per minute, lasting for several days or even weeks. The temperature remained normal; the respiratory movements were generally slowed; and usually there was observed paralysis of the posterior members Choleraic diarrhœa was invariably present. Death usually took place in a few days, or at the farthest in four or five weeks. As a rule, it appeared that larger doses caused labored respiration, violent retching, and contracted pupils. A rapid lowering of temperature, 0.5 ° to 5.° C., was sometimes observed. The appearances that presented *post mortem* were much like those observed in cardiac syncope.

They believed they had discovered a volatile organic poison in the exhaled breath and the moisture condensed from it. This poison they believed to be of the nature of an organic alkaloid, or a ptomaine not unlike Brieger's ptomaine (16).

In further reports, in 1888, (17), they state that none of eleven rabbits in which the condensed pulmonary vapor had been injected into the vascular system in doses of 12 to 30 c. c. survived, but of eight rabbits receiving an injection of from 4 to 8 c. c., three were living after the lapse of from four to five weeks, but were then weak. When the fluid was injected under the skin of the thorax and [illegible] rabbits died rapidly. The results were much the same as [illegible] reported in other cases. The quantity of the condensed liquid injected in these cases was: 20 c. c. in one case, 25 c. c. in three cases, 31 c. c. in one case, 40 c. c. in one case, and 44 c. c. in another case. After death, considerable congestion of the viscera was noted, especially of the lungs. No appearance of [illegible] was noted. The brain and its membranes were congested, but without effusion. The condensed liquid turns concentrated sulphuric acid yellow. [illegible] is reduced by ammoniacal nitrate of silver solution as well as by chloride of gold. After boiling in a closed vessel it is still toxic, showing that the poison is not a micro-organism. The boiled lung liquid poisons with more rapidity than that which has not been sterilized, and may kill a pigeon and a guinea-pig as well as a rabbit; it may kill by being injected into the rectum or into the stomach; a guinea-pig two months old was killed within twelve hours by an injection of 3 c. c. into the peritoneal cavity. If injected into the lungs this liquid produces rapid congestion followed by true inflammation and red hepatization.

In an experiment with two dogs it was arranged that one breathed ordinary air and the second inhaled air which came from the lungs of the other. The dogs were of the same weight, 15 kilograms. The experiment continued for six hours and forty minutes. No appreciable or immediate consecutive accidents were produced.

In a second experiment the pulmonary liquid was collected from dogs through a tracheotomy tube to exclude impurities furnished by the mouth. The air inhaled was first washed to remove dust. The moisture in the air expired was condensed, and the liquid collected in a flask surrounded by ice. At the moment of injection this liquid was filtered, and was then injected at the temperature of the laboratory, about 12° C. If the animal was kept immovable from 12 to 16 hours, inflammation of the air passages was produced. The liquid of the first hours came from a thoroughly sound lung, and in the later hours from a diseased lung. The two were collected separately and tried separately. For one kilogram of the animal, for each hour, the mean quantity of fluid obtained was 0.38 grammes, varying from 0.28 to 0.48 grammes. It was greater in the beginning and lessened the longer the animal was kept in a fixed position. It was injected into the marginal vein of the ear of a rabbit by means of a syringe, 75 c. c. being injected. When the injection did not exceed 40 to 50 c. c. the time occupied by the injection was from 6 to 15 minutes. Experiments made by injections upon the dog were negative without exception. Experiments made upon the rabbit produced lesions, but the relation between these and the injections was uncertain.

Dastre and Loye, in 1888, (18), reported that they had exposed one dog to the expired breath of another for six hours without noting any effects. They inoculated animals with the condensed moisture of respiration, as follows:

5 rabbits,	each	33	to	75	c. c.	of the	fluid.	Results	negative.
2 guinea-pigs,	"	5	"	7	"	"	"	"	"
2 dogs,	"	30	"	53	"	"	"	"	"
2 frogs,	"	2	"	3	"	"	"	"	"
2 rabbits,	"	50	"	100	"	"	"	Died.	
A young dog,				30	"	of water.		"	

They found that 50 to 70 c. c. of the condensed fluid of respiration (20 to 35 c. c. per kilo.) could be injected into the veins of the ear of a dog without producing any of the symptoms reported by Brown-Séquard and d'Arsonval. They observed one death during the injection of 190 c. c. (60 c.c. per kilo.), yet by control experiments with water they obtained a more remarkable result—a rapid death from the injection of 30 c. c. of distilled water (25 c. c. per kilo.).

Russo-Giliberti and Alessi, in 1888, (19), reported experiments confirming the results obtained by Dastre and Loye.

Wurtz, in 1888, (20), attempted to obtain the "ptomaine" of Brown-Séquard and d'Arsonval from the fluid condensed from expired air. By expiring through a 1 per cent. solution of oxalic acid he obtained, besides ammonia, a volatile organic base which was precipitated by Bouchardet's reagent and by potassio-mercuric iodide. With platinic chloride it formed a double salt, crystallizing in short needles, and a soluble salt with auric chloride. When heated to 100° C. it gave off a peculiar odor. This basic substance, he thought, might be regarded as a leucomaine.

Brown-Séquard and d'Arsonval, in 1889, (21), reported a new form of experiment by means of which they obtained additional evidence in support of their former statements. The new form of experiment consisted in confining animals (rabbits) in a series of metallic cages connected by means of rubber tubing, through which a constant current of air is aspirated. The animal in the last cage of the series receives air that has traversed the entire series of cages, and is loaded with the impurities from the lungs of the animals in the other cages. This animal succumbs, after a time, to the atmospheric conditions present. After another interval of some hours, the animal in the next to the last cage also dies; the first and second animals usually remaining alive. They could not attribute the death of these animals to excess of carbonic acid in the atmosphere of the cages, because they rarely found more than 3 per cent. of this gas in the last jar with small animals, or 6 per cent. with larger animals. On placing absorption tubes containing concentrated $H_2 SO_4$ between the last two cages, the animal in the last cage remained alive, while that in the cage before it was the first to die. They concluded from these facts, that the death of the animals was produced by a volatile poison, which poison is absorbed by the H_2SO_4, which thus saves the life of the animal in the last cage.

They stated (22) that any alkali used to absorb carbonic acid from expired air would also change the organic poison, and proposed an apparatus by means of which the organic poison should be supplied to the fresh air entering the jars by volatilizing it from fluid condensed from the expired air.

Von Hofmann-Wellenhof, in 1888, (23), found that when he injected large quantities of the condensed fluid of respiration at 12° C., instead of at 37° C.—intravenous injection,—a resemblance of the results obtained by Brown-Séquard and d'Arsonval was produced. Under such circumstances he observed muscle weakness, slowing of respiration, fall of temperature, and dilatation of the pupils, though the animals remained alive. He injected 10 rabbits with 6 to 30 c. c. of the fluid warmed to the body temperature, all the results being negative. Three other animals were injected in the jugular vein—one receiving 28 c. c. of the fluid, another 25 c. c. of distilled water, and a third 50 c. c. of distilled water. There was no difference in the symptoms noted in the animals. He noticed symptoms of depression only after injecting 50 c. c., or more, of the fluid. In a series of 17 experiments with inoculations of from 30 to 50 c. c. each of the fluid, in 12 there appeared haemoglobinuria; 6 of these died. As the result of his experiments, he concluded that the existence of a volatile poison in the expired air of healthy human beings has not been demonstrated by his experiments; this being a direct contradiction of the results of Brown-Séquard and d'Arsonval, as were also those of Dastre and Loye.

Uffelmann, in 1888, (24), found that there was a perceptible increase in organic matter in the atmosphere of a sleeping-room occupied by several persons for some hours, increasing in amount with the length of time the room was occupied.

Lehmann and Jessen, in 1890, (25), collected 15–20 c. c. of condensed fluid per hour from the breath of a person exhaling through a glass spiral laid in ice. The fluid was always clear as water, odorless, and of neutral reaction. Nessler's reagent showed the presence of ammonia constantly, with good teeth but little, sometimes merely a trace, with bad teeth, more, though never more than 10 mg. of NH_4Cl in one litre. Traces of HCl were also constantly found. A small sediment remained on evaporation, ranging from 39 to 86.1 mg. per litre of fluid. This they believed to originate from the glass vessel; being probably calcium oxalate. They tested its reducing power upon solution of permanganate of potash, making two control determinations. The first determination showed 3.6 mg. of O for the oxidation of 1 L.; the second, 4.2 mg. of O. They were unable to obtain any alkaloid reaction in the condensed fluid, or in its distillates, by means of $PtCl_4$, $AuCl_3$, KCdI, KBiI, KI, Bouchardet's reagent, K_2CrO_6, picric acid, metawolframic acid, or phosphowolframic acid. Only sublimate gave at times an opalescence which, like the yellow coloration of the Nessler reagent, pointed to traces of NH_3. Neither could they succeed, according to the method of Würtz, in obtaining a lime or oxalic acid-free filtrate. The ammoniacal silver solution, according to Brown-Séquard and d'Arsonval's method, failed to give the desired reaction—remaining clear. They confined a man, clothed in his working clothes, in a zinc cage for about one-half an hour, then allowed a boy and girl to inhale the air from the cage. No ill effects, except increase of respirations to 30 and 40 per minute, were noticeable. They had complete negative results from inoculations of condensed fluid into animals.

Lipari and Crisafulli, in 1889–90, (26), reported results which were in accord with those of Dastre and Loye, and directly opposed to those of Brown-Séquard and d'Arsonval. They could find no organic principle possessing toxic properties in the expired breath of healthy persons.

Margouty, in 1891, (27), reported the results of experiments similar to those of Hammond, and also of experiments in injecting fluid condensed from expired air into animals. His results did not correspond to those reported by Hammond, and there was no evidence of toxic properties in the injected fluids.

Haldane and Smith, in 1892, (28), published an account of experiments in which an air-tight chamber, 6 feet 2 inches high, 2 feet 11 inches wide, and 3 feet 11 inches long, was employed. Samples of air for analysis were drawn off through a tube placed in the wall of the chamber, about three feet from the floor. When one person remained in this chamber until the vitiation was from ten to twenty times as great as in the most crowded and worst ventilated public buildings, there was no perceptible odor or sense of oppression. Air vitiated to such an extent as to completely prevent a match from burning had no appreciable effect upon the subject of the experiment. In other experiments hypernœa and other phenomena produced were apparently due to the increased proportion of carbonic acid.

With rabbits weighing 1800 grammes, hæmaturia was produced when the amount of boiled distilled water injected passed beyond 100 c. c., and, therefore, 80 c. c. were taken as the maximum dose.

To obtain the condensed liquid from the lungs, a man expired through a Liebig condenser, in the jacket of which was flowing a stream of ice-cold water. The condensation liquid was collected in a flask, the bulb of which was buried in ice; and when the required amount (80 c. c.) had been obtained, it was at once injected into the subcutaneous tissue of the back. Six rabbits were thus injected, each with 80 c. c. of the fluid, with no evident disturbance of health in any of them; 80 c. c. to a rabbit corresponds to a dose of about 3 litres to a man. They also repeated the experiments of Brown-Séquard and d'Arsonval in supplying to the animals air charged with organic matter drawn directly from the lungs of other animals. Two large rabbits were placed in an air-tight chamber and a current of air drawn through this was supplied to two young rabbits under observation; no effect was produced.

Merkel, in 1892, (29), reported an experiment in which four air-tight glass vessels, of 1½ litres capacity, were connected by means of glass tubes; a mouse being placed in each vessel. Between the third and fourth vessels a Geissler absorption tube, containing sulphuric acid, was interposed. Air was now drawn slowly through the vessels by means of an aspirator, so that the second mouse breathed the air from the first, the third from that of the second, etc. The result was, just as in the experiment of Brown-Séquard and d'Arsonval, that the mouse in the third vessel died first, after 16–20 hours, while that in the fourth vessel remained alive.

The conclusion is drawn that, as the fourth mouse remained alive, the death of the third cannot have been due to excess of carbonic acid, or deficiency of oxygen in the air, but must have been caused by the presence of some volatile substance which is absorbed or destroyed by sulphuric acid.

The symptoms presented by the mice before death were at first restlessness and gradually increasing acceleration of respiration, afterward slowing of respiration, and finally spasmodic deep respirations, becoming constantly less frequent until the advent of death. The proportion of carbonic acid in the air led through the glass vessels was not poisonous; it amounted in the highest case to 1.5 per cent.

Merkel also conducted the expired breath through HCl with the idea of combining the organic matter with it, and believed he was successful, but the quantities of the "salts" produced were so small that determination of their chemical nature was impossible. His experiments upon animals with this body, obtained from its combination by neutralization of the acid, gave negative results.

He concludes that the expired breath of healthy persons contains a volatile poison in extremely small quantities; being probably a base which is poisonous in its gaseous state, but loses its toxicity after combination with acids. His belief in the toxicity of the organic matter contained in the expired breath of human beings is based solely upon the results he obtained in the "Brown-Séquard and d'Arsonval" experiment.

Haldane and Smith, in 1893, (30), repeated the "Brown-Séquard" experiment, using five bottles, each of a capacity of 1 to 1½ litres, connected by means of tubes. A mouse was placed in each bottle and ventilation established through the whole system by means of a filter-pump; a small meter being placed between the last bottle and the pump. Specimens of air leaving the last bottle were drawn off at intervals for analysis. Full-grown mice were used. The mice in the last two bottles were exposed to the full effect of the vitiated air for 53 hours without detriment.

In a second experiment an absorption tube containing pumice-stone saturated with sulphuric acid was placed between the last two bottles. This experiment was continued for thirty hours; no serious effects were observed. The amount of ventilation furnished was from 12 to 24 litres per hour. The mice remained normal after having been in the bottle three days and the percentage of carbonic acid in the last bottle had varied from 2.4 to 5.2, averaging about 3.

They state that these experiments, like their former ones on rabbits and man, are distinctly against the theory that a volatile poison, other than carbonic acid, exists in the expired air.

Beu, in 1893, (31), reported the results of experiments, made under the direction of Uffelmann, in which the condensed moisture of expired air was collected by the methods usually employed, taking the precaution to cleanse his apparatus with solution of $KMnO_4$ and distilled water, and likewise sterilizing the apparatus before it was brought into use. The saliva is collected in a Woulff bottle attached before the condenser. The amount of air expired, measured by a gas meter, was found to be 3000 litres in eight hours, from which he collected 100 c. c. of fluid. A distinct ammonia reaction was obtained upon the addition of Nessler's reagent. Nitrate of silver failed to show the presence of chlorine.

Its reducing power upon solution of permanganate of potash showed 50 mg. of oxygen necessary to oxidize one litre of fluid, or 15 mg. in 24 hours, which denotes 0.0017 mg. per litre of expired air. The alkaloid reaction with $AuCe_3$, KI, phosphomolybdate of potash, gave negative results.

He expired 500 litres through 150 c. c. of a 1 per cent. solution of HCl—then evaporating to dryness on the water-bath, a yellowish-brown deposit remained. This deposit, dissolved in distilled water, formed a fatty layer on the surface of the slightly yellow fluid. The whole quantity, 1.5 g., was warmed to the body temperature and injected under the skin of the back of a white mouse without producing observable symptoms. This fluid had a distinct odor not comparable to anything.

He next confined a mouse in a sealed glass vessel, having a globe attached with potash solution to absorb the carbonic acid; 3200 expirations of air were conducted into the glass vessel during the three hours—no effect noticeable. In a second experiment the carbonic acid was not absorbed, the experiment lasting four hours—no effect.

He repeated the "Brown-Séquard" experiment, using white mice in four glass cages. The death of the animals, he believes, was due to changes in the temperature and the accumulation of moisture in the jars. He believes the protection afforded by H_2SO_4 in Brown-Séquard and d'Arsonval's experiments was due to its abstraction of the moisture from the air. An acute poisoning through the organic matters contained in the expired air he believes to be impossible, or at least as not shown by anything in his experiments.

Rauer, in 1893, (32), used white mice confined in glass vessels of about 1½ litres capacity, the bottom of which was covered with oats. The cork was perforated by three tubes; one of these passed down near the bottom of the vessel and served for the entrance of the air; the second terminated just below the cork and served for the exit of air; and the third extended down to about the height of the animal but was usually closed, this was only used for the removal of air for its chemical examination. In the beginning, thermometers and hygrometers were used in the vessels, but they were found to be unimportant and were abandoned. The whole apparatus was connected with a large aspirator.

In an experiment with five animals and a ventilation of four litres per hour, the carbonic acid was found to amount to 9.3 per cent. after five hours. In another experiment with six animals and with a ventilation of 2½ litres per hour, he inserted four absorption tubes with soda-lime between the last two jars, and a Geissler tube containing concentrated H_2SO_4 between the fourth and fifth. The sixth animal remained alive while the fifth died earlier than the fifth animal in the first experiment. He concludes that there is no organic poison in expired air, death being due to the excess of carbonic acid in the atmospheres of the jars.

Sanfelice, in 1893, (33), reported that he had repeated the "Hammond" experiment, using a flask of about 5 litres capacity, the animal dying in six or seven hours. He is undecided as to the existence of a volatile expiratory poison, though he thinks that other factors, for instance, heat radiation, have an important influence upon the results.

Lübbert and Peters, in 1894, (34), reported that they had repeated the "Brown-Séquard" experiment, placing a guinea-pig in each of a series of four flasks. Between the third and fourth flasks they placed a combustion tube through which the air coming from the third flask was conducted, passing over red-hot cupric oxide, to remove the organic matter. Before reaching the fourth flask, the air was again cooled by conducting it through a cylinder surrounded with ice. In this manner all moisture contained in the air was condensed. From this cylinder the air passed through a series of twelve U-tubes, each made from a piece of tubing 80 cm. in length and of 2 millimeters internal diameter. During its passage through these U-tubes the air assumed a temperature of about 18° C. as it entered the fourth flask. The results obtained by this arrangement substantiated the conclusions they had formed from conducting the experiment in the ordinary manner, that the cause of death was traceable to the high per cent. of carbonic acid. The removal of the organic matter by combustion failed to save the life of the animal in the last jar when the carbonic acid had increased to 11 or 12 per cent. After the absorption of the carbonic acid by means of soda-lime the last animal remained alive. They conclude, therefore, that the poisonous expiratory poison of Brown-Séquard and d'Arsonval does not exist, but that death is produced by the excess of carbonic acid in the flasks.

Brown-Séquard and d'Arsonval, in 1894, (35), reported further experiments, and at the same time gave fuller details as to all their experiments and the apparatus employed. They had inoculated over one hundred animals with the condensed fluid of respiration and believed in the truth of their former statements as firmly as ever. They could not understand the failures on the part of the other experimenters. They emphatically reaffirm that the expired breath of man and animals contains a volatile organic poison producing the results reported by them, and that these results are not produced by excess of carbonic acid or deficiency of oxygen in the air.

From the foregoing summary of the reports of different experimenters, it will be seen that widely different results have been reported by them, but that the majority of the later investigators agree in denying that the exhaled breath of healthy human beings or of animals contains a poisonous organic alkaloid, or any poisonous product other than carbonic acid, yet in any case positive results require an explanation which shall account for the facts.

DR. BERGEY'S EXPERIMENTS.

The first experiments made by Dr. Bergey were to ascertain whether the condensed moisture of air expired by men in ordinary, quiet respiration, contains any particulate organic matters, such as micro-organisms, epithelial scales, etc. The test for micro-organisms was made by having an adult man expire for from twenty to thirty minutes through sterilized melted gelatin, which was then preserved as a culture for from twenty to thirty days. In the first trial, six, and in the second two colonies of common air organisms developed; but when special care was taken to thoroughly sterilize the vessels used, the result was that in two consecutive trials the gelatin remained sterile. Epithelial scales and other particulate matters were sought for by condensing the vapor of the exhaled breath and examining the product with the microscope, with and without the use of stains. In six preparations thus examined no bacteria or epithelial cells were found. This result was to be expected, since neither bacteria nor wetted particles pass into the air from the surface of fluids, or from moist surfaces, unless the air currents are sufficiently powerful to take up particles of the liquid itself in the form of spray.

Abbott (36), in his paper on "Sewer-Gas," reports some experiments made to determine the possibility of conveying micro-organisms from liquid culture media by means of a current of air bubbling through such media; also by means of ordinary baker's yeast inoculated into media containing from 1 to 5 per cent. of glucose. No bacteria were carried from the culture by the exploding air-bubbles produced by the yeast, but a current of air equal to 3½ litres in six hours, bubbling through a liquid culture, carried with it some of the organisms in the culture.

The determinations of ammonia in the condensed fluid of expired air, the estimation of its reducing power upon solution of permanganate of potash, and its reaction with various reagents (see Appendix, Section II.), were made with fluids collected from a healthy man, from a man with a tracheal fistula following excision of the larynx, the expired air not coming in contact with the mouth or the pharynx, and from a man suffering from well marked tuberculosis of the lungs. In each case the amount of ammonia and of albuminoid ammonia in the fluid was very small, as shown by Table B in the appendix, the average being, in grams per litre of fluid:

	Free Ammonia.	Albuminoid Ammonia.
Healthy man	.019	.081
Man with tracheal fistula	.00046.	.00036.
Consumptive	.003.	.0034.

The oxidizable matter in these fluids, as shown by their reducing power on a solution of permanganate of potash, was determined, and the details are given in Table C in the appendix. The average results, stated in milligrammes of oxygen consumed per litre of condensed fluid, are as follows: Healthy man, 10.72; man with tracheal fistula, 13.49; consumptive, 19.34. The high average for the man with the tracheal fistula is due to a single observation, for which the figure was 24.916. Omitting this, the average for the three other observations would be 9.68.

The average for five specimens of fluid condensed from the expired air of a healthy man four hours after he had taken a meal was 11.98, while the average for six specimens from the breath of the same man half an hour after the meal was only 3.86. For two specimens from the same man collected three and a half and four hours after a meal, but just after the mouth had been thoroughly rinsed with warm water, the average was 2.49. These results indicate that the ammonia and oxidizable organic matter in the condensed fluid were, to a large extent, due to products of decomposition of organic matters in the mouth. The well known fact that the amount of oxygen absorbed and of carbonic acid given off varies according to whether the person is fasting or has recently taken a meal, may possibly be in part due to the same cause, but the results obtained by Birkholz (37) indicate that it can only be in part. Ransome (11) reports no marked difference in the amount of ammonia, or of oxidizable organic matter, as determined by the permanganate test, contained in the fluids collected from the exhaled breath soon after a meal and in that collected from a fasting person. Beu (31) found a much higher proportion of oxidizable matter in the fluid condensed from his own breath (50 mg. of oxygen required per litre of fluid) than was found in Dr. Bergey's experiments. His results indicated the exhalation of 15 mg. of organic matter in 24 hours, the corresponding figure from Ransome's results being 20 mg. About 12 c. c. of fluid was collected from about 335 litres of air expired per hour, being nearly equal to the results obtained by Beu (31), who condensed 100 c. c. of the fluid from three cubic metres of air expired in eight hours.

Renk (38, p. 162) gives a table showing that in an average quantity of 9000 litres of air expired in a day by a healthy man, the amount of moisture may be from 200 to 400 grammes, depending on the temperature and relative moisture of the inspired air. With air containing 50 per cent. of moisture inspired at 25° C., the amount of moisture is 293 grammes, or about the result given by Beu, referred to above.

Lehmann and Jessen (25) found that between 3 and 4 mg. of oxygen were required to one litre of fluid to effect oxidation, and note that more ammonia was present in the fluid collected from a person with decayed teeth than in that obtained from a person whose teeth were sound. The very considerable differences in the amounts of ammonia and of oxidizable matter found in the fluids condensed from expired air by different experimenters, and by the same experimenter in fluids obtained from the same person at different times, are probably due to several different causes and their combinations. The amount of fluid condensed per litre of expired air varies from .003 to .004 c. c. The soundness and cleanliness of the mouth and teeth influence the amount of ammonia and oxidizable matter expired. Variations in the amount of organic matter contained in the inhaled air may possibly influence the result, but this influence must be slight. Ransome's results indicate that the age, health, and vigor of the person may affect the amount of organic matter exhaled, and Dr. Bergey's experiments with the fluid obtained from the consumptive patient show that a smaller proportion of ammonia and a larger amount of oxidizable matter were present in it than in the fluid collected from a healthy man. It should be remembered, also, that it is extremely difficult to obtain accurate results in quantitative determinations of such very minute amounts of ammonia and oxidizable matters as are found in expired air, and a part of the differences in results obtained is no doubt due to unnoted differences in the details of the experiments.

The results of tests for the presence of an organic alkaloid in the condensed fluids obtained by Dr. Bergey were negative, corresponding to those reported by Lehmann and Jessen (25) and by Ben (31).

The results of attempts to condense the moisture of the air in the hospital ward (Appendix, III., 3) were not satisfactory, and the determinations of ammonia in the fluid obtained are not comparable, except that they show that the placing of a dust filter in front of the condensing apparatus causes a marked reduction in the proportion of ammonia in the condensed fluid. The evaporation equalled the condensation except on days when the external air was saturated with moisture, hence no moisture was collected on clear days, but on such days some dust particles may have accumulated in the apparatus which had no filter.

Some experiments were made to determine the amount of oxidizable matters in atmospheric air, the results of which are given in Table F, in the appendix. These results differ greatly, some showing a mere trace of organic matter, others showing an amount which consumed .204, .340, and .558 grammes of oxygen per 1000 cbm. of air. The great differences in the amount of ammonia in air found by different observers as tabulated by Renk (38, p. 40), and as reported by Remsen (39), Miss Talbot (40), Nekam (41), Archarow (42), and Abbott (36), while evidently in part due to differences in methods of experiment, must be more largely due to differences in the amount of organic dusts in the air in different places or in the same place at different times, than to differences in the amount of ammoniacal gases or organic vapors in the air, and the same is true with regard to the differences in the amount of oxidizable organic matter in the air reported by Angus Smith (12), Carnelly and Mackey (43), and others.

Several series of experiments were made to determine the nature of the gaseous mixtures in which small animals die with symptoms of asphyxia. The first of these series were repetitions of the experiments reported by Hammond and described above. Mice and sparrows were used. The details are given in the Appendix IV., 1, and the results in Table G. It was found impossible, by Hammond's method, to absorb all the carbonic acid produced by an animal, and it will be seen by Table G, that at the time of death of the sparrows, the carbonic acid had increased until it formed from 12.27 to 14.08, or an average for eight experiments of 13.24 per cent. of the air, while the oxygen had diminished to from 3.25 to 5.61, or an average of 4.67 per cent. of the air. The symptoms observed were those produced by insufficiency of oxygen, and there was no evidence that death was due to organic matters in the air. The duration of life in the animals confined was from three to six hours, being much longer than that reported by Hammond using a slightly smaller vessel, viz. less than one hour, and corresponds to the results reported by Sanfelice (33), who found that the animals lived from six to seven hours. When the experiment was so modified that all the carbonic acid was removed from the air breathed by the animal—as described in the appendix, the animal did not die in seven hours, although the percentage of oxygen had been reduced to 18.35, as shown by Table H in the appendix. These experiments, therefore, furnish no evidence of the existence of an organic poison in the expired air, but the method of absorbing carbonic acid by an alkali is said by Brown-Séquard and d'Arsonval (22) to change the organic poison which they claim to be present, and hence these experiments are not conclusive on this point.

A series of experiments was also made upon mice and sparrows to determine the time required to produce death by asphyxia when the animal is confined in a jar of known capacity, when no provision is made for removing carbonic acid and moisture, or for supplying fresh air, and also to determine the proportions of carbonic acid and of oxygen existing in the enclosed air at the time of death. In connection with these experiments it was also sought to determine the influence which high or low temperatures of the air would have on the result. The data derived from these experiments are shown in Table I in the Appendix.

A mouse weighing 21 grams, placed in a jar of 1000 c. c. capacity at a temperature of 30 ° C., lived four hours; in a jar of 2000 c. c. capacity a similar mouse lived seven and a half hours; in one case when the room temperature was 25.5 ° C., in another case when the room temperature was 5 ° C. In the first case death occurred when the amount of carbonic acid was 12, and that of the oxygen 8.6 per cent. of the mixture; in the second case, the proportions were 13.2 per cent. of carbonic acid and 6.4 per cent of oxygen; and in the third case, 10 per cent. of carbonic acid and 9.2 per cent. of oxygen. There are considerable differences in susceptibility to the effects of an impure atmosphere in individual mice, but when a mouse is placed in a closed jar containing ordinary atmospheric air, the time required to produce death is usually that required to produce the proportions of carbonic acid and of oxygen indicated above, and, hence, is in proportion to the size of the jar. A mouse should live about twice as long in a jar of 2000 c.c. as in one of 1000 c. c., other conditions as to temperature, etc., being the same, and commencing with ordinary atmospheric air.

The duration of life in the experiments with atmospheric air in closed vessels, making due allowance for variations in the air volume, coincides quite closely with the duration of life in the "Hammond" experiment. The air analyses at death of the animals in the two forms of experiment, also gave very similar results. In comparing the results shown in Tables G and I, it is necessary to bear in mind the differences in the size of the jars and in the weight of the animals used in the several experiments. As a general rule, the animal dies when the carbonic acid has increased to between 12 and 13 per cent. and the oxygen has diminished to between 5 and 6 per cent. Is death due to the increase in the carbonic acid, or to the diminution in the oxygen, or to both?

Some data for answering this question are presented in Table L, which shows the results obtained by placing animals in gaseous mixtures containing various proportions of carbonic acid, oxygen, and nitrogen. The animals experimented on were mice, rats, rabbits, guinea-pigs, and sparrows. From this table it will be seen that the diminution in oxygen in the inspired air was the most important factor in producing death, and that so long as the oxygen is present in the proportion of 6 per cent. and upwards, carbonic acid may be present to the amount of 20 per cent. without causing death. When the carbonic acid forms much more than 20 per cent. of the mixture, say 30 to 40 per cent., the oxygen must form at least 12 per cent. to preserve life.

If the proportion of oxygen in the mixture be reduced, the duration of life is shortened, as will be seen from the following extract from Table L:

No.	Weight grams.	At beginning of experiment.			At end of experiment.			Duration of life.	Capacity of jar.
		CO_2 %	O %	N. %	CO_2 %	O %	N. %		
8	18	0	11.35	88.65	6.56	4.14	89.3	$3\frac{1}{2}$ hours.	2280 c. c.
9	15	0	11.35	88.65	7.43	3.58	89.0	$4\frac{1}{6}$ "	2280 "
10	17	0	11.35	88.65	7.52	3.16	89.2	$4\frac{1}{6}$ "	2280 "

In these experiments the proportion of oxygen was reduced to about one-half of that in the normal atmosphere, and the duration of life was also reduced about one-half. The jars were a little larger than those used in the experiments reported in Table I. The proportion of oxygen present at the death of the animal was between 3 and 4 per cent., or lower than in the cases reported in Table I, while the carbonic acid had increased to only about 7 per cent. instead of 12 per cent., as in Table I. The smaller proportion of carbonic acid here present seems to have allowed a greater reduction in the proportion of the oxygen. These results correspond with those obtained with mixtures of gases by Paul Bert (7, page 518), who concluded that carbonic acid when inhaled is really a poison, and with the results of the elaborate researches of Friedländer and Herter (14), which lead to the same conclusion.

In this connection the observations of Richardson (8) are of interest. His experiments were made chiefly with mice placed in jars having a capacity of 635 c. c. In such a jar containing ordinary atmospheric air at 12.8° C., a mouse weighing 18.8 grams became comatose in 1$\frac{5}{6}$ hours, which is, he says, the average duration of life under such conditions. At a temperature of 6.6° C., the animal dies in forty minutes. In an atmosphere of pure oxygen, at 6.6° C., the animal will live only two-thirds as long as in atmospheric air, while at a temperature of 21° C. it will remain conscious for three hours and lives twelve hours, and at 10° C. it remains conscious for two hours and lives three or four hours. With atmospheric air, the modifications, he says, are less distinctly marked.

The results of similar experiments made with air, and with different mixtures of gases, at different temperatures, are given in Table J in the Appendix. These results show that the duration of life, in confined places, is influenced to a very marked degree by temperature, and that this influence is independent of the richness of the air in oxygen. Experiments Nos. 3 and 17 noted in Table J indicate that an atmosphere consisting of 90 per cent. of oxygen and 10 per cent. of nitrogen does not support life quite as long as does ordinary atmospheric air when the temperature is 0° C., while at a temperature of 50° C. the atmosphere rich in oxygen supports life much longer than the ordinary atmosphere, as is shown by experiments Nos. 5 and 15 in the table. The gradual rise in temperature which must have taken place in the experiments previously referred to, was probably but a small factor in the results obtained, because, as shown in the tables for those experiments, the duration of life and the proportion of oxygen present at death bear a constant relation to each other. This they fail to do in the "Richardson" experiments.

The toleration which is acquired by an animal by prolonged sojourn in an atmosphere which is gradually becoming richer in carbonic acid and poorer in oxygen, makes it impossible to compare the results as to duration of life in such experiments with the results of experiments in which the animal is placed at once in an atmosphere containing abnormal proportions of these gases, so far as the effects of increase of carbonic acid and diminution of oxygen are concerned, but it is evident from the results reported in Tables I and J, that death does not occur in atmospheres in which the carbonic acid does not exceed 10 per cent. unless the oxygen is reduced to below 7 per cent. of the mixture.

A series of experiments was made by injecting into animals the fluid condensed from the air expired by healthy persons and by a man with a tracheal fistula, from whom it was possible to obtain such fluid without contamination from the exhalations from the mouth. The details of these experiments, and of the results obtained, are given in the Appendix, VI. The injections were made into the general circulation in rabbits, and into the peritoneal cavities of rabbits, guinea-pigs, and white rats, following the methods employed by Brown-Séquard and d'Arsonval (15) and by v. Hofmann-Wellenhof (23). The number of animals inoculated with the condensed fluid of respiration was thirteen, in four sets. The fluid was collected with the greatest care in a sterilized apparatus; subsequent cultures made from it indicating that it was sterile. It was warmed to about 35° C., before injection. The proportion injected, as compared with the body weight of the animals, was, in some instances, less than that used by Brown-Séquard and d'Arsonval, in others greater than the smallest quantities used by them with fatal effects. The results obtained, with the amount of fluid injected in each case, are shown in Table K, given in the Appendix.

In most of the animals no observable disturbance of health was produced, nor did this condition alter in the course of several months during which they were kept under observation. One rabbit died thirty-two days after having received an injection into its peritoneal cavity of 5 c.c. of fluid condensed from the breath of a man with tracheal fistula. The results of *post-mortem* examination showed focal necrosis in the liver, but no ecchymoses and hemorrhages in the lungs and intestines, such as are reported as a characteristic result of such injections by Brown-Séquard and d'Arsonval. Three other rabbits which had received injections of the condensed fluid, and had remained apparently perfectly well from six weeks to seven months, were killed and careful *post-mortem* examinations made. The results of these examinations showed that there was no special disease or degeneration in the organs of these animals.

The results of this series of experiments are, therefore, in accord with those reported by v. Hofmann-Wellenhof (23), and indicate that fluid condensed from the pulmonary exhalations of man has no toxic or specially injurious effect when injected into animals, and that there is no evidence that such fluid contains an organic poison.

The attempt to collect condensed moisture from the air of the hospital ward was but partially successful, as has been stated above, and a sufficient amount of the fluid to make injection experiments was not directly obtained. To overcome this difficulty the air of the ward was drawn over sterilized glycerine which was then diluted with distilled water, and the product injected into animals. The results are shown in Table E in the Appendix. Three of the animals thus injected died between four and six weeks later, but the *post-mortem* examinations failed to show any clear connection between the injection and the fatal result. As it was shown that the fluid collected and the dust in the ward contained several species of bacteria, including pathogenic forms, it was to be expected that more definite results would have been obtained, but the power of the cells and tissues to resist the pathogenic organisms was sufficient to prevent their action in each case, except, perhaps, in one, in which the abscess produced may have been due to pyogenic bacteria in the injected fluid.

A number of experiments were made in which animals, in a series of bell jars, were caused to breathe air which became more contaminated with the products of respiration as it passed through the series, being a repetition of the experiments of Brown-Séquard and d'Arsonval. The form of the apparatus used, and the details as to the results obtained in each of the thirty-three experiments of this kind, are given in the Appendix, VII. These experiments were performed on sparrows, mice, guinea-pigs, and rabbits.

It was very difficult to keep the apparatus absolutely air-tight, and, no doubt, some of the discrepancies in the results, at least for the earlier experiments, are due to slight leakage of air through some one or more of the numerous joints. The more concordant results in the later experiments indicate that these defects had been obviated.

In the great majority of cases death was evidently due to the diminution in the oxygen and increase in the carbonic acid—the proportions of these gases present in the jar when an animal died being about the same as in the experiments reported in Table 1, *i. e.*, the oxygen was reduced to between 4 and 6 per cent. and the carbonic acid increased to from 12 to 14 per cent. The mode of death of the animals was similar to that observed in slow asphyxia, and the results of careful *post-mortem* examination and microscopic investigation do not indicate the effects of any organic poison.

The insertion of absorption tubes containing caustic alkalies between the bell jars, to absorb the carbonic acid, as in experiments Nos. 6 to 14, and of concentrated sulphuric acid, as in experiments Nos. 15, 18, and 19, did not give results corresponding to those reported by Brown-Séquard and d'Arsonval.

In these experiments the animals were in an atmosphere of less pressure than the external air, the diminution amounting usually to about 2 mm. of mercury, but there is no reason to suppose that this exerted any influence upon the results obtained.

Experiments Nos. 17, 18, and 19 show that the mice became habituated, to a certain extent at least, to the conditions under which they were placed, and could live in an atmosphere which was almost immediately fatal to a fresh mouse placed in it. This had already been demonstrated by Bernard (5). In the case of several mice, this power to resist the foul atmosphere was preserved for from three to eight days after they had been removed from the jar, so that they had a certain degree of permanent immunity (See experiment 18, C.). Experiments Nos. 20 to 28 were made to see if it was possible to develop such an immunity, and the results obtained indicate such a possibility, but further investigation will be necessary to settle this important point. At present it is uncertain to what extent the immunity observed in a few mice was possessed by them before they were experimented on, or was produced by their first exposures to the vitiated atmospheres.

From the data accumulated with reference to the composition of the atmosphere in these bell jars by repeated analyses at short intervals, compared with the results reported by Brown-Séquard and d'Arsonval, it seems probable that the cases in which the last animal in the series survived some of the others, and a low percentage of carbonic acid was found in the jar, should be attributed entirely to defects either in methods of air analyses or in the apparatus, or in both. If, however, the life of the last animal was apparently saved by H_2SO_4 in Dr. Bergey's experiments, it was due to leakage in the connections from the increased resistance caused by the interposition of the absorption tube. This is an important fact, which is in direct opposition to the theory of Brown-Séquard and d'Arsonval with regard to the influence of the H_2SO_4 in the absorption tubes. The great differences in individual susceptibility of different animals must also be taken into account in considering the results of these experiments; for example, in experiment No. 11, sparrow No. 4 died when the percentage of oxygen was 9.34, and that of carbonic acid was only 2.79, while No. 5 lived until the percentage of oxygen was reduced to 3.53. In some mice there seems to be a very considerable immunity against the asphyxiating effect of an atmosphere poor in oxygen and rich in carbonic acid.

The duration of life of individual animals in experiments of this kind depends upon the size of the bell jars in relation to the size of the animal, on the amount of fresh air supplied, on conditions of temperature and moisture, and on individual peculiarities of the animal and it seems probable that variations in these factors will account for the different results obtained by different experimenters. The symptoms in the animals which died were those of death by slow asphyxia.

In experiment No. 33, with a series of six rabbits confined for forty-two days, the proportion of carbonic acid in the last two jars, for the greater part of the time, was between 4 and 7 per cent. and that of oxygen between 12 and 16 per cent. None of the animals died or were seriously ill. Those in the first three and in the fifth jar gained in weight, those in the fourth and sixth lost slightly in weight.

The results of blood-corpuscle counts made for five of these animals at the close of the experiment, and again thirty-eight days afterward, show an average increase during this period of 158,600 red, and 5,400 white corpuscles per cubic millimetre, an amount which has little significance. Microcytes were found in the blood of the animals immediately after the experiment, but none were found thirty-eight days later.

The organs of a number of the animals that died in these experiments were preserved in alcohol and examined microscopically. The changes noted *post mortem* were those of profound venous congestion of all the internal organs. The lungs were frequently so charged with venous blood that the portions preserved for microscopic examination failed to float in water. The right side of the heart was usually dilated with a large firm venous clot, the left ventricle was in most instances contracted. The liver, on incision, bled freely, as did also the kidneys and spleen, the blood being quite dark and venous. All the capillaries were unusually prominent, being filled with venous blood; this was particularly noticeable in the small intestine, and in the membranes of the brain.

Microscopic examination of the organs presented a picture coinciding with the gross *post-mortem* appearances. In the lungs the capillaries were found to be distended with blood, occluding in many cases the lumen of the alveoli and air cells, and presenting a typical picture of passive hyperæmia. In the liver, kidneys, and spleen, as well as in the intestines, the capillaries were likewise overloaded with blood. Pathological changes were but rarely noted, and some of these, such as slight proliferation of connective-tissue elements between the tubules of the kidney, and, in rarer instances, in the inter-lobular spaces of the liver, are such as are occasionally found in animals which have not been subjected to such conditions, and may, therefore, have existed in the animals at the beginning of the experiment. All the changes which were constantly present may properly be attributed to the action of the carbonic acid and the low percentage of oxygen in the atmosphere, interfering with the circulation and aëration of the blood. The lesions reported by Brown-Séquard and d'Arsonval as characteristic in such cases were not seen. No focal necroses or peculiar uniform degenerative changes were found. The results of these experiments, therefore, do not agree with those reported by Brown-Séquard and d'Arsonval—and furnish no evidence of the existence of an organic poison in the air expired by animals.

CONCLUSIONS

I. The results obtained in this research indicate that in air expired by healthy mice, sparrows, rabbits, guinea pigs, or men, there is no peculiar organic matter which is poisonous to the animals mentioned (excluding man), or which tends to produce in these animals any special form of disease. The injurious effects of such air observed appeared to be due entirely to the diminution of oxygen, or the increase of carbonic acid, or to a combination of these two factors. They also make it very improbable that the minute quantity of organic matter contained in the air expired from human lungs has any deleterious influence upon men who inhale it in ordinary rooms, and, hence, it is probably unnecessary to take this factor into account in providing for the ventilation of such rooms.

II. In ordinary quiet respiration, no bacteria, epithelial scales, or particles of dead tissue are contained in the expired air. In the act of coughing or sneezing, such organisms or particles may probably be thrown out.

III. The minute quantity of ammonia, or of combined nitrogen, or other oxidizable matters, found in the condensed moisture of human breath appears to be largely due to products of the decomposition of organic matter which is constantly going on in the mouth and pharynx. This is shown by the effects of cleansing the mouth and teeth upon the amount of such matters in the condensed moisture of the breath, and also by the differences in this respect between the air exhaled through a tracheal fistula and that expired in the usual way.

IV. The air in an inhabited room, such as the hospital ward in which experiments were made, is contaminated from many sources besides the expired air of the occupants, and the most important of these contaminations are in the form of minute particles or dusts. The experiments on the air of the hospital ward, and with the moisture condensed therefrom, show that the greater part of the ammonia in the air was probably connected with dust particles which could be removed by a filter. They also showed that in this dust there were micro-organisms, including some of the bacteria which produce inflammation and suppuration, and it is probable that these were the only really dangerous elements in this air.

V. The experiments in which animals were compelled to breathe air vitiated by the products of either their own respiration or by those of other animals; or were injected with fluid condensed from expired air, gave results contrary to those reported by Hammond, by Brown-Séquard and d'Arsonval, and by Merkel, but corresponding to those reported by Dastre and Loye, Russo Giliberti and Alessi, Hofmann-Wellenhof, Rauer, and other experimenters referred to in the preliminary historical sketch of this report, and make it improbable that there is any peculiar volatile poisonous matter in the air expired by healthy men and animals, other than carbonic acid. It must be borne in mind, however, that the results of such experiments upon animals as are referred to in this report may be applicable only in part to human beings. It does not necessarily follow that a man would not be injured by continually living in an atmosphere containing 2 parts per 1000 of carbonic acid and other products of respiration, of cutaneous excretion, and of putrefactive decomposition of organic matters, because it is found that a mouse, a guinea-pig, or a rabbit, seems to suffer no ill effects from living under such conditions for several days, weeks, or months, but it does follow that the evidence which has heretofore been supposed to demonstrate the evil effects of bad ventilation upon human health should be carefully scrutinized.

VI. The effects of reduction of oxygen and increase of carbonic acid to a certain degree appear to be the same in artificial mixtures of these gases as in air in which the change of proportion of these gases has been produced by respiration.

VII. The effect of habit, which may enable an animal to live in an atmosphere in which, by gradual change, the proportion of oxygen has become so low and that of the carbonic acid so high that a similar animal brought from fresh air into it dies almost immediately, has been observed before, but we are not aware that a continuance of this immunity produced by it had been previously noted. The experiments reported in the Appendix, VII., 17 to 28, show that such an immunity may either exist normally or be produced in certain mice, but that these cases are very exceptional, and it is very desirable that a special research should be made to determine, if possible, the conditions upon which such a continuance of immunity depends.

VIII. An excessively high or low temperature has a decided effect upon the production of asphyxia by diminution of oxygen and increase of carbonic acid. At high temperatures the respiratory centres are affected, where evaporation from the skin and mucous surfaces is checked by the air being saturated with moisture; at low temperatures the consumption of oxygen increases, and the demand for it becomes more urgent.

So far as the acute effects of excessively foul air at high temperatures are concerned, such, for example, as appeared in the Black Hole at Calcutta, it is probable that they are due to substantially the same causes in man as in animals.

IX. The proportion of increase of carbonic acid and of diminution of oxygen, which has been found to exist in badly ventilated churches, schools, theatres, or barracks, is not sufficiently great to satisfactorily account for the great discomfort which such conditions produce in many persons, and there is no evidence to show that such an amount of change in the normal proportion of these gases has any influence upon the increase of disease and death-rates which statistical evidence has shown to exist among persons living in crowded and unventilated rooms. The Report of the Commissioners appointed to inquire into the regulations affecting the sanitary conditions of the British Army (1), properly lays great stress on the fact that in civilians at soldiers' ages, in twenty-four large towns, the death-rate per 1000 was 11.9, while in the foot-guards it was 20.4, and in the infantry of the line 17.9, and showed that this difference was mainly due to diseases of the lungs occurring in soldiers in crowded and unventilated barracks. These observations have since been repeatedly confirmed by statistics derived from other armies, from prisons, and from the death-rates of persons engaged in different occupations, and, in all cases, tubercular disease of the lungs and pneumonia are the diseases which are most prevalent among persons living and working in unventilated rooms, unless such persons are of the Jewish race. But consumption and pneumonia are caused by specific bacteria, which, for the most part, gain access to the air-passages by adhering to particles of dust which are inhaled, and it is probable that the greater liability to these diseases of persons living in crowded and unventilated rooms, is, to a large extent, due to the special liability of such rooms to become infected with the germs of these diseases. It is, however, by no means demonstrated, as yet, that the only deleterious effect which the air of crowded barracks or tenement-house rooms, or of foul courts and narrow streets, exerts upon the persons who breathe it, is due to the greater number of pathogenic micro-organisms in such localities. It is quite possible that such impure atmospheres may affect the vitality and the bactericidal powers of the cells and fluids of the upper air-passages with which they come in contact, and may thus predispose to infections, the potential causes of which are almost everywhere present, and especially in the upper air-passages and in the alimentary canal of even the healthiest persons, but of this we have, as yet, no scientific evidence. It is very desirable that researches should be made on this point.

X. The discomfort produced by crowded, ill-ventilated rooms in persons not accustomed to them is not due to the excess of carbonic acid, nor to bacteria, nor, in most cases, to dusts of any kind. The two great causes of such discomfort, though not the only ones, are excessive temperature and unpleasant odors. Such rooms as those referred to are generally overheated, the bodies of the occupants, and, at night, the usual means of illumination, contributing to this result.

The cause of the unpleasant, musty odor which is perceptible to most persons on passing from the outer air into a crowded, unventilated room is unknown; it may, in part, be due to volatile products of decomposition contained in the expired air of persons having decayed teeth, foul mouths, or certain disorders of the digestive apparatus, and it is due, in part, to volatile fatty acids given off with, or produced from, the excretions of the skin, and from clothing soiled with such excretions. It may produce nausea and other disagreeable sensations in specially susceptible persons, but most men soon become accustomed to it, and cease to notice it, as they will do with regard to the odor of a smoking-car, or of a soap factory, after they have been for some time in the place. The direct and indirect effects of odors of various kinds upon the comfort, and perhaps also upon the health, of men are more considerable than would be indicated by any tests now known for determining the nature and quantity of the matters which give rise to them. The remarks of Renk (38, p. 174) upon this point merit consideration. Cases of fainting in crowded rooms usually occur in women, and are connected with defective respiratory action due to tight lacing or other causes.

Other causes of discomfort in rooms heated by furnaces or by steam are excessive dryness of the air, and the presence of small quantities of carbonic oxide, of illuminating gas, or of arsenic derived from the coal used for heating.

XI. The results of this investigation, taken in connection with the results of other recent researches summarized in this report, indicate that some of the theories upon which modern systems of ventilation are based are either without foundation or doubtful, and that the problem of securing comfort and health in inhabited rooms requires the consideration of the best methods of preventing or disposing of dusts of various kinds, of properly regulating temperature and moisture, and of preventing the entrance of poisonous gases like carbonic oxide derived from heating and lighting apparatus, rather than upon simply diluting the air to a certain standard of proportion of carbonic acid present.

It would be very unwise to conclude, from the facts given in this report, that the standards of air supply for the ventilation of inhabited rooms, which standards are now generally accepted by sanitarians as the result of the work of Pettenkofer, De Chaumont, and others, are much too large under any circumstances, or that the differences in health and vigor between those who spend the greater part of their lives in the open air of the country hills, and those who live in the city slums, do not depend in any way upon the differences between the atmospheres of the two localities except as regards the number and character of micro-organisms.

BIBLIOGRAPHY.

1. General report of the commission appointed for improving the sanitary condition of Barracks and Hospitals. Fol., London, 1861.

2. Leblanc (F.) Recherches sur la composition de l'air confiné. Ann. d. chim. et. phys., Par., 1842, V, 223–268.

3. Regnault (V.) and Reisset (J.) Recherches chimiques sur la respiration des animaux des diverses classes. Ann. de chim. et phys., Par., 1849, 3. s., XXVI, 299–519, 2 pl.

4. Friedländer (C.) and Herter (E.) Ueber die Wirkung des Sauerstoffmangels auf den thierischen Organismus. Ztschr. f. physiol. Chem., Strassb., 1879, III, 19–53.

5. Bernard (C.) Leçons sur les effets de substance toxiques et médicamenteuses. 8vo, Paris. 1857.

6. Valentin (G.) Ueber Athmen im geschlossenen Raume. Ztschr. f. rat. Med., Leipz. and Heidelb., 1861, 3. s., X, 33–100.

7. Bert (P.) Leçons sur la physiologie comparée de la respiration ; professées au museum d'histoire naturelle. 8vo, Paris, 1870.

8. Richardson (B. W.) On certain of the phenomena of life. Tr. M. Soc. Lond., 1861, I, 53–128.

9. Pettenkofer (M.) and Voit (C.) Untersuchungen über die Respiration. Ann. d. chem. u. pharm., Leipz. u. Heidelb., 1862–3, 2. suppl. bd., 52–70.

9. Pettenkofer (M.) Ueber die Respiration. Ann. d. chem. u. pharm., Leipz., u. Heidelb., 1862–3, 2. suppl. bd., 1–52.

9. Pettenkofer (M.) Ueber die Bestimmung des luftförmigen Wassers in Respirations-Apparate. Sitzungsb. d. bayer. Akad. d. Wissensch., München, 1862, II, 152–161.

9. Pettenkofer (M.) Ueber die Ausscheidung von Wasserstoffgas bei der Ernährung des Hundes mit Fleisch und Stärkmehl oder Zucker. Sitzungsb. d. bayer. Akad. d. Wissensch., München, 1862, II, 88–91.

10. Hammond (W. A.) A treatise on hygiene with special reference to the military service. 8vo, Philadelphia, 1863.

11. Ransome (A.) On the organic matter of human breath in health and disease. J. Anat, and Physiol., Lond., 1870, IV, 209–217, 1 tab.

12. Smith (R. A.) Air and rain : the beginnings of a chemical climatology. 8vo, London, 1872.

13. Seegen (J.) and Nowak (J.) Versuche über die Ausscheidung von gasförmigen Stickstoff aus den im Körper umgesetzten Eiweissstoffen. Arch. d. ges. Physiol., Bonn., 1879, XIX, 347–415.

14. Hermans (J. T. F.) Ueber die vermeintliche Ausathmung organischer Substanzen durch den Menschen. Ein Beitrag zur Ventilationsfrage. Arch. f. Hyg., München u. Leipz., 1883, I, 1–40.

15. Brown-Séquard and d'Arsonval. Démonstration de la puissance toxique des exhalations pulmonaires provenant de l'homme et du chien. Compt. rend. Soc. de biol., Par., 1887, 8. s., IV, 814–818.

16. Brown-Séquard and d'Arsonval. Resemblances entre l'action toxique de certaines ptomaines et celle du poison pulmonaire. Compt. rend. Soc. de biol., Par., 1888, 8. s., V 108–110.

17. Brown-Sequard and d'Arsonval. Recherches démonstrant que l'air expire par l'homme et les mammifères, à l'éclat de sante, contient un agent toxique très puissant. Compt. rend. Acad. d. sc., Par., 1888, CVI, 106–112

17. Brown-Sequard and d'Arsonval. Nouvelles recherches démonstrant que les poumons secretent un poison extrêmement violent qui en sort avec l'air expiré. Compt. rend. Soc. de biol., Par., 1888, 8. s., V, 33–54.

17. Brown-Sequard and d'Arsonval. Sur quelques points importante relatifs à la durée de la survie des lapins apres l'injection sous-cutanee du liquide contenant le poison de l'air expire. Compt. rend. Soc. de biol., Par., 1888, 8. s., V, 121–172.

17. Brown-Séquard and d'Arsonval. Remarques sur la valeur des faits qui nous ont servi a demontrer la toxicité de l'air expiré. Compt. rend Soc. de biol., Par., 1888, 8. s., V, 99–101

17. Brown-Sequard and d'Arsonval. Nouvelles remarques à l'egard du poison pulmonaire. Compt rend. Soc. de biol., Par., 8. s., V, 54–56.

18. Dastre and Loye. Recherches sur la toxicité de l'air expiré. Compt. rend. Soc. de biol., Par., 1888, 8. s., V, 91–99.

19. Russo-Giliberti (A.) and Alessi (G.) Sulla tossicità dell' aria aspirata. Boll. Soc. d'ig. di Palermo, 1888, III, 331–340.

20. Würtz (R.) Sur la présence des bases volatiles dans le sang et dans l'air expiré. Compt. rend. Acad. d. sc., Par., 1888, CVI, 213.

21. Brown-Séquard and d'Arsonval. Nouvelles recherches démonstrant que la toxicité de l'air expiré ne depend pas de l'acide carbonique. Compt. rend. Acad. d. sc., Par., 1889, CVIII, 267–272.

22. Brown-Sequard and d'Arsonval. Description d'un appareil permittant de faire respirer a plusieurs animaux de l'air libre et sur quant à ses proportions d'oxygene et d'acide carbonique, mais contenant des quantités considérables du poison de l'aire expire. Compt. rend Soc. de biol., Par., 1888, 8. s., V, 110.

23. von Hofmann-Wellenhof (G.) Enthält die Expirationsluft gesunder Menschen ein flüchtiges Gift? Wien. klin. Wochnschr., 1888, I, 753–755.

24. Uffelmann (J.) Luftuntersuchen, ausgeführt im hygienischen Institut der Universität Rostock. Arch. f. Hyg., München u. Leipz., 1888, VIII, 262–350.

25. Lehmann (K. B.) and Jessen (F.) Ueber die Giftigkeit der Expirationsluft. Arch. f. Hyg., Munchen u. Leipz., 1890, X, 367–381.

26. Lipari (G.) and Crisafulli (G.) Richerche sperementali sull' aria espirata dall' uomo allo stato normale. Sicilia med., Palermo, 1889, I, 229. Also, transl. [Abstr.]: Arch. de physiol. norm. et path., Par., 1890, 5. s., II, 679.

27. Margouty (B. M. E.) Du rôle des matieres animales dans la nocivite de l'air expiré. 4to, Bordeaux, 1891.

28. Haldane (J.) and Smith (J. L.) The physiological effects of air vitiated by respiration. J. Path. and Bacteriol., Edinb. and Lond., 1892–3, I, 168–186.

29. Merkel (S.) Neue untersuchungen über die Giftigkeit der Expirationsluft. Arch. f. Hyg., München u. Leipz., 1892, XV, 1–28.

30. Haldane (J.) and Smith (J. L.) The toxic action of expired air. J. Path. and Bacteriol., Edinb. and Lond., 1892-3, I, 318-321.

31. Beu (J.) Untersuchungen über die Giftigkeit der Expirationsluft. 8vo, Rostock, 1893. Also in Ztschr. f. Hyg., Leipz., 1893, XIV, 64-75.

32. Rauer. Untersuchungen über die Giftigkeit der Expirationsluft. Ztschr. f. Hyg., Leipz., 1893, XV, 57-71.

33. Sanfelice (F.) Sull' aria di alcune ambienti abitali. Ann. d. Ist. d'ig. Sper. d. R. Univ. di Roma, 1893, n s., III, 399-436.

34. Lübbert (A.) and Peters (R.) Ueber die Giftwirkung der Ausathmungsluft. Pharm. Centralhalle, Dresd., 1894, 541-548. *Also*, [Abstr.]: Hyg. Rundschau, Berl., 1894, IV, 1118.

35. Brown-Séquard and d'Arsonval. Nouvelles recherches démonstrant que la toxicité de l'air expiré dépend d'une poison provenant des poumons et non de l'acide carbonique. Arch. de phys. norm. et. path., Par., 1894, 5. s.. XVI, 113-124.

36. Abbott (A. C.) Chemical, physical, and bacteriological studies upon air over decomposing substances, with special reference to their application to the air of sewers. Tr. Cong. Am. Phys. and Surg., New Haven, 1894, III, 28-62.

37. Birkholz (W.) Ueber den Einfluss der Temperatur und der Ernährung auf ihr Kohlensäurepruduktion im Thierkörper. Inaug. diss 8vo, Erlangen, 1889.

38. Renk (F.) Die Luft. Handb. d. Hyg., 8vo, Leipz., 1886, 1. Th. 2. Abth. 2 Hft., 1-242.

39. Remsen (I.) Report on the subject of organic matter in the air. Bull. Nat. Bd. Health, Wash., 1880-1, 517-521.

40. Talbot (M.) Technol. Quarterly, 1887, I, 29.

41. Nékám (L. A.) Ueber die Untersuchungen der organischen Substanzen der Luft. Arch. f. Hyg., München u. Leipz., 1890, XI, 396-409.

42. Archarow (J.) Ueber die Bestimmung der organischen Stoffe der Luft vermittelst Kaliumpermanganat. Arch. f. Hyg., München u. Leipz., 1891, XIII, 229-246.

43. Carnelly (T.) and Mackie (W.) The determination of organic matter in air. Proc. Roy. Soc., Lond. (1886), 1887, XLI, 238-247.

44. Friedländer (C.) and Herter (E.) Ueber die Wirkung der Kohlensäure anf den thierischen Organismus. Ztschr. f. physiol. Chem., Strassb., 1878-9, II, 99-148.

APPENDIX.

DETAILS OF METHODS EMPLOYED, AND RESULTS OBTAINED, IN EXPERIMENTS UPON THE EFFECTS OF EXPIRED AIR.

BY

DAVID HENDRICKS BERGEY, B. S., M. D.

(The numbers in parentheses refer to the bibliographical list appended to the report.)

I.—Four experiments were made to determine whether the air expired by man contains micro-organisms. The results are shown in the following table.

TABLE A.

No.	Date.	Culture medium.	Amount of medium.	Time in breathing.	Number of colonies.	Time under observation.	Remarks.
	1893					Days.	
1	Dec. 29	Gelatin.	150 c. c.	30 min.	6	30	Common air organisms.
	1894						
2	Jan. 10	"	" "	" "	2	30	" " "
3	Feb. 7	"	" "	" "	0	30	Sterile.
4	Mch. 3	"	" "	20 "	0	20	"

In these experiments the expired breath was conducted through melted gelatin contained in the apparatus shown in Fig. 1, for 20 to 30 minutes. The gelatin was then hardened by rolling the flask in a shallow basin containing ice-water, thus distributing the culture in a thin layer over the bottom [illegible] flask. The cultures were kept under observation for 20 to 30 days. About 150 c.c. of the gelatin was used for each experiment. The glass tube, b, of the apparatus used, which served for the entrance of the expired air, was inserted far enough to just impinge upon the culture medium in the flask, so that the air produced a slight agitation of the fluid in passing through the apparatus.

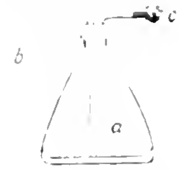


FIG. 1.—Apparatus for determining the presence of bacteria in expired breath.

Description of the apparatus used for determining the presence of bacteria in expired breath. Fig. 1, a, represents a half litre Erlenmeyer flask closed with a rubber stopper having two openings. Each of these openings is closed by a glass tube bent at right angles above the stopper.

b, represents the longer glass tube which reaches nearly to the bottom of the flask. This tube has a small bulb-shaped enlargement blown into its upper end, which serves to retain any saliva that might flow into the tube. This tube serves as the mouthpiece through which the air enters the apparatus. When not in use, the mouth-piece is closed with a small cotton plug. The internal diameter of the tube is seven mm.

c, the shorter tube is bent at right angles and terminates just below the stopper. The external end of this tube is closed with a cotton plug to prevent the entrance of micro-organisms from this side of the apparatus. The internal diameter of this tube is also seven mm.

The organisms which developed in these cultures were all of the same character—a small yellow bacillus which is quite common in the air of the laboratory. In the experiments in which gelatin remained sterile, the precaution had been taken to sterilize the apparatus with dry heat for an hour previous to introducing the gelatin, besides the subsequent sterilization of the culture medium on three successive days. If, after standing in the working room for several days, it was found that the culture medium was sterile, the expired breath was then conducted through the apparatus and the culture was kept under observation (for the time specified in the table) at the room temperature. The nature of the organisms that developed in the first two experiments, and the absence of any growth in the others, makes it probable that they developed from spores that survived the fractional sterilization of the culture medium. It is improbable that they were carried in the expired breath.

Several attempts were made to use bouillon and litmus milk instead of gelatin, as the culture medium. Neither of the former media was found to be suitable for the purpose.

Careful examination of the fluid condensed from the expired air was made with high powers, both in hanging drops, and in six dried and stained preparations, but nothing resembling bacteria or epithelium was found. A few amorphous particles, a few minute apparently crystalline masses, and here and there a fragment resembling vegetable fibre, were all that could be seen.

II.—A series of experiments was made to determine the amount of ammonia, of albuminoid ammonia, and of oxidizable matters contained in the fluids condensed from expired air.

The apparatus used in collecting the condensed vapor from expired breath is represented in Fig. 2, the condenser of which is laid in ice. Each time before this apparatus was brought into use, the condenser was boiled out with either a solution of bichromate of potash and sulphuric acid, or with alkaline permanganate of potash, then freely rinsed with twice distilled water until entirely free from the cleansing solutions used. The apparatus was then quickly connected together and placed in a large steam sterilizer for an hour. The condenser was then packed in ice and the breath exhaled through the apparatus, using but little greater expiratory force than in ordinary respiration. In several of the experiments a gas meter was attached after the apparatus, in order to measure the volume of air exhaled. This was found to approximate a third of a cubic metre per hour, during which time as much as 12 c. c. of moisture was collected.

The amount of air expired in ordinary quiet respiration ranges from 400 to 500 litres per hour. It is evident that the diminished amount exhaled in the experiment did not represent the full respiratory capacity; the reduction observed having its cause, in all probability, in the slightly greater effort required to conduct the expired breath through the apparatus. It was noted that the number of expirations ranged from twelve to fifteen per minute, the ordinary rate being about eighteen per minute. This was also caused by the slight obstruction to the respiratory current prolonging the expiratory movement. Inhalation took place through the nose.

DESCRIPTION OF FIGURE 2.

This apparatus was used to condense moisture from the expired breath. It consists of a glass mouth-piece, *a*, having an internal diameter of seven millimetres; its length being twenty centimetres. The distal end of this tube is bent at an obtuse angle and is connected with a glass tube of similar size, bent at right angles, and inserted through one of the openings of the rubber stopper of the wide-mouthed flask *b*. The other opening of this stopper carries a similar glass tube, also bent at right angles, attached to the proximal arm of the condenser *c*. To the distal arm of the condenser is attached another glass tube, also bent at right angles, passing through one of the openings of the rubber stopper of the wide-mouthed flask *e*. The other opening in this stopper carries a glass tube of similar size, also bent at right angles, passing nearly to the bottom of the flask. The different parts of the apparatus are connected together by means of short pieces of stout, closely fitting rubber tubing. The small wide-mouthed flask *b* serves as a receptacle for saliva. The tubing in the stopper closing its mouth terminates just below its inner surface. The condenser *c* is U-shaped, with each of its arms bent at right angles about half-way down to the lower dilated portion, and has an internal diameter of seven millimetres. The dilated portion of the condenser is twelve centimetres in length and four centimetres in its external diameter. The small wide-mouthed flask *e* is nearly filled with small, pea-sized pieces of pumice-stone saturated with concentrated sulphuric acid. This serves to arrest the organic matter in any air that might accidentally enter from this side of the apparatus. The U-shaped condenser rests in a square glass dish *d*, 20 x 8 x 8 centimetres in its external dimensions, containing cracked ice.

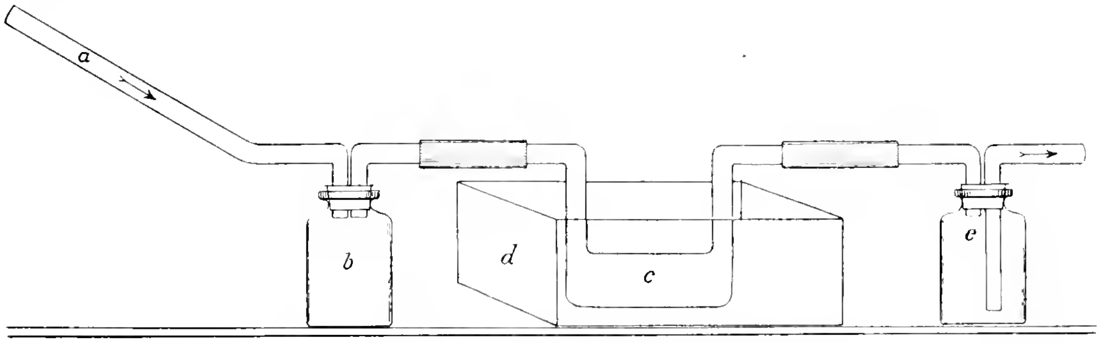


FIG. 2.—Apparatus to condense moisture from the expired breath.

In order to adapt the mouth-piece of this apparatus to the fistulous opening in the throat of the man that had had his larynx removed, the proximal end of the mouth-piece was attached to a porcelain mouth-piece used for speaking-tubes. This was padded with several layers of cheese cloth, and the loose end of this tied around his neck to hold it in position. In this manner he was able to exhale through the apparatus without any difficulty.

Some of the condensed fluid was collected from my own breath and that of other healthy persons; other portions were collected from a man having a permanent fistulous opening in his throat through which he breathed; there being no connection whatever with the mouth and upper air passages. Some fluid was also collected from the breath of a man suffering from advanced tubercular disease of the lungs.

The amount of free and albuminoid ammonia in this condensed fluid, as estimated according to the well-known method of Wanklyn, Chapman, and Smith, is shown in Table B, together with the amount of fluid used in each of these determinations and the time required to collect these portions of fluid. A definite portion of the fluid was diluted with 500 c. c. of twice distilled water, and the ammonia in a like quantity of the same water was determined simultaneously and deducted from the amount found in the diluted fluid. The minute quantities of ammonia found in each of these determinations required the greatest care in manipulation to avoid all sources of contamination in the collection of the fluid as well as subsequently in the distillation and Nesslerization. The greatest care had to be exercised, therefore, in cleansing all apparatus and also in the preparation of the different reagents.

The fluid for the first seven determinations was collected from my own breath, and, for the next thirteen determinations, from the breath of the man with the tracheal fistula. The remainder of the determinations were made on the fluids collected from the breath of the consumptive.

TABLE B.

DETERMINATION OF FREE AND ALBUMINOID AMMONIA IN CONDENSED FLUID OF RESPIRATION.

No.	Amount of fluid used.	Grams per litre of fluid.		Time and amount collected.		Date.	Remarks.
		Free NH$_3$.	Alb. NH$_3$.	Minutes.	c.c. of fluid.		
1	5 c. c.	.0198	.005	60	10	1893. Dec. 15	My own breath.
2	5 "	.031	.004	55	10	" 20	" " "
3	5 "	.0314	.0038				" " "
4	5 "	.0026	.0162	60	12	" 28	" " "
5	5 "	.0028	.016				" " "
6	4 "	.0245	.004	55	8.5	1894. Jan. 1	" " "
7	4 "	.022	Defective.				" " "
8	5 "	.0004	.0002			" 16	Mr. Hickey's breath.
9	5 "	.0006	.0002				(Tracheal fistula.)
10	5 "	.0003	.0002			" 19	" "
11	5 "	.0003	.0002				" "
12	5 "	.0004	.0006			" 22	" "
13	5 "	* Failure.	* Failure.				" "
14	5 "	.0005	.0005			" 25	" "
15	5 "	.0006	.0006				" "
16	5 "	.0004	.0005			" 26	" "
17	5 "	.0004	.0005				" "
18	10 "	.0007	.0005			" 29	" "
19	10 "	.0006	.0002			" 30	" "
20	21.5 "	.0003	.0001			Feb. 1	" "
21	15 "	.0058	.0003	65	15	1895. Jan. 18	Consumptive person.
22	12 "	.0034	.0005	60	12.5	Feb. 7	" "
23	15 "	.0023	.0033	120	20	" 13	" "
24	10 "	.0005	.0095	120	16	" 19	" "

The amount of organic matters present in the condensed fluid, as shown by its reducing power upon solution of permanganate of potash, is represented in Table C, the results being calculated to Mg. of O. consumed to one litre of the condensed fluid. The table also shows the amount of fluid used in each of the determinations and the time required to collect such amount. In three of the experiments the amount of air expired is also given. These determinations were made according to the methods now in common use for the determination of organic matter in water as modified by Kubel; the fluid being diluted with a definite amount of distilled water, the reducing power on permanganate of which was simultaneously determined and deduced from the results obtained. The ebullition of the fluid was always carefully timed—the time being five minutes.

---

* Merely a trace found.

TABLE C.

DETERMINATION OF OXIDIZABLE MATTER IN CONDENSED MOISTURE OF RESPIRATION.

No.	Date.	Time and amount collected.		Amount used c.c.	Mgm. of O consumed to 1 litre.	Amount of air expired Litres.	Remarks.
		Hours.	c.c. of fluid.				
	1894.						
1	Jan. 31	1	3.5	3.5	8.01		D. Hickey's breath (tracheal fistula).
2	" 31	1	4	4	11.68		" " " "
3	" 31	1	3	3	9.3458		" " " "
4	" 31	1	1.5	1.5	24.916		" " " "
5	Sept. 6	3	35	25	12.04	982.5	My own breath.
6	" 12	1	12	10	8.89	333.3	" " "
7	" 17	35 min.	8	8	11.25	176	Dr. Gillespie's breath.
	1895.						
8	Jan. 26		7.5	7	6.86		Consumptive's "
9	" 29	20 "	4.75	4.75	18.30		Four hours after last meal.*
10	" 29	20 "	4.25	4.25	2.27		Half hour " " "
11	" 30	15 "	4	4	Failure		Three and a half hours after last meal.
12	" 30	15 "	4	4	Failure.		Half hour after last meal.
13	" 31		16	16	19.32		Consumptive's breath
14	" 31	15 "	3.75	3.75	10.40		Four hours after last meal.
15	" 31	15 "	3.75	3.75	2.60		Half hour " " "
16	Feb. 1	15 "	4.5	4.5	7.57		Three and a half hours after last meal.
17	" 1	10 "	3	3	8.10		Half hour after last meal.
18	" 2	15 "	3.8	3.8	10.105		Three hours " " "
19	" 2	15 "	3.5	3.5	15.485		Halt hour " " "
20	" 2	60 "	9.75	9.75	7.50		Consumptive's breath.
21	" 4	15 "	4	4	10.90		Four hours after last meal.
22	" 4	15 "	4	4	9.70		Four and a half hours after last meal, antiseptic mouth wash.
23	" 6	15 "	3.8	3.8	12.76		Four and a halt hours after last meal.
24	" 19	120 "	16	5	19.12		Consumptive's breath.
25	" 28	15 "	3.75	3.75	Failure.		One and a half hours after meal.
26	" 28	60 "	6.25	6.25	33.90		Consumptive's breath.
27	" 28	10 "	3.25	3.25	8.83		Three and a half hours after meal.
28	" 28	10 "	2.75	2.75	3.47		Four hours after meal, mouth rinsed with warm water.
29	Mch. 1	10 "	2.50	2.50	7.56		Four hours after meal.
30	" 1	10 "	2.75	2.75	3.47		Half hour " "
31	" 2	15 "	3.75	3.75	2.62		Three hours " "
32	" 2	15 "	3.25	3.25	1.515		Three and a half hours after meal, mouth rinsed with warm water.
33	" 2	15 "	4	4	1.23		Half hour after last meal.

The fluids for these determinations were collected from the breath of the man with the tracheal fistula; from the breath of the consumptive; and from my own breath and that of another healthy person. With the exception of one of the results obtained with fluid collected from the breath of the man with the tracheal fistula, which result is out of accord with the others (cause unknown), the determinations show no marked variation in the amount of oxidizable matter, whatever the source of the fluid or conditions of the person from whose breath it was collected, though only a few experiments were made. Just before collecting the fluid for several of the later deter-

---

* The fluids for the determinations before and after meals were collected from my own breath.

m[illegible] the mouth was well rinsed in a weak solution of formalin or with warm water. A [illegible] 2 Mg. [illegible] O per litre in the 23d from the amount required for the fluid collected [illegible] day before, seems to have resulted from the use of the antiseptic mouth wash, in others a [illegible] reduction was brought about by simply rinsing the mouth several times with warm water.

Several efforts were made to obtain evidence as to the chemical nature of the condensed fluid collected from my own breath. Eighty (80) litres of expired air were conducted through 50 c. c. of a [illegible] per cent. solution of oxalic acid in ten minutes. This fluid gave a decided yellowish-brown color with 1 c. c. of Nessler's reagent, showing at least five times as much ammonia as was present in the distilled water used to make the oxalic acid solution. The fluid condensed from exhaled breath, obtained by conducting the breath through a condensing apparatus laid in ice, was tested with the following reagents for the presence of a volatile organic alkaloid: $AuCl_3$, $PtCl_4$, Ammon. Molybdate, $AgNO_3$; reaction negative. Nessler's reagent produced a yellow color, and a few drops of a 10 per cent. solution of $HgCl_2$ with a few drops of a 10 per cent. solution of KI also gave a yellow color.

The results of the tests, though few in number, gave no evidence of the presence of expiratory products other than those indicated by the determinations of ammonia, and the reducing power on solution of permanganate of potash.

III.—Experiments with fluid condensed from the air of a large surgical ward in the University Hospital, with and without filtration of the air.

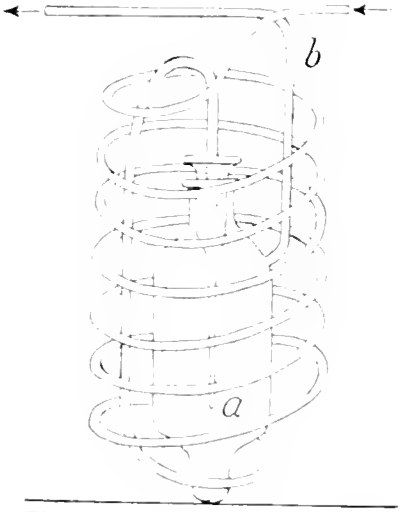


Fig. 3.—Condenser of [illegible] in Fig. 4. [illegible]

Several efforts were made to collect moisture from the air of a crowded surgical ward of the Hospital by means of a large glass funnel, sealed at the neck and filled with ice. A small beaker was placed beneath the funnel to collect any moisture condensing on its exterior. This method proved unsuccessful, and was abandoned. An apparatus, shown in Fig. 3, and arranged as shown in Fig. 4, was placed on a mantel over an unused open fire-place at one end of the ward.

Description of the apparatus used to condense the moisture in the air of the hospital ward:

Fig. 3 represents the condenser, consisting of *a*, a small glass receptacle eleven centimetres in height and three centimetres in diameter at its widest part, and having a capacity of 50 c. c. This receptacle has two openings, the one at the top being closed with a closely fitting, hollow, glass stopper; the second opening consists of a glass tube coming obliquely from the expanded portion near the top, and at a distance of three centimetres bends upward along the side of the receptacle. This serves as the exit tube to the receptacle, while the air enters through the hollow glass stopper closing the other opening. Each of the tubes has an internal diameter of four millimetres. The spiral portion of the condenser consists of a piece of block tin tubing, *b*, three metres in length, and five millimetres in internal diameter. This is connected with the entrance tube of the receptacle by means of a short piece of rubber tubing, and with the dust filter by a longer piece of rubber tubing. The exit tube of the receptacle has a piece of glass tubing, thirty centimetres in length, and five centimetres in internal diameter, fused to its end. This is bent at right angles near its upper extremity, and connected with the gas meter by means of a piece of rubber tubing.

Fig. 4, represents the apparatus as arranged in the hospital ward. *a* represents an inverted bell-jar with the condenser packed in ice. The bell-jar is supported by an iron tripod, *b*. The dust filter, consisting of a glass tube loosely packed with asbestos, is represented at *c*, and is attached to a stative by means of a clamp, while *e* represents the gas meter, and *f* the water faucet in the lavatory. The meter is connected with the faucet by means of a long piece of block-tin tubing of 1¼ centimetres internal diameter. *g* represents the Chapman water pump attached to the faucet.

The dust filter, *c*, is twenty centimetres in length, consisting of a narrow portion four centimetres long and three millimetres in internal diameter, and of a wider portion sixteen centimetres long and twelve millimetres in internal diameter.

The condenser was cleansed by rinsing it with a solution of bichromate of potash and sulphuric acid, then removing all trace of this solution by rinsing it repeatedly with twice distilled water. The cleansing of the apparatus was greatly facilitated by attaching it to a Chapman water pump in the laboratory, and drawing the cleansing solution and distilled water through it in large quantities. It was then placed in the inverted bell jar, packed in ice, and connected with the meter and pump in the hospital ward.

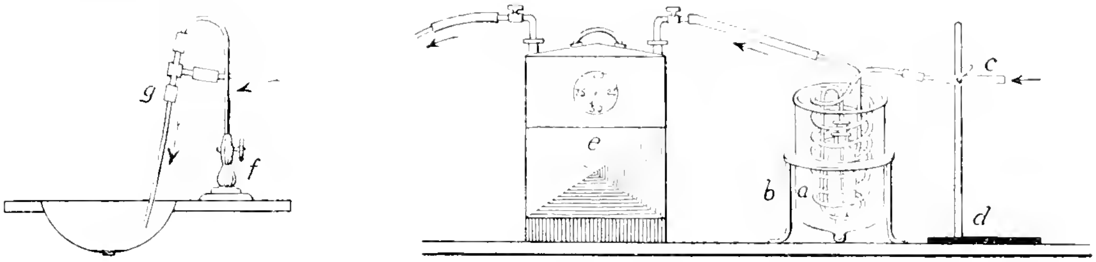


FIG. 4.—Apparatus used to condense moisture from the air of the Hospital Ward.

With this apparatus a small amount of fluid was collected on days when the atmosphere was saturated with moisture, but if this fluid was allowed to remain in the receptacle during several days of clear weather it slowly evaporated. However, enough fluid was collected in this manner to make several determinations of the free and albuminoid ammonia in it. The results thus obtained are shown in Table D; the first and third experiments showing results obtained without placing a dust filter of asbestos before the condenser. The second and fourth experiments show the results obtained by attaching such a dust filter.

TABLE D.

DETERMINATION OF FREE AND ALBUMINOID AMMONIA IN THE MOISTURE CONDENSED FROM THE AIR OF THE HOSPITAL WARD.

No.	Date.	Time.	Litres of air aspirated.	Amt. of moisture condensed.	Grms. per 1000 cbm. air.		No. of bacteria per c. c. of fluid.	Remarks.
					Free NH_3.	Alb. NH_3.		
	1894	Hours.						
1	Dec. 13	43½	4612.9	3. c. c.	0.0210	0.0028	3140	No dust filter.
	1895							
2	Jan. 9	41½	3990.3	7. "	0.00075	0.00125	1331	Dust filter.
3	" 18	34¼	1669.7	3. "	0.0012	0.0015		No dust filter.
4	Mch. 4	33	1980.0	2.6 "	0.0015	0.0010		Dust filter.

Microscopic examination of the fluid condensed from the air of the hospital ward showed: a number of small amorphous particles—black, yellow, and colorless; a few small crystals, a few epithelial scales, small bits of vegetable fibre, and a few bacteria.

Cultures made from this fluid showed numerous colonies of moulds, numerous common air and water organisms, some of which rapidly liquefied the gelatin of the cultures. B. pyocyanus was found in one instance, in others a yellow sarcina, and yeasts of different colors. Besides these a [illegible] Bacillus [illegible] was found in most of the cultures; in one [illegible] very large numbers and excluded nearly all the other forms [illegible] plates exposed in the ward, and in the cultures from dust collected [illegible].

O[illegible] which had [illegible] on the [illegible] and mantel during the night [illegible] cotton swab and [illegible] upon gelatin plates. The cultures in [illegible] did not differ greatly from those made from the fluid, except that the moulds were [illegible] other organisms [illegible] in the cultures from the fluid.

[illegible] exposed to the [illegible] of the ward showed the same character of organisms as in the [illegible] and those which developed from the dust collected in the vicinity [illegible]. In addition to the species already noted, colonies of staphylococcus aureus [illegible] were also noted in these plates.

The small amount of fluid collected from the air of the hospital ward in the manner stated, and the rapidity with which it evaporated on dry days, made it impossible to collect a sufficient quantity to inoculate it into animals. To overcome this difficulty a small quantity of sterilized glycerine (7.5 to 10 c.c.) was aspirated through the condensers after it had been cleansed. It is doubted, however, whether this served to withdraw an appreciable amount of moisture from the air. After aspirating air through the apparatus for several days it was brought to the laboratory and the fluid in the receptacle transferred to a small sterilized flask. The condenser was then washed out by aspirating [illegible] c.c. of twice distilled water (sterilized) through it. This was added to the fluid poured from the receptacle, thoroughly mixed with it, and inoculated into animals. The glycerine in the fluid inoculated into the animals was diluted at least 50 per cent. Three sets of animals were inoculated and each time a control animal was inoculated with equal parts of glycerine and distilled water that had been sterilized for one hour. The results of these experiments are shown in Table E.

TABLE E.

[illegible]ECTION OF BACTERIA, ETC., FROM THE ATMOSPHERE OF THE HOSPITAL WARD, USING GLYCERINE IN THE ABSORPTION APPARATUS.

No.	Date.	Time.	Litres of air Aspirated.	Amt. of glycerine (c.c.)	Weight of rabbit and amt. of fluid injected.						No. of bacteria in dilute fluid, per c.c.
					Weight.	c.c.	Weight.	c.c.	Weight. (control animal.)	c.c.	
	1894.	Hours.			Grams.		Grams.		Grams.		
1	Dec. 5	47½	13338.8	10 c.c.							900
2	" 11	69½		10 "							450
	1895.										
3	Jan. 1	47½	7754.2	7.5 "	3[illegible]	6	113[illegible]	2	1025	2	2675
4	" 3	44[illegible]	7669.3	7.5 "	22[illegible]5	6	2355	6	2255	6	1893
5	" 5	52½	4024.2	7.5 "	107[illegible]	6	1250	6	1400	6	1640

The animals inoculated with the products collected from the air of the hospital ward in the manner stated were under observation for two months. Three of these animals died during the time they were under observation. The control animal of the third series died after twelve days. This animal was observed to be in poor health for several days before its death. On examination, *post mortem*, it was found to have had a good-sized abscess in the right axillary fossa, which had ruptured externally; the liver presented numerous whitish bands and foci on all of its surfaces and throughout its interior. A number of echinococcus cysts were found adherent to the liver, [illegible]. The kidneys were normal in size and appearance, and the capsule was [illegible]. The other organs appeared normal.

Cultures were taken from the abscess, blood, lungs, liver, spleen, and kidneys. Those from the [illegible] were the only ones developing any growth. The prevailing organisms in the cultures from the abscess were staphylococcus albus and aureus.

Cover-slip preparations were made from the abscess, blood, lungs, liver, spleen, and kidney. Those from the site of the abscess were the only ones showing any organisms; numerous cocci, with a few bacilli, were observed.

Microscopic examination of the organs hardened in alcohol and mounted in celloidin: The liver presented some increase of connective-tissue elements between the lobules. The whitish bands on the surface of the organ, noted at the autopsy, were found to be due to this increase in connective-tissue elements in the inter lobular spaces. No change was noticed in the liver cells themselves. All the other organs were found to be normal.

The nature of the substances inoculated into this control animal (6 c. c. of equal parts of sterilized glycerine and distilled water) and the antiseptic precautions observed in the inoculation make it doubtful whether the source of infection is traceable to the experiment. The changes noted in the liver are of such a nature as to indicate their production by causes preceding even those which brought about the death of the animal.

Rabbit No. 2 of the first series, having received 2 c. c. of the fluid obtained by aspirating the air of the hospital ward through the condensing apparatus moistened with sterilized glycerine, died after 35 days. Autopsy: Half-grown rabbit, poorly nourished, and adipose all used up, presented nothing important externally. Internally: A small amount of clear fluid in the abdominal cavity; the liver is somewhat darker than normal, mottled, and contains a few psorosperms. Spleen is normal. Kidneys and adrenals are normal in appearance. The right lung is considerably congested, being readily torn; the left is also slightly congested. The right side of the heart is filled with dark fluid blood; the left side is nearly empty. Several echinococcus cysts were found in the abdominal cavity.

Cover-slip preparations were made from the abdominal fluid, the kidneys, liver, spleen, lung, and blood; all proved negative.

The organs were preserved in alcohol and mounted in celloidin for microscopic examination.

Microscopic examination of the organs: Left lung showed the capillaries and larger vessels very much dilated and filled with blood. Infiltration of leucocytes was noted here and there. Right lung showed marked proliferation of cells and infiltration of leucocytes. Many of the air cells were obliterated. The liver, kidneys, and spleen were normal.

Rabbit No. 1 of the second series, inoculated with the fluid obtained from the air of the hospital ward, died after 38 days. Autopsy: Full-grown rabbit, shows numerous bruises and lacerations of the skin over various parts of the body. Many of the wounds along the sides and back show ecchymoses under the skin. Adipose not all used up. Internally: Liver slightly darker and somewhat larger, apparently, than normal. Spleen is larger than normal. Kidneys embedded in fat, normal in appearance. Lungs and heart normal. Blood is dark and fluid.

Cover-slips were made from all the organs with negative results.

The organs were preserved in alcohol and mounted in celloidin for microscopic examination.

Microscopic examination of the organs: No abnormalities could be found in any of the organs; all appearing to be normal.

The remaining rabbits of these series showed no symptoms of any deleterious influence from the fluid inoculated. No swelling or formation of abscess was noted in any of them.

Rabbit No. 2 of the first series evidently died of lung disease, as shown at *post mortem*. As to the causation of this disease, it is impossible to venture an opinion. Rabbit No. 1 of the second series died of causes which left apparently no manifestations pointing to their nature.* Rabbit No. 3 (control) of the third series evidently died from the effects of the extensive axillary abscess. As to the source of the infection, no decided opinion can be given. Probably the infection gained an entrance through the inoculation wound.

Some experiments were made to determine the amount of oxidizable matter in atmospheric air. At first a measured amount of air was slowly aspirated through twice distilled water, and the amount of oxidizable matter extracted from the air estimated according to the method used for determin-

---

*Death may have resulted from injury, as shown by the contusions and wounds noted at autopsy. These wounds were probably inflicted by other rabbits in the same cage.

ing the oxidizable matters in the condensed fluid of respiration. In the later experiments the air was conducted through two flasks—the first containing 100 c.c. of a 1 per cent. solution of sulphuric acid, the second 100 c.c. of a 1 per cent. solution of potassium hydroxide. After aspirating a measured amount of air through these solutions, 50 c.c. of each were mixed together and the amount of oxidizable matter determined as in the earlier experiments. The results are shown in Table F.

TABLE F.

DETERMINATIONS OF OXIDIZABLE ORGANIC MATTERS IN ATMOSPHERIC AIR.

No.	Absorbent used.	Amount sol. c.c.	Litres of air aspirated.	Time of aspiration.	O consumed to 1,000 cub. m. of air.	Date.	Remarks.
				Hours	Grms.	1894	
1	Distilled H_2O	125	200	20	.340	Aug. 20	Laboratory air.
2	" "	150	240	22	*Failure	" 21	" "
3	" "	150	240	20	.121	" 22	" "
4	" "	150	240	20	.058	" 23	" "
5	" "	150	240	20	Failure	" 24	" "
6	" "	150	240	20	Failure	" 25	" "
7	" "	150	240	20	Failure	" 26	" "
8	" "	150	300	20	.030	" 27	" "
9	" "	150	320	20	.059	" 29	" "
10	" "	150	280	20	.085	" 30	" "
11	" "	150	309	20½	.013	Sept. 6	" "
12	" "	100	900	50	.204	" 8	" "
13	" "	150	360	24	Failure	" 11	" "
14	" "	150	360	20	Failure	" 12	" "
15	A 1% solution H_2SO_4 A 1% " KHO	100 100	1000	22	.558	" 18	External "
16	" "	100 100	911.25	20	.086	Oct. 2	" "
17	" "	100 100	690.5	20	.068	" 3	" "
18	" "	100 100	433	20	.062	" 4	" "
19	" "	100 100	447	22	.007	" 6	" "

These experiments were made at a season of the year when the windows of the laboratory were open most of the time and the amount of dust floating in the laboratory air must have been about equal to that in the external air. The method employed to obtain the oxidizable matter from the external air is preferable to that employed for the laboratory air, and, since equal portions of the solutions used neutralize each other, they have no objectionable influence upon the process of determination of the oxidizable matter.

In several instances a portion of the water, containing the oxidizable matter extracted from the air, was treated with $AgNO_3$, $HgCl_2$, $AuCl_3$, $PtCl_4$, K_4FeCy_6, $K_6Fe_2Cy_{12}$, KHO, $Ba(HO)_2$, H_2SO_4, I, and with phosphomolybdic acid, am. molybdate, but no reaction was obtained with any of these, either in hot or cold solution. Nessler's reagent gave a deep yellow color, and $HgCl_2$ with KI produced a lemon-colored precipitate, rapidly changing to red, with deposit of HgI_2.

IV.—Experiments on mice and birds confined in glass jars, by the method used by Hammond (10).

The exact conditions under which Hammond conducted his experiment are not given in his treatise, and the size of the jar he used is uncertain. Taking the relative sizes of the animal, jar, and the other parts of the apparatus shown in the accompanying figure, it seems probable that he used a jar of at least four litres' capacity. In the apparatus used for our experiments, two- and four-

*By "Failure" is meant that merely a trace of organic matter was found.

litre jars were used. The arrangements for the absorption of moisture, CO_2, and for the introduction of fresh air, were the exact counterparts of these arrangements in Hammond's apparatus, judging from his description and engraving. Fresh air was supplied at intervals of one-half to one hour. This was accomplished by attaching a graduated aspirator to the Geissler potash bulbs containing the $Ba(HO)_2$ solution.

The results obtained in these experiments are shown in Table G. Hammond claims that in his experiments a mouse invariably died within one hour. In our experiments all the animals lived over three hours, and some even longer than six hours. The great difference in the duration of life for different animals may be accounted for in the varying susceptibility of different animals of the same species to the atmospheric conditions in the jar, but the still greater difference in the duration of life in our experiments, as compared with Hammond's results, cannot be attributed to the same cause, and, since it is not known positively what the capacity of the jars was which he used it would be useless to speculate on the point.

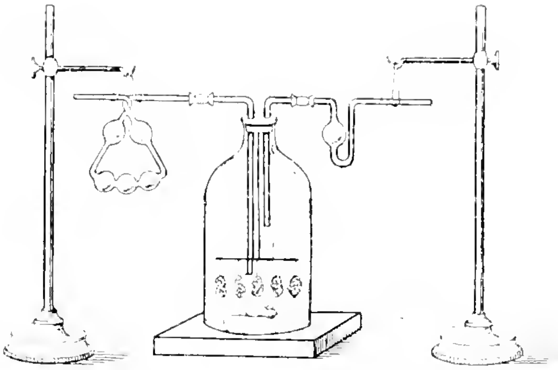


Fig. 5.—Hammond's apparatus.

Fig. 5 shows Hammond's apparatus as given in his treatise (Fig. 10, p. 170), and is an accurate representation of the apparatus used by us, except that it does not show the graduated aspirator connected with the free end of the Geissler potash bulbs, by means of which a known amount of fresh air was introduced at stated intervals during the experiment.

TABLE G.

THE "HAMMOND EXPERIMENT."

No.	Date.	Capacity of the jar.	Amt. of air aspirated.	Time.	Animal.	Weight.	Exam. of air.		Remarks.
							CO_2.	O.	
	1893.			H'rs.		Grms.	%	%	
1	Dec. 15	4000 c. c.	250 c. c.	5	Sparrow.	20			Alive ; revived.
2	" 16	" "	185 "	5½	"	20			" "
3	" 18	" "	600 "	6	Mouse.	14			" "
4	" 19	" "	600 "	6	"	15			" "
5	" 20	2000 "	300 "	6	"	14			" "
6	" 20	" "	300 "	6	"	15			"
7	" 21	4000 "	225 "	5	Sparrow.	26			" Same animal.
8	" 22	" "	225 "	5	"	26			"
	1894.								
9	Feb. 9	" "	300 "	3	"				Died.
10	" 9	" "	350 "	4	"				"
11	" 10	" "	400 "	3¼	"				"
12	" 10	" "	400 "	3¼	"				"
13	" 12	" "	500 "	5¼	"				"
14	" 12	" "	350 "	3⅔	"				"
15	Mch. 6	" "	550 "	6½	"	23	13.80	5.61	"
16	" 6	" "	550 "	4¾	"	23	13.75	5.60	"
17	" 7	" "	250 "	5¼	"	21	13.04	4.75	"
18	" 7	" "	250 "	5½	"	21	12.50	4.875	"
19	" 9	" "	250 "	4¾	"	25	12.79	5.59	"
20	" 9	" "	350 "	6⅜	"	21	12.27	3.94	"
21	" 10	" "	200 "	4⅔	"	25	14.08	3.74	"
22	" 10	" "	200 "	4½	"	22	13.69	3.25	"

For determination of the proportions of CO_2 and of O in the air of the jar at the end of the [illegible] Bunte's gas burette, represented in Fig. 6. For rapid determinations [illegible] soon learns to manage it easily and obtain [illegible] other methods. It is not claimed that the results so [illegible] resulting from the use of this burette is a constant [illegible] experiments reported on, and is without influence on [illegible]

[illegible] the upper portion is of larger size than the lower, which is [illegible] extending from zero near the bottom to 100 c. c. just below the expanded portion above, and from the zero mark down to 10 c. c. near the lower extremity of the tube. The capacity from the 100 c. c. mark to the three-way stopcock, *b*, closing its upper end, is 50 c. c., making the entire capacity of the tube 160 c. c. The lower end is closed by means of a simple glass stopcock, *e*. *c* represents a small cup at the top with marks at 20 and 25 c. c. respectively, thus facilitating the measurement of the contained volume of gas at a constant pressure of known amount of water in the cup.

f represents an iron stand to which the burette is firmly clamped.

d represents a glass tube of wider calibre surrounding the burette, filled with water and serving as a water-jacket to prevent rapid changes in temperature of the gases under examination.

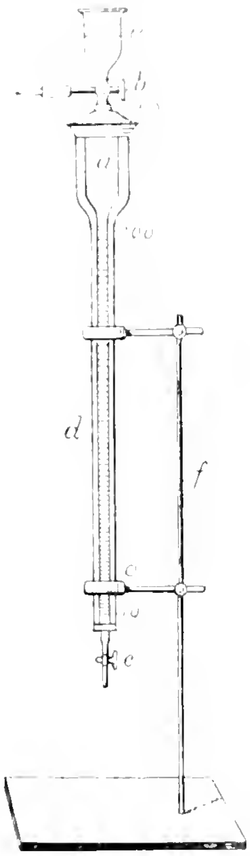


Fig. 6. B[illegible] G[illegible]
Burette [illegible]

METHOD OF USING BUNTE'S GAS BURETTE.

The burette is filled with water and the three-way stopcock closing its upper end is so turned as to communicate through it with the external air, or with the vessel containing the air to be analyzed, by means of a short piece of rubber tubing connecting this stopcock with such vessel. By opening the stopcock, closing its lower end, some of the water, say 150 c. c., is allowed to flow out, and the air or gas to be analyzed flows in to take its place. When the desired amount of the sample of air has been taken, the lower stopcock is quickly closed and the three-way stopcock is turned half-way round, thus bringing it in communication with the small cup at the top, which should also be filled with water to its 25 c. c. mark. The pressure of the contained air is now equalized and the communication with the cup is closed. A few drops of water always lodge just below the upper stopcock; these must be dislodged by gently tapping the iron stand on the floor. In a few minutes the volume of air may be read off. The burette is then connected at its lower end with a Chapman water pump and a portion of the water in it is drawn off. The water in the cup is then poured out and about 1[illegible] c. c. of a [illegible] per cent. solution of sodium or potassium hydroxide poured into it, and in turning the stopcock, this flows in to take the place of the water just removed. The fluid and air in the burette are now gently agitated, at intervals, for five minutes, the cup is again filled with water to the 25 c. c. mark, the stopcock again opened, and the pressure of the gas equalized. If any of the water flows into the burette more must be poured into the cup to retain the gas under the original pressure of 25 c. c. of water in the cup. This part of the operation requires some care and practice in order to prevent the escape of any of the contents of the burette or the entrance of external air. When the pressure is again equalized the volume of gas is again read off, the reduction in volume representing the amount of CO_2 absorbed; this is readily calculated to the per cent. of the original volume of gas.

The burette is now once more attached to the Chapman water pump to remove a portion of the fluid in the burette. About 1[illegible] c. c. of a 12 per cent. solution of pyrogallic acid is poured into the cup and allowed to flow in. The fluid and gas are gently agitated, at intervals, during five minutes, the pressure equalized as before, the volume of gas read off, and the calculations for O. made as before. In most instances N. is the only gas remaining.

From the determinations of the proportions of CO_2 and of O, in the air of the jar, after death of the animal, in the Hammond experiments, it is evident that two factors were operative in killing it. These were the low percentage of O, present and the high percentage of CO_2, which the arrangements instituted for the absorption of this gas had failed to remove. In a short time the exterior of the sponges became coated with $BaCO_3$ while the $Ba(HO)_2$ in the interior became inoperative. This can be demonstrated by determining the alkalinity of the fluid expressed from the sponges, at the end of the experiment, with solution of oxalic acid. Another fact which substantiates such a conclusion is that of the clouding of the $Ba(HO)_2$ in the Geissler potash bulbs quite early in the experiment from the CO_2 in the air aspirated from the jar in supplying fresh air. While the solution of $Ba(HO)_2$ used in the sponges was twice the strength of that usually employed in CO_2 determinations in the Pettenkofer flask method, the amount of solution which can be taken up by the sponges of the size used (about 10 c. c. each) is entirely too small to absorb more than a fractional part of the CO_2 generated by an animal during the time of an experiment.

The mode of death in these experiments presented such a close similarity to that noted in cases of CO_2 poisoning, under other circumstances, that it was impossible to distinguish it from death produced by that gas. Judging from the air analyses at death of the animals, from the constancy of the symptoms and the close similarity of the gaseous contents of the jars at death of the animals, and, besides these, the absence of any positive indications of the presence and action of other poisonous expiratory products as manifested either by the action of the animals or the mode in which death took place, it is safe to conclude that the low percentage of O, together with the high percentage of CO_2, in the atmosphere of the jars, were the principal causes of death. The mode of death differed in no particular from that noted in the case of animals dying in the closed vessels, in the "Brown-Séquard" experiments, or in those made with artificial gaseous mixtures where sufficient oxygen was present to support life for several hours. Another fact, observed likewise in all the other forms of experiment reported on, was the prompt revival of the animals when removed from the jars and supplied with fresh air. In exceptional cases, where the animal was not removed until death was certain to take place in a very short time, the revival of the animal did not follow on removal from the jar, but death supervened at a shorter or longer period after removal. The failure of these animals to revive might be attributed to the presence of *ante-mortem* clots within the heart cavities produced by the long-continued respiration of such high percentages of Co_2 as existed in the atmosphere of the jars in this and the other experiments. The prompt revival of the animals removed from the jars a little earlier appears to be an additional indication that the symptoms produced in these experiments had been due to the relative proportions of O and CO_2 present in the atmosphere which the animals breathed. The effects of an organic volatile poison would not allow such rapid recovery, and would most probably manifest itself by continued ill-health on the part of the animals subjected to it.

Some animals vitiated the contained air more rapidly than others, so that, while there is a close relation between the composition of the atmosphere at the end of the experiments, it is evident that the degree of respiratory interchange determined the duration of life for each individual. The room temperature for these experiments was very nearly constant—18° to 25° C.

A further attempt was made by modifying the apparatus. This modification is shown in Fig. 7. Here the CO_2 is absorbed by passing the air, issuing from the bell-jar containing the animal, through five Pettenkofer absorption tubes, each containing 100 c. c. of a strong solution of $Ba(HO)_2$ [10 g. $Ba(HO)_2 + 8H_2O$ to 1 L.]. In addition to this, the air is passed through two Pettenkofer tubes, each containing 100 c. c. of Buchner's alkaline pyrogallate solution, to remove some of the O from the air. The moisture is absorbed by $CaCl_2$ placed in a shallow vessel, covered with a perforated porcelain plate, in the bottom of the bell-jar.

DESCRIPTION OF THE APPARATUS USED IN THE MODIFIED "HAMMOND" EXPERIMENT, FIG. 7.

a represents a one-litre bell-jar resting on a ground-glass plate, and contains a shallow vessel with $CaCl_2$. The vessel containing the $CaCl_2$ is covered with a perforated porcelain plate on which the mouse under experiment is placed.

[illegible] two aspirating flasks, of four litres' capacity, partially filled with saturated salt solution. By reversing their positions these aspirators give a continuous current of air. The rubber stopper [illegible] of each flask carries two glass tubes with glass stopcocks, and the apparatus [illegible] to maintain the air current in the same direction by closing one, and opening the other, of the glass stopcocks when the flasks are reversed in their positions.

The Pettenkofer tubes containing the Ba(HO)₂ are attached to the stative *c*, and those containing the pyrogallate solution to the stative *d*.

e represents a stopcock in the tubing connecting the aspirators. This serves to control or [illegible] the aspiration.

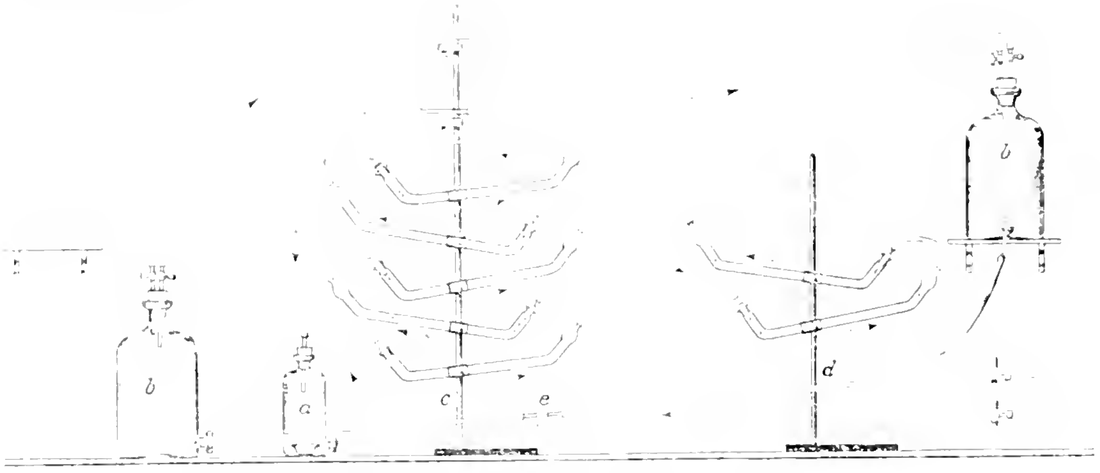


Fig. 7.—Modified Hammond Apparatus (devised by [illegible]).

The results obtained with this modification of the apparatus are shown in Table II. The same animal was used in each of the six different experiments performed, and it failed to succumb to the conditions present in any of them. In the later experiments, in which the animal was placed in a one litre bell jar, it failed to reduce the proportion of O in the volume of air within the apparatus (about six litres) to such an extent as to endanger its life, even with the additional reduction of O taking place in the two Pettenkofer tubes containing Buchner's solution of alkaline pyrogallate. The percentage of CO₂ remained quite low through the absorption by the Ba(HO)₂ in the five Pettenkofer tubes. The construction of the apparatus permitted the continuous circulation of the air within the apparatus so that the animal was constantly breathing air that had been breathed and

TABLE II.

MODIFIED "HAMMOND" EXPERIMENT.

No.	Date.	Animal.	Weight.	Aspirator.	Number of absorbers.	Capacity of air.	Time.	Examination of air.		Remarks.
								CO₂.	O.	
	1894.		Grams.				Hours.	%.	%.	
1	Oct. 24	White mouse.	23	Continuous.	5 Ba(HO)₂ tubes.	4200 c.c.	7¼			Mouse quite sick.
2	" 25	"	"	"	"	" "	8½			" " "
3	" 26	"	"	"	"	1,200 c.c.	6			" " "
4	" 27	"	"	"	{ 5 Ba(HO)₂ { 2 Pyro.	" "	4¼	.33	9.44	Previous aspiration 2 hours.
5	" 31	"	"	"	"	" "	7		18.35	Previous aspiration 12 hours.
6	Nov. 3	"	"	"	"	" "	6¼			Previous aspiration 10 hours.

rebreathed before. The direction of the air current through the apparatus is shown by the position of the arrows in the figure. By changing the position of the aspirating flasks, and turning the stop-cocks in the glass tubing inserted through the stoppers closing the upper openings of the aspirators, the current was maintained in the same direction as before, and the entrance of external air was thereby prevented.

The results obtained show that, with the absorption of the CO_2 as generated, the mouse remained relatively comfortable in the atmosphere present and that no deleterious effects developed from the continued rebreathing of the air confined within the apparatus. The animal seemed to be somewhat oppressed toward the close of each experiment, but revived quickly after removal from the apparatus.

The air contained in the two aspirating flasks was retained each time in the later experiments. Consequently in these experiments the fresh air supply comprised only that which was enclosed in the Pettenkofer tubes, the rubber connecting tubes, and in the bell-jar containing the animal. In several of the later experiments the volume of air within the apparatus was aspirated continuously through all its parts for some hours before beginning the experiment. In this manner the pure air-supply was reduced to one litre, the amount of air in the bell-jar containing the animal.

V.—Experiments to determine the proportions of CO_2 and of O in the air of a glass vessel in which small animals (mice and birds) had remained until death was produced, and the effects of different temperatures upon the duration of life and on the composition of the residual atmosphere after death in such cases.

The results obtained in these experiments are shown in Table I. At the room temperature death did not take place until the amount of oxygen present was too low to support life. At a higher or lower temperature there was a slightly shorter duration of life, varying with the amount of increase or reduction of the temperature.

TABLE I.

EXPERIMENTS WITH ANIMALS IN CLOSED VESSELS—ATMOSPHERIC AIR.

No.	Date.	Capacity of the jar.	Temperature.	Time.	Animal.	Weight.	Exam. of air.		Remarks.
							CO_2.	O.	
	1893			Hours.		Grams.	%	%	
1	Nov. 27	1000 c. c.	29.5° C.	4	Mouse.	18⅕	13.818		
2	" 28	" "	25. C.	3⅚	"	18¾	17.66		
3	Dec. 5	2000 "	23.5 C.	5	"	22¾			
4	" 6	" "	23.5 C.	7½	"	15⅖	17.30		
5	" 14	" "		8½	"	11⅗	13.12		
6	1894	1000 "	29. ° C.	3⅙	"	19½			
7	Jan. 26	" "	30. ° C.	4	"	21	12.00	8.60	
8	" 27	" "	30.5 C.	4⅙	"	11	12.00	8.60	
9	" 30	2000 "	31. C.	4	"	21			
10	Feb. 1	" "	31. ° C.	4⅙	"				
11	" 2	" "	7.5 C.	7	"		12.60	8.00	
12		" "	5. C.	7½	"		10.00	9.20	
13		" "	25.5 C.	7½	"		13.20	6.40	Cold-water cloths applied to the outside of the jar at temperature of 11° C.
14		" "	24. ° C.		"		11.90	7.50	
15	" 9	" "		2	Sparrow.				
16	" 9	" "		2$\frac{1}{10}$	"				
17	" 13	" "	27.5° C.	2¾	"		12.75	5.86	
18	" 13	" "	27.5° C.	2¼	"				
19	Mch. 28	7000 c. c.	30. ° C.	9	"	24	13.28	4.89	
20	" 29	" "	29.5 C.	7¾	"	23	13.485	7.37	
21	" 30	" "	11.5° C.	9¾	"	23	13.00	6.929	
22	" 31	" "	12. ° C.	8⅙	"	22	87.97	5.534	

[illegible] temperature upon the duration of life in a confined space (and even in the open [illegible] Richardson's experiments (5), is presented in Table J. [illegible] experiments show that the duration of life is very perceptibly shortened [illegible] as well as at a lower temperature than 18° to 25° C.

TABLE J

"RICHARDSON" EXPERIMENT

[illegible]	[illegible]	[illegible]	Weight	[illegible]	Temperature	Atmosphere	Time	Final Gas CO₂	Final Gas O	Remarks
	1894		Grams	c.c.						
1	Nov. 5	White mouse	22	612	45° C.	Air	5 min	1.06	18.25	Died
2	" 5	"	22	"	7.5 "	"	2 hrs	12.7	3.7	"
3	" 5	"	21½	"	"	"	1 "	11.4	6.35	"
4	" 5	"	2[illegible]	"	16.2 "	"	3 "	13.5	2.6	"
5	" 6	"	16	"	5 "	"	20 min			Flask plunged in hot water open at top.
6	" 6	Gray mouse	2[illegible]	122	42 "	"	3 "			Same as in No. 4. Remained alive.
7	" 6	"	12	"	50 "	"	21 "			Same as in Nos. 4 and 5. Died.
8	" 6	White mouse		625	48 "	"	7 "			Rapid current of air aspirated through the flask.
9	" 6	"	22	"	10.5 "	76.59 O 23.41 N	4½ hrs			
10	" 6	"		"			20 min.	22.36	39.44	Same flask as No. 9. Mouse introduced at death of No. 9.
11	" 9	"	16	"	10 "	92.8 O 9.2 N.	4¼ hrs.			
12	" 9	"		"			2 "	25.20	47.20	Same flask as No. 11. After death of No. 11.
13	" 9	Gray mouse.	21	"	13 "	92.8 O 9.2 N.	3¼ "			
14	" 9	"		"	20 "		26 min	28.21		After death of No. 13.
15	" 1[illegible]	White mouse.	18	"	5 "	92.8 O 9.2 N.	3½ hrs.			
16	" 1[illegible]	"	21	"	30.5 "		1½ "	19.34	55.3	After death of No. 15
17	" 1[illegible]	"	16	"	4.5 "	97.8 O. 9.2 N	54 min.			
18	" 1[illegible]	"	22	"	1[illegible] "		47 "	24.03	60.05	After death of No. 17
19	" 13	"	12	"	18 "	Air.	2½ hrs			
20	" 13	"	13	"	18 "		1 min	14.47	4.27	After death of No. 19
21	" 13	"	12	"	4[illegible] "	Air.	55 "			
22	" 13	"	13	"	7.5 "		34 "	17.76	7.45	After death of No. 21

An interesting condition noted in autopsies upon a number of the animals that succumbed to the conditions in the "Richardson" experiment was that of the blood in the heart of the animal. In the cases where death supervened in a short time, the heart blood was fluid and seemed to lack the power of coagulation, while in those cases in which death resulted after several hours' confinement in the flask, the cavities of the heart contained firm, dark clots of blood. This condition of the blood was, no doubt, due to the influence of the CO generated by the animal during the experiment.

CHART I.—SHOWING RELATIVE PROPORTIONS OF CO_2 AND OF O, AND THE RELATIVE DURATION OF LIFE IN THE EXPERIMENTS IN CLOSED VESSELS.

Key
Represents relative per cent. of CO_2 at close of exp.
—x—x— " " " " O " "
" " duration of life.
—o—o— " " room temperature.

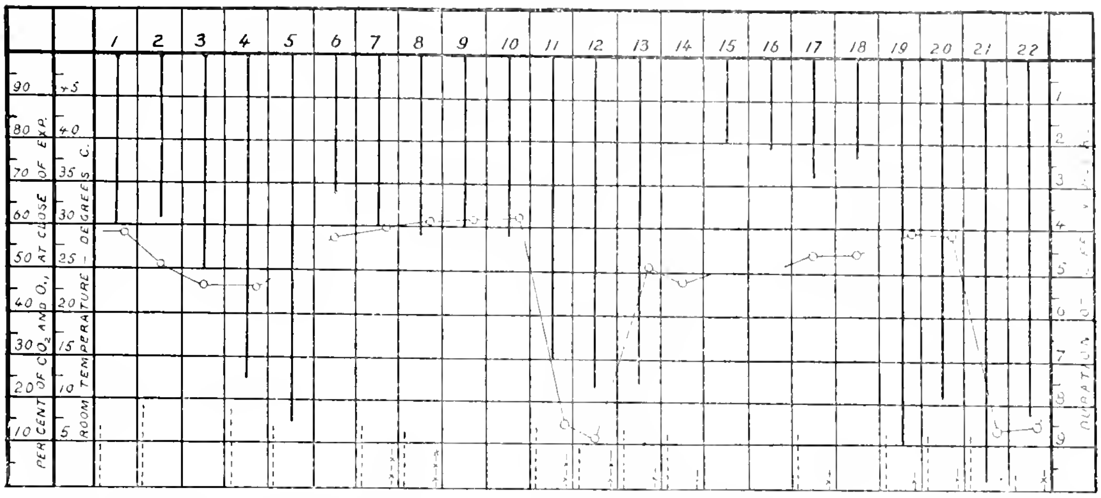


Chart I. shows the relative duration of life, the relative proportions of CO_2 and of O at death of the animal, in the experiments with animals in closed vessels containing atmospheric air.

CHART II.—SHOWING RELATIVE DURATION OF LIFE, PROPORTIONS OF N AND O AT BEGINNING OF EXPERIMENTS, WITH THE TEMPERATURE OF THE ATMOSPHERES IN THE "RICHARDSON" EXPERIMENTS.

Key
···· Represents relative per cent. of N.
—x—x—x " " " " " O.
" " duration of life.
—o—o—o " " temperature in the flask.

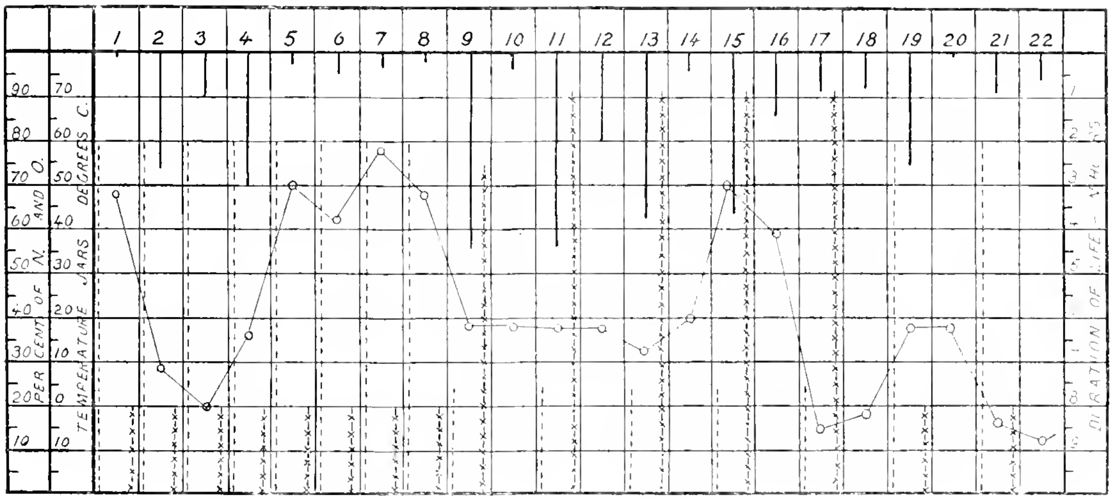


Chart II. shows the relative duration of life, the relative proportions of N and of O at the beginning of each of the "Richardson" experiments, also the temperature curve for the entire series.

TABLE K.

EXPERIMENTS WITH ARTIFICIAL ATMOSPHERES.

[illegible]	[illegible]		[illegible]	[illegible]	[illegible]	[illegible]			[illegible]	After Experiment			Respiratory Quotient $\frac{CO_2}{O}$
						CO_2	O	N		CO_2	O	N	
1	April	3	Mouse		228		4.9	95.1	30 sec.	.12	4.47	95.41	0.0045
2	"	3	"		"		84.	16.	1¼ hrs.	[illegible]	58.73	16.91	0.3405
3	May	25	Rabbit	1092	37,000	.04	20.7	79.26	5½ "	14.27	4.70	81.04	3.0356
4	June	6	Guinea-pig	473	4,000	.04	20.7	79.26	1¾ "	15.26	4.29	80.45	3.5571
	"	4	"	565	"	.68	5.30	93.93	43 min.	8.59	2.31	89.10	3.6796
6	May	5	Mouse		2282		83.07	16.93	13¾ hrs.	25.53	58.65	14.70	0.4404
7	"	5	"		"		83.07	16.93	15¼ "	21.06	61.78	17.16	0.3408
8	"	21	"	16	"		11.35	88.65	3 "	6.56	4.14	89.30	1.5845
9	"	21	"	15	"		11.35	88.65	4½ "	7.43	3.58	89.00	2.0754
10	"	21	"	17	"		11.35	88.65	4½ "	7.52	3.16	89.22	2.3797
11	"	21	"	8½	"		9.75	90.25	6½ "	5.41	3.34	91.25	1.6197
12	"	21	"	8½	"		9.75	90.25	1½ "	4.51	2.84	92.65	1.5880
13	"	21	"	11	"		9.75	90.25	6¾ "	5.17	2.87	91.96	1.8013
14	"	25	"	16	"		8.23	91.77	4 "	4.18	2.52	93.30	1.6587
15	"	25	"	8	"		8.23	91.77	1 min.	.03	6.48	92.89	0.0072
16	"	25	"	15	"		8.23	91.77	3½ hrs.	3.85	2.54	94.61	1.5157
17	June	1	"	22	"		5.7	94.30	4 min.	.58	4.91	94.51	0.1181
18	"	1	"	17	"		5.70	94.30	2 "	.77	5.40	93.83	0.1425
19	May	26	"	12	"		5.70	94.30					
20	"	24	"	12	"	.58	5.42	94.00	3 min.				
21	"	24	"	8	"	.58	5.42	94.00	2 "				
22	"	24	"	8	"	.58	5.42	94.00	2½ "	.79	5.75	93.46	0.1273
23	June	1	"	11	"	12.03	21.61	66.36	8½ hrs.	18.01			
24	"	1	"	12	"	12.03	21.61	66.36	8½ "	21.02			
25	April	29	"		"	13.30	3.72	82.98	30 sec.	13.40	3.70	82.90	3.6216
26	May	1	"		"	14.05	22.60	63.35	7 hrs.	24.65	11.40	64.05	2.1622
27	"	1	"		"	14.05	22.60	63.35	8½ "	25.12	10.00	64.90	2.5100
28	"	1	"		"	14.05	22.60	63.35	8¼ "	28.32	7.40	64.28	3.8243
29	"	11	Rabbit	1357	37,000	11.28	19.64	69.08	8½ "	19.16	4.27	75.57	4.4871
30	"	15	"	1755	"	22.47	22.23	55.30	5 "	20.10	4.89	75.01	4.2962
31	"	15	Mouse		228	21.00	12.00	67.00	2 "	19.70	8.93	71.37	2.2060
32	"	15	"		"	21.00	12.00	67.00	2¾ "	20.02	8.41	71.57	2.3781
33	"	15	"		"	21.00	12.00	67.00	5½ "	21.80	6.54	71.66	3.3333
34	"	4	"		"	21.05	16.65	61.40	52 min.	21.45	15.70	62.85	1.3662
35	"	4	"		"	21.05	16.65	61.40	2¼ hrs.	23.15	12.815	63.985	1.8064
36	"	4	"		"	21.05	16.65	61.40	4½ "	22.70	11.43	65.87	1.0772
37	June	9	Rabbit	1442	37,000	17.00	13.82	69.18	7½ "	16.14	2.07	81.69	5.4343
38	"	9	Guinea-pig	478	4,000	15.00	21.00	64.00	1¼ "	16.07	2.77	81.06	5.8014
39	"	11	Gray rat	Full grown	37,000	17.81	3.88	88.25	1¾ "	11.13	8.55	80.32	1.3017
40	May	31	Mouse	21	2282	25.47	18.00	56.53	¾ "	27.11	16.20	56.69	1.6734
41	"	31	"	19	"	25.47	18.00	56.53	1¾ "	27.47	17.53	55.00	1.5670
42	"	31	"	16	"	25.47	18.00	56.53	1⅓ "	27.42	16.83	55.75	1.6292
43	June	11	Guinea-pig	758	4,000	37.[illegible]	21.[illegible]	4[illegible]	1 "	17.83	2.77	79.40	6.4368
44	"	12	Gray rat	Half grown	"	37.5	22.50	4[illegible]	1½ "	17.25	4.63	78.12	3.7257
45	"	13	Rabbit	2255	37,000	56.75	43.25		5 "	20.40	3.71	75.89	5.4986
46	"	13	Guinea-pig	742	4,000	62.50	21.25	16.25	1½ "	27.09	4.30	68.61	6.2870
47	"	12	Mouse		2280	81.36	18.64		1 min.	81.36	18.64		4.3648
48	"	12	"		"	81.36	18.64		1 "	81.36	18.64		4.3648

In order to ascertain whether an atmosphere which had served for respiration, once or oftener, affected an animal differently from an atmosphere made up artificially from pure gases to the same proportions as found in the analysis of the atmospheres in the different experiments reported on, a series of experiments was undertaken to determine the effects of gaseous mixtures made up of varying proportions of CO_2, O, and of N. The results obtained in this series of experiments are shown in Table K, giving the capacity of the jar, the weight of the animal, the composition of the atmosphere before and after the experiment, and the duration of life in such an atmosphere. The construction of artificial atmospheres, and the introduction of an animal into such an atmosphere without considerable alteration of the proportions of the different gases, through the accidental introduction of atmospheric air, was not always found an easy matter. The chief difficulty was unfortunately a fundamental one, in that the CO_2 was not entirely free from atmospheric air; the oxygen contained more than 10 per cent. of N; while the attempt to obtain pure N from atmospheric air by means usually employed for this purpose—burning out the O with phosphorus—gave variable results with each attempt, the proportion of O remaining after the absorption of the P_2O_5 usually ranged from 2 to 5 per cent. Under these circumstances it will be seen that there was an almost insurmountable difficulty to the construction of an atmosphere having the exact proportions of the different gases predetermined for it, and abundant evidence of this difficulty was obtained from analyses of the mixtures after sufficient time had been allowed, as was supposed, for the diffusion of the gases.

The thorough diffusion of the components of gaseous mixtures appears to be a slow process. Twenty four hours, or longer, was usually allowed for this to take place, yet from the variable lengths of time during which animals of the same size and apparently possessing the same amount of vitality could survive in atmospheres of equal volume made up from the same mixture, and the variable proportions of the different gases found on analysis after death of the animals exposed to these atmospheres, show that perfect diffusion had not always taken place. These discrepancies in the construction of the gaseous mixtures are to be regretted, though they are not great enough to vitiate the value of the experiments taken as a whole. The positive character of the results is too evident to allow these difficulties to have much weight.

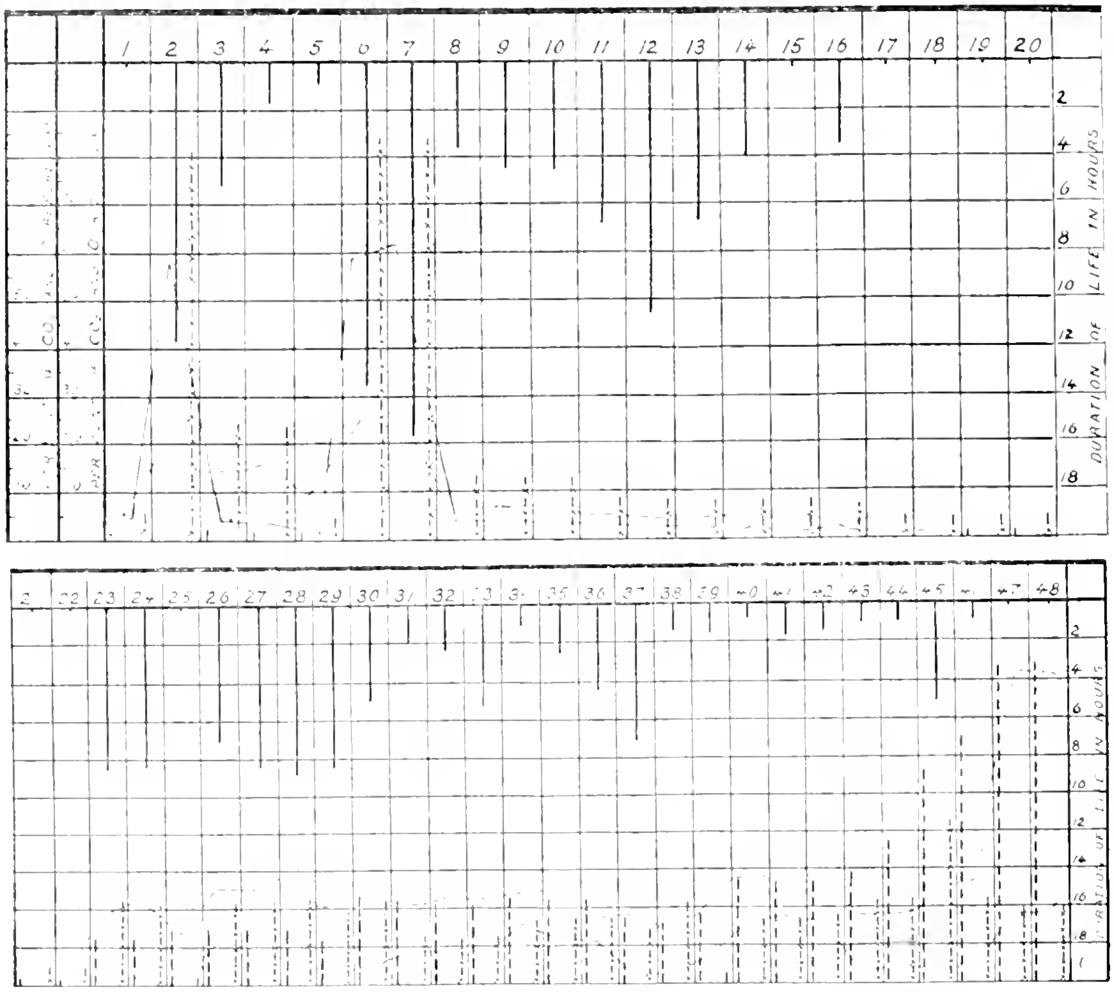
There is an uncertain feature in the determinations of the proportions of CO_2 in the gaseous mixtures, after death of the animal, in those instances where this gas was originally present in high percentages. On this account it would be well to bear in mind that the third column representing the proportions of the different gases present at death, marked N, represents, in fact, the gases which failed to be absorbed in the gas-burette by the solutions of caustic soda and of pyrogallic acid used to absorb the CO_2 and O present. There is no doubt as to the presence of the proportions of CO_2, as stated in the different experiments, before placing the animal in the mixture. Whether a large proportion of the CO_2 was likewise absorbed by the animal, it is impossible to say. There is no probability that such was the case. A part of the loss of CO_2 may also be accounted for in the method employed in making the gaseous mixtures. These mixtures were made by displacing water from the jars which were to contain them. The water may have taken up the CO_2 more readily than the other gases, especially where this was the first gas introduced into the jar, and may, therefore, have been a slight source of variation in the composition of the mixture; yet, it seems, from analysis made just before placing the animal in the mixture, that the loss in this manner was very small. The desired proportion of CO_2 was usually present, even after twenty-four hours had been allowed for diffusion to take place.

Chart III. shows the results obtained in these experiments as to the relative duration of life and the relative proportions of CO_2 and of O at the beginning of the experiment, as well as at death of the animal. In comparing this chart with Chart I., it must be remembered that in this series of experiments the composition of the atmosphere was a different and variable one, while in the series of experiments shown in Chart I., the composition of the atmosphere at the beginning of the experiment was invariably the same—*i.e.*, atmospheric air. This fact, along with the variations in size of jar for different animals, explains the longer or shorter duration of life in this series of experiments as compared with that presented in Chart I. The very important influences of these [illegible] kept in mind constantly in comparing these two charts, as well as in comparing [illegible] any of the other forms of experiment.

CHART [illegible] Experiments with the Artificial Gaseous Mixtures.

[illegible] after the experiment

[illegible]



The mode of death in these experiments, when sufficient O was present to support life for several hours, was similar to that noted in the "Hammond" experiments, in the experiments with atmospheric air in closed vessels, and in the "Brown-Sequard" experiments, and could not be distinguished from death in CO_2 poisoning. When such an amount of O was not present, death was often almost instantaneous, following, at the longest, within five minutes after the animal was placed in the jar. After a few gasps and several violent struggles, life became extinct.

A number of the animals used in this series of experiments were examined *post mortem*. The gross appearances presented in these animals were of the character of those found ordinarily in cases of CO_2 poisoning. Intense venous engorgement was noted in all the organs and tissues.

The heart invariably contained large, firm blood clots, dark in color, extending from the auricles into the ventricles. This was usually most marked on the right side.

Microscopic examination of the organs, hardened in alcohol and mounted in celloidin, presented no other constant conditions than those brought about by the mode of death—the extensive venous engorgement. The very slight pathological changes noted in isolated cases, from the rapidity with which death ensued on exposure to the atmospheric conditions present, must be attributed to causes antedating the time of the experiment by a considerable period. The changes here referred to were mostly of the nature of interstitial changes present in the liver and kidneys. No trace of the poisonous effects of any other respiratory products was noted in any of the animals examined.

The results obtained strengthened to a satisfactory degree the conclusions drawn from the results obtained in the other experiments reported on. It was shown that in the absence of a sufficient proportion of O in the artificial gaseous mixture to support life—at least 5 per cent.—the animal speedily succumbed. On the other hand, CO_2 could be present in quite large proportions, as long as sufficient O was also present to support life for some time, and no untoward effects were manifested. The different animals used in these experiments—sparrows, rats, mice, guinea-pigs, and rabbits—manifested no distinct differences in susceptibility to the conditions present.

VI.—Experiments in the inoculation of animals with the moisture condensed from the exhaled breath, as conducted by Brown-Séquard and d'Arsonval, by Hofmann-Wellenhoff, and others. Four series of animals were inoculated with the fluid as shown in Table L.

SERIES I.—The fluid, clear, limpid in character and without odor, of which 21 c. c. had been collected from the breath of a healthy person on December 5, 1893, was warmed by holding the receptacle containing it in a vessel of warm water, about 35° C. A rabbit, weighing 1870 g., received $1\frac{3}{4}$ c. c. into the large vein at the margin of the ear. Another rabbit, weighing 1820 g., also received $1\frac{3}{4}$ c. c. in the same manner. A guinea-pig, weighing 220 g., received $4\frac{1}{2}$ c. c. into the peritoneal cavity. A second guinea-pig, weighing 280 g., also received $4\frac{1}{2}$ c. c. into the peritoneal cavity. A third guinea-pig, weighing 220 g., received $4\frac{1}{2}$ c. c. of sterilized distilled water into the peritoneal cavity as a control.

These animals were kept under careful observation for more than a month, and as nothing unusual in their condition presented itself, they were released.

SERIES II.—On January 18, 1894, 20 c. c. of the fluid had been condensed from the breath of the man having the tracheal fistula. The fluid was warmed by holding the receptacle containing it in a vessel of warm water, about 36° C.

Of this fluid 5 c. c. were injected into the peritoneal cavity of each of three white rats; a fourth rat receiving 5 c. c. of sterilized distilled water into the peritoneal cavity as a control experiment.

INOCULATIONS WITH CONDENSED FLUID OF EXPIRED BREATH.

TABLE L.

SERIES I.

No.	Date.	Animal.	Weight.	Amount of fluid injected.	Remarks.
	1893		Grams.		
1	Dec. 5	Rabbit	1870	$1\frac{3}{4}$ c.c.	Under observation over a month. Healthy.
2	"	"	1820	$1\frac{3}{4}$ "	" " " " "
3	"	Guinea-pig	220	$4\frac{1}{2}$ "	" " " " "
4	"	"	280	$4\frac{1}{2}$ "	" " " " "
5	"	"	220	$4\frac{1}{2}$ "	Control—inoculated with sterilized distilled water.

SERIES II

	1894				
1	Feb. 2	White rat	175	5 c.c.	Still alive and healthy.
2	"	"	[illegible]	5 "	Died 9-6, 1894, from other causes.
3	"	"	148	5 "	Still alive and healthy.
4	"	"	112	5 "	Control—inoculated with sterilized distilled water.

SERIES III

1	Feb. 2	Rabbit	1500	7.5 c.c.	Killed after 45 days.
2	"	"	2150	1 "	Still under observation. Healthy.
3	"	"	880	5 "	Died after 28 days.
4	"	"	[illegible]	5 "	Control—inoculated with sterilized distilled water.

SERIES IV

1	May 3	Rabbit	1161	10 c.c.	Still under observation. Healthy.
2	"	"	[illegible]	1 "	Killed 11-2, 1894. Healthy.
3	"	"	1750	1 "	" " "
4	"	"	1350	1 "	Still under observation. Healthy.

These animals were under close observation for several months without noting any alteration in their condition. One of them has since died (Sept. 6, 1894) from other causes. The others continue well.

SERIES III. On February 1, 1894, 44 c.c. of the fluid had been collected from the exhalations of the man having the tracheal fistula. This fluid was again warmed, as before, to about 35° C., and injected into the peritoneal cavity of rabbits as follows:

No. 1. Weight, 1500 g.; 7.5 c.c. of fluid.
No. 2. " 2150 g.; 1 c.c. " "
No. 3. " 880 g.; 5 c.c. " "
No. 4. " [illegible] g.; 5 c.c. " sterilized distilled water.

Rabbit No. 3 of this series died during the night of March 4, 1894, and an autopsy held the next morning showed the following conditions[*]:

Young female rabbit. Externally: Not very thin, adipose not quite used up. Internally: On opening the abdominal cavity the organs were found in normal position. Stomach and large intestines well filled. Liver slightly enlarged, no spots; shows lobular appearance well marked; rather pale in color, as are all the organs and tissues (albino). Gall bladder well filled with pale bile. Small intestines moderately filled; no change in their appearance; Peyer's patches not enlarged. Appendix not inflamed. Spleen not enlarged. Kidneys normal in size. Adrenals small. Lungs normal, rather pale. Heart rather pale, contracted on left side, right side filled with blood.

Cultures were taken from the liver, spleen, blood, and abdominal fluid and all proved negative.

Microscopic examination of the organs: Kidney. Presents some blood-vessels which contain an increased amount of white blood corpuscles. Glomeruli are slightly swollen, showing a small

---

[*] Autopsy made by Dr. Olmsted.

amount of infiltration. Slight increase of connective tissue between the tubules. Large blood vessels are very much dilated. Areas of slight extravasation. A certain amount of cloudy swelling. Liver—Shows large number of small areas of cell-death necrotic areas. Breaking up of cells and fragmentation of the nuclei, which is almost identical with the conditions found in diphtheria. Adrenals—No change apparent. Spleen No change apparent. The teased heart muscle, treated with acetic acid, shows possibly a trace of fatty degeneration. No "widespread ecchymoses and hemorrhages in the lungs and intestines" were found, as reported by Brown-Sequard and d'Arsonval.

On March 20, 1894, rabbit No. 1 of this series was killed in order to study the condition of its organs and compare the results with the conditions found in rabbit No. 3. Weight before death, 1830 g., gain 330 g. It seemed to be in perfect health.

On opening the abdominal cavity the organs were found in normal position. No increase of peritoneal fluid. On the liver a number of points (psorosperms ?), one a depression ½ mm. in depth, grayish-white in appearance, were noted; mostly on the left lobe. Several other small areas—whitish in appearance, sharply limited in their outline, smaller than the last, not distinctly depressed, usually two, three, or more together—were found scattered over the upper and lower surfaces of the liver. The liver is dark in color, lobules well marked out; of about normal size and consistency. Cutting into the liver there is the usual amount of hemorrhage. Spleen—Small, if anything, it is contracted, otherwise of normal appearance. Adrenals appear normal. Kidneys—Embedded in usual amount of fat. Normal in size, color, and consistency. Small echinococcus cyst in the great omentum, and another in the liver. Intestines normal in appearance. Heart normal in appearance. Portion of muscle teased with salt solution and treated with acetic acid shows no fatty change. Lungs normal in appearance.

Cultures were taken from the peritoneal fluid, liver, spleen, kidneys, and blood. All proved negative.

Microscopic examination of the organs: Liver—Contains a small hemorrhage at the depressed part noted at autopsy. The other spots noted are found to be entirely superficial. Slight increase of connective-tissue elements. Engorgement of a capillary noted. Kidney—Nephritis manifested by some congestion of vessels, proliferation of the connective-tissue cells between the tubules and around the glomeruli; an occasional glomerulus being quite contracted. Spleen shows an increased amount of pigment.

The remaining rabbits of this series have continued well to the present time.

Series IV.—On March 30, 1894, 45 c. c. of the condensed fluid had been collected from the breath of a healthy person. This was again warmed to 35° C., and injected into the peritoneal cavities of four rabbits, each receiving 10 c. c. of the fluid; their weights were as follows: 1161 g., 1359 g., 1400 g., and 1759 g.

On November 2, 1894, the rabbits of this series having remained healthy, Nos. 2 and 3 were killed in order to study the condition of their organs, and determine whether they presented organic lesions traceable to the fluid injected. They were in perfect health as far as might be judged from their appearances.

On *post-mortem* examination all the organs in these animals were found to be normal. Nor was any abnormality to be noted in microscopic examination of the organs.

The remaining animals of this series continue well to the present time.

The pathological conditions noted in the cases of rabbits Nos. 1 and 3 of Series III., are not unusual in these animals, as they are very commonly found in normal animals reared in the laboratory and in those purchased from dealers.* It is unsafe to infer, therefore, that any of the conditions noted in these animals were due to the action of the fluid injected.

The sterility of the fluid injected into the animals in this series of experiments was tested each time by the inoculation of portions of it into tubes of melted gelatin; these were then hardened according to Esmarch's method. In two instances several colonies of a yellow bacillus, common to

---

* This fact has also been noted by Dr. Abbott. His observations have not yet been published.

[illegible] In [illegible] other instances the cultures remained [illegible] were taken from the portions remaining after the animals [illegible] probably account for the contaminations noted. There is no [illegible] were contaminated in the exhaled breath while collecting the [illegible] of the organisms which developed in these cultures indicates [illegible] while the fluid was being warmed and inoculated into the animals.

VII. The experiments consisting in [illegible] to breathe air recently expired by other animals. These experiments are designated as "Brown-Séquard" experiments. The apparatus used consists of a series of bell jars, four to six in number, connected together by means of glass and rubber tubing, and so arranged that a continuous current of air is conducted through the entire series. The apparatus is shown in Fig. 8. The first animal receives pure air only, the second animal receives the air coming from the bell jar containing the first animal, the third that coming from the second, while the last animal receives air that has traversed the entire series, and, consequently, contains the impurities added to it in its course through all the other jars.

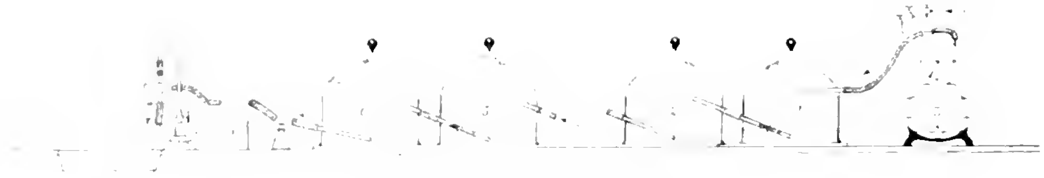


FIG. 8.—Brown-Séquard apparatus.

KEY TO "BROWN-SÉQUARD" APPARATUS—FIG. 8.

The Nos. 1, 2, 5, 6 represent four of the six bell jars in the series.

a, represents the gas meter.

b, represents a small Erlenmeyer flask containing about 100 c. c. of water. The bubbles produced by the air passing through the water show whether aspiration is regular or not.

c, represents a Woulff bottle attached between the Erlenmeyer flask and pump to prevent the entrance of water into the apparatus when there is negative pressure in the apparatus.

d, represents the water tap.

e, represents a Chapman water pump, which creates the suction and maintains the ventilation.

The glass and rubber tubing connecting the different parts of the apparatus, as shown in the figure, has an internal diameter of nine mm., while that used to connect the seven-litre bell jars was only five mm. in its internal diameter.

DESCRIPTION OF THE "BROWN-SÉQUARD" APPARATUS—FIG. 8.

The bell jars rest on large ground-glass plates, and, in order to produce an air-tight joint, the base of the bell jar is well rubbed with beef suet (well adapted for this purpose). In addition to this, the joint is sealed with melted paraffine. If this work is carefully done there is no possibility of leakage at these joints. The bell jars are connected together by means of glass tubing bent at right angles and inserted through a perforated rubber cork fitted into the openings near the top and bottom of the jar. The air enters the apparatus through the gas-metre. The metre is connected with the first jar by means of rubber tubing attached to the glass tube inserted into the upper opening of the jar. After passing through this jar it takes its exit by means of the glass tube inserted into the lower opening, and connected with a similar glass tube inserted into the upper opening of the second jar by means of a short piece of rubber tubing. It takes the same course through all the jars.

The bell jars shown in the figure represent those used for the rabbits, and have a capacity of [illegible] c. c. A wooden box, four inches in depth and just large enough to allow the bell jar to be placed over it, was placed in each of these bell jars. These boxes contained fine dry sawdust to a depth of about five cm., thus forming a comfortable bed for the animals, and at the same time absorbing the urine. In the last experiment (No. 33) it was found necessary to change the sawdust in these boxes every eight to twelve days. When the sawdust was changed each week the animals remained comfortable.

The bell jars used for the mice, sparrows, and guinea pigs were exactly similar in construction to those represented in the figure, but only of 7000 c. c. capacity. For these animals a false bottom of wire netting was placed in the bell jars instead of the boxes with sawdust. This arrangement served to keep the mice and sparrows dry and comfortable, but was less satisfactory with the guinea pigs.

For the mice and sparrows sufficient food and water were placed in the jar at the beginning to last to the close of the experiment. For the guinea-pigs and rabbits this was impossible; these being fed daily on cabbage leaves introduced through one of the openings in the jars. By arresting the aspiration of air through the apparatus for a few minutes there was very little opportunity for any change to take place in the confined air while the animals were being fed.

In order to facilitate the taking of samples of air from the bell jars, a T-tube was inserted between each of the last three jars. The Bunte gas-burette was attached to the stem of one of these T-tubes and the air aspirated from the jar by the force of the water flowing out of the lower opening of the burette. By placing a screw clamp on the rubber connections on either side of the T-tube it was possible to take a sample of air from the jar before or after it, as might be desired. By stopping the aspirating pump there was rarely any difficulty in taking a sample of air from any of the jars in the manner stated. On two or three occasions a slight negative pressure in the jar, caused by the small amount of ventilation taking place, prevented the aspiration of a sufficient amount of air (100 to 150 c.c.) to accomplish its analysis in the burette. Otherwise no trouble was experienced in the taking of samples of air as desired. The gas-burette was connected with the T-tubes by means of a short piece of rubber tubing attached to the stem of these tubes and ordinarily closed with a short glass rod. The rubber tubing was attached to the three-way stopcock of the burette.

The results in the thirty-three experiments performed upon sparrows, mice, guinea pigs, and rabbits are shown in the following tables.

In these experiments, as well as in those previously reported, the disturbance of the heat-regulating function may have contributed to the results.

Absorbers containing caustic soda or potash, or soda lime, were used in experiments 6 to 14 between the third and fourth, and the fourth and fifth jars of the series to absorb the CO_2 from the air passing into the last two jars. This arrangement failed to save the lives of the animals in these two jars. In experiments 15, 18, and 19, an absorption-tube containing concentrated H_2SO_4 was placed between the last two jars. The results obtained in these three experiments do not differ from those obtained without the H_2SO_4 absorbers, and, therefore, give no evidence whatever of the protective influence claimed for such absorbers. The primary cause of death, low percentage of O, was still present and active.

Experiments 20 to 28 were made with the hope of producing some slight tolerance to the atmospheric conditions present in these experiments on the part of an animal subjected to such conditions for a considerable time. While there is positive evidence that a mouse living under these conditions for several days can withstand an atmosphere that instantly kills a fresh mouse, the number of experiments made are insufficient to prove that such tolerance has any great degree of permanency; yet the results obtained with the mice carried through the series of experiments from 20 to 28 indicate the probability that the tolerance obtained is maintained for at least several days afterward, and that such animal is less likely to die when again quickly placed into such an atmosphere than one that had not had such an experience.

The guinea-pigs used in experiment 30 seemed to be unable to withstand, with equal facility with the mice and sparrows, the atmospheric conditions to which they were subjected. Several of them succumbed to œdema of the lungs during the second week of the experiment, but since this is the only experiment in which these animals were used, a positive opinion on this point cannot be given.

The rabbits in experiment 31 were supposed, at the time, to have succumbed to the oppressive heat of the laboratory owing to the season of the year, but the later experiments would indicate an insufficient amount of air was aspirated through the bell jars, and it is evident that leakage took place through some of the connections because of the irregular order in which death took place.

The last experiment was made to determine what the results would be when the proportion of CO_2 was kept as low as Brown-Séquard and d'Arsonval claim for their experiments. It was found impossible to aspirate sufficient air per hour to bring about this result. However, sufficient air was aspirated to prevent the reduction of the O to proportions that were insufficient to support life. By this means it was possible to continue the experiment for six weeks without losing any of the animals, or producing any grave symptoms in any of them.

In this experiment mercurial manometers were attached between the first and second, and between the fifth and sixth bell jars to ascertain the amount of negative pressure, if any, brought about by the conditions or by the form and arrangement of the apparatus. A difference of about three millimetres was noted between the fifth and sixth bell jars, while no difference was noted between the first and second. It was also ascertained, by placing a clamp on the rubber tubing connecting the fifth and sixth jars, and continuing the aspiration, that the amount of negative pressure required to break one of the glass plates on which the jars rested, as occurred in experiment 32, was 105 millimetres. From this it may be inferred that at times a greater negative pressure existed than that noted in the last experiment. Such extreme negative pressure as was found necessary to break a glass plate 45 × 45 × 0.6 centimetres could only occur upon the entire arrestation of the air-current from some accident to the apparatus. Under ordinary circumstances we do not believe that the amount of negative pressure differed to any extent from that found in the last experiment.

The proportions of CO_2 and of O present at the time of death bear a constant relation to each other in the different experiments. The duration of life in each instance was dependent entirely upon the rapidity of the air current circulating through the apparatus. This statement, however, requires further explanation. If the average rate of ventilation per hour for an entire experiment is taken, it will be found to vary considerably in the different experiments. This is evident when it is stated that in experiment 7 the rate had been 9.8 litres per hour up to the time of the death of the animal in the third jar; in experiment 8 the rate had been 3.8 litres per hour at the death of the fifth animal; in experiment 9 the rate had been 11.9 litres per hour at the death of No. 5; at the death of No. 3, in experiment 14, 10.2 litres per hour; at the death of Nos. 3, 4, and 5, in experiment 15, 3.45 litres per hour; at the death of Nos. 3, 4, and 5, in experiment 16, only 1.9 litres per hour; at the death of No. 5, in experiment 10, 3.55 litres per hour. From these figures it will be seen that the average rate of ventilation per hour for an experiment is not the most important factor. By referring to the tables giving the details for each of the 33 experiments it will be noted that the rate of ventilation was frequently changed. It was usually increased considerably in the evening and again decreased the next morning. Frequent changes in the rate during the day were also necessary, because it is practically impossible to get a perfectly steady current with the water pump. In carefully regulating the rate of ventilation, the lives of the animals were controlled at will, and it is upon the rapidity of the air-current toward the close of the experiment that the duration of life depended in each case.

The rabbits used in the last "Brown-Séquard" experiment were weighed at the end of the experiment and their weight then as compared with their weight at the beginning of the experiment was as follows:

No. 1,	before	820 g.,	after	1052 g.,	gain	232 g.
" 2,	"	900 g.,	"	1055 g.,	"	155 g.
" 3,	"	917 g.,	"	1190 g.,	"	273 g.
" 4,	"	1125 g.,	"	1047 g.,	loss	78 g.
" 5,	"	1220 g.,	"	1352 g.,	gain	132 g.
" 6,	"	1665 g.,	"	1544 g.,	loss	121 g.

At the death of No. 4, six days after the close of the experiment, the loss in its weight was found to have been caused by the presence of psorosperms in its liver. This organ was literally filled with masses of these bodies. The loss of weight in No 6, in the absence of any other observable causes, may be safely attributed to its position in the series of bell jars, and, therefore, to the impurity of the atmosphere which it breathed. The estimations of the proportions of CO_2 and of O present in this bell jar, as found from day to day, denote atmospheric conditions that were undoubtedly unfavorable to the full performance of its bodily functions. It ate less ravenously than the other animals and was frequently in a stupid, drowsy condition.

At the close of this experiment an examination of the blood of these rabbits was also made and the proportion of corpuscles per cubic millimetre determined with the Thoma Zeiss hæmocytometer, with the following results :

No. 1,	5,170,000	red, and	24,000	white per cubic mm.
" 2,	5,337,000	" "	21,000	" " " "
" 3,	4,510,000	" "	18,000	" " " "
" 4,	4,150,000	" "	10,000	" " " "
" 5,	4,950,000	" "	15,000	" " " "
" 6,	4,375,000	" "	16,000	" " " "

Here again there is evidence that the conditions existing in these bell jars were injurious to some extent ; most so in the last jars. No. 4 presents evidence of an influence more serious in its nature than that presented by the other animals, and this has since been found to have originated from causes within its own body.

Microcytes were noted in the blood of these animals. These immature corpuscles seemed to be more numerous in Nos. 4, 2, and 1 ; the blood of the other animals presenting only a few of these bodies.

Thirty-eight days after the termination of the experiment a second examination was made of the blood of the five remaining animals, with the following results :

No. 1,	4,400,000	red, and	20,000	white per cubic mm.
" 2,	4,500,000	" "	15,000	" " " "
" 3,	5,160,000	" "	30,000	" " " "
" 5,	4,960,000	" "	30,000	" " " "
" 6,	5,890,000	" "	20,000	" " " "

The first and second animals show a slight reduction and the third and sixth an increase in the number of corpuscles. No microcytes or blood-plates were noticed this time.

The weight of these animals at the time of this second examination of the blood was as follows :

No. 1,	1040 g.,	lost 12 g.,	since close of experiment.
" 2,	1045 g.,	" 10 g.,	" " " "
" 3,	1265 g.,	gained 75 g.,	" " " "
" 5,	1405 g.,	" 53 g.,	" " " "
" 6,	1545 g.,	" 1 g.,	" " " "

The loss of weight in the first and second animals may be due to the change of food. The gain in the others is no doubt due to the better atmospheric conditions under which they are now living.

Post mortem examinations of a number of the animals dying in the "Brown-Séquard" experiments were made with the greatest care. The organs were preserved in alcohol and mounted in celloidin for the microscopic examination. The gross appearances presented by the animals showed a constant similarity to the appearances noted in the animals used in the experiments with artificial gaseous mixtures. The constant appearances noted were those of intense venous engorgement of all the organs and tissues. The heart cavities contained firm, dark clots of blood, filling both auricles and ventricles, those on the right side being usually much larger than those on the left. No inflammatory changes or serous exudates were found in any instance.

Microscopic examination of the organs presented no constant feature aside from the manifestations produced by the cause and mode of death. Engorgement of the blood vascular system was noted everywhere with usually some degree of infiltration in the lung. No degenerative changes were constantly present. Those found in isolated cases—such as a slight increase of connective-tissue elements between the tubules of the kidneys and about the glomeruli, and small areas of proliferation of connective-tissue elements in the liver—cannot be safely attributed to the experiment. This opinion is strengthened by the short duration of the experiments, and it is probable that the changes were due to ante-experimental causes.

The mode of death as observed in these experiments presented certain constant features which were undistinguishable from those produced by slow asphyxia under other circumstances. There was a period of excitement, followed, in the course of time, by a period of progressive depression. The breathing, at first rapid, generally became slower, with perceptible lengthening of the respiratory pauses, accompanied at a later period by marked expiratory efforts. Along with these respiratory changes was usually noted a progressive muscular weakness gradually deepening into paralysis of the posterior members. The animal moves about with evident difficulty, and finally sinks down, remains lying on the side or back, without any other movements than those of respiration. It now presents a comatose condition from which it cannot be aroused by striking the sides of the bell jar. Death usually ensues through the gradual lengthening of the respiratory pauses passing into an entire failure of respiration. In a small proportion of the cases, life becomes extinguished through one or two convulsive seizures.

No. 1. BROWN-SÉQUARD EXPERIMENT.

Commenced at 5 P.M., March 2, 1894. Sparrows in 1 litre flasks. 4 in series.

The + mark indicates the death of the animal.

Time.	No. 1.		No. 2.		No. 3.		No. 4		Remarks.
	CO_2.	O.	CO_2.	O.	CO_2.	O.	CO_2	O.	
$17\frac{1}{2}$ hrs.									48.5 litres aspirated each hour; too rapid.
$17\frac{3}{4}$ "									Changed to 2.85 litres per hour.
$18\frac{3}{4}$ "						+			No. 3 died. Symptoms of CO_2 poison.
$19\frac{1}{4}$ "									Experiment stopped.

No. 2. BROWN-SÉQUARD EXPERIMENT.

Commenced at 11.45 A.M., March 3, 1894. Sparrows in 7-litre bell jars. 5 in series.

Time.	No. 1. 21 g.		No. 2 21 g.		No. 3 21 g.		No. 4. 21 g.		No. 5.		Remarks.
	CO_2.	O.	CO_2.	O.	CO_2.	O.	CO_2.	O.	CO_2.	O	
4¾ hrs.										+	36.8 litres aspirated. No. 5 died.
19¼ "								+			No. 4 died during night. Others lively.
22 "											No. 3 still comfortable.
27 "						+					No. 3 died.
29¾ "		+		+							Nos. 1 and 2 dead.
48¼ "			2.85	16.99	5.01	15.65	6.07	12.63	7.36	13.40	Examination of air after death of each bird.

No. 3. BROWN-SÉQUARD EXPERIMENT.

Commenced at 12.15 P.M., March 5, 1894. Sparrows in 7-litre bell jars. 5 in series.

Time.	No. 1. 22 g.		No. 2. 19 g.		No. 3. 27 g.		No. 4. 26 g.		No. 5. 25 g.		Remarks.
	CO_2.	O.	CO_2.	O.	CO_2.	O.	CO_2.	O.	CO_2.	O.	
20¾ hrs.											Current 11.6 litres per hour.
22½ "											Current reduced; now 6 litres per hour.
29½ "										+	No. 5 died.
29¾ "						+		+			Nos. 3 and 4 dead. Experiment stopped.

No. 4. BROWN-SÉQUARD EXPERIMENT.

Commenced at 9 30 A.M., March 7, 1894. Sparrows in 7-litre bell jars. 5 in series.

Time.	No. 1. 21 g.		No. 2. 22 g.		No. 3. 23 g.		No. 4. 25 g.		No. 5. 21 g.		Remarks.
	CO_2.	O.	CO_2.	O.	CO_2.	O.	CO_2.	O.	CO_2.	O.	
13¾ hrs.		+		+		+		+		+	All the birds are dead. No record of amount of air aspirated.
			14.30	4.485	14 01	3.635					Examination of air after death.

No. 5. Brown-Séquard Experiment.

Commenced at 6 P.M., March 8, 1894. Sparrows in 7-litre bell jars. 5 in series.

Time.	No. 1. 21 g.		No. 2. 21 g.		No. 3. 26 g.		No. 4. 22 g.		No. 5. 25 g.		Remarks.
	CO_2.	O.	CO_2.	O.	CO_2.	O.	CO_2.	O.	CO_2.	O.	
14¾ hrs.				†		†		†		†	Nos. 3, 4, and 5 dead.
18¾ "											No. 2 died.
24 "		†									No. 1 died during night.
	10.83	6.93	13.545	3.755	13.25	4.35	13.78	3.465	14.195	3.965	Examination of air after death.

No. 6. Brown-Séquard Experiment.

Commenced at 8.45 A.M., March 12, 1894. Sparrows in 7-litre bell jars. 5 in series.

Time.	No. 1. 23 g.		No. 2. 23 g.		No. 3. 23 g.		No. 4. 23 g.		No. 5. 27 g.		Remarks.
	CO_2.	O.	CO_2.	O.	CO_2.	O.	CO_2.	O.	CO_2.	O.	
8 hrs.							13.77	4.06	8.02	3.97	CO_2 absorbers. Absorbers changed, saturated. Nos. 3, 4, and 5 are greatly oppressed. All are alive.
8½ "											Experiment terminated.

No. 7. Brown-Séquard Experiment.

Commenced at 9.15 A.M., March 13, 1894. Sparrows in 7-litre bell jars. 5 in series.

Time.	No. 1. 23 g.		No. 2. 23 g.		No. 3. 23 g.		No. 4. 23 g.		No. 5. 27 g.		Remarks.
	CO_2.	O.	CO_2.	O.	CO_2.	O.	CO_2.	O.	CO_2.	O.	
5¾ hrs.							1.11	19.22	1.49	17.42	56.6 litres aspirated. Absorbers acting.
7½ "						†					No. 3 died. Nos. 1 and 2 much oppressed. Experiment continued.
8½ "							2.02	19.20	4.77	14.23	84.9 litres aspirated.
8¾ "		†		†							Nos. 1 and 2 died. Nos. 4 and 5 still unaffected. Experiment continued.
22 "											169.8 litres aspirated. Nos. 4 and 5 well. Experiment terminated.
26 "											Nos. 4 and 5 well.
26¼ "					12.39	4.155	3.08	17.20	2.61	17.78	Examination of air after death.

No. 8. BROWN-SÉQUARD EXPERIMENT.

Commenced at 3.45 P.M., March 14, 1894. Sparrows in 7-litre bell jars. 5 in series.

Time.	No. 1. 29 g.		No. 2 23 g		No. 3. 27 g.		No. 4. 26 g.		No. 5. 27 g.		Remarks.
	CO_2.	O.	CO_2.	O	CO_2.	O.	CO_2.	O.	CO_2.	O.	
18 hrs.											106 litres aspirated. Birds all well.
19¼ "							4.28	7.73	4.52	7.12	Nos. 3 and 4 showing signs of oppression.
20¾ "											
30 "							4.82	5.01	3.27	3.95	No. 5 most affected.
31¼ "										+	No 5 died. 121.75 litres aspirated. No. 4 quite sick.
						+		+			Nos. 3 and 4 died in night. 141.5 litres aspirated and experiment stopped.
47¼ "					8.56	9.665*	0.96	10.06*	2.875	3.56	Examination of air after death.

No. 9. BROWN-SÉQUARD EXPERIMENT.

Commenced at 11.30 A.M., March 16, 1894. Sparrows in 7-litre bell jars. 5 in series.

Time.	No. 1. 29 g.		No. 2. 23 g.		No. 3. 26 g.		No. 4. 24 g.		No. 5. 24 g.		Remarks.
	CO_2.	O.	CO_2.	O.	CO_2.	O.	CO_2.	O.	CO_2.	O.	
4½ hrs.							.001036	13.37	.001047	12.67	CO_2 absorbers. 39.6 litres aspirated.
6½ "											Current increased.
22 "							1.29	16.41	2.01	14.92	290 litres aspirated, or 13 litres per hour. All are well.
22¼ "											357.9 litres aspirated. All birds well.
30 "						+		+		+	All died during night (aspiration practically nil).
46¾ "					18.01	1.51	16.68	0.468	13.065	2.545	Examination of air after death.

---

* These air analyses were made several hours after death, and considerable alteration must have occurred through ventilation in the interval.

No. 1. Brown-Séquard Experiment.

Commenced at 9.15 A.M., March 20, 1894. Sparrows in 7-litre bell jars. 5 in series.

Time	No. 1, 28 g.		No. 2, 28 g.		No. 3, 27 g.		No. 4, 27 g.		No. 5, 24 g.		Remarks
	CO_2	O_2	CO_2	O_2	CO_2	O_2	CO_2	O_2	CO_2	O_2	
3 hrs											CO_2 absorbers: all are slightly oppressed.
3¼ "							3.08	12.24[1]	6.73	12.11	
5¼ "							4.27	7.34	2.61	9.04	
6¼ "							5.22	6.89	2.86	7.50	
7¼ "							5.69	5.69	4.79	5.74	
8 "											Current increased for the night.
											25.5 litres aspirated. All are somewhat oppressed.
23 "							1.114	16.49	0.503	15.79	All are lively. 360.8 litres aspirated, current reduced.
24¼ "							3.23	12.46	1.20	14.72	Becoming oppressed.
25¼ "							5.60	9.74	3.60	9.88	
26¼ "							8.28	8.65	5.27	9.14	
27¼ "							7.82	5.65	5.11	7.71	
28¼ "							9.08	3.13	6.20	6.84	All are very much oppressed.
29¼ "							9.51	—	6.34	5.50	
30¼ "							9.42	4.07	6.42	4.86	No. 4 died.
31 "										†	Nos. 3 and 5 died.
				†							No. 2 died. No. 1 released. Revived; exp. stopped.
32½ "			15.14	3.145	14.34	4.775	10.965	3.50	10.51	3.77	Examination of air after death.

No. 11. BROWN-SÉQUARD EXPERIMENT.

Commenced at 11.45 A.M., March 22, 1894. Sparrows in 7-litre bell jars. 5 in series.

Time.	No. 1. 28 g.		No. 2. 29 g.		No. 3. 29 g.		No. 4. 25 g.		No. 5. 26 g.		Remarks.
	CO_2.	O.	CO_2.	O.	CO_2.	O.	CO_2.	O.	CO_2.	O.	
$3\frac{1}{4}$ hrs.							1.41	14.20	0.96	12.98	CO_2 condensers.
						+					No. 3 died. Replaced by a fresh bird, weight 29 g. Experiment continued.
$3\frac{1}{2}$ "					4.86	13.965					
$5\frac{1}{4}$ "							2.06	11.06	1.28	11.30	34 litres aspirated.
											Current increased.
$20\frac{3}{4}$ "											152.8 litres aspirated.
21 "							1.40	12.92	1.09	12.76	$8\frac{2}{5}$ litres per hour during night.
22 "							1.83	12.02	5.19	9.07	Current reduced.
							2.16	11.11	6.39	7.90	All somewhat oppressed.
23 "							2.48	9.45	7.30	6.23	
24 "								+			No. 4 quite sick.
25 "							2.79	9.34	7.70	5.65	No. 4 died. Nos. 3 and 5 show great oppression.
26 "									6.93	4.86	
27 "									6.405	4.29	
										+	No. 5 died.
28 "									6.76	3.53	
$28\frac{1}{4}$ "						+					No. 3 died. No. 2 much oppressed.
											8.5 litres aspirated last 9 hrs. Exp. stopped. Nos. 1 and 2 died during night.
$29\frac{3}{4}$ "			14.525	4.29	15.00	4.30	3.49	9.545	8.31	3.395	Examination of air after death.

No. 12. Brown-Séquard Experiment.

Commenced at 3.45 P.M., March 24, 1894. Sparrows in 7 litre bell jars. 5 in series.

Time.	No. 1, 24 g.		No. 2, 25 g.		No. 3, 20 g.		No. 4, 27 g.		No. 5, 25 g.		Remarks.
	CO_2	O	CO_2	O	CO_2	O	CO_2	O	CO_2	O	
2 hrs.											31 litres aspirated. Current slightly increased.
19 "											334.5 litres aspirated.
24½ "											All lively. $Ba(HO)_2$ absorber renewed.
											469.75 litres aspirated.
41¼ "											Nos. 3, 4, and 5 oppressed.
42¾ "							5.018	5.047	2.264	6.436	426.75 litres aspirated.
43¼ "							3.457	5.857	1.577	4.08	Current reduced.
44½ "											No. 5 died.
46¼ "								+			No. 4 died.
47½ "						+					No. 3 died. 448.75 litres aspirated. No. 2 oppressed.
50 "											Nos. 1 and 2 oppressed, No. 2 most so.
65¾ "											Experiment stopped. Both revived. 543.5 litres aspirated.
					14.77	3.412	4.293	1.36	3.729	3.449	Examination of air after death.

No. 13. Brown-Séquard Experiment.

Commenced at 12.45 P.M., March 27, 1894. Sparrows in 7-litre bell jars. 5 in series.

Time.	No. 1. 24 g.		No. 2. 25 g.		No. 3. 26 g.		No. 4. 25 g.		No. 5. 25 g.		Remarks.
	CO₂.	O.	CO₂.	O.	CO₂.	O.	CO₂.	O.	CO₂.	O.	
½ hrs.											8 litres aspirated. Current reduced.
2½ "											35 litres aspirated.
3½ "							1.12	14.565	0.676	13.636	
5 "											53 litres aspirated. Current increased for night.
20¼ "							4.00	11.279	2.827	10.556	249 litres aspirated. All lively.
21½ "							4.00	8.279	3.29	7.055	Nos. 3, 4, and 5 becoming oppressed.
23¼ "											
25 "							4.644	6.145	3.76	4.524	All are much oppressed.
26¼ "							1.655	7.685	1.054	5.80	Current slightly increased.
28½ "											307 litres aspirated. Current increased for night.
28¾ "											523 litres aspirated. All are well.
44¼ "							4.477	11.94	2.468	11.974	566 litres aspirated. Leakage, meter changed to other end of bell jars.
46¼ "											
47 "							5.365	9.365	3.518	8.60	All showing signs of oppression.
47¾ "							4.609	8.45	3.041	7.794	
48¾ "							4.113	7.498	4.03	5.95	
49¾ "							4.938	5.508	4.25	4.54	
50¾ "							4.932	4.545	6.327	3.894	
51½ "										+	No. 5 died.
53 "						+		+			Nos. 3 and 4 died.
54¼ "				+							No. 2 died. No. 1 released.
54¾ "											Experiment stopped.
			14.746	2.186	13.92	3.912			6.4875	3.4395	Examination of air after death.

No. 14. [illegible]

[illegible] March [illegible], 1904 [illegible] May [illegible] 5 [illegible]

Time.	No. 1. CO₂	No. 1. O	No. 2. CO₂	No. 2. O	No. 3. CO₂	No. 3. O	No. 4. CO₂	No. 4. O	No. 5. CO₂	No. 5. O	Remarks.
5¼ hrs.											[illegible] aspirated. Current increased. Nos. 3, 4, and 5 slightly oppressed.
21 "							.275	13.600	[illegible]	14.76	157 litres aspirated.
22½ "							1.706	14.58	2.[illegible]34	13.00	No. 5 [illegible] slightly oppressed.
24 "							3.07	11.11	3.357	[illegible]	[illegible] litres aspirated.
26¼ "							3.25	[illegible]	[illegible]	[illegible]	Nos. 3, 4, and 5 slightly oppressed.
27½ "							2.075	9.213	2.777	[illegible]	
28¼ "							[illegible]	[illegible]	[illegible]	5.020	
29 "											
30 "											266 litres aspirated. Current increased. All more or less oppressed.
46 "											303 litres aspirated. All still oppressed. Current reduced.
69½ "											413 litres aspirated. No. 5 died in night. Others very sick.
71 "											No. 3 died.
71½ "											414 litres aspirated.
											No. 4 died.
73¼ "											415 litres aspirated.
76 "					12.4	3.53	5.470	3.277	7.176	4.53	Aspiration stopped. 417 litres aspirated.
											Examination of air after death.

No. 15. Brown-Séquard Experiment.

Commenced 12 M., April 2, 1894. Mice in 5 [illegible] bell jars.

Time.	No. 1. 19.5 g.		No. 2. 17 g.		No. 3. [illegible]		No. 4. [illegible]		No. 5. [illegible]		[illegible]
	CO_2.	O.	CO_2.	O.	CO_2.	O.	CO_2.	O.	CO_2.	O.	
15 hrs.					3.830	15.350	8.671	8.671			2 litres aspirated.
15½ “					7.805	9.55	9.30	5.531	7.75		Leakage.
17 “							7.48	5.357		9.93	
18 “							7.60	5.30	6.45	9.24	5.0 litres aspirated.
19¼ “											5.5 litres aspirated.
19½ “											17 litres aspirated.
22 “											19.5 litres aspirated. Current increased.
23 “											109 litres aspirated.
30 “							1.765	13.84	1.78	14.30	
40½ “							2.40	13.10	2.30	12.517	
41½ “							3.72	12.51	3.717	11.630	
42¾ “							3.867	11.22	5.048	10.22	
44 “							5.05	9.53	5.57	9.40	
45¼ “							5.17	9.79	3.78		142.5 litres aspirated.
46¾ “										....	142.5 litres aspirated.
47¾ “											
62½ “							6.845	7.60	1.08	6.06	All somewhat oppressed.
63¼ “							7.40	7.67	2.35	4.70	183 litres aspirated.
64½ “							7.29	7.20	3.03	3.08	185 litres aspirated.
65¾ “							7.40	6.37	3.59	3.96	All considerably oppressed.
66⅓ “							7.75	5.80	2.02	3.86	
67⅓ “							7.310	6.178	3.26	3.58	
68⅓ “							7.27	6.04	3.43	3.33	
69⅓ “							8.22	5.10	3.63	2.15	
70¼ “							8.25	4.78	1.00	2.96	
71 “							7.61	5.39	3.44	3.25	
71¾ “											Current increased; 189.5 litres aspirated. *All much oppressed.*
86¾ “							3.60	12.93	2.35	13.65	All quite lively; 367 litres aspirated. All absorbers renewed.
87¼ “							5.240	12.58	3.19	12.77	
88½ “							5.450	12.32	4.14	12.15	
89½ “							7.47	10.34	5.465	10.546	All absorbers acting poorly.
90¼ “							7.00	9.875	6.22	9.707	
92¼ “							8.37	9.335	6.340	9.519	
93¼ “							9.17	8.508	7.66	8.141	
94¼ “							9.67	7.375	8.395	7.397	
95¼ “							9.93	7.35	8.318	7.68	373 litres aspirated. Current slightly increased.
96 “				+		+		+		+	Nos. 2, 3, 4, and 5 dead; 382 litres aspirated. Experiment stopped.
110½ “			10.930	6.52	12.60	4.55	12.28	3.93	12.31	4.86	Examination of air after death of mice.

No. 16. BROWN-SÉQUARD EXPERIMENT.

Commenced at [illegible] M., April 9, 1894. Mice in 7-litre bell jars. 5 in series.

Time.	No. 1, 7 g.		No. 2, 15 g.		No. 3, 18 g.		No. 4, 25 g.		No. 5, 19 g.		Remarks.
	CO_2	O	CO_2	O	CO_2	O	CO_2	O	CO_2	O	
7½ hrs											7.5 litres aspirated. All oppressed. Current increased.
											81.5 litres aspirated.
22½ "											Current reduced.
											80 litres aspirated. All except No. 1 oppressed. Current increased.
31 "						†		†		†	92.5 litres aspirated. Nos. 3, 4, and 5 died in night.
47 "											The experiment stopped.
					16.317	3.8	13.3	4.02	12.05	5.437	Examination of air after death.

No. 17. Brown-Séquard Experiment.

Commenced at 12 M., April 11, 1894. Mice in 7 litre bell jars [illegible] in serie[illegible]

Time.	No. 1. 7 g.		No. 2. 15 g.		No. 3. 16 g.		No. 4. 23 g.		No. 5. 17 g.		Remark.
	CO_2.	O.	CO_2.	O.	CO_2.	O.	CO_2.	O.	CO_2.	O.	
5¾ hrs											9.5 litres aspirated. All slightly oppressed. Current increased.
21¼ "											47 litres aspirated. Current reduced somewhat.
30 "											53.5 litres aspirated. All oppressed; current again increased.
44¾ "											122.5 litres aspirated; all lively again.
51½ "							13.48	8.80	12.118	8.325	
52½ "							12.129	7.067	12.045	7.41	
53 "											131.5 litres aspirated. All more or less oppressed. Current increased.
68 "											179 litres aspirated. All lively again. Current considerably reduced.
68½ "							11.346	7.88	12.78	6.92	
69½ "							12.09	7.38	12.75	6.519	
71½ "							12.007	7.49	13.35	5.76	
72½ "							13.66	6.256	14.285	6.405	
75 "							15.13	4.59	15.13	4.36	
76 "							15.08	4.13	15.26	3.86	
77 "							15.613	3.83	15.91	3.47	186.5 litres aspirated. Current increased. All oppressed.
79½ "											293.5 litres aspirated. All are lively again.
104¼ "											Current somewhat reduced for the next 24 hours.
117½ "							10.919	7.00	11.11	6.536	
118½ "							10.919	7.08	11.73	7.00	
119½ "							11.068	6.297	11.74	5.68	
121½ "							11.11	5.465	12.535	5.22	
122½ "							12.63	4.689	12.737	4.94	
123½ "							12.65	4.506	13.08	4.17	360.5 litres aspirated. All show considerable depression.
124½ "							12.989	4.29	13.96	3.77	
121¼ "										a	
122¼ "										b	Mice are much oppressed. The experiment is now stopped. All revived. 364.5 litres aspirated.
125 "										c	
125 "								d			
125 "						e					
125¼ "											

a. Fresh house mouse placed in No. 5 jar. Died in two minutes.
b. " white " " " 5 " Lived to end of experiment.
c. " " " " " 5 " Died in half a minute.
d. " " " " " 4 " Died in half an hour.
e. " " " " " 3 " Died in six minutes.

[illegible]

[illegible]

					[illegible] All are [illegible] oppressed. Current increased.
					[illegible] litres [illegible]. All [illegible].
					150 [illegible] litres [illegible] aspirated. Current continued.
					219 litres. All are more or less oppressed.
[illegible]	[illegible]	[illegible]	12.8[illegible]	7.0[illegible]	
12	1	7.[illegible]5	13.77	5.69	
15.15		6.27[illegible]	14.37[illegible]	4.943	
1[illegible].94		6.945	13.945	5.46	Experiment stopped. All living; also white mouse placed in No. 5, and small gray mouse in No. 4, as well as mouse d.

[illegible]

No. 19. BROWN-SÉQUARD EXPERIMENT.

Commenced at 10.30 A.M., April 20, 1894. Mice in 7-litre bell jars. 5 in series. H_2SO_4 absorber.

Time.	No. 1, 7 g.		No. 2, 7 g.		No. 3, 7 g.		No. 4, 18 g.		No. 5, 33 g.		Remarks.
	CO_2.	O.	CO_2.	O.	CO_2.	O.	CO_2.	O.	CO_2.	O.	
6 hrs.											18.5 litres aspirated. All show oppression.
23 "											133.5 litres aspirated. All oppressed. Current reduced slightly.
29 "							7.627	11.716	10.58	8.226	Current the same.
30 "							8.568	10.029	10.69	7.418	144 litres aspirated. All are oppressed. Current increased.
31 "											213 litres; current the same.
47½ "											306.5 litres. All are oppressed. Current reduced.
70¼ "							9.637	9.73	11.238	7.809	
76¼ "							9.62	9.15	11.258	7.238	
78½ "											324 litres aspirated. Current increased.
79¼ "											406 litres aspirated. Current reduced.
94½ "							5.87	13.22	7.70	11.267	
95¼ "							9.159	—	10.87	7.40	
102¾ "											421 litres aspirated. Current the same.
103¼ "											428.5 litres. Nos. 3, 4, and 5 are very sick.
118¾ "										a	
118¾ "										b	
118¾ "								c			
118¾ "										d	
118¾ "										+	No. 5 died.
119 "											The others are very sick, especially No. 4.
120½ "							13.73	4.23	14.12	3.816	
121½ "											No. 4 died. Experiment stopped. Others soon revived.

a No. 4 of last experiment placed in No. 5 jar; died in two minutes.

b White mouse, used in Experiment 17, placed in No. 5 jar; died in two and one-half minutes.

c White mouse, used in Experiment 17, placed in No. 4 jar, died in three and one-half minutes.

d Small mouse, used in Experiment 17, placed in No. 5 jar; died in one minute.

[illegible] EXPERIMENTS

April 25, 1894 [illegible] June 5, 1894. Mice [illegible] 7-litre bell-jars

[illegible]

	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]				[illegible] aspirated. Current [illegible]
[illegible]				17[illegible] litres aspirated. All comfortable.
25				45 litres aspirated. All slightly depressed. Current increased.
35				130.5 litres aspirated. All depressed. Current reduced.
40 "				147 litres aspirated. Considerably depressed. Current increased.
65 "				224.5 litres aspirated. All lively. Current reduced.
75 "				332 litres aspirated. Current continued.
[illegible]				355 litres aspirated. No. 5 died; No. 4 greatly depressed.
[illegible] "				357 litres aspirated. Experiment stopped; all soon revived.

[illegible] Experiment 21, after intermission of two days. May 1, 1894.

				Fresh mouse in No. 5.
[illegible]				20 litres aspirated. All lively. Current reduced.
[illegible] "				145.5 litres aspirated. Current the same.
[illegible] "				160 litres aspirated. Current increased, showing depression.
[illegible]				341.5 litres aspirated. All lively again. Current reduced.
[illegible]				351.5 litres aspirated. Depressed. Current increased.
[illegible]				459 litres aspirated. All more comfortable. Current reduced.
[illegible]				466.5 litres aspirated. Experiment stopped.

Continued as Experiment 22, after interval of three days. May 7, 1884.

7 hrs.			12 litres aspirated. All slightly oppressed. Same current.
23¼ "			68.5 litres aspirated. All considerably oppressed. Same current.
31 "			76.5 litres aspirated. All much oppressed. Current increased.
47¼ "			202.5 litres aspirated. Current reduced slightly.
55½ "			222.5 litres aspirated. Current the same.
71 "		+b	243 litres aspirated. No. 4 died in the night; other oppressed.
71¼ "			
72 "			248.5 litres aspirated. Experiment stopped; all soon revived.

Continued as Experiment 23, after interval of three days. May 11, 1884.

6¾ hrs.		4	18 litres aspirated. Four mice placed in No. 4.
29¾ "		+ +	59.5 litres aspirated. Two mice in No. 4 are dead; removed.
40¼ "			109.5 litres aspirated.
48½ "			122.5 litres aspirated.
60½ "			147.5 litres aspirated.
70¾ "	+	+ +	148 litres aspirated. Two remaining mice in No. 4 died; also No. 3.
70¾ "			Experiment discontinued; soon revived.

Continued as Experiment 24, after interval of two days. May 16, 1884.

3 hrs.	Fresh mice in Nos. 3 and 4. 22.5 litres aspirated. Current continued.
23½ "	121.5 litres aspirated. All lively.
47½ "	211.5 litres aspirated. All more or less oppressed.
65½ "	270 litres aspirated. All more or less oppressed.
71½ "	325 litres aspirated. All more or less oppressed.
74½ "	341.5 litres aspirated. Considerably oppressed; experiment stopped.

Continued as Experiment 25, after interval of two days. May 21, 1894.

21½ hrs.	103.5 litres aspirated. All much oppressed; same current.
28 "	130 litres aspirated. All much oppressed; same current.
45 "	198.5 litres aspirated. All much oppressed; same current.
52¼ "	266.5 litres aspirated. All much oppressed; same current.
69¾ "	323.5 litres aspirated. All much oppressed; same current.
75 "	340 litres aspirated. Experiment stopped; all soon revived.

Continued as Experiment 26, after interval of one day. May 25, 1894.

7¾ hrs.	4.5 litres aspirated. All depressed; current increased.
22¾ "	147 litres aspirated. All depressed; same current.
71¾ "	302.5 litres aspirated. Sunday between.
78 "	304.5 litres aspirated. Experiment stopped; all soon revived.

Continued as Experiment 27, after interval of one day. May 29, 1894.

4 hrs.	5 litres aspirated. Show oppression; current increased.
20¼ "	69 litres aspirated. Current reduced.
24¾ "	74 litres aspirated. Much oppressed; current increased.
27¼ "	77 litres aspirated. Current again increased.
44¼ "	146 litres aspirated. More lively; current reduced.
52¼ "	152.5 litres aspirated. Current increased.
68¼ "	301.5 litres aspirated. Current reduced.
75 "	317 litres aspirated. Experiment stopped; revived.

Continued as Experiment 28, after interval of one day. June 2, 1894.

4¼ hrs.	7 litres aspirated. Current increased.
21¾ "	134.5 litres aspirated. Same current.
45 "	227.5 litres aspirated. Current reduced.
52¼ "	258 litres aspirated. Same current continued.
68¾ "	305 litres aspirated. Current again reduced.
75 "	434 litres aspirated. Experiment stopped; revived.

---

a No. 1 of Experiment 17 placed in No. 5; died in one-half minute.
b No. 3 of Experiment 19 placed in No. 4; died in three minutes.
c No. 2 of Experiment 17 placed in No. 5; died in one minute.

No. 29. BROWN-SÉQUARD EXPERIMENT.

Commenced at 5.15 P.M., June 5, 1894. Mice in 7-litre bell jars. 5 in series.

Time.	No. 1.	11 g	No. 2.	9 g.	No. 3.	12 g.	No. 4.	16 g.	No. 5.	19 g.	Remarks.
	CO_2.	O.	CO_2.	O.	CO_2.	O.	CO_2.	O.	CO_2	O.	
16 hours.											121 litres aspirated. Current reduced; all are lively.
24 "											129 litres. Current increased; some oppression.
40½ "											301.5 litres. Current reduced.
47¼ "											335.5 litres aspirated. Current increased; some oppression.
64¼ "											451 litres. Current reduced.
70 "							10.51	11.80	7.45	5.80	
72½ "											460 litres. Current same; some oppression.
87½ "											535.5 litres. Current much reduced.
94¼ "											541 litres. Current increased; greatly oppressed.
96½ "											545.5 litres. Current same.
113¾ "								+		+	Nos. 4 and 5 died in the night.
114 "										a	No. 1 of last experiment placed in jar No. 5; remained alive.
114 "								b			No. 2 of last experiment placed in jar No. 4; alive.
114 "						c					No. 3 of last experiment placed in jar No. 3; alive.
114¼ "											565.5 litres aspirated.
115¼ "											567 litres aspirated; all mice alive; experiment stopped.

No. 3.—[illegible] EXPERIMENT.

Commenced at 3.15 P.M., June 13, 1894. Guinea-pigs in 7-litre bell-jars; 5 in series.

		No. 1	No. 2	No. 3	No. 4	No. 5	Remarks
[illegible]		[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]							Nos. 4 and 5 are oppressed. Current 24 litres per hour.
1[illegible]							No. 5 dead. Great negative pressure. Fresh air supplied, and
21¼	"					Wt. 575	No. 5 replaced by a fresh guinea-pig. Experiment continued.
43[illegible]						2[illegible]	6 litres per hour; all are lively.
51¼							Animals fed; bell-jars cleaned. Animals replaced.
75¼	"						Animals fed; all well and dry; 6[illegible] litres per hour.
94[illegible]	"						Again fed; all lively and dry in bottom of cages.
115¾	"						3 litres per hour; Nos. 4 and 5 oppressed; animals fed.
122¼	"						5 litres per hour; animals fed.
139	"						8 litres per hour; cages cleaned; animals fed.
146[illegible]	"						4 litres per hour; animals fed; all oppressed.
163¼	"						5 litres per hour; animals fed.
171¼	"						5 litres per hour; animals fed.
187[illegible]	"						45 litres per hour; animals fed.
194[illegible]	"						No. 1 dead of oedema of lungs; experiment continued with 4 animals.
211¾	"						No. 3 died in night of oedema of lungs. Experiment continued.
235¾	"						Nos. 2, 4, and 5 living, but much oppressed. Experiment stopped.

[illegible] No. 5 and three [illegible] experiment. No autopsy.

No. 31. BROWN-SEQUARD EXPERIMENT.

Commenced at 5.15 P.M., June 25, 1894. Rabbits in 37 litre bell jars. 5 in series.

Time.	No. 1 1850 g.		No. 2 1325 g.		No. 3 1504 g.		No. 4 [illegible]		No. 5 [illegible]		Remarks.
	CO_2	O.	CO_2.	O.	CO_2	O	CO_2	O	CO_2	O	
16 hours											60 litres per hour aspirated.
24 "											34 litres per hour; some oppression.
40¼ "				+		+					Nos. 2 and 3 died in the night. Experiment stopped.

No. 32. BROWN-SEQUARD EXPERIMENT.

Commenced at 10.15 A.M., December 4, 1894. Rabbits in 37-litre bell jars. 6 in series.

Time.	No. 1. 2175 g.		No. 2 1045 g.		No. 3. 1065 g.		No. 4 2025 g.		No. 5. 2500 g.		No. 6. 3043 g.		Remarks.
	CO_2.	O.	CO_2.	O.	CO_2.	O.	CO_2.	O	CO_2.	O	CO_2.	O.	
3¾ hrs.							3.91	15.87			5.33	14.19	120 litres per hour aspirated.
4¾ "									4.13	14.47	5.08	13.17	
5¾ "									4.13	14.56	5.02	13.62	
20¼ "									5.55	14.07	6.17	13.67	
27½ "							4.18	14.25			6.19	11.32	
29¾ "									6.00	14.19	7.21	13.86	
46¾ "									4.13	15.05	4.83	14.00	
51½ "							4.38	14.74			5.88	12.26	
53 "									6.10	13.20	7.17	11.90	
54 "									5.28	13.90	6.05	12.40	
71½ "									3.47	15.46	4.05	13.83	
74¼ "									5.92	12.82	6.81	11.46	
78¼ "									5.81	13.69	7.38	11.82	
94¾ "		+		+		+		+		+			All the rabbits are smothered except No. 6. The glass plate under No. 6 broke during the night and arrested the aspiration of air through the other bell jars.

No. 33. Brown-Séquard Experiment.

[illegible] 2.45 P.M., December 8, 1904. Rabbits in 37-litre bell jars. 6 in series.

	No. 1 [illegible] g		No. 2 [illegible] g		No. 3 [illegible] g		No. 4 [illegible] g		No. 5 [illegible] g		No. 6 [illegible] g		Remarks
[illegible]	CO_2	O_2	CO_2	O_2	CO_2	O_2	CO_2	O_2	CO_2	O_2	CO_2	O_2	
1													80 litres per hour aspirated.
2									3.51	16.73	3.63	14.62	
3									3.43	15.39	4.32	13.86	72 litres per hour aspirated.
4													Larger glass tubing used to connect the bell jars. 100 litres per hour aspirated.
5									1.39	16.68	1.61	15.51	
6									1.58	16.27	1.72	14.49	
7									4.94	14.43	4.88	13.86	
8									4.31	15.29	4.46	14.98	
9									4.31	15.29	4.46	14.98	Cages cleaned out; 148 litres per hour aspirated.
10									2.51	16.69	2.72	15.69	
11													
12									1.08	16.38	1.59	16.30	130 litres per hour aspirated.
13									2.37	16.11	2.51	15.54	
14									1.69	16.60	1.09	15.43	
15													
16									1.75	16.55	2.23	15.67	Cages cleaned out.
17													
18									4.07	15.22	5.24	13.88	
19									4.09	15.15	5.53	13.74	
20									4.91	16.01	6.16	15.46	
21									4.51	15.58	5.85	14.00	
22													
23									7.61	11.81	7.75	11.63	Cages cleaned out; 130 litres per hour aspirated.
24									4.88	15.03	6.32	13.63	
25									5.58	14.20	6.52	13.35	120 litres per hour aspirated.
26									5.38	14.18	6.31	12.73	
27									6.84	14.00	6.51	14.11	125 litres per hour aspirated.
28									6.68	13.26	6.69	13.00	
29													
30									6.26	13.71	7.44	12.53	
31							4.89	14.87			7.11	12.74	
32							4.77	15.38			7.59	12.92	
33									6.39	13.37	7.81	11.77	110 litres per hour aspirated.
34					4.23	15.76					7.46	11.14	
35									5.74	14.17	8.02	11.69	Cages cleaned out; No. 6 not well; due to filth.
36													
37									6.67	13.55	7.77	12.45	No. 6 has fully recovered.
38									4.42	14.44	5.44	13.06	115 litres per hour aspirated.
39									5.29	13.51	6.81	12.05	
40					4.86	14.88					7.02	12.54	
41													
42									5.74	14.15	6.94	13.19	Experiment stopped.
	[illegible] g		[illegible] g		1192 g.		1247 g.		1352 g.		1544 g.		Weight of animal at close of experiment.

INDEX.

SMITHSONIAN CONTRIBUTIONS TO KNOWLEDGE.
1033

Hodgkins Fund.

ARGON,

A NEW CONSTITUENT OF THE ATMOSPHERE.

BY

LORD RAYLEIGH AND PROFESSOR WILLIAM RAMSAY.

CITY OF WASHINGTON:
PUBLISHED BY THE SMITHSONIAN INSTITUTION.
1896.

SMITHSONIAN CONTRIBUTIONS TO KNOWLEDGE.
1033

Hodgkins Fund.

ARGON,

A NEW CONSTITUENT OF THE ATMOSPHERE.

BY

LORD RAYLEIGH AND PROFESSOR WILLIAM RAMSAY.

CITY OF WASHINGTON:
PUBLISHED BY THE SMITHSONIAN INSTITUTION.
1896.

The Knickerbocker Press, New York

ADVERTISEMENT.

The present memoir was submitted by Lord Rayleigh and Professor Ramsay, in competition for one of the Hodgkins Fund prizes offered by the Smithsonian Institution in a circular dated March 31, 1893. The competition closed December 31, 1894; and on August 9, 1895, the Award Committee, having completed its examination of the 218 papers submitted by contestants, granted the first prize, of $10,000, for a treatise embodying some new and important discovery in regard to the nature or properties of atmospheric air, to Lord Rayleigh, of London, and Professor William Ramsay, of the University College, London, for the discovery of "ARGON," a new element of the atmosphere.

The Committee was composed of the following members: Doctor S. P. Langley, Chairman, ex-officio; Doctor G. Brown Goode, appointed by the Secretary of the Smithsonian Institution; Assistant Surgeon-General John S. Billings, U. S. A., by the President of the National Academy of Sciences; and Professor M. W. Harrington, by the President of the American Association for the Advancement of Science. The Foreign Advisory Committee, as first constituted, was represented by Monsieur J. Janssen, Professor T. H. Huxley, and Professor von Helmholtz; and after the death of the latter, Doctor W. von Bezold was added.

The memoir is here presented in the form in which it was submitted to the Committee. A revised version, re-edited, with additional matter, was, with the consent of the Smithsonian Institution, published in the Philosophical Transactions.

S. P. LANGLEY,

SECRETARY.

Washington City, May, 1896.

ARGON,

A NEW CONSTITUENT OF THE ATMOSPHERE.

By Lord Rayleigh and Professor William Ramsay.

> "Modern discoveries have not been made by large collections of facts, with subsequent discussion, separation, and resulting deduction of a truth thus rendered perceptible. A few facts have suggested an *hypothesis*, which means a *supposition*, proper to explain them. The necessary results of this supposition are worked out, and then, and not till then, other facts are examined to see if their ulterior results are found in Nature."—De Morgan, "A Budget of Paradoxes," Ed. 1872, p. 55.

I.—Density of Nitrogen from Various Sources.

In a former paper[1] it has been shown that nitrogen extracted from chemical compounds is about one-half per cent lighter than "atmospheric nitrogen."

The mean numbers for the weights of gas contained in the globe used were as follows:

From nitric oxide	2.3001
From nitrous oxide	2.2990
From ammonium nitrite	2.2987

while for "atmospheric" nitrogen there was found:

By hot copper, 1892	2.3103
By hot iron, 1893	2.3100
By ferrous hydrate, 1894	2.3102

At the suggestion of Prof. Thorpe experiments were subsequently tried with nitrogen liberated from *urea* by the action of sodium hypobromite. The carbon and hydrogen of the urea are supposed to be oxidized by the reaction to CO_2 and

---

[1] *Proceedings of the Royal Society*, vol. LV, p. 340, 1894.

H_2O, the former of which would be retained by the large excess of alkali employed. It was accordingly hoped that the gas would require no further purification than drying. If it proved to be light, it would at any rate be free from the suspicion of containing hydrogen.

The hypobromite was prepared from commercial materials in the proportions recommended for this analysis of urea—100 gms. caustic soda, 250 c. c. water, and 25 c. c. of bromine. For our purpose about 1½ times the above quantities were required. The gas was liberated in a bottle of about 900 c. c. capacity in which a vacuum was first established. The full quantity of hypobromite solution was allowed to run slowly, so that any dissolved gas might be at once disengaged. The urea was then fed in, at first in a dilute condition, but as the pressure rose, in a ten per cent solution. The washing out of the apparatus, being effected with gas in a highly rarefied state, made but a slight demand upon the materials. The reaction was well under control, and the gas could be liberated as slowly as desired.

In the first experiment the gas was submitted to no other treatment than slow passage through potash and phosphoric anhydride, but it soon became apparent that the nitrogen was contaminated. The "inert and inodorous" gas attacked vigorously the mercury of the Topler pump and was described as smelling like a dead rat. As to the weight, it proved to be in excess even of the weight of atmospheric nitrogen.

The corrosion of the mercury and the evil smell were in great degree obviated by passing the gas over hot metals. For the fillings of June 6th, 9th, 13th, the gas passed through a short length of tube containing copper in the form of fine wire heated by a flat Bunsen burner, then through the furnace over red-hot iron and back over copper oxide. On June 19th the furnace tubes were omitted, the gas being treated with the red-hot copper only.

The results, reduced so as to correspond with those above quoted, were:

June	6th	2.2978
"	9th	2.2987
"	13th	2.2982
"	19th	2.2994
	Mean	2.2985

Without using heat it has not been found possible to prevent the corrosion of the mercury. Even when no urea is employed and air, simply bubbled through the hypobromite solution, is allowed to pass with constant shaking over mercury contained in a U-tube, the surface of the metal was soon fouled. When *hypochlorite* was substituted for *hypobromite* in the last experiment there was a decided improvement, and it was thought desirable to try whether the gas prepared from hypochlorite and urea would be pure on simple desiccation. A filling on June 25th gave as the weight 2.3343, showing an excess of 36 mg., as compared with other chemical nitrogen, and of about 25 mg. as compared with atmospheric nitrogen. A test with alkaline pyrogallate appeared to prove the absence from this gas of free oxygen, and only a trace of carbon could be detected when considerable quantity of the gas was passed over red-hot cupric oxide into a solution of baryta.

Although the results relating to urea-nitrogen are interesting for comparison with that obtained from other nitrogen compounds, the original object was not attained on account of the necessity of retaining the treatment with hot metals. We have found, however, that nitrogen from ammonium nitrite may be prepared without the employment of hot tubes, whose weight agrees with that above quoted. It is true that the gas smells slightly of ammonia, easily removable by sulphuric acid, and apparently also of oxides of nitrogen. The solution of potassium nitrite and ammonium chloride was heated in a water bath, of which the temperature rose to the boiling point only towards the close of operations. In the earlier stages the temperature required careful watching in order to prevent the decomposition taking place too rapidly. The gas was washed with sulphuric acid, and after passing a Nessler test, was finally treated with potash and phosphoric anhydride in the usual way.

The following results have been obtained:

July 4th	2.2983
" 9th	2.2989
" 13th	2.2990
Mean	2.2987

It will be seen that in spite of the slight nitrous smell there is no appreciable difference in the densities of gas prepared from ammonium nitrite with and without the treatment by hot metals. The result is interesting as showing that the agreement of numbers obtained for chemical nitrogen does not depend upon the use of a red heat in the process of purification.

The five results obtained in more or less distinct ways for chemical nitrogen stand thus:

From nitric oxide	2.3001
From nitrous oxide	2.2990
From ammonium nitrite purified at a red heat	2.2987
From urea	2.2985
From ammonium nitrite purified in the cold	2.2987
Mean	2.2990

These numbers, as well as those above quoted for "atmospheric nitrogen," are subject to a deduction of 0,0006 for the skrinkage of the globe when exhausted.[1] If they are then multiplied in the ratio of 2.3108 : 1.2572, they will express the weights of the gas in grammes per litre. Thus, as regards the mean numbers, we find as the weight per litre under standard conditions of chemical nitrogen 1.2505, that of atmospheric nitrogen being 1.2572.

It is of interest to compare the density of nitrogen obtained from chemical compounds with that of oxygen. We have $N_2 : O_2 = 2.2981 : 2.6276 = 0.87471$; so that if $O_2 = 16$, $N_2 = 13.9954$. Thus when the comparison is with chemical nitrogen the ratio is very nearly that of 16 : 14. But if "atmospheric nitrogen" be substituted, the ratio of small integers is widely departed from.

To the above list may be added nitrogen prepared in yet another manner, whose weight has been determined subsequently to the isolation of the new dense constituent of the atmosphere. In this case nitrogen was actually extracted from air by means of magnesium. The nitrogen thus separated was then converted into ammonia by action of water upon the magnesium nitride and afterwards liberated in the free state by means of calcium hypochlorite. The purification was conducted in the usual way, and included passage over red-hot copper and copper oxide. The following was the result:

Globe empty, Oct. 30th, Nov. 5th	2.82313
Globe full, Oct. 31st	.52395
Weight of gas	2.29918

It differs inappreciably from the mean of other results, viz., 2.2990, and is of special interest as relating to gas which at one stage of its history formed part of the atmosphere. Another determination with a different apparatus of the density of "chemical" nitrogen from the same source, magnesium nitride, which had been prepared by passing "atmospheric" nitrogen over ignited magnesium, may here be recorded. The sample differed from that previously mentioned, inasmuch as it had not been subjected to treatment with red-hot copper. After treating the nitride with water, the resulting ammonia was distilled off, and collected in hydrochloric acid; the solution was evaporated to dryness; the dry ammonium chloride was dissolved in water, and its concentrated solution added to a freshly prepared solution of sodium hypobromite. The nitrogen was collected in a gas-holder over water

---

[1] "On the Densities of the Principal Gases," *Proceedings of the Royal Society*, vol. LIII, p. 134, 1893.

which had previously been boiled, so as at all events partially to expel air. The nitrogen passed into the vacuous globe through a solution of potassium hydroxide, and through two drying tubes, one containing soda-lime, and the other, phosphoric anhydride.

At 18.38° C., and 754.1 mm. pressure, 162.843 c. c. of this nitrogen weighed 0.18963 gramme. Hence,

Weight of 1 litre at 0° C. and 760 mm. pressure, 1.2521 gramme. The mean result of the weight of 1 litre of "chemical" nitrogen has been found to equal 1.2505. It is therefore seen that "chemical" nitrogen, derived from "atmospheric" nitrogen, without any exposure to red-hot copper, possesses the usual density.

Experiments were also made, which had for their object to prove that the ammonia, produced from the magnesium nitride, is identical with ordinary ammonia, and contains no other compound of a basic character. For this purpose, the ammonia was converted into ammonium chloride, and the percentage of chlorine determined by titration with a solution of silver nitrate which had been standardized by titrating a specimen of pure sublimed ammonium chloride. The silver solution was of such a strength that one cubic centimetre precipitated the chlorine from 0.001701 gramme of ammonium chloride.

I. Ammonium chloride from orange-colored sample of magnesium nitride.

0.1106 gramme required 43.10 cubic centimetres of silver nitrate, = 66.35 p. c. of chlorine.

II. Ammonium chloride from blackish magnesium nitride.

0.0118 gramme required 43.6 cubic centimetres of silver nitrate, = 66.35 p. c. of chlorine.

III. Ammonium chloride from nitride containing a large amount of unattacked magnesium.

0.0630 gramme required 24.55 cubic centimetres of silver nitrate, = 66.30 p. c. of chlorine.

Taking for the atomic weights: of hydrogen, H = 1.0032; of nitrogen, N = 14.04; and of chlorine, Cl = 35.46, the theoretical amount of chlorine in ammonium chloride is 66.27 p. c.

From these results—nitrogen prepared from magnesium nitride obtained by passing "atmospheric" nitrogen over red-hot magnesium has the density of "chemical" nitrogen, and that ammonium chloride prepared from magnesium nitride contains practically the same percentage of chlorine as pure ammonium chloride—it may be concluded that red-hot magnesium withdraws from "atmospheric" nitrogen no substance capable of forming a basic compound with hydrogen.

2. REASONS FOR SUSPECTING A HITHERTO UNDISCOVERED CONSTITUENT IN AIR.

When the discrepancy of weights was first encountered, attempts were naturally made to explain it by contamination with known impurities. Of these the most likely appeared to be hydrogen, present in the lighter gas in spite of the passage over red-hot cupric oxide. But inasmuch as the intentional introduction of hydrogen into the heavier gas, afterwards treated in the same way with cupric oxide, had no effect upon its weight, this explanation had to be abandoned, and finally it became clear that the difference could not be accounted for by the presence of any known impurity. At this stage it seemed not improbable that the lightness of the gas extracted from chemical compounds was to be explained by partial dissociation of nitrogen molecules N_2 into detached atoms. In order to test this suggestion, both kinds of gas were submitted to the action of the silent electric discharge, with the result that both retained their weights unaltered. This was discouraging, and a further experiment pointed still more markedly in the negative direction. The chemical behavior of nitrogen is such as to suggest that dissociated atoms would possess a high degree of activity, and that even though they might be formed in the first instance their life would probably be short. On standing they might be expected to disappear, in partial analogy with the known behavior of ozone. With this idea in view a sample of chemically prepared nitrogen was stored for eight months. But at the end of this time the density showed no sign of increase, remaining exactly as at first.[1]

Regarding it as established that one or other of the gases must be a mixture, containing as the case might be an ingredient much heavier or much lighter than ordinary nitrogen, we had to consider the relative probabilities of the various possible interpretations. Except upon the already discredited hypothesis of dissociation, it was difficult to see how the gas of chemical origin could be a mixture. To suppose this would be to admit two kinds of nitric acid, hardly reconcilable with the work of Stas and others upon the atomic weight of that substance. The simplest explanation in many respects was to admit the existence of a second ingredient in air from which oxygen, moisture, and carbonic anhydride had already been removed. The proportional amount required was not great. If the density of the supposed gas were double that of nitrogen, one-half per cent only by volume would be needed; or if the density were but half as much again as that of nitrogen, then one per cent would still suffice. But in accepting this explanation, even provisionally, we had to face the improbability that a gas surrounding us on all sides and present in enormous quantities could have remained so long unsuspected.

---

[1] *Proceedings of the Royal Society*, vol. LV, p. 344, 1894.

The method of most universal application by which to test whether a gas is pure or a mixture of components of different densities is that of diffusion. By this means Graham succeeded in effecting a partial separation of the nitrogen and oxygen of the air, in spite of the comparatively small difference of densities. If the atmosphere contains an unknown gas of anything like the density supposed, it should be possible to prove the fact by operations conducted upon air which had undergone atmolysis. If, for example, the parts least disposed to penetrate porous walls were retained, the "nitrogen" derived from it by the usual processes should be heavier than that derived in like manner from unprepared air. This experiment, although in view from the first, was not executed until a later stage of the inquiry (§ 6), when results were obtained sufficient of themselves to prove that the atmosphere contains a previously unknown gas.

But although the method of diffusion was capable of deciding the main, or at any rate the first, question, it held out no prospect of isolating the new constituent of the atmosphere, and we therefore turned our attention in the first instance to the consideration of methods more strictly chemical. And here the question forced itself upon us as to what really was the evidence in favor of the prevalent doctrine that the inert residue from air, after withdrawal of oxygen, water, and carbonic anhydride, is all of one kind.

The identification of "phlogisticated air" with the constituent of nitric acid is due to Cavendish, whose method consisted in operating with electric sparks upon a short column of gas confined with potash over mercury at the upper end of an inverted U-tube.[1] This tube (M) was only about $\frac{1}{10}$ inch in diameter, and the column of gas was usually about one inch in length. After describing some preliminary trials, Cavendish proceeds: "I introduced into the tube a little soap-lees (potash), and then let up some dephlogisticated (oxygen) and common air, mixed in the above-mentioned proportions, which, rising to the top of the tube (M), divided the soap-lees into its two legs. As fast as the air was diminished by the electric spark, I continued adding more of the same kind, till no further diminution took place; after which a little pure dephlogisticated air, and after that a little common air, were added, in order to see whether the cessation of diminution was not owing to some imperfection in the proportion of the two kinds of air to each other; but without effect. The soap-lees being then poured out of the tube, and separated from the quicksilver, seemed to be perfectly neutralized, and they did not at all discolor paper tinged with the juice of blue flowers. Being evaporated to dryness, they left a small quantity of salt, which was evidently nitre, as appeared by the manner in which paper, impregnated with a solution of it, burned."

---

[1] Experiments on Air, *Philosophical Transactions*, vol. LXXV, p. 372, 1785.

Attempts to repeat Cavendish's experiment in Cavendish's manner have only increased the admiration with which we regard this wonderful investigation. Working on almost microscopical quantities of material and by operations extending over days and weeks, he thus established one of the most important facts in chemistry. And what is still more to the purpose, he raises as distinctly as we could do, and to a certain extent resolves, the question above suggested. The passage is so important that it will be desirable to quote it at full length:

"As far as the experiments hitherto published extend, we scarcely know more of the phlogisticated part of our atmosphere, than that it is not diminished by lime-water, caustic alkalies, or nitrous air; that it is unfit to support fire, or maintain life in animals; and that its specific gravity is not much less than that of common air; so that, though the nitrous acid, by being united to phlogiston, is converted into air possessed of these properties, and consequently, though it was reasonable to suppose, that part at least of the phlogisticated air of the atmosphere consists of this acid united to phlogiston, yet it was fairly to be doubted whether the *whole* is of this kind, or whether there are not in reality many different substances confounded together by us under the name of phlogisticated air. I therefore made an experiment to determine whether the whole of a given portion of the phlogisticated air of the atmosphere could be reduced to nitrous acid, or whether there was not a part of a different nature to the rest, which would refuse to undergo that change. The foregoing experiments indeed in some measure decided this point, as much as the greatest part of the air let up into the tube lost its elasticity; yet as some remained unabsorbed it did not appear for certain whether that was of the same nature as the rest or not. For this purpose I diminished a similar mixture of dephlogisticated and common air, in the same manner as before, till it was reduced to a small part of its original bulk. I then, in order to decompound as much as I could of the phlogisticated air which remained in the tube, added some dephlostigated air to it and continued the spark until no further diminution took place. Having by these means condensed as much as I could of the phlogisticated air, I let up some solution of liver of sulphur to absorb the dephlogisticated air; after which only a small bubble of air remained unabsorbed, which certainly was not more than $\frac{1}{120}$ of the bulk of the phlogisticated air let up into the tube; so that if there is any part of the phlogisticated air of our atmosphere which differs from the rest, and cannot be reduced to nitrous acid, we may safely conclude that it is not more than $\frac{1}{120}$ part of the whole."

Although Cavendish was satisfied with his result, and does not decide whether the small residue was genuine, our experiments about to be related render it not improbable that his residue was really of a different kind from the main bulk of the "phlogisticated air," and contained the gas now called argon.

Cavendish gives data[1] from which it is possible to determine the rate of absorption of the mixed gases in his experiment. The electrical machine used "was one of Mr. Nairne's patent machines, the cylinder of which is 12½ inches long, and 7 in diameter. A conductor of 5 feet long and 6 inches in diameter was adapted to it, and the ball which received the spark was placed two or three inches from another ball fixed to the end of the conductor. Now when the machine worked well, Mr. Gilpin supposes he got about two or three hundred sparks a minute, and the diminution of the air, during the half hour which he continued working at a time, varied in general from 40 to 120 measures, but was usually greatest when there was most air in the tube, provided the quantity was not so great as to prevent the spark from passing readily." The "measure" spoken of represents the volume of one grain of quicksilver, or 0.0048 c. c.; so that an absorption of one cubic centimetre of mixed gas per hour was about the most favorable rate. Of the mixed gas about two-fifths would be nitrogen.

3. Methods of Causing Free Nitrogen to Combine.

The concord between the determinations of density of nitrogen obtained from sources other than the atmosphere having made it at least possible that some heavier gas exists in the atmosphere, hitherto undetected, it became necessary to submit atmospheric nitrogen to examination with the view of isolating, if possible, the unknown and overlooked constituent, or it might be constituents.

Nitrogen, however, is an element which does not easily enter into direct combination with other elements; but with certain elements, and under certain conditions, combination may be induced. The elements which have been directly united to nitrogen are (a) boron, (b) silicon, (c) titanium, (d) lithium, (e) strontium and barium, (f) magnesium, (g) aluminum, (h) mercury, (i) hydrogen, and (k) oxygen, the last two by help of an electrical discharge.

(a) *Nitride of boron* was prepared by Wöhler and Deville,[2] by heating amorphous boron to a white heat in a current of nitrogen. Experiments were made to test whether the reaction would take place in a tube of difficultly fusible glass; but it was found that the combination took place at a bright-red heat to only a small extent, and that the boron, which had been prepared by heating powdered boron oxide with magnesium dust, was only superficially attacked. Boron is therefore not a convenient absorbent for nitrogen.

---

[1] *Philosophical Transactions*, vol. LXXVIII, p. 271, 1788.

[2] *Annales de Chemie* (3), 52, p. 82.

(b) *Nitride of silicon* also requires for its formation a white heat, and complete union is difficult to bring about. Moreover it is not easy to obtain large quantities of silicon. This method was therefore not attempted.

(c) *Nitride of titanium* is said to have been formed by Deville and Caron,[2] by heating titanium to whiteness in a current of nitrogen. This process was not tried by us. As titanium has an unusual tendency to unite with nitrogen, it might, perhaps, be worth while to set the element free in presence of atmospheric nitrogen, with a view to the absorption of the nitrogen. This has, in effect, been already done by Wöhler and Deville; they passed a mixture of the vapor of titanium chloride and nitrogen over red-hot aluminum, and obtained a large yield of nitride. It is possible that a mixture of the precipitated oxide of titanium with magnesium dust might be an effective absorbing agent at a comparatively low temperature.

(d), (e) *Lithium* at a dull-red heat absorbs nitrogen,[4] but the difficulty of obtaining the metal in quantity precludes its application. On the other hand, *strontium* and *barium*, prepared by electrolyzing solutions of their chlorides in contact with mercury, and subsequently removing the mercury by distillation, are said by Maquenne[5] to absorb nitrogen with readiness. Although we have not tried these metals for removing nitrogen, still our experience with their amalgams has led us to doubt their efficacy, for it is extremely difficult to free them from mercury by distillation, and the product is a fused ingot, exposing very little surface to the action of the gas. The process might, however, be worth a trial. Nitrogen is also known to be converted into cyanides when passed over a mixture of baryta and carbon, and this may possibly prove to be the most efficient method of effecting its removal on a large scale.

(f) *Nitride of magnesium* was prepared by Deville and Caron (*loc. cit.*) during the distillation of impure magnesium. It has been more carefully investigated by Briegleb and Geuther,[6] who obtained it by igniting metallic magnesium in a current of nitrogen. It forms an orange-brown, friable substance, very porous, and it is easily produced at a bright red heat. When magnesium, preferably in the form of thin turnings, is heated in a combustion tube in a current of nitrogen, the tube is attacked superficially, forming a coating of magnesium silicide. As the temperature rises to bright redness, the magnesium begins to glow brightly, and combustion takes place, beginning at that end of the tube through which the gas is introduced. The combustion proceeds regularly, the glow extending down the

---

[1] Schützenberger, *Comptes Rendus*, 89, 644.

[2] *Annalen der Chemie und Pharmacie*, 101, 360.

[3] *Ibid.*, 73, 34.

[4] Ouvrard, *Comptes Rendus*, 114, 120.

[5] *Ibid.*, 114, 25 and 220.

[6] *Annalen der Chemie und Pharmacie*, 123, 228.

tube, until all the metal has united with nitrogen. The heat developed by the combination is considerable, and the glass softens; but by careful attention and regulation of the rate of the current, the tube lasts out an operation. A piece of combustion tubing of the usual length for organic analysis, packed tightly with magnesium turnings, and containing about 30 grammes, absorbs between seven and eight litres of nitrogen. It is essential that oxygen be excluded from the tube, otherwise a fusible substance is produced, possibly nitrate, which blocks the tube. With the precaution of excluding oxygen, the nitride is loose and porous, and can easily be removed from the tube with a rod; but it is not possible to use a tube twice, for the glass is generally softened and deformed.

(g) *Nitride of aluminum* has been investigated by Mallet.[1] He obtained it in crystals by heating the metal to whiteness in a carbon crucible. But aluminum shows no tendency to unite with nitrogen at a red heat, and cannot be used as an absorbent for the gas.

(h) Garresheim[2] states that he has induced combination between nitrogen and mercury; but the affinity between these elements is of the slightest, for the compound is explosive.

(i) The union of hydrogen with nitrogen to form ammonia in presence of an acid seems to proceed at a fair rate under the influence of electric sparks from a battery and coil; but an attempt to increase the rate by use of the alternating current from a dynamo has not so far succeeded.

The process of removing nitrogen by a combination with oxygen is treated in § 2, 4, and 8.

4. EARLY EXPERIMENTS ON SPARKING NITROGEN WITH OXYGEN IN PRESENCE OF ALKALI.

In our earliest attempts to isolate the suspected gas by the method of Cavendish, we used a Ruhmkorff coil of medium size actuated by a battery of five Grove cells. The gases were contained in a test tube standing over a large quantity of weak alkali, and the current was conveyed in wires insulated by inverted U-shaped glass tubes passing through the liquid round the mouth of the test tube. The inner platinum ends of the wire were sealed into the glass insulating tubes, but reliance was not placed upon the sealings. In order to secure tightness in spite of cracks, mercury was placed in the bends. This disposition of the electrodes complicates the apparatus somewhat and entails the use of a large

---

[1] *Transactions of the Chemical Society*, 1876, II, 349.

[2] *Annalen der Chemie und Pharmacie*, 195, 373.

depth of liquid in order to render possible the withdrawal of the tubes, but it has the great advantage of dispensing with sealing electrodes into the principal vessel, which might give way and cause the loss of the experiment at the most inconvenient moment. With the given battery and coil a somewhat short spark, or arc, of about 5 mm. was found to be more favorable than a larger one. When the mixed gases were in the right proportion, the rate of absorption was about 30 c. c. per hour, or 30 times as fast as Cavendish could work with the electrical machine of his day.

To take an example, one experiment of this kind started with 50 c. c. of air. To this, oxygen was gradually added until, oxygen being in excess, there was no perceptible contraction during an hour's sparking. The remaining gas was then transferred at the pneumatic trough to a small measuring vessel, sealed by mercury, in which the volume was found to be 1.0 c. c. On treatment with alkaline pyrogallate, the gas shrank to .32 c. c. That this small residue could not be nitrogen was argued from the fact that it had withstood the prolonged action of the spark, although mixed with oxygen in nearly the most favorable proportion.

The residue was then transferred to the test tube with an addition of another 50 c. c. of air and the whole worked up with oxygen as before. The residue was now 2.2 c. c., and after removal of oxygen .76 c. c.

Although it seemed almost impossible that these residues could be either nitrogen or hydrogen, some anxiety was not unnatural, seeing that the final sparking took place under somewhat abnormal conditions. The space was very restricted, and the temperature (and with it the proportion of aqueous vapor) was unduly high. But any doubts that were felt upon this score were removed by comparison experiments in which the whole quantity of air operated on was very small. Thus when a mixture of 5 c. c. of air with 7 c. c. of oxygen was sparked for 1¼ hours, the residue was 0.47 c. c. and after removal of oxygen 0.06 c. c. Several repetitions having given similar results, it became clear that the final residue did not depend upon anything that might happen when sparks passed through a greatly reduced volume, *but was in proportion to the amount of air operated upon.*

No satisfactory examination of the residue which refused to be oxidized could be made without the accumulation of a larger quantity. This, however, was difficult of attainment at the time in question. The gas seemed to rebel against the law of addition. It was thought that the cause probably lay in the solubility of the gas in water, a suspicion since confirmed. At length, however, a sufficiency was collected to allow of sparking in a specially constructed tube, when a comparison with the air spectrum taken under similar conditions proved that at any rate the gas was not nitrogen. At first scarcely a trace of the principal nitrogen lines could be seen, but after standing over water for an hour or two these lines became apparent.

We now proceed to give an account of the early experiments with magnesium.

5. EARLY EXPERIMENTS ON WITHDRAWAL OF NITROGEN FROM AIR BY MEANS OF RED-HOT MAGNESIUM.

It having been proved that nitrogen at a bright-red heat was easily absorbed by magnesium, best in the form of turnings, an attempt was successfully made to remove that gas from the residue left after eliminating oxygen from air by means of red-hot copper.

The preliminary experiment was made in the following manner: A combustion tube, A, was filled with magnesium turnings, packed tightly by pushing them in with a rod. This tube was connected with a second piece of combustion tubing, B, by means of thick-walled indiarubber tubing, carefully wired; B contained copper oxide, and in its turn was connected with the tube C D, one-half of which contained soda-lime, previously ignited to expel moisture, while the other half was filled with phosphoric anhydride. E is a measuring vessel, and F was connected with a gas-holder containing "atmospheric nitrogen."

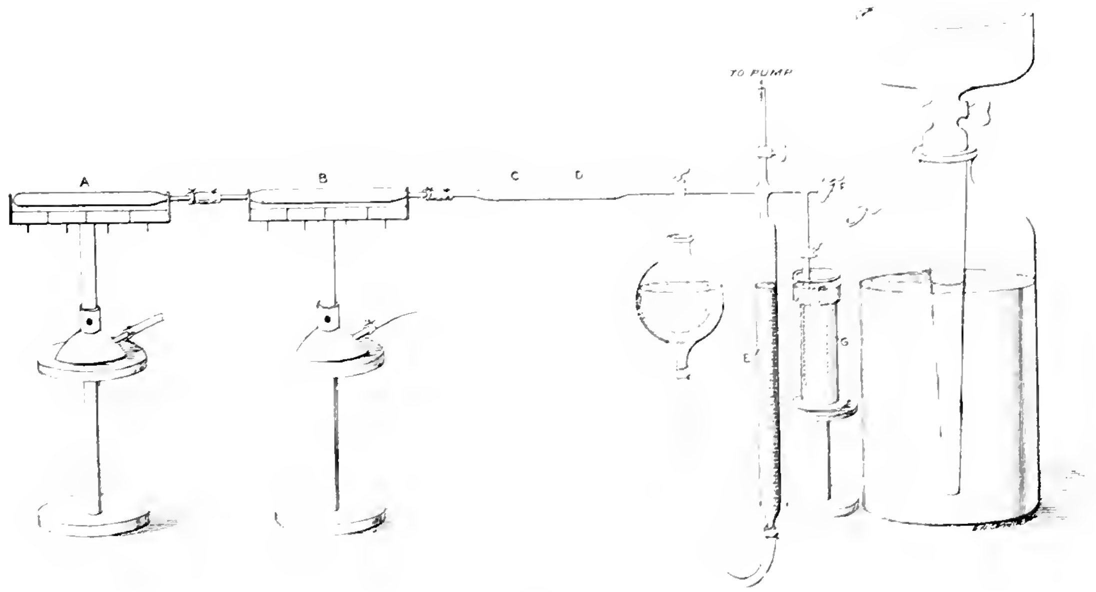


Fig. 1.

In beginning an experiment, the system of tubes, which was heated with long-flame burners, was pumped empty; a little hydrogen was formed by the action of the moisture in the tube on the metallic magnesium; it was oxidized by the copper oxide and absorbed by the phosphoric pentoxide. A gauge attached to a Sprengel's pump, connected with the apparatus, showed when a vacuum had been reached. A quantity of nitrogen was then measured in E, and admitted into contact with the red-hot magnesium. Absorption took place rapidly at first and then slowly as shown by the gauge on the Sprengel's pump. A fresh quantity was then measured and admitted, and these operations were repeated until no more could be absorbed. The system of tubes was then pumped empty by means of the Sprengel's pump, and the gas was collected. The magnesium tube was then detached and replaced by another. The unabsorbed gas was returned to the measuring-tube by a device shown in the figure (G), and the absorption recommenced. After 1094 cubic centimetres of gas had thus been treated, there was left about 50 cubic centimetres of gas, which resisted rapid absorption. It still contained nitrogen, however, judging by the diminution of volume which it experienced when allowed to stand in contact with red-hot magnesium. Its density was, nevertheless, determined by weighing a small bulb of about 40 cubic centimetres capacity first with air, and afterwards with the gas. The data are these:

(a) Weight of bulb and air — that of glass counterpoise.....	0.8094 gramme
Weight of bulb alone — " " "	0.7588 "
Weight of air....................................	0.0506 gramme
(b) Weight of bulb and gas — that of glass counterpoise.....	0.8108 gramme
Weight of bulb alone — " " "	0.7588 "
Weight of gas....................................	0.0520 gramme

Taking as the weight of a litre of air 1.29347 gramme, the mean of the latest results, and of oxygen (= 16) 1.42961 gramme,[1] the density of the residual gas is 14.88.

---

[1] The results on which this and the subsequent calculations are based are as follows (the weights are those of 1 litre):

	Air.	Oxygen.	Nitrogen.	Hydrogen.
Regnault	1.29349	1.43011	1.25647	0.08988
Von Jolly	1.29383	1.42971	1.25819	....
Leduc	1.29330	1.42910	1.25700	0.08985
Rayleigh	1.29327	1.42952	1.25718	0.09001

Regnault's numbers have an approximate correction applied to them by Crafts. The mean of these numbers is taken, that of Regnault for nitrogen being omitted, as there is reason to believe that his specimen was contaminated with hydrogen.

Air.	Oxygen.	Nitrogen.	Hydrogen.
1.29347	1.42961	1.25749	0.08991

This ratio gives for air the composition by volume:

Oxygen..	20.91 p. c.
Nitrogen...	79.09 "

a result verified by experiment.

It is of course to be understood that these densities of nitrogen refer to atmospheric nitrogen, that is, to air from which oxygen, water vapor, carbon dioxide, and ammonia have been removed.

This result was encouraging, although weighted with the unavoidable error attaching to the weighing of a very small amount. Still the fact remains that the supposed nitrogen was heavier than air. It would hardly have been possible to make a mistake of 2.7 milligrammes.

It is right here to place on record the fact that this first experiment was to a great extent carried out by Mr. Percy Williams, to whose skill in manipulation and great care its success is due, and to whom we desire here to express our thanks.

Experiments were now begun on a larger scale, the apparatus employed being shown in Fig. 2.

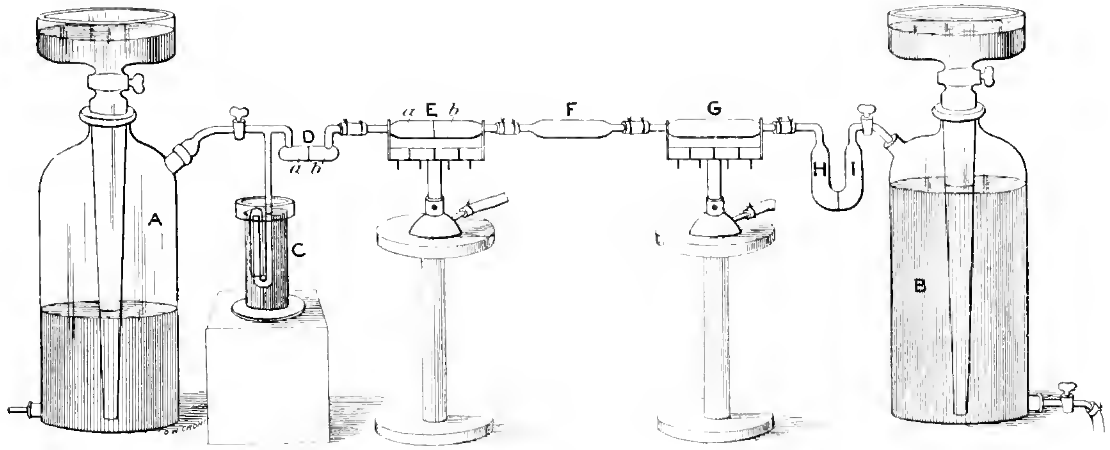


FIG. 2.

A and B are large glass gas-holders of about 10 litres capacity. C is an arrangement by which gas could be introduced at will into the gas-holder A, either by means of an india-rubber tube slipped over the open end of the U-tube, or, as shown in the figure, from a test tube. The tube D was half filled with soda-lime (*a*), half with phosphoric anhydride (*b*). Similarly the tube E, which was kept at a red heat by means of the long-flame burner, was filled half with very porous copper (*a*) reduced from dusty oxide by heating in hydrogen, half with copper oxide in a granular form (*b*). The next tube, F, contained granular soda lime, while G contained magnesium turnings, also heated to bright redness by means of a long-flame burner. H contained phosphoric anhydride, and I soda-lime. All joints were sealed, excepting those connecting the hard-glass tubes E and G, to the tubes next them.

The gas-holder A having been filled with nitrogen, prepared by passing air over red-hot copper, and introduced at C, the gas was slowly passed through the system of tubes into the gas-holder B, and back again. The magnesium in the tube G having then ceased to absorb, was quickly removed and replaced by a fresh tube. This tube was, of course, full of air, and before the tube G was heated, the air was carried back from B towards A by passing a little nitrogen from right to left. The oxygen in the air was removed by the metallic copper and the nitrogen passed into the gas-holder A, to be returned in the opposite direction to B.

In the course of about ten days, most of the nitrogen had been absorbed. The magnesium was not always completely exhausted; usually the nitride presented the appearance of a blackish-yellow mass, easily shaken out of the tube. It is needless to say that the tube was always somewhat attacked, becoming black with a coating of magnesium silicide. The nitride of magnesium, whether blackish or orange, if left for a few hours exposed to moist air, was completely converted into white, dusty hydroxide, and during exposure it gave off a strong odor of ammonia. If kept in a stoppered bottle, however, it was quite stable.

It was then necessary in order to continue the absorption to carry on operations on a smaller scale, with precautions to exclude atmospheric air as completely as possible. There was at this stage a residue of 1500 cubic centimetres.

The apparatus was therefore altered to that shown in Fig. 3 so as to make it possible to withdraw all the gas out of the gas-holder A. The left-hand exit led to the Sprengel's pump; the compartment (*a*) of the drying tube B was filled with soda-lime, and (*b*) with phosphoric anhydride. C is a tube into which the gas could be drawn from the gas-holder A. The stopcock, as shown, allows gas to pass through the horizontal tubes and does not communicate with C; but a vertical groove allows it to be placed in communication either with the gas-holder, or with the apparatus to the right. The compartment (*b*) of the second drying tube D

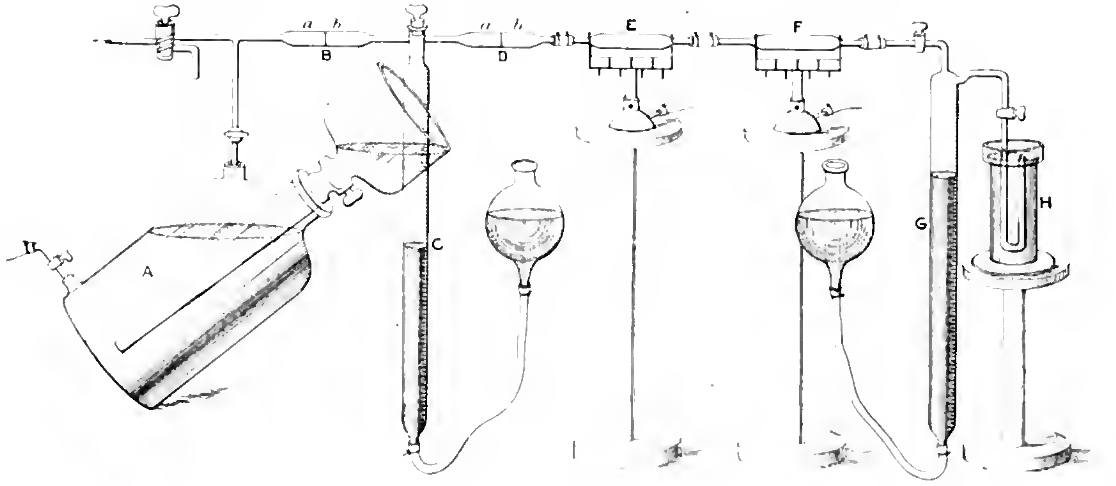


Fig. 3.

contained phosphoric anhydride, and (*a*) soda-lime. The tube D communicated with a hard-glass tube, E, heated over a long-flame burner; it was partly filled with metallic copper, and partly with copper oxide. This tube, as well as the tube F, filled with magnesium turnings, was connected to the drying tube with india-rubber. The gas then entered G, a graduated reservoir, and the arrangement H permitted the removal or introduction of gas from or into the apparatus. The gas was gradually transferred from the gas-holder to the tube C, and passed backwards and forwards over the red-hot magnesium until about 200 cubic centimetres were left. It was necessary to change the magnesium tube, which was made of smaller size than formerly, several times during the operation. This was done by turning out the long-flame burners and pumping off all gas in the horizontal tubes by means of the Sprengel's pump. This gas was carefully collected. The magnesium tube was then exchanged for a fresh one, and after air had been exhausted from the apparatus, nitrogen was introduced from the reservoir. Any gas evolved from the magnesium (and apparently there was always a trace of hydrogen, either occluded by the magnesium, or produced by the action of aqueous vapor on the metal) was oxidized by the copper oxide. Had oxygen been present, it would have been absorbed by the metallic copper, but the copper preserved its red appearance without alteration, whereas a little copper oxide was reduced during the series of operations. The gas, which had been removed by pumping, was reintroduced at H, and the absorption continued.

The volume of the gas was thus, as has been said, reduced to about 200 cubic centimetres. It would have been advisable to take exact measurements, but, unfortunately, some of the original nitrogen had been lost through leakage; and a natural anxiety to see if there was any unknown gas led to pushing on operations as quickly as possible.

The density of the gas was next determined. The bulb or globe in which the gas was weighed was sealed to a two-way stopcock, and the weight of distilled and air-free water filling it at 17°.15 was 162.654 grammes, corresponding to a capacity of 162.843 cubic centimetres. The shrinkage on removing air completely was 0.0212 cubic centimetre. Its weight when empty should therefore be increased by the weight of that volume of air, which may be taken as 0.000026 gramme. This correction, however, is perhaps hardly worth applying in the present case.

The counterpoise was an exactly similar bulb, of equal capacity, and weighing about 0.2 gramme heavier than the empty globe. The balance was a very sensitive one by Oertling, which easily measured one-tenth of a milligramme. By the process of swinging, one-hundredth of a milligramme would be determined with fair accuracy.

In weighing the empty globe, 0.2 gramme was placed on the same pan as that which hung from the end of the beam to which it was suspended and the final weight was adjusted by means of a rider, or by small weights on the other pan. This process practically leads to weighing by substitution of gas for weights. The bulb was always handled with gloves, to avoid moisture or grease from the fingers.

Three experiments, of which it is unnecessary to give details, were made to test the degree of accuracy with which a gas could be weighed, the gas being dried air, freed from carbon dioxide. The mean result gave for the weight of 1 litre of air at 0° and 760 mm. pressure, 1.2935 gramme. Regnault found 1.29340, a correction having been applied by Crafts to allow for the estimated alteration of volume caused by the contraction of his vacuous bulb. The mean result of determinations by several observers is 1.29347; while one of us found 1.29327.

The globe was then filled with the carefully dried gas.

Temperature, 18°.80; pressure, 759.3 mm.

Weight of 162.843 c.c. of gas	0.21897	gramme.
Weight of 1 litre gas at 0° and 760 mm.	1.4386	"
Density, that of air compared with O = 16, being 14.476	16.100	"

It is evident from these numbers that the dense constituent of the air was being concentrated. As a check, the bulb was pumped empty and again weighed; its weight was 0.21903 gramme. This makes the density 16.105.

It appeared advisable to continue to absorb nitrogen from this gas. The first tube of magnesium removed a considerable quantity of gas; the nitride was converted into ammonium chloride, and the sample contained 66.30 p. c. of chlorine, showing, as has before been remarked, that if any of the heavier constituent of the atmosphere had been absorbed, it formed no basic compound with hydrogen. The second tube of magnesium was hardly attacked; most of the magnesium had melted, and formed a layer at the lower part of the tube. That which was still left in the body of the tube was black on the surface, but had evidently not been much attacked. The ammonium chloride which it yielded weighed only 0.0035 gramme.

The density of the remaining gas was then determined. But as its volume was only a little over 100 cubic centimetres, the bulb, the capacity of which was 162 cubic centimetres, had to be filled at reduced pressure. This was easily done by replacing the pear-shaped reservoir of the mercury gas-holder by a straight tube, and noticing the level of the mercury in the gas-holder and in the tube which served as a mercury reservoir against a graduated mirror scale by help of a cathetometer at the moment of closing the stopcock of the density bulb.

The details of the experiment are these:

Temperature 19.12 C. Barometric pressure 749.8 mm. (corr.)
Difference read on gas-holder and tube 225.25 mm. (corr.)
Actual pressure, 524.55 mm.
Weight of 162.843 cubic centimetres of gas .... 0.17913 gramme
Weight of 1 litre at 0° and 760 mm. pressure .... 1.7054 "
Density .... 19.086 "

This gas is accordingly at least 19 times as heavy as hydrogen.

A portion of the gas was then mixed with oxygen, and submitted to a rapid discharge of sparks for four hours. It contracted, and on absorbing the excess of oxygen with pyrogallate of potassium the contraction amounted to 15.4 per cent of the original volume. The question then arises: If the gas contained 15.4 per cent of nitrogen of density 14.014 and 84.6 per cent of other gas, and if the density of the mixture were 19.086, what would be the density of the other gas? Calculation leads to the number 20.0.

A vacuum-tube was filled with a specimen of the gas of density 19.086, and it could not be doubted that it contained nitrogen, the bands of which were distinctly visible. It was probable therefore that the true density of the pure gas lay not far from 20 times that of hydrogen. At the same time many lines were seen which could not be recognized as belonging to the spectrum of any known substance.

Such were the preliminary experiments made with the aid of magnesium to separate from atmospheric nitrogen, its dense constituent. The methods adopted in preparing large quantities will be subsequently described.

6. PROOF OF THE PRESENCE OF ARGON IN AIR, BY MEANS OF ATMOLYSIS.

It has already (§ 2) been suggested that if "atmospheric nitrogen" contains two gases of different densities, it should be possible to obtain direct evidence of the fact by the method of atmolysis. The present section contains an account of carefully conducted experiments directed to this end.

The atmolyser was prepared (after Graham) by combining a number of "church-warden" tobacco pipes. At first twelve pipes were used in three groups, each group including four pipes connected in series. The three groups were then connected in parallel, and placed in a large glass tube, closed in such a way that a partial vacuum could be maintained in the space outside the pipes by a water pump. One end of the combination of pipes was open to the atmosphere, or rather was connected with the interior of an open bottle containing sticks of caustic alkali, the object being mainly to dry the air. The other end of the combination was connected to a bottle aspirator, initially full of water, and so arranged as to draw about 2 per cent of the air which entered the other end of the pipes. The gas collected was thus a very small proportion of that which leaked through the pores of the pipes, and should be relatively rich in the heavier constituents of the atmosphere. The flow of water from the aspirator could not be maintained very constant, but the rate of 2 per cent was never much exceeded. The necessary 4 litres took about 16 hours to collect.

The air thus obtained was treated exactly as ordinary air had been treated in determinations of the density of atmospheric nitrogen. Oxygen was removed by red-hot copper, followed by cupric oxide, ammonia by sulphuric acid, moisture and carbonic anhydride by phosphoric anhydride and potash.

The following are the results:

Globe empty, July 10, 14	2.81789
Globe full, Sept. 15 (12 pipes)	.50286
	2.31503
Ordinary atmospheric nitrogen	2.31016
Difference +	.00487
Globe empty, Sept. 17	2.81345
Globe full, Sept. 18 (12 pipes)	.50191
	2.31154
	2.31016
Difference +	.00138
Globe empty, Sept. 21	2.82320
Globe full, Sept. 20 (12 pipes)	.51031
	2.31289
	2.31016
Difference +	.00273
Globe empty, Sept. 21, Oct. 30	2.82306
Globe full, Sept. 22 (12 pipes)	.51140
	2.31166
	2.31016
Difference +	.00150

The mean excess of the four determinations is .00262 gramme, or, if we omit the first, which depended upon a vacuum weighing of two months old, .00187 gramme.

The gas from prepared air was thus in every case denser than from unprepared air, and to an extent much beyond the possible errors of experiment. The excess was, however, less than had been expected, and it was thought that the arrangement of the pipes could be improved. The final delivery of gas from each of the groups in parallel being so small in comparison with the whole streams concerned, it seemed possible that each group was not contributing its proper share, and even that there might be a flow in the wrong direction at the delivery end of one or two of them. To meet this objection, the arrangement in parallel had to be abandoned, and for the remaining experiments 8 pipes were connected in simple series. The porous surface in operation was thus reduced, but this was partly compensated for by an improved vacuum. Two experiments were made under the new conditions:

Globe empty, Oct. 30, Nov. 5	2.82313
Globe full, Nov. 3 (8 pipes)	.50930
	2.31383
Ordinary atmospheric nitrogen	2.31016
Difference +	.00367
Globe empty, Nov. 5, 8	2.82355
Globe full, Nov. 6 (8 pipes)	.51011
	2.31344
Ordinary atmospheric nitrogen	2.31016
Difference +	.00328

The excess being larger than before is doubtless due to the greater efficiency of the atmolysing apparatus. It should be mentioned that the above recorded experiments include all that have been tried, and the conclusion seems inevitable that "atmospheric nitrogen" is a mixture, and not a simple body.

It was hoped that the concentration of the heavier constituent would be sufficient to facilitate its preparation in a pure state by the use of prepared air in substitution for ordinary air in the oxygen apparatus. The advance of 3½ mg. on the 11 mg. by which atmospheric nitrogen is heavier than chemical nitrogen, is indeed not to be despised, and the use of prepared air would be convenient if the diffusion apparatus could be set up on a large scale and be made thoroughly self-acting.

7. NEGATIVE EXPERIMENTS TO PROVE THAT ARGON IS NOT DERIVED FROM NITROGEN FROM CHEMICAL SOURCES.

Although the evidence of the existence of argon in the atmosphere, derived from the comparison of densities of atmospheric and chemical nitrogen and from the diffusion experiments, appeared overwhelming, we have thought it undesirable to shrink from any labor that would tend to complete the verification. With this object in view, an experiment was undertaken and carried to a conclusion on November 13th, in which 3 litres of chemical nitrogen, prepared from ammonium nitrite, were treated with oxygen in precisely the manner in which atmospheric nitrogen had been found to yield a residue of argon. In the course of operations an accident occurred, by which no gas could have been lost, but of such a nature that from 100 to 200 c. c. of air must have entered the working vessel. The gas remaining at the close of the large scale operations was worked up as usual with battery and coil until the spectrum showed only slight traces of the nitrogen lines. When cold, the residue measured 4 c. c. This was transferred, and after treatment with alkaline pyrogallate to remove oxygen, measured 3.5 c. c. If atmospheric nitrogen had been employed, the final residue should have been about 30 c. c. Of the 3.5 c. c. actually left, a good part is accounted for by the accident alluded to, and the result of the experiment is to show that argon is not formed by sparking a mixture of oxygen and chemical nitrogen.

A similar set of experiments was carried out with magnesium. The nitrogen, of which three litres were used, was prepared by the action of bleaching-powder on ammonium chloride. It was circulated in the usual apparatus over red-hot magnesium, until its volume had been reduced to about 100 cubic centimetres. An equal volume of hydrogen was then added, owing to the impossibility of circulating a vacuum. The circulation then proceeded until all absorption had apparently stopped. The remaining gas was then passed over red-hot copper oxide into the Sprengel's pump, and collected. As it appeared still to contain hydrogen, which had escaped oxidation, owing to its great rarefaction, it was passed over copper oxide for a second and a third time. As there was still a residue, measuring 12.5 cubic centimetres, the gas was left in contact with red-hot magnesium for several hours, and then pumped out; its volume was then 4.5 cubic centimetres. Absorption was, however, still proceeding when the experiment terminated, for at a low pressure the rate is exceedingly slow. This gas, on being examined with the spectroscope, contained both hydrogen and nitrogen, and failed to show the red lines of argon. The amount of residue attainable from three litres of atmospheric nitrogen should have amounted to a large multiple of the quantity actually obtained.

8. SEPARATION OF ARGON ON A LARGE SCALE.

To separate nitrogen from "atmospheric" nitrogen on a large scale, by help of magnesium, several devices were tried. It is not necessary to describe them all in detail. Suffice it to say that an attempt was made to cause a store of "atmospheric nitrogen" to circulate by means of a fan, driven by a water-motor. The difficulty encountered here was leakage at the bearing of the fan, and the introduced air, on coming into contact with the magnesium, produced a cake which blocked the tube. It might have been possible to remove oxygen by metallic copper; but instead of thus complicating the apparatus, a water-injector was made use of to induce circulation. Here also it is unnecessary to enter into details. For, though the plan worked well, and although about 120 litres of "atmospheric" nitrogen were absorbed, the yield of argon was not large, about 600 cubic centimetres having been collected. This loss was subsequently discovered to be due partially at least to the relatively high solubility of argon in water. In order to propel the gas over magnesium, through a long combustion tube packed with turnings, a considerable water-pressure, involving a large flow of water, was necessary. The gas was brought into intimate contact with this water, and presuming that several thousand litres of water ran through the injector, it is obvious that a not inconsiderable amount of argon must have dissolved. Its proportion was increasing at each circulation, and consequently its partial pressure also increased. Hence, towards the end of the operation, at least, there is every reason to believe that a serious loss had occurred.

It was next attempted to pass "atmospheric nitrogen" from a gas-holder first through a combustion-tube of the usual length packed with metallic copper reduced from the oxide; then through a small U-tube containing a little water, which was intended as an index of the rate of flow; the gas was then dried by passage through tubes filled with soda-lime and phosphoric anhydride, and it next passed through a long iron tube (gas-pipe) packed with magnesium turnings, and heated to bright redness in a second combustion-furnace. After the iron tube followed a second small U-tube containing water, intended to indicate the rate at which the argon escaped into a small gas-holder placed to receive it. The nitrogen was absorbed rapidly, and argon entered the small gas-holder. But there was reason to suspect that the iron tube is permeable by argon at a red heat. The first tube-full allowed very little argon to pass. After it had been removed and replaced by a second, the same thing was noticed. The first tube was difficult to clean; the nitride of magnesium forms a cake on the interior of the tube, and it was very difficult to remove it; moreover, this rendered the filling of the tube troublesome, inasmuch as its interior was so rough that the magnesium turnings could only with difficulty be forced down. However, the permeability to argon, if such be the case, appeared to have decreased. The iron tube was coated internally with a skin of magnesium nitride, which appeared to diminish its permeability to argon. After all the magnesium in the tube had been converted into nitride (and this was easily known, because a bright glow proceeded gradually from one end of the tube to the other), the argon remaining in the iron tube was "washed" out by a current of nitrogen; so that, after a number of operations, the small gas-holder contained a mixture of argon with a considerable quantity of nitrogen.

On the whole, the use of iron tubes is not to be recommended, owing to the difficulty in cleaning them, and the possible loss through their permeability to argon. There is no such risk of loss with glass tubes, but each operation requires a new tube, and the cost of the glass is considerable if much nitrogen is to be absorbed. Tubes of porcelain were not tried; but they are hardly likely to succeed, for the glaze in the interior would certainly be destroyed by the action of the red-hot magnesium, and the roughening of the surface would render them as difficult to empty and refill as the iron tubes were found to be.

By these processes 157 litres of "atmospheric nitrogen" were reduced in volume to about 2.5 litres in all of a mixture of nitrogen and argon. This mixture was afterwards circulated over red-hot magnesium in order to remove the last portions of nitrogen.

As the apparatus employed for this purpose proved very convenient, a full description of its construction is here given. A diagram is shown in Fig. 4 which sufficiently explains the arrangement of the apparatus. A is the circulator. It consists of a sort of Sprengel's pump (*a*), to which a supply of mercury is admitted from a small reservoir (*b*). This mercury is delivered into a gas-separator (*c*), and the mercury overflows into the reservoir (*d*). When its level rises, so that it blocks the tube (*f*), it ascends in pellets or pistons into a reservoir (*e*) which is connected through (*g*) with a water-pump. The mercury falls into (*b*), and again passes down the Sprengel-tube (*a*). No attention is therefore required, for the

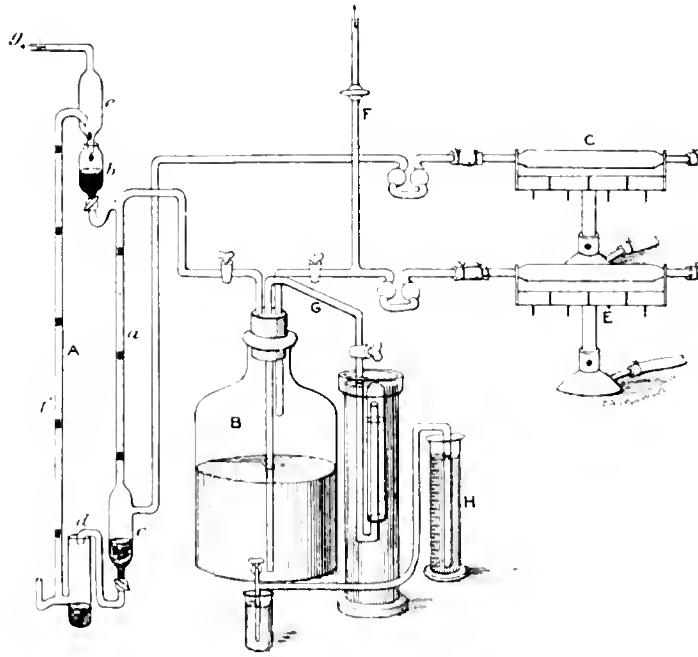


FIG. 4.

apparatus works quite automatically. This form of apparatus was first suggested by Dr. Collie.

The gas is drawn from the gas-holder B, and passes through a tube C, which is heated to redness by a long-flame burner, and which contains in one half metallic copper, and in the other half copper oxide. This precaution is taken in order to remove any oxygen which may possibly be present, and also any hydrogen or hydrocarbon. In practice, it was never found that the copper became oxidized, or the oxide reduced. It is, however, useful to guard against any possible contamination. The gas next traversed a drying-tube D, the anterior portion containing ignited soda-lime, and the posterior portion phosphoric anhydride. It then passed through E, a piece of combustion-tube, drawn out at both ends, filled with magnesium turnings, and heated by a long-flame burner to redness. After registering the rate of circulation by passing a small U-tube with bulbs, filled with water, it again entered the gas-holder B.

After the magnesium-tube E had done its work, the stopcocks were all closed and the gas was turned down, so that the burners might cool. The mixture of argon and nitrogen remaining in the system of tubes was pumped out by a Sprengel's pump through F, collected in a large test tube, and reintroduced into the gas-holder B through the side-tube G, which requires no description. The magnesium-tube was then replaced by a fresh one; the system of tubes was exhausted of air; argon and nitrogen were admitted from the gas-holder B; the copper oxide-tube and the magnesium-tube were again heated; and the operation was repeated until absorption ceased. It was easy to decide when this point had been reached, by making use of the graduated cylinder H, from which water entered the gas-holder B. It was found advisable to keep all the water employed in these operations, for it had become saturated with argon. If gas was withdrawn from the gas-holder, its place was taken by this saturated water.

The absorption of nitrogen proceeds very slowly towards the end of the operation, and the diminution in volume of the gas is not greater than four or five cubic centimetres per hour. It is therefore somewhat difficult to judge of the end-point, as will be seen when experiments on the density of this gas are described. The magnesium-tube, towards the end of the operations, was made so hot that the metal was melted in the lower part of the tube, and sublimed in the upper part. The argon and residual nitrogen had therefore been thoroughly mixed with gaseous magnesium, during its passage through the tube E.

To avoid possible contamination with air in the Sprengel's pump, the last portion of gas collected from the system of tubes was not readmitted to the gas-holder B, but was separately stored.

The argon was collected in two operations. First the quantity made by absorption by magnesium in glass tubes with the water-pump circulator was purified. Later, after a second supply had been prepared by absorption in iron tubes, the mixture of argon and nitrogen was united with the first quantity and circulated, by means of the mercury circulator, in the gas-holder B. Attention will be drawn to the particular sample of gas employed in describing further experiments made with the argon.

By means of magnesium, about seven litres of nitrogen can be absorbed in an hour; the changing of the tubes of magnesium, however, takes some time: consequently the largest amount absorbed in one day was nearly thirty litres.

The principal objection to the oxygen method of isolating argon, as hitherto described, is the extreme slowness of the operation. An absorption of 30 c. c. of mixed gas means the removal of but 12 c. c. of nitrogen. At this rate eight hours are required for the isolation of 1 c. c. of argon, supposed to be present in the proportion of 1 per cent.

In extending the scale of operations we had the great advantage of the advice of Mr. Crookes, who a short time ago called attention to the flame rising from platinum terminals which convey a high-tension alternating electric discharge, and pointed out its dependence upon combustion of the nitrogen and oxygen of the air.[1] Mr. Crookes was kind enough to arrange a demonstration at his own house with a small alternating current plant, in which it appeared that the absorption of mixed gas was at the rate of 500 c. c. per hour, or nearly twenty times as fast as with the battery. The arrangement is similar to that first described by Spottiswoode.[2] The primary of a Ruhmkorff coil is connected directly with the alternator, no break or condenser being required, so that in fact the coil acts simply as a high-potential transformer. When the arc is established the platinum terminals may be separated beyond the initial striking distance.

The plant with which the large scale operations have been made consists of a De Meritens alternator, kindly lent by Professor J. J. Thomson, and a gas-engine. As transformer, one of Swinburne's hedgehog pattern has been employed with success, but the ratio of transformation (24:1) is scarcely sufficient. A higher potential, although perhaps not more efficient, is more convenient. The striking distance is greater, and the arc is not so liable to go out. Accordingly most of the work to be described has been performed with transformers of the Ruhmkorff type.

The apparatus has been varied greatly, and it cannot be regarded as having even yet assumed a completely satisfactory and final form. But it will give a suffi-

---

[1] *Chemical News*, vol. LXV, p. 301, 1892.

[2] A mode of exciting an induction-coil. *Philadelphia Magazine*, vol. VIII, p. 390, 1829.

cient idea of the method if we describe an experiment in which a tolerably good account was kept of the air and oxygen employed. The working vessel was a glass flask of about 1500 c. c. capacity, and stood neck downwards over a large jar of alkali. As in the small scale experiments the leading-in wires were insulated by glass tubes, suitably bent and carried through the liquid up the neck. For the greater part of the length iron pipes were employed, but the internal extremities were of platinum, doubled upon itself at the terminals from which the discharge escaped. The glass projecting tubes must be carried up for some distance above the internal level of the liquid, but it is desirable that the arc itself should not be much raised above that level. A general idea of the disposition of the electrodes will be obtained from the figure (5). To ensure gas tightness these bends were occupied by mercury. A tube for the supply or withdrawal of gas was carried in the same way through the neck.

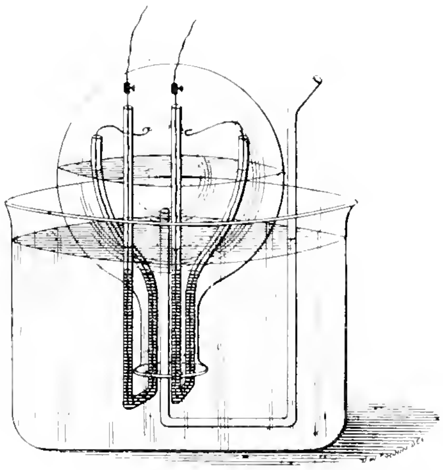


FIG. 5.

The Ruhmkorff employed in this operation was one of medium size. When the mixture was rightly proportioned and the arc of full length, the rate of absorption was about 700 c. c. per hour. A good deal of time was lost in starting, for especially when there is soda on the platinum, the arc is liable to go out if lengthened prematurely. After seven days the total quantity of air led in amounted to 7925 c. c. and of oxygen (prepared from chlorate of potash) 9137 c. c. On the eighth and ninth days oxygen alone was added, of which about 500 c. c. was consumed, while there remained about 700 c. c. in the flask. Hence the proportion in which the air and oxygen combined was as 79 : 96. On the eighth day there was about three hours' work, and the absorption slackened off to about one-quarter of the previous rate. On the ninth day (September 8th) the rate fell off still more, and, after three hours' work, became very slow. The progress towards removal of nitrogen was examined from time to time with the spectroscope, the points being approximated and connected with a small Leyden jar. At this stage the yellow nitrogen line was faint, but plainly visible. After about four hours' more work the yellow line had disappeared, and for two hours there had been no visible contraction. It will be seen that the removal of the last part of the nitrogen was very slow, mainly on account of the large excess of oxygen present.

The final treatment of the residual 700 c. c. of gas was on the model of the small scale operations already described.

By means of a pipette the gas was gradually transferred to a large test tube standing over alkali. Under the influence of sparks (from battery and coil) passing all the while, the superfluous oxygen was consumed with hydrogen fed in slowly from a voltameter. If the nitrogen had been completely removed, and if there were no unknown ingredient in the atmosphere, the volume under this treatment should have diminished without limit. But the contraction stopped at a volume of 65 c. c., and the volume was taken backwards and forwards through this as a minimum by alternate treatment with oxygen and hydrogen added in small quantities, with prolonged intervals of sparking. Whether the oxygen or the hydrogen were in excess could be determined at any moment by a glance at the spectrum. At the minimum volume the gas was certainly not hydrogen or oxygen. Was it nitrogen? On this point the testimony of the spectroscope was equally decisive. No trace of the yellow nitrogen line could be seen even with a wide slit and under the most favorable conditions.

When the gas stood for some days over water the nitrogen line again asserted itself, and many hours' sparking with a little oxygen were required again to get rid of it. As it was important to know what proportions of nitrogen could be made visible in this way, a little air was added to gas that had been sparked for some time subsequently to the disappearance of nitrogen in its spectrum. It was found that about 1½ per cent was clearly, and about 3 per cent was conspicuously, visible. About the same numbers apply to the visibility of nitrogen in oxygen when sparked under these conditions, that is, at atmospheric pressure, and with a jar in connection with the secondary terminals.

When we attempt to increase the rate of absorption by the use of a more powerful electric arc further experimental difficulties present themselves. In the arrangement already described, giving an absorption of 700 c. c. per hour, the upper part of the flask becomes very hot. With a more powerful arc the heat rises to such a point that the flask is filled with steam and the operation comes to a standstill. The remedy is to be found in the use of a larger vessel submerged, at any rate as regards its upper portion, in water. In the later experiments a globe of about 7 litres capacity, intended for showing the combustion of phosphorus in oxygen, was employed. The neck was inclined upwards at an angle of about 45° and was closed air-tight by a cork, through which were led the necessary tubes. The lower part of the globe is occupied by about 3 litres of a 5 per cent solution of caustic soda, the solution rising to within about half an inch of the platinum terminals. The upper half of the globe is kept cold by water applied externally. With this apparatus an absorption of 3 litres of mixed gas per hour can be attained,—about 3000 times the rate at which Cavendish could work.

9. DENSITY OF ARGON PREPARED BY MEANS OF OXYGEN.

No direct determination has yet been made of the density of argon isolated by the oxygen method, but a fair estimate may be founded upon the data relating to the volumes already recorded, on the assumption that the accurately known densities of atmospheric and chemical nitrogen differ on account of the presence of argon in the former and that during the treatment with oxygen nothing is oxydized except nitrogen. Thus if

D = density of chemical nitrogen,
D = " atmospheric nitrogen,
d = " argon,
L = proportional volume of argon in atmospheric nitrogen.

the law of mixtures gives:

$$Ld + (1 - L)\,D = D'$$

or

$$d = D + \frac{D' - D}{L}$$

In this formula $D' - D$ and L are both small, but they are known with fair accuracy. From the data already given

$$L = \frac{65}{\cdot 79 \times 7925},$$

whence if (on an arbitrary scale of reckoning) $D = 2.2990$, $D = 2.3102$, we find $d = 3.378$. Thus if N_2 be 14 or O_2 be 16, the density of argon is 20.6.

It had been hoped that further data might have been obtained respecting the proportional volume of argon in atmospheric nitrogen, but accidents difficult to avoid in operations so risky and so extended have hitherto stood in the way.

10. DENSITY OF ARGON PREPARED BY MEANS OF MAGNESIUM.

It has already been stated that the density of the residual gas from the first and preliminary attempt to separate oxygen and nitrogen from air by means of magnesium was 19.086, and allowing for contraction on sparking with oxygen the density is calculable as 20.01. The following determinations of density were also made:

(a) After absorption in glass tubes, the water circulator having been used, and subsequent circulation by means of mercury circulator until the rate of contraction had grown slow:

162.843 cubic centimetres, measured at 757.7 mm. (corr.) pressure and 16°.81 C., weighed 0.2683 gramme. Hence,

Weight of 1 litre at 0° and 760 mm. . . . . 1.7541 grammes.
Density compared with hydrogen (O = 16) 19.64

This gas was again circulated over red-hot magnesium for two days. Before circulation it contained nitrogen, as was evident from its spectrum; after circulating, nitrogen appeared to be absent, and absorption had completely stopped, and the density was again determined.

(b) 162.843 cubic centimetres, measured at 745.4 mm. (corr.) pressure and 17°.25 C., weighed 0.2735 gramme. Hence,

Weight of 1 litre at 0° and 760 mm. . . . . 1.8206 grammes.
Density compared with hydrogen (O = 16) 20.38

Several portions of this gas having been withdrawn for various purposes were somewhat contaminated with air, owing to leakage, passage through the pump, etc. All these portions were united in the gas-holder with the main stock, and circulated for eight hours, during the last three of which no contraction occurred. The gas removed from the system of tubes by the mercury-pump was not restored to the gas-holder, but kept separate.

(c) 162.843 cubic centimetres, measured at 758.1 mm. (corr.) pressure and 17°.09 C., weighed 0.27705 gramme. Hence,

Weight of 1 litre at 0° and 760 mm. . . . . 1.8124 grammes.
Density compared with hydrogen (O = 16) 20.28

The contents of the gas-holder were subsequently increased by a mixture of nitrogen and argon from 37 litres of atmospheric nitrogen, and after circulating, density was determined. The absorption was, however, not complete.

(d) 162.843 cubic centimetres, measured at 767.6 mm. (corr.) pressure and 16°.31 C., weighed 0.2703 gramme. Hence,

Weight of 1 litre at 0° and 760 mm. . . . . 1.743 grammes.
Density compared with hydrogen (O = 16) 19.54

The gas was further circulated, until absorption had apparently ceased. This took about 6 hours. Density was again determined.

(e) 162.843 cubic centimetres, measured at 767.7 mm. (corr.) pressure and 15°.00 C., weighed 0.2773 gramme. Hence,

Weight of 1 litre at 0° and 760 mm	1.7784 grammes.
Density compared with hydrogen (O = 16)	19.90

(f) A second determination was carried out, without further circulation.

162.843 cubic centimetres, measured at 769.0 mm. (corr.) pressure and 16°.00 C., weighed 0.2773 gramme. Hence,

Weight of 1 litre at 0° and 760 mm	1.7820 grammes.
Density compared with hydrogen (O = 16)	19.94

It is better to leave these results without comment at this point, and to return to them later.

11. SPECTRUM OF ARGON.

Vacuum tubes were filled with argon prepared by means of magnesium at various stages in this work, and an examination of these tubes has been kindly undertaken by Mr. Crookes, to whom we wish to express our cordial thanks for the exhaustive study to which he has subjected its spectrum. The first tube was filled with the early preparation, of density 19.09, which obviously contained some nitrogen. A photograph of its spectrum was taken, and compared with a photograph of the spectrum of nitrogen; and it was at once evident that a spectrum different from that of nitrogen had been registered.

The second specimen of argon submitted to examination was that of density 20.38. The light emitted from it is of a crimson color, with a blue or lilac shade. The electrodes were of platinum. The spectrum seen in this tube has nothing in common with that of nitrogen, nor indeed, so far as we know, with that of any known substance. But one peculiarity must be chronicled. When the current is passed from the induction coil in one direction, that end of the capillary next the positive pole appears of a redder, and that next the negative pole of a bluer hue. An explanation of this phenomenon is probably to be found in a paper by Mr. E. C. C. Baly,[1] in which he describes experiments on a mixture of two gases. One of his final conclusions is:

"That when an electric current is passed through a rarefied mixture of two gases, one is separated from the other and appears in the negative glow." We

---

[1] *Proceedings of the Physical Society*, 1893, p. 147.

regard it therefore as not improbable that the residual gas from the atmosphere, which we have up to now termed "argon," may be in reality a mixture of two gases, which have not as yet been separated. Should this hypothesis turn out to be correct on further examination, we propose for the name of the second gas "apathes," both words suggesting inactivity; that these names are justified will appear when the attempts to form compounds of the gases are described. For the present, however, we shall term the gas, or the mixture, "argon."

It was found possible by Mr. Crookes to partially separate the spectra by directing the slit of the spectroscope at one end of the capillary tube. He has kindly furnished us with the following table of approximate wave-lengths. The numbers indicate the relative intensity of the lines, 10 denoting a line of maximum brightness. The results are the means of three sets of very concordant measurements.

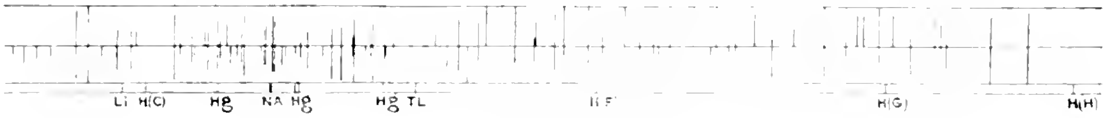


Fig. 6.

I. Red. (+)	II. Blue. (—)	I.	II.	I. Red. (- -)	II. Blue. (—)	I.	II.
——	612.0	—	6	561.0	561.0	9	6
609.9	—	4	—	556.7	556.7	2	2
605.8	605.8	2	2	555.8	555.8	10	8
604.4	604.4	3	3	552.0		1	—
603.2	603.2	8	8	550.1	550.1	2	1
592.6	592.6	4	4	549.8	549.8	8	8
590.9	590.9	6	5	545.6	545.6	6	6
588.7	588.7	6	7	544.6	——	2	-
585.8	——	4		542.1	542.1	4	2
583.4	——	2	- -		528.9	—	4
580.3	——	1	—	525.8	525.8	6	6
577.1	577.1	2	1	521.5	521.5	7	7
574.6	574.6	6	4	519.2	— —	10	—
568.5		2	—	516.1	516.1	9	9
564.5	564.5	9	6	— —	514.0		10
				506.2	506.2	4	10
				501.4	501.4	4	2
				——	500.7		9

Centre of a hazy band, probably resolvable.
Sharp edge of wide line extending to 588.0
Hazy line.

I. Red. (+)	II. Blue. (−)	I.	II.	I. Red. (+)	II. Blue. (−)	I.	II.
496.3	496.3	4	9	—	448.2	—	6
493.8	493.8	2	10	443.0	443.0	8	10
487.8	487.8	4	10	439.7	439.7	2	10
485.3	485.3	2	9	—	438.0	—	8
480.1	480.1	6	10	—	437.1	—	8
476.7	476.7	4	9	434.7	434.7	4	10
473.5	473.5	2	9	433.8	433.8	9	9
473.0	473.0	2	9	430.4	430.4	8	5
470.2	470.2	8	8	427.2	427.2	8	8
—	466.0	—	10	426.2	426.2	6	6
462.5	—	6	—	425.6	425.6	6	3
461.3	461.3	6	10	420.0	420.0	9	8
459.6	459.6	2	9	415.6	415.6	9	9
458.1	458.1	2	9				
—	454.7	—	9				
451.3	451.3	9	2				

Two of the most characteristic lines, which are easily seen in an ordinary pocket spectroscope, and which served at once to identify the gas, are in the least refrangible part of the red end of the spectrum. Their wave-lengths are 696.56, 705.64 *M.* They cannot be mistaken for lines of any other substance, because they are so much less refrangible than any other conspicuous red lines. We append a slip on which Mr. Crookes has registered the lines of both spectra.

Mr. Crookes has compared the spectra of the two samples of gas, one prepared by means of magnesium, the other by sparking with oxygen; the gases were both in vacuum tubes. He says:

"There can be no doubt as to their identity in all the chief lines." Professor Schuster has also kindly made a comparison of the spectra of the two samples of gas, using a Leyden jar, and sparking at atmospheric pressure. He states that the ten chief lines of both spectra are identical. These observations place it beyond question that the gas produced by both processes is the same in the main; but until the absolute identity of both spectra is proved, it is possible that one sample *may* contain some gas not present in the other.

12. SOLUBILITY OF ARGON IN WATER.

The tendency of the gas to disappear when manipulated over water in small quantities having suggested that it might be more than usually soluble in that liquid, special experiments were tried to determine the degree of solubility.

The most satisfactory measures relating to the gas isolated by means of oxygen were those of September 28th. The sample contained a trace of oxygen, and (as judged by the spectrum) a residue of about 2 per cent of nitrogen. The procedure and the calculations followed pretty closely the course marked out by Bunsen,[1] and it is scarcely necessary to record the details. The quantity of gas operated upon was about 4 c. c., of which about 1½ c. c. were absorbed. The final result for the solubility was 0.0394 at 12° C., about 2½ times that of nitrogen.

Similar results have been obtained with argon prepared by means of magnesium. At a temperature of 13°.9, 131 arbitrary measures of water absorbed 5.3 of argon. This corresponds to a solubility in distilled water, previously freed from dissolved gas by boiling in vacuo for a quarter of an hour, and admitted to the tube containing argon without contact with air, of 4.05 c. c. of argon per 100 of water.

The fact that the gas is more soluble than nitrogen would lead us to expect it in increased proportion in the dissolved gases of rain water. Experiments have been devised to test this conjecture, but hitherto time has been wanting for carrying them out. As regards spring water, it is known that many thermal springs emit considerable quantities of gas, hitherto regarded as nitrogen. The question early occurred to us, as to what proportion, if any, of the new gas was contained therein. A notable example of a nitrogen spring is that at Bath examined by Daubeny in 1833. With the permission of the authorities of Bath, Dr. Arthur Richardson was kind enough to collect for us about 10 litres of the gases discharged from the King's Spring. A rough analysis on reception showed that it contained scarcely any oxygen and but little carbon dioxide. Two determinations of density were made, the gas being treated in all respects as air, prepared by diffusion and unprepared, was treated for the isolation of atmospheric nitrogen. The results were:

October 29th	2.30513
November 7th	2.30532
Mean	2.30522

The weight of the "nitrogen" from the Bath gas is thus about half-way between that of chemical and "atmospheric" nitrogen, suggesting that the proportion of argon is *less* than in air, instead of greater, as had been expected.

13. Attempt at Liquefaction.

Up till now, argon has not been liquefied. A simple experiment has been made with the original sample of gas, of density 19.4, which certainly contained a considerable amount of nitrogen. On compressing it in a pressure-apparatus to

---

[1] *Gasometry*, p. 141.

between 80 and 100 atmospheres, and cooling to 90° by means of boiling nitrous oxide, no appearance of liquefaction could be observed.

Further experiments in this direction are in contemplation.

14. THE RATIO OF THE SPECIFIC HEATS OF ARGON.

In order to gain knowledge regarding the elementary or compound nature of argon, experiments were made on the velocity of sound in it. It will be remembered that from the velocity of sound, the ratio of the specific heat at constant pressure to that at constant volume can be deduced by means of the equation

$$n\lambda = v = N\frac{e}{d}(1 + \alpha t)\frac{C_p}{C_v}$$

where λ is the wave-length of the sound, v its velocity, e the isothermal elasticity, d, the density, $(1 + \alpha t)$ the temperature-correction, C_p the specific heat at constant pressure, and C_v that at constant volume. In comparing two gases at the same temperature, each of which obeys Boyle's law with sufficient approximation, many of these terms disappear, and the ratio of specific heats of one gas may be deduced from that of the other, if known, by the simple proportion

$$\lambda^2 d : \lambda'^2 d' :: 1.41 : x$$

where for example λ and d refer to air, of which the ratio is 1.41, according to observations by Röntgen (1.4053), Wüllner (1.4053), Kayser (1.4106), and Jamin and Richard (1.41).

The apparatus adopted, although in principle the same as that usually employed, differed somewhat from the ordinary pattern, inasmuch as the tube was a narrow one of 2 mm. bore, and the vibrator consisted of a glass rod, sealed into one end of the tube, so that about 15 cm. projected outside the tube while 15 cm. was contained in the tube. By rubbing the projecting part longitudinally with a rag wet with alcohol, vibrations of exceedingly high pitch took place, causing waves in the gas, which registered their nodes by the usual device of lycopodium powder. The temperature was that of the atmosphere and varied little from 17°.5; the pressure was also atmospheric, and varied only one millimetre during the experiments. Much of the success of these experiments depends on so adjusting the length of the tube as to secure a good echo, else the wave-heaps are indistinct. But this is easily attained by attaching to its open end a piece of thick-walled india-rubber tubing, which can be closed by a clip at a spot which is found experimentally to produce good heaps at the nodes.

The accuracy of this instrument has frequently been tested; but fresh experiments were made with air, carbon dioxide, and hydrogen, so as to make certain that reasonably reliable results were obtainable. Of these an account is here given.

Gas in tube.	No. of observations in each set.		Half wave-length.		Ratio $\frac{C_p}{C_v}$
	I	II	I.	II.	
Air	3	2	19.60	19.59	1.410 Assumed.
CO_2	3		15.11	--	1.276 Found.
H_2	3	—	73.6	--	1.376 Found.

To compare these results with those of previous observers, the following numbers were obtained for carbon dioxide: Cazin, 1.291; Röntgen, 1.305; De Lucchi, 1.292; Muller, 1.265; Wüllner, 1.311; Dulong, 1.339; Masson, 1.274; Regnault, 1.268; Amagat, 1.299; and Jamin and Richard, 1.29. It appears just to reject Dulong's number, which deviates so markedly from the rest; the mean of those remaining is 1.288, which is in sufficient agreement with that given above. For the ratio of the specific heats of hydrogen, we have: Cazin, 1.410; Röntgen, 1.385; Dulong, 1.407; Masson, 1.401; Regnault, 1.400; and Jamin and Richard, 1.410. The mean of these numbers is 1.402. This number appears to differ considerably from the one given above. But it must be noted, first, that hydrogen is difficult to obtain perfectly pure; second, that the wave-length which should have been found is 74.5, a number differing but little from that actually found; third, that the waves were long and that the nodes were somewhat difficult to place exactly; and fourth, that the atomic weight of hydrogen has been taken as unity, whereas it is more likely to be 1.01, if oxygen, as was done, be taken as 16. The atomic weight 1.01 raises the found value of the ratio to 1.391, a number differing but little from the mean value found by other observers.

Having thus established the trustworthiness of the method we proceed to describe our experiments with argon.

Five series of measurements were made with the sample of gas of density 19.943. It will be remembered that a previous determination with the same gas gave as its density 19.904. The mean of these two numbers was therefore taken as correct, viz., 19.923.

The individual measurements are:

I.	II	III.	IV	V.	Mean.
18.16	18.14	18.02	18.04	18.03	18.08 mm.

for the half wave-length. Calculating the ratio of the specific heats, the number 1.653 is obtained.

It will be noticed that this is the theoretical ratio for a monatomic gas, that is, a gas in which all energy imparted to it in raising its temperature at constant volume is expended in generating translational motion. The only other gas of which the ratio of specific heats has been found to fulfil this condition is mercury at a high temperature.[1] The extreme importance of these observations will be discussed later.

15. ATTEMPTS TO INDUCE CHEMICAL COMBINATION.

A great number of attempts were made to induce chemical combination with the argon obtained by use of magnesium, but without any positive result. In such a case as this, however, it is necessary to chronicle negative results, if for no other reason but that of justifying the name, argon. These will be detailed in order.

(a) *Oxygen in presence of caustic alkali.*—This need not be further discussed here; the method of preparing argon is based on its inactivity under such conditions.

(b) *Hydrogen.*—It has been mentioned that in order to free argon from excess of oxygen, hydrogen was admitted, and sparks passed to cause combination of hydrogen and oxygen. Here again caustic alkali was present, and argon appeared to be unaffected.

A separate experiment was, however, made in absence of water, though no special pains was taken to dry the mixture of gases. The argon was admitted up to half an atmosphere pressure into a bulb, through whose sides passed platinum wires, carrying pointed poles of gas-carbon. Hydrogen was next admitted until atmospheric pressure had been obtained. Sparks were then passed for four hours by means of a large induction coil, actuated by four storage cells. The gas was confined in a bulb closed by two stopcocks, and a small U-tube with bulbs, like that shown in Fig. 4 was interposed, to act as a gauge, so that if expansion or contraction had taken place, the escape or entry of gas would be observable. The apparatus, after the passage of sparks, was allowed to cool to the temperature of the atmosphere, and on opening the stopcock the level of water in the U-tube remained unaltered. It may therefore be concluded that, in all probability, no combination had occurred; or that if it had, it was attended with no change of volume.

(c) *Chlorine.*—Exactly similar experiments were performed with dry, and afterwards with moist, chlorine. The chlorine had been stored over strong sulphuric acid for the first experiment, and came in contact with dry argon. Three hours' sparking produced no change of volume. A drop of water was admitted into the bulb. After four hours' sparking, the volume of the gas, after cooling, was

---

[1] Kundt and Warburg, *Pogg. Ann.*, 127, p. 497, and 135, pp. 337 and 527, and 157, p. 353.

diminished by about $\frac{1}{10}$ cubic centimetre, due probably to the solution of a little chlorine in the small quantity of water present.

(d) *Phosphorus.*—A piece of combustion-tubing, closed at one end, containing at the closed end a small piece of phosphorus, was sealed to the mercury reservoir containing argon; connected to the same reservoir was a mercury gauge, and a Sprengel's pump. After removing all air from the tubes argon was admitted to a pressure of 600 mm. The middle portion of the combustion-tube was then heated to bright redness, and the phosphorus was distilled slowly from back to front, so that its vapor should come into contact with argon at a red heat. When the gas was hot, the level of the gauge altered; but on cooling, it returned to its original level, showing that no contraction had taken place. The experiment was repeated several times, the phosphorus being distilled through the red-hot tube from open to closed end, and *vice versa.* In each case, on cooling, no change of pressure was observed. Hence it may be concluded that phosphorus at a red heat is without action on argon. It may be remarked parenthetically that no gaseous compound of phosphorus is known which does not possess a volume different from the sum of those of its constituents. That no solid compound was formed is sufficiently proved by the absence of contraction. The phosphorus was largely converted into the red modification during the experiment.

(e) *Sulphur.*—An exactly similar experiment was performed with sulphur, again with negative results. It may therefore be concluded that sulphur and argon are without action on each other at a red heat. And again, no gaseous compound of sulphur is known in which the volume of the compound is equal to the sum of those of its constituents.

(f) *Tellurium.*—As this element has a great tendency to unite with heavy metals, it was thought worth while to try its action. In this, and in the experiments to be described, a different form was given to the apparatus. The gas was circulated over the reagent employed, a tube containing it being placed in the circuit. The gas was dried by passage over soda-lime and phosphoric anhydride; it then passed over the tellurium or other reagent, then through drying tubes, and then back to the gas-holder. That combination did not occur was shown by the unchanged volume of gas in the gas-holder; and it was possible, by means of the graduated cylinder which admitted water to the gas-holder, to judge of as small an absorption as half a cubic centimetre. The tellurium distilled readily in the gas, giving the usual yellow vapor; and it condensed quite unchanged, as a black sublimate. The volume of the gas, when all was cold, was unaltered.

(g) *Sodium.*—A piece of sodium weighing about half a gramme was heated in argon. It attacked the glass of the combustion-tube, which it blackened, owing to liberation of silicon, but it distilled over in drops into the cold part of the tube. Again no change of volume occurred, nor was the surface of the distilled sodium tarnished; it was brilliant, as it is when sodium is distilled *in vacuo*. It may probably also be concluded from this experiment that silicon, even while being liberated, is without action on argon.

The action of compounds was then tried; those chosen were such as lead to oxides or sulphides. Inasmuch as the platinum-metals, which are among the most inert of elements, are attacked by fused caustic soda, its action was investigated.

(h) *Fused and red-hot caustic soda.*—The soda was prepared from sodium, in an iron boat, by adding drops of water cautiously to a lump of the metal. When action had ceased, the soda was melted, and the boat introduced into a piece of combustion-tube placed in the circuit. After three hours' circulation no contraction had occurred. Hence caustic soda has no action on argon.

(i) *Soda-lime at a red heat.*—Thinking that the want of porosity of fused caustic soda might have hindered absorption, a precisely similar experiment was carried out with soda-lime, a mixture which can be heated to bright redness without fusion. Again no result took place after three hours' heating.

(j) *Fused potassium nitrate* was tried under the impression that oxygen plus a base might act where oxygen alone failed. The nitrate was fused and kept at a bright-red heat for two hours, but again without any diminution in volume of the argon.

(k) *Sodium peroxide.*—Yet another attempt was made to induce combination with oxygen and a base, by heating sodium peroxide to redness in a current of argon for over an hour, but also without effect. It is to be noticed that metals of the platinum group would have entered into combination under such treatment.

(l) *Persulphides of sodium and calcium.*—Soda-lime was heated to redness in an open crucible, and some sulphur was added to the red-hot mass, the lid of the crucible being then put on. Combination ensued, with formation of polysulphides of sodium and calcium. This product was heated to redness for three hours in a brisk current of argon, again with negative result. Again, metals of the platinum group would have combined under such treatment.

(m) Some argon was shaken in a tube with nitro-hydrochloric acid. On addition of potash, so as to neutralize the acid, and to absorb the free chlorine and nitrosyl chloride, the volume of the gas was barely altered. The slight alteration was evidently due to solubility in the aqueous liquid, and it may be concluded that no chemical action took place.

(n) Bromine water was also without effect. The bromine vapor was removed with potash.

(o) Lastly, a mixture of potassium permanganate and hydrochloric acid, involving the presence of nascent chlorine, had no action, for on absorbing chlorine by means of potash, no alteration in volume had occurred.

We do not claim to have exhausted the possible reagents. But this much is certain, that the gas deserves the name "argon," for it is a most astonishingly indifferent body, inasmuch as it is unattacked by elements of very opposite character, ranging from sodium and magnesium on the one hand, to oxygen, chlorine, and sulphur on the other. It will be interesting to see if fluorine also is without action, but for the present that experiment must be postponed, on account of difficulties of manipulation.

16. General Conclusions.

It remains, finally, to discuss the probable nature of the gas or gases which we have succeeded in separating from atmospheric air, and which we provisionally name *argon*.

That argon is present in the atmosphere, and is not manufactured during the process of separation, is amply proved by many lines of evidence.

First: Atmospheric nitrogen has a high density, while chemical nitrogen is lighter. That chemical nitrogen is a uniform substance is proved by the identity of properties of samples prepared by several different processes, and from several different compounds. It follows, therefore, that the cause of the high density of atmospheric nitrogen is due to the admixture with a heavier gas. If that gas possesses the density of 20 compared with hydrogen as unity, atmospheric nitrogen should contain of it approximately one per cent. This was found to be the case, for on causing the nitrogen of the atmosphere to combine with oxygen in presence of alkali, the residue amounted to nearly one per cent.

Second: This gas has been concentrated in the atmosphere by diffusion. It is true that it has not been freed from oxygen and nitrogen by diffusion, but the process of diffusion increases relatively to nitrogen the amount of argon in that portion which does not pass through the porous walls. That this is the case is proved by the increase of density of that mixture of argon in nitrogen.

Third: It is in the highest degree improbable that two processes, so different from each other as those which have yielded argon should each manufacture the same product. The explanation is simple if it be granted that these processes merely eliminate nitrogen from an atmospheric mixture.

Fourth: It has been shown that pure nitrogen prepared from its compounds leaves an insignificant residue when caused to enter into combustion with oxygen or with magnesium.

There are many other lines of argument which suggest themselves; but we think it will be acknowledged that those given above are sufficient to establish the existence of argon in the atmosphere.

It is practically certain that the argon prepared by means of electric sparking with oxygen is in the main identical with argon prepared by aid of magnesium. The samples have in common:

First: Spectra which already have been shown to be identical as regards the ten brightest lines.

Second: They have approximately the same density. It is true that an actual determination of the density of the sample prepared by sparking has not been carried out; but its density, determined indirectly, agrees with sufficient approximation with that found for the sample prepared by means of magnesium.

Third: The two samples have practically the same solubility in water.

The question whether argon is of an elementary or a compound nature is settled according to the usually accepted theory by the ratio of its specific heats in favor of the former supposition. The argument may be stated thus: The kinetic energy of a gas, due to the motion of its molecules, is proportional to the absolute temperature. A rise of temperature increases the kinetic energy both of the molecules as a whole, as well as of the atoms which are constituents of the molecules. If, however, the gas-molecule consists of a single atom, inter-atomic motion within the molecule is excluded, and the motion of the molecule through space, or its translational motion, alone remains to be considered. The specific heat at constant volume, C_v, of a gas whose molecules consist of free atoms corresponds only to the energy due to their translation through space. The specific heat at constant pressure includes besides the heat equivalent of work done during expansion. The work done by gases during expansion, however, is practically equal for all gases, seeing that their coefficients of expansion and compressibility are practically the same. This quantity can easily be calculated to be 2.00 calories per gram-molecule for a pressure of 760 mm. and a rise of temperature of 1° C.

The ratio of the kinetic energy of a gas due to the translational motion of its molecules to the total energy contained in the gas has been shown by Clausius[1] to be expressed by the equation

$$\frac{K}{H} = \frac{\frac{3}{2}(C_p - C_v)}{C_v}$$

where K is the energy of the moving molecules, and H the total energy contained

---

[1] *Poggendorff's Annalen*, 1857, 100, p. 377.

in the gas, both expressed as heat; C_v is caused both by molecular and atomic motion. Now as the specific heats are practically independent of temperature,

$$\frac{K_1 - K_0}{H_1 - H_0} = \frac{\frac{3}{2}(C_p - C_v)}{C_v}$$

$H_1 - H_0 = C_v$, or specific heat at constant volume; and $K_1 - K_0$, which may be termed M, is the proportion of this heat which is employed in producing and maintaining translational motion of the molecules. Therefore

$$\frac{M}{C_v} = \frac{\frac{3}{2}(C_p - C_v)}{C_v}; \text{ and } \frac{C_p - C_v}{M} = \frac{2}{3}$$

In words, the heat used in expanding the gas bears to the heat producing molecular motion 2 : 3. Hence the ratio $M = \frac{3}{2} \times 2.00 = 3.00$. The specific heat of the molecular weight taken in grammes of a monatomic gas is therefore 3.00 calories for constant volume, and for constant pressure, 3.00 + 2.00 = 5.00. The ratio between these numbers is 1 : 1.66; and this ratio has been found experimentally for mercury gas by Kundt and Warburg (*loc. cit.*). That it has also been found for argon is equally a proof of the monatomic nature of its molecules. A monatomic gas can only be an element, or a mixture of elements, and hence it follows that argon is not of a compound nature.

From Avogadro's law, the density of a gas is half its molecular weight; now the density of argon is approximately 20, hence its molecular weight must be 40. But its molecule is identical with its atom; hence its atomic weight, or, if it be a mixture, the mean of the atomic weights of the constituents of that mixture, regard being had to the proportion in which they are present, must be 40.

Chemists will recognize this fact as of the most startling nature; but the data are clear, and we can only welcome any confirmation by independent experimenters.

We are not yet able to state with certainty whether argon is a mixture, or, if it be, of how many elements it consists. The spectroscopic evidence points in favor of at least two components; but of itself it is not conclusive. Attempts will be made to effect a separation, if possible, of the elements which give such dissimilar spectra, when the current passes from positive to negative, or in the contrary direction. But, as yet, time has not allowed of any experiments with such an object.

The relation of argon to other elements remains to be discussed. We inclined for long to the view that it (or they) was possibly the representative of the three elements which might be expected to follow fluorine in the periodic table. Such elements should have atomic weights between 19, the atomic weight of fluorine, and 23, the atomic weight of sodium. But this view is completely put out of court by the discovery of the monatomic nature of its molecules. We are therefore led to look for a gap for an element of atomic weight 40. The series in this neighborhood is: Chlorine 35.5; a possible trio of elements with atomic weights between that of chlorine and that of potassium; potassium 39; calcium 40; scandium 44. There can be no doubt that potassium, calcium, and scandium follow legitimately their predecessors in the vertical columns, lithium, beryllium, and boron; and that they are in almost certain relation with rubidium, strontium, and (but not so certainly) yttrium. If argon be a single element then there is reason to doubt whether the periodic classification of the elements is complete; whether, in fact, elements do not exist which cannot be fitted among those of which it is composed. On the other hand, if argon be a mixture of two elements they might find place in the eighth group; one after chlorine, and the other after bromine. Necessarily the last must needs be present in very small proportion.

In conclusion, it need excite no astonishment that argon is so indifferent to reagents. For mercury, although a monatomic element, forms compounds which are by no means stable at a high temperature in the gaseous state; and as for the physical condition of argon, that of a gas, we possess no knowledge why carbon, with its low atomic weight, should be a solid, while nitrogen is a gas, except in so far as we ascribe molecular complexity to the former, and comparative molecular simplicity to the latter. Argon, with its comparatively low atomic weight, and its molecular simplicity, might well be expected to rank among the gases. And its inertness, which has suggested its name, sufficiently explains why it has not previously been discovered among compound bodies.

We would suggest for this gas, assuming provisionally that it is not a mixture, the symbol A.

SMITHSONIAN CONTRIBUTIONS TO KNOWLEDGE.
1034

Hodgkins Fund.

ATMOSPHERIC ACTINOMETRY

AND THE

ACTINIC CONSTITUTION OF THE ATMOSPHERE.

BY

E. DUCLAUX,

Professor of Physics in the Agronomical Institute, Paris.

CITY OF WASHINGTON:
PUBLISHED BY THE SMITHSONIAN INSTITUTION.
1896.

SMITHSONIAN CONTRIBUTIONS TO KNOWLEDGE.
1034

Hodgkins Fund.

ATMOSPHERIC ACTINOMETRY
AND THE
ACTINIC CONSTITUTION OF THE ATMOSPHERE.

BY
E. DUCLAUX,
Professor of Physics at the Agronomical Institute, Paris.

CITY OF WASHINGTON:
PUBLISHED BY THE SMITHSONIAN INSTITUTION.
1896.

The Knickerbocker Press, New York

ADVERTISEMENT.

The present memoir is a translation of the treatise entitled "Sur l'actinométrie atmosphérique et sur la constitution actinique de l'atmosphère," submitted by Professor Emile Duclaux, in competition for one of the Hodgkins Fund prizes offered by the Smithsonian Institution in a circular dated March 31, 1893. The competition closed December 31, 1894; and on August 9, 1895, the Award Committee, having completed its examination of the 218 papers submitted by contestants, granted honorable mention to Professor Duclaux and recommended his memoir for publication by the Smithsonian Institution.

The Committee was composed of the following members: the Secretary of the Institution S. P. Langley, Chairman, ex-officio: Doctor G. Brown Goode, appointed by the Secretary of the Smithsonian Institution; Assistant Surgeon-General John S. Billings, appointed by the President of the National Academy of Sciences; and Professor M. W. Harrington, appointed by the President of the American Association for the Advancement of Science. The Foreign Advisory Committee, as first constituted, was represented by Monsieur J. Janssen, Professor T. H. Huxley, and Professor von Helmholtz; and after the death of the latter, Doctor W. von Bezold was added.

S. P. LANGLEY,

SECRETARY.

Washington City, May, 1896.

Atmospheric Actinometry and the Actinic Constitution of the Atmosphere.

By E. Duclaux,

Professor of Physics in the Agronomical Institute, Paris.

ATMOSPHERIC ACTINOMETRY.

The progress made by science leads us more and more to attribute to chemical rays a special action, which is different from and, to a certain extent, independent of that of the calorific and luminous rays. The chemical radiations of the sun, reaching the limits of our atmosphere, become modified while passing through it, according to a law which is peculiar to them; and, so far as can be seen in so new a subject, their absorption is not the same as that of the calorific or luminous parts of the spectrum.

Photographers, especially those who take landscapes, well know that days which are equally warm or equally luminous do not always give the same results for the same length of exposure, and that there are days when, for some unknown reason, the chemical impression is much slower than on others.

Another argument may be drawn from what often happens in northern lands, where vegetation, which is well known to be specially susceptible to the power of chemical rays, makes much more rapid progress than in temperate regions, notwithstanding the fainter light and the lower temperature.

To what are such differences due? What law does the chemical absorption of the atmosphere obey, and on what does it depend? Ought we to attribute it to its normal elements: oxygen, nitrogen, carbonic acid, and water vapor? Then it should have some general uniformity. Or ought we to see in it, on the contrary, the action of solid or volatile elements, which incessantly reach it from the bare or from the cultivated soil? Then it should have a local character, leading to a multiplicity of chemical climates. These are very important questions, for which science has as yet no answer; not that the subject has not already been thoroughly investigated, but because in all the actinometric inquiries proposed so far, sufficient care has not been bestowed upon the separation of chemical action from luminous and calorific effects.

The process which best shows the incorrectness of the methods employed heretofore is that of Messrs. Bunsen and Roscoe, which depends upon a mixture of chlorine and of hydrogen, exposed to the light. The intensity of the chemical action is then estimated by the quantity of hydrochloric acid formed in a given time, or rather by the diminution of volume which necessarily follows. This method has two grave defects. One is that reaction may take place from the effect of heat quite as well as from that of chemical rays, and that consequently it does not separate the two actions which it is important to isolate. The second, much more serious, defect is this, that the reaction is extremely exothermic and continues, when once begun, under the influence of the heat which it develops. There is, therefore, no proportionality between the active cause and the effect it produces. The cause is simply provocative and starts a mechanism, which continues to work independently. It is true that an effort is made to reduce to a minimum the work of this mechanism, by operating only with very small quantities of gas and by multiplying the cooling surfaces, in such a way that the phenomenon constantly requires a new excitation in order to continue. But this is not sufficient to relieve the method of the charge of lacking proportionality between cause and effect, which renders the measurements almost illusory, in spite of the care taken by Messrs. Bunsen and Roscoe to discuss them.

We find the same defects, though perhaps a little less seriously, in the often employed method which depends upon the reduction of ferric oxalate by light. Since the first observation by Dobereiner, H. Draper, Marchand, and G. Lemoine have studied this reaction. As in the preceding case the oxalate, or the equivalent mixture of ferric chloride and oxalic acid, is reduced by the action of heat alone, and although this reduction is slow, it operates as a source of error. Moreover, the liquid is colored and loses its color in proportion as the process continues. Hence the conditions of absorption are modified during the process and this by a phenomenon which is to a certain degree external. Finally, the reaction is still sufficiently exothermic to require that this property should be taken into account. All these defects have been corrected, so far as possible, by M. G. Lemoine, who has for some time been making a careful study of the process, but the method loses thus that neatness and that simplicity which are so desirable.

The ideal would be attained by the discovery of a limpid and transparent liquid which would not change while the reaction went on, becoming the seat of an easily measurable, chemical phenomenon, which could be the result of no action except that of heat. Can we go any farther in our demands and require that it should not be exothermic in any degree? M. Berthelot does not think so, and believes that the addition of energy resulting from the absorption of calorific, luminous, or chemical radiation would not be sufficient to produce a chemical phenomenon which, while going on, would not give rise to a small amount of heat. I do not very well see why a calorific absorption of solar radiation might not compensate for some heat of combination, and even permit a slightly endothermic reaction to appear. I have endeavored to discover some simple method, which, complying with this programme, could be interpreted without ambiguity, but I have not succeeded. I have been compelled to content myself with an old, well known reaction—the oxidation which weak solutions of oxalic acid undergo upon exposure to light.

These solutions are and remain transparent. The oxalic acid in them is transformed into carbonic acid, which disappears by diffusion, so that the oxidation which it has undergone can be easily ascertained by an acidimetric determination made before and after its exposure to light. The reaction thus produced is faintly exothermic, to be sure, but as only very weak solutions are taken, for it is well not to exceed 2 or 3 grammes of crystallized oxalic acid per litre, there is no reason why we should be troubled about the error which arises from this fact. Moreover, the liberation of heat, which results from combustion, even if it should be perceptible, would remain without effect, for oxalic acid oxidizes only with extreme slowness under the influence of heat alone.

Exp.—10 c. c. of a solution of oxalic acid, titrating 19 c. c. of lime-water per litre, was heated on a water bath to nearly 95°, in a flask of 125 c. c.
After heating 4 hours, the titre is 18.5 c. c. Loss 2.6 per cent.
" " 8 " " " 18.0 " " 5.2 "

Exp.—10 c. c. of another solution, titrating 16.6 c. c. of lime-water per litre, was heated an hour and a half to 115°.
The titre falls only to 16.2 c. c. and 16.4 c. c.

During the days of greatest heat, the temperature hardly exceeds 50° in the shallow vessels, in which the liquid is exposed to the sun. It may, therefore, be assumed that neither the solar heat nor the heat produced by combustion have any perceptible effect upon the transformation of the oxalic acid, which may, on fine days, reach or even exceed 50 per cent of the acid contained in the solution.

As the calorific rays have hardly any power, it would be desirable to eliminate the action of the luminous rays also, but the chemical radiations are so closely intermingled with the latter that it is difficult to separate them. Let us be content, therefore, for the present, to know that our solution of oxalic acid is peculiarly affected by the action of the luminous and the chemical parts of the spectrum. We shall soon find reasons to believe that it is the chemical part alone which acts. But we have first to investigate the manner by which combustion is produced before we can determine what influences cause it.

Study of the Process.

Oxalic acid, dissolved in water and exposed to light, absorbs oxygen, and changes almost entirely into carbonic acid. There appears also a little formic acid, but in almost infinitesimal quantities. Hence it follows, as we have seen, that we can ascertain the quantity of oxidized acid by a simple acidimetric determination.

INFLUENCE OF CONCENTRATION.

In order to study the actinometric process, the first thing to discover is the degree of concentration which gives the largest amount of sensibility. In order to know this I exposed to the sun, under precisely the same conditions, during three fine days from June 4th to June 6th, including about 36 hours of insolation, four liquids, containing, respectively, per litre:

	grm.	grm.	grm.	grm.
	63	31.5	12.6	0.3 of oxalic acid;
that is,	1	$\frac{1}{2}$	$\frac{1}{5}$	$\frac{1}{10}$ of an equivalent,

per litre. At the end of this time, an acidimetric analysis gave me the quantities of acid which had been burnt, and I computed from this the proportion of acid which had disappeared from each of the vessels.

The figures were the following, counted in milligrammes per litre:

	1 Equiv.	$\frac{1}{2}$ Equiv.	$\frac{1}{5}$ Equiv.	$\frac{1}{10}$ Equiv.
Quantity of acid burnt,	2,500	2,800	4,700	3,300
Proportion,	4 %	9 %	38 %	52 %

To reach the maximum in the absolute quantity of acid consumed we must, therefore, operate with solutions neither too concentrated nor too weak. Solutions which are too concentrated oxidize slowly, and the variation in chemical value is often noted with difficulty. It is, on the other hand, very easy to measure this variation with solutions which are rather weak, because it represents a notable fraction of the primitive value. But, on the other hand, when the liquid has been weakened by the sun, the last portions burn quite slowly. There are, therefore, two dangers to avoid.

After various trials I decided upon a solution whose variation of titre during the most favorable days should not exceed one half of the initial value. This is a solution containing about $\frac{1}{2}$ an equivalent or about 3 grammes of oxalic acid per litre. Ten cubic centimetres of this liquid are saturated by about an equal volume of common lime-water, so that the daily variation of the titre amounts to 4 or 5 c. c. of lime-water, a quantity which can be measured down to $\frac{1}{100}$ by means of a burette. The accuracy which we thus obtain is more than sufficient, as we shall presently see.

INFLUENCE OF THE DEPTH OF SOLUTION.

In discussing the question of oxidation, we must consider the part played by the ease with which oxygen penetrates into the depths of the solution. We can easily calculate that the 10 c. c. of oxalic solution, which are used in each one of the experiments, require for complete combustion about 3 c. c. of oxygen, a quantity greatly superior to that which is already dissolved. Whatever the facility may be with which this gas penetrates into a liquid, which is subjected for 8 to 10 hours to insolation in free contact with the air, we may well ask if a solution of oxalic acid oxidizes in the sun in the same way in a vessel of shallow depth, in which its thickness is small, as in a cone-shaped glass or in a round tube. The following experiment furnishes an answer to this question:

Exp.—On August 16th, 17th, and 18th, I exposed to the sun 10 c. c. of a $\frac{1}{20}$ normal solution of oxalic acid, as follows:

(a) In a cone-shaped glass,

(b) In an ordinary test tube,

(c) In a Bohemian glass mattrass with flat bottom.

To secure uniformity of temperature, the cylindrical tube *b* was placed upright in the mattrass *c*; the exposure continued from 8 o'clock A.M. till 3.30 in the evening. The following proportions of acid were consumed:

	a	b	c
August 16th,	29 %	— %	95 %
" 17th,	34	14	97
" 18th,	34	13	84
" 19th,	31	14	87

Thus, everything else being equal, the proportion of acid consumed is much greater in a vessel with a flat bottom than in a cylindrical tube. The difference is indeed so very striking, that the difficulty with which oxygen penetrates the solution does not suffice to explain it.

A combustion of 13 per cent, produced in 7 hours in the 10 c. c. of liquid, contained in the mattrass *b*, has not required more than 0.4 c. c. of oxygen; in other words, about 6 times the normal quantity dissolved in the solution. When we think of the rapidity with which deaërated water aerates itself anew, it is hard to believe that it was the oxygen which was wanting, and we are thus led to believe that the chemical action was at fault. If the incident ray does not bring with it an excess of chemical energy, the superficial layers absorb as much as is available, and there is none left for the lower strata, even though all the needful oxygen should be at hand to burn the acid which is present.

The question is of some importance, because it teaches us the quantum of chemical action which may be expected from light in the vicinity of the soil, and consequently, also, the degree of atmospheric absorption. In order to get information on this subject, let us operate with shallow, cylindrical vessels, which are at most a centimetre high at the rim, so that there can be no stagnation of air above the liquid, and that the oxygen always has easy access to the latter. If the actinic influence is deficient in the incident light, we must be able to put in evidence the influence of the surface and the depth of the liquid. For equal depths the combustion will have to be proportional to the surface. For equal surfaces with different depths, combustion, if limited to the superficial layers, should not increase with the volume and the depth of the solution, or at least not increase so rapidly. This is exactly what experience shows.

Exp.—Into two cylindrical, very shallow vessels, having the same surface, I poured 10 and 20 c. c. of a half-deci-normal solution of oxalic acid. After a rather dark and somewhat stormy day, I find that 28 per cent. of the acid has been burnt in the vessel that held 10 c. c., and only 23 per cent. in the other. As it held twice as much liquid as the other, the absolute quantities of acid burnt are relatively 28 and 46, while the depths of solution were in the ratio of 1 to 2. Combustion, therefore, increases less quickly than depth. As the latter has not exceeded a centimetre in the vessel in which it was greatest, and as, moreover, the total combustion was very slight, we cannot admit that oxygen was wanting. But the solar rays, deprived of their chemical radiations, which were rendered active by their passage through the superficial strata, reached the lower layers very much weakened, although the luminous transparency of the two liquids was perfect.

There exists then a kind of shifting of the actinic rays during the passage of the light through the first layers which it encounters; and, whether these rays are not abundant or whether the absorption be very efficient and the medium very opaque for them, the weakening process is very rapid. In return, when the surface alone is allowed to vary, while the height of the liquid remains unchanged, the effect of combustion is proportional to the surface, and consequently to the volume.

Exp.—I procured two cylindrical vessels with flat bottoms, of Bohemian glass, the bottom surfaces of which were as 1 to 2. I exposed them to the sun, one with 10 c. c., the other with 20 c. c. of one and the same half-deci-normal solution of oxalic acid. The quantities of burnt acid have always been in the proportion of 1 to 2, in a long series of experiments, with an approximation equal to that which the process of analysis should demand.

We shall have to avail ourselves of all these results when we try to ascertain the cause of atmospheric absorption. Let us be content, for the time being, with drawing a practical conclusion from them, namely, that it is desirable always to work with vessels of the same dimensions, and with equal quantities of solution, if we wish to obtain figures that can be compared with each other.

I employ small blown vessels of Bohemian glass, with flat bottoms, such as are found in trade. I choose them of the same dimensions, or nearly so, which can easily be ascertained by fitting together their edges and noting whether they have nearly the same external diameter. It is not necessary to carry accuracy any farther, considering all the inevitable irregularities connected with measurement.

Those which I have used measured about 4.5 centimetres in diameter, and 10 c. c. of liquid had there a thickness of about 6 millimetres. When I was at work in the country, in the Cantal or in the Puy-de-Dome, where the clouds of atmospheric dust are not calcareous, I left them freely exposed to the air upon a small table, so placed as to face the south and to expose them to the sun all day long. The heating which takes place in them is never very great, as the following experiments show; although they were not made in a flat vessel, but in a cone-shaped glass with a foot. The heating is less by 4° or 5° C. when working with a flat vessel.

Exp.—The same glass with a foot and containing 10 c. c. of a half-deci-normal solution of oxalic acid was exposed from the 15th to the 27th of August, 1885, daily to the sun. Every day the mean pressure, the maximum temperature of the liquid, and the aspect of the sky were carefully noted. Here follow the proportions of acid burnt on the different days, during which the weather was very fine. The experiments were made at Fau, in the Cantal, at an altitude of about 700 metres.

Date		Barom. Pressure.	Max. Temper.	Combustion.	Condition of the Sky.
August	15.	712 mm.	36.8	21 %	Fine. Slight cirrus.
"	16.	712 "	37.5	29 %	Fine.
"	17.	710 "	37.5	34 %	"
"	18.	710 "	37.5	32 %	"
"	19.	705 "	35.9	32 %	East wind. Clear sky
"	20.	705 "	35.2	30 %	" " " "
"	21.	705 "	30	21 %	Cirro-cumulus. Fresh weather.
"	22.	705 "	25	24 %	Sky clouded in the morning.
"	23.	705 "	22	22 %	" " " " Cumulus.
"	24.	710 "	30	27 %	Sky overcast.
"	25.	710 "	25	25 %	Stormy weather. Rain at night.
"	26.	705 "	30	30 %	" " Cumulus.
"	27.	700 "	29	26 %	" " "

The most active combustions correspond to the highest maximum temperatures, but only because both of them indicate, each in its own way, the presence of a livelier and more active sunlight. When the sky is overcast or shows cumuli, the solar combustion may be more powerful than when there are cirri, even though the maximum temperature should be lower.

In no case, as will be seen, has the temperature of the solution risen to a sufficiently high level to affect the chemical combustion which takes place there. We may, however, if we wish it, secure ourselves against this cause of error by causing the light vessels which contain the solution of oxalic acid, to float on a water-bath. They will then, during the day on which they are exposed to the sun, be heated a few degrees only. This is a method which I have adopted only during the hottest and driest days. The water-bath served as much to restrain evaporation as to prevent heating of the solution.

INFLUENCE OF THE AGE OF THE SOLUTION.

We now reach an unexpected fact, namely: that a fresh solution of oxalic acid does not behave like an older solution of the same strength, and appears much more refractory to the action of the sun. It becomes sensitive only very slowly, and it requires even several weeks for that end, when it is kept in diffused light.

Exp. On September 5, 1885, I compared an old solution of oxalic acid, containing $\frac{1}{40}$ equivalent (1.575 grm.) of this acid per litre, with another liquid, which I prepared at that moment, of the same strength. The common titre of these two solutions amounted to 22.8 c. c. of lime-water for 20 cubic centimetres.

At the close of the day (September 5th), which had been rather foggy, two insolated vessels containing the older liquid titrated together

> 16.2 c. c. of the same lime-water and had consequently lost 6.6 c. c. of their original strength. Two vessels with the new solution titrated together 21.7 c. c. and had consequently lost not more than 1.1 c. c. The new solution is therefore nearly 6 times less sensitive than the other.
>
> The next day, the weather being fine, the losses amounted to 1.5 c. c. for the new solution and to 8.5 c. c. for the old. This is about the same ratio as on the day before.
>
> On September 12th, after a fine day, four trials gave me the same results, losses of 9.3 c. c. for the old solution, and of 5.9 c. c. for the newly made. The difference in sensitiveness was less marked than six days previously.
>
> On September 25th, twenty days later, the losses became 8.6 c. c. for the first liquid, and 7.7 c. c. for the second. This is not yet equality, which was reached only in the month of October, after a little more than a month.

The fact that two liquids of different ages reach at the end of some time the same degree of sensitiveness, proves that there must be a maximum. We shall, however, soon see that this is not a *maximum maximorum*. However this may be, if the solution of oxalic acid has once reached this maximum, it differs in no way from what it was at first, neither from a chemical nor from a physical point of view; it gives by evaporation the same crystallized acid, and its acidimetric value is unchanged. A molecular activity, however, has been at work, upon which I shall not dwell just here. I will state now only two important facts concerning it: one is that it requires time for its completion, and the other that it betrays itself by easier oxidizability under the influence of solar radiations.

The only phenomenon which in our present state of knowledge may be compared to that which we have just discovered, is the increase of sensitiveness observed in sensitized collodion which has been allowed to rest and to grow old for a few days. This fact is well known to photographers. It may make us think also, by analogy, of the variations in the rotatory power of sugar solutions, some hours after their preparation up to the moment when they become stable. It is admitted that these few hours are necessary to enable the sugar molecules to spread uniformly throughout the solution and to assume the orientation necessary to stable equilibrium. But all these analogies are remote. The phenomenon deserves being investigated by itself, and we have here only to face its practical consequences.

These may be summed up in a few words: that it is desirable to allow the oxalic acid solution to acquire such sensitiveness before using. This is all the easier since these solutions can become sensitive in a concentrated state and preserve this sensitiveness even after being diluted. One can then provide a mother-liquor, so to speak, which may be made sensitive and which afterwards may be diluted as necessity arises. Ordinarily I used to prepare a normal solution to the amount of several litres, containing 13 grammes per litre, which I kept for some weeks under diffused light, and subsequently diluted, in fractions, to the twentieth or fortieth degree. One litre of this mother-liquid, rendered duly sensitive, may thus serve for 2000 tests. In all the comparative experiments which will be mentioned in this memoir, I have always taken pains to work with identical liquids and such as had the same sensitiveness.

We are now possessed of our actual working process, which amounts to this: To expose to the sun during the day a shallow dish, containing 20 c. c. of a half-deci-normal solution of oxalic acid, which has become sensitive by time, and to measure at the close of the day, by a titration with lime-water, the quantity of acid which has disappeared by oxidation.

Let us now see what results have been obtained by this process.

ACTINOMETRIC MEASUREMENTS.

Since the year 1885 I have made several series of actinometric measurements, especially during fine weather and at times when I was sufficiently master of my own time to secure to them the regularity which they require. All these experiments, made at different times and at different places, are not absolutely alike, since the solutions used might have undergone some change. But such variations amount to little from one year to another, and to almost nothing in the course of the same year, as I have been able to determine repeatedly; for every time when I changed the solution, I exposed simultaneously two or more vessels with old and with new material, and I always found that the solar combustion was the same for both, up to that degree of approximation which the measurements demand.

While operating with two or more vessels containing one and the same liquid, it does not always happen that we find the same result for all at the close of the day. There are irregularities in the process, some of which will be explained presently, while the others have until now defied all efforts at explanation, so sudden are they and so exceptional. There is no other remedy for this than to eliminate such out-of-the-way cases, which are always rare, making every day a trial with 3 or 4 vessels and keeping, of the figures thus obtained, only those which are concordant.

It is in this way that the following observations have been made. For each of them a record has been kept of the proportion of oxalic acid burned in 10 c. c. of a half-deci-normal solution exposed to the sun. Furthermore the state of the sky has been recorded and the principal incidents of the day of insolation.

Special attention has been paid to verifying the solar and antisolar lights[1] which were very frequent during the first years in which these observations were made and which have never been absent since that time. I have described the aspect they assumed in the countries in which I began my observations. The more I study them, the more I consider them as solely due to the presence of aqueous vapor at very great heights in the atmosphere. We shall have to examine, from this point of view, their influence on the phenomena of solar combustion.

The tables which follow are also intended to show the very considerable variation which the quantities of oxalic acid consumed present from day to day. The combustion, which is almost completely absent on cloudy or rainy days, may reach or even exceed 50 per cent of the acid during bright and luminous days. But there are also some very bright days, during which combustion is feeble, and twice it has happened that I was unable to take photographs for want of proper light, being deceived by the apparent brightness of the day on which I was working.

I shall quote my observations very nearly in the order in which I made them, from the moment when I had regulated the process of measurement; and in connection with each one of these sets of observations I shall cite the facts which they have revealed to me and which subsequent observations have only confirmed.

OBSERVATIONS OF THE YEAR 1885.

Made at Fau (Cantal). Altitude 800 metres. Country of meadows and of woods. Volcanic soil. (Andesite and basalt of the plateau.)

I have inserted above (page 8) some observations which I made at the end of August with the solution in a conical glass. The combustion is a little less rapid than in the vessels of Bohemian glass which I used in experiments of a later date. Here follow those made in September and October. S. and A. S. represent solar lights in the west and anti-solar lights.

---

[1] See, on this subject, a note inserted in the *Comptes Rendus de l'Académie des Sciences*, vol. XCIX, p. 714.

Date		Combustion	Remarks
September	2	32 %	Rain the night before. Clear weather. S. faint.
"	3	0	Rainy and stormy day. No sun.
"	4	7 %	Glimpses of the sun. Barometer rises again.
"	5	13	Day partly sunny, partly rainy.
"	6	7 %	Rain in the morning; a little sun in the evening.
"	7	7 %	" " " " " " " " " "
"	8	28 %	Day in appearance similar to the two preceding.
"	9	7 %	Fog and rain in the morning; sun in the evening. S. and A. S. continuous during more than an hour.
"	10	35	Very fine day. S. and A. S.
"	11	28	Rainy in the morning. Clearing in the evening. S. and A. S. very bright.
"	12	36 %	Fine day, corona around the moon. S. and A. S.
"	13	22 %	A fine day. Cirrus. In the evening, at sunset clouds in the west project their shadow in the east upon anti-solar lights. There are besides, in the neighborhood of this light, small cloudlets, the violet-red color of which is exactly the same, except as regards intensity, as that of the anti-solar light. An irregular corona around the moon, fringed and elongated in certain directions by cirrus-streamers to the four points.
"	14	21 %	A very fine and very hot day. S. and A. S. very fine.
"	15	27 %	A very fine and very hot day. S. and A. S. feeble.
"	16	35 %	" day and slight cirrus. No S. and A. S.
"	17	21 %	" cirrus and cirro-cumulus. At night storm.
"	18	17 %	Quite fine in the morning. Cloudy in the evening. Rain and storm at 6 o'clock P.M.
"	19	17 %	A day divided between sun and clouds.
"	20	34 %	A fine day. S. and A. S.
"	21	29 %	" " Cirrus and cirro-cumulus.
"	22	33 %	Fine day without clouds. S. and A. S. fine but short lived.
	23	32 %	Fine day without clouds. Fine but short-lived S. and A. S.
"	24	29 %	Numerous cirri in the evening. Cumulus and storm. Barometer falls.
"	25	1 %	Dark and cold day. Lunar halo of 22°.
"	26	13 %	Middling day. Some glimpses of the sun.
"	27	0 %	Rainy weather in the morning. Dark and cold all day.
"	28	4 %	A few glimpses of the sun.
"	29	3 %	Fog and rain all day.
"	30	2 %	Rain in the morning, in the evening fog. No sun.
October	1	3 %	Rain in the morning; very little sun in the evening. S. and A. S. Violet mist in the valley.
"	2	12 %	Quite a fine day. In the evening violet lights very perceptible in the neighborhood of *Venus*, whose brilliancy is very great.
"	3	20 %	Sky cloudy all day.
"	4	11 %	Fine in the morning; in the evening dark.
"	5	24 %	A fine day. Very few clouds. S. and A. S.
"	6	12 %	Foggy day.
"	7	1 %	Rain all day.
"	8	24	Fine day, autumn like. Sun rather veiled.
"	9	13	Rain in the morning; sun in the evening.
"	10	6	Rain all day. Rare glimpses of the sun.
"	11	13	Rain in the morning; a little sun in the evening.
"	12	12	Covered sky; rare glimpses of the sun.
"	13	7 %	Sky overcast; cold weather. North wind. Frost at night.
"	14	22	Fine in the morning, overcast in the evening.
"	15	4	Dark and rainy day.
"	16	13 %	Rainy in the morning; in the evening breaks in the clouds.

Date.		Combustion.	Remarks.
October	17	19 %	Very fine day, from beginning to end.
"	18	18 %	" " " In the evening cirrus and halo of 22°. Barometer falls.
"	19	18 %	Dark in the morning, a little sun in the evening. Incessant rain after 3 o'clock P.M
"	20	5 %	Rainy day. No sun.
"	21	9 %	" "
"	22	4 %	" "
"	23	24 %	Quite a fine day, in spite of east wind which rose very high after 9 o'clock.
"	24	3 %	Rainy day from beginning to end.
"	25	14 %	Partly sun and partly rain. Two currents in the air, one from the south, superior, carrying off cirri ; the other from the north, inferior, with clouds. The latter finally dominates and after having brought up intermittent and slight rains, it gives a cool night.
"	26	2 %	A rainy day.
"	27	15 %	Stormy at night. Day quite fine.
"	28	3 %	Rainy day.
"	29	5 %	" Rare glimpses of light.

These two months of uninterrupted observation prove already that the solar combustion passes through very different values within 24 hours. These changes are sometimes very sudden and exceed especially those of the thermometer, the barometer, and even those of the average brightness of the day. The actinometric effect does not show, therefore, that approximate constancy, which makes it relatively so easy to measure the other effects of solar radiation ; it requires a very close and minute investigation.

While it amounts to little or nothing at all in overcast and rainy weather, it rises very perceptibly during fine, sunny days ; but it seems to be subject to other influences yet beside those which we have mentioned when we spoke of "a fine day," "fine weather," etc. If we find, in fact, that the days from the 20th to the 24th September resemble each other very closely, as far as their external physiognomy is concerned, and are also very much alike in point of actinometry, we have on the other hand the example of October 17th, 18th, and 19th, during which the degree of combustion was the same, and this although the weather had been very fine during the first two days and very indifferent during the last. An instance of the opposite nature is offered to us by the 6th, 7th, and 8th of September, which differed very much in their actinometric aspect, whilst they resembled each other so far as their external physiognomy was concerned.

It would be interesting to find out under what influences these variations are produced. In the meantime, until we reach that point, let us notice that the combustion on the finest days in October does not amount to as much as that obtained on the finest days in September, and that the latter again do not equal the fine days in August, mentioned on page 8, if we bear in mind that the experiments mentioned on that page were made in a cone-shaped glass, capable of holding the bulb of a thermometer and not, like those made in September, with shallow vessels in which the figures would have been much higher.

One might be tempted to see here the effect of the lessened length of days. But, in order to avoid this influence, the length of exposure has been everywhere precisely the same: from 8.30 A.M. to 1.30 P.M. There is, therefore, an influence due to the seasons, which we must also endeavor to trace back to its true cause. For this purpose we can only collect the greatest possible amount of evidence.

RESULTS OF OBSERVATIONS MADE IN 1886 AND 1887.

I made for this end several series of experiments in 1886 and 1887, at Paris, in the Cantal, and at Oreines, at the foot of the Puy-de-Dome. Unfortunately I cannot report them here in detail, having mislaid the papers which contained the record. I can only indicate the general results which I have retained in my memory, because they served as a starting-point for new investigations. In the first place I again found evidence of the almost perfect independence between the degree of solar combustion of oxalic acid, and the occurrence of solar and anti-solar lights. If there are any examples of coincidence between an active combustion and the presence of such lights, it is because these lights appear only in fine weather. But there are also other cases in which combustion is very rapid and when those lights are altogether missing. If they play any part at all, it seems to be one quite secondary, and this view agrees very fairly with the hypothesis that the phenomenon is due to the presence of aqueous vapors in the upper regions of the atmosphere. It is, of course, well known that liquid water or water in the form of steam influences the activity of actinic combustion very little.

Another very important result is this: that the maxima of the figures of combustion during the finest days are higher in spring than in summer. The difference did not strike me as quite so marked as between summer and autumn. As to the maximum in spring I have always found it very clearly marked during observations carried on for four years, and an example of this will be found, unfortunately too limited in its nature, when I shall speak of my experiments of 1888.

The maximum in spring appears alike in Paris and in the country. But I have also found that solar combustion was less intense in Paris than in the Cantal or in the Puy-de-Dome; this difference appears not only in the high figures connected with the oxalic acid, but I have found it also in a long series of experiments, which I had undertaken in order to study the transformations which several organic substances undergo in the solar light, and which offer a greater resistance than oxalic acid. These I had been compelled to leave in the light for weeks and for months before the attack was complete. They thus summed up the influence to which they had been subjected during the length of the exposure. Now this phenomenon required, generally, for its termination, much more time, sometimes three or four times more, in Paris than in the country.

Among the facts of this kind I can only quote one which I find I had by chance inserted in a work intended for the examination of another question. A deci-normal solution of tartaric acid which was every day exposed from 10 A.M. till 2 P.M. to the sun in Paris, had lost by combustion in seven months and a half only 10 per cent of its acid, while in the Cantal an identical solution had lost in two months 47 per cent. This involves a combustion about fifteen times more rapid, and although the length of exposure was a little greater every day in the Cantal than in Paris, and although the quantum of solar combustion increases more rapidly than the length of exposure, this is not enough to make up for the difference. In another case involving the combustion of glucose in an alkaline liquid, I found that to take two years in Paris which had required only three months in the Cantal.

Finally, this experiment teaches us also that average years do not resemble each other and that, if there are some which are rich in chemical radiations, there are poor ones also. These differences between one year and another, from this point of view, appeared to me more marked than in any other respect. We have shown above the most striking inequalities between consecutive days of the same season. They recur, less markedly, for consecutive years.

These statements which, I repeat, I regret not being able to support by figures, suggest a number of problems for which I have begun to seek a solution.

In the first place, the fact that active combustion is stronger on fine days in spring than in summer and in autumn, shows that there must be another cause of action than the influence of temperature, or the height of the sun above the horizon. We are naturally led to think of the influence of the volatile organic products which vegetation scatters in the air during summer, and which, if they are capable of being oxidized, absorb and utilize for their own benefit the chemical radiations of the light which passes through the atmosphere, preventing them from reaching the soil. We are confirmed in this view by what has been said before (page 6) concerning the relative poverty of solar light, at the time when it reaches us, in radiations able to oxidize oxalic acid.

In the second place, the difference between the sum total of the annual radiations at Paris and at the Cantal, or on the high table-lands of the Puy-de-Dome, leads us to ask if the question of altitude may not perhaps be of importance. Two identical vessels, containing the same solution and exposed during the same time at different heights in the atmosphere—will they or will they not undergo the same degree of oxidation?

INFLUENCE OF ALTITUDE.

I begin with the last question, because the documents which helped me to solve it were lost, together with those which gave the results of the experiments already mentioned, and I must therefore be very brief in my treatment.

In order to solve this problem I installed myself at the foot of the Puy-de-Dome in the little village of Orcines, and I made a number of experiments simultaneously in the garden of the house in which we lived, and on the terrace of the observatory on the Puy-de-Dome, where M. Humandon kindly undertook to expose and to remove again at certain fixed hours the vessels containing the oxalic acid which had been rendered sensitive. The two stations are distant from each other 4 kilometres in a direct line. The vertical difference amounts to about 400 metres. The incline, therefore, between the two stations does not count for much, and they cannot be considered as being upon the same vertical line. Experiments made on the top and at the foot of the Eiffel tower would have been more satisfactory in this respect. But at the Eiffel tower I should have had to apprehend encountering difficulties of another kind, especially the want of homogeneousness between the layers of the atmosphere. For the lower ones which had swept populous parts of the city could, in that amount, no longer be considered equivalent to the upper parts. What tempted me to choose the station of the Puy-de-Dome was exactly this homogeneousness of the whole region so far as its vegetation was concerned. The Puy-de-Dome is surrounded to a great distance by a dry, almost deserted country, covered with woods and largely with heather, while some portions are absolutely bare in places where pozzolanes crop out of the soil or in those immense overflows of lava of recent date, which are called "cheires," and which defy any attempt at cultivation. One of these "cheires" cropped out close to the house in which I dwelt, and I imagine that, on the whole, there was no reason why the air on the top and that of the table-land from which the mountain rises, should be heterogeneous. In spite of these favorable circumstances I did not find that the combustion at the observatory was very different from that at Orcines. It exceeded the latter a little, on an average, but with exceptional results in one or the other direction, so as to prevent any positive conclusion. I remember that my estimates showed an increase of altitude accompanying an increase of actinic intensity, but that they were not such as to prove it. This conclusion diminishes my regret at having mislaid the data.

INFLUENCE OF OXIDIZABLE SUBSTANCES SUSPENDED IN THE AIR

With this second question I have been more successful, since comparative experiments can here be made with far more precision than elsewhere. All that is necessary is to expose in one and the same place two vessels containing the same oxalic solution; one being made to float upon water contained in a deep crystallizing pan in such a way that a layer of stagnant aqueous vapor may be kept above the surface of the liquid which it contains. The other vessel floats in like manner, and under the same conditions, on the surface of some turpentine or of any other essential oil. It is always found that combustion is far less advanced in the second than in the first vessel. As I said before, I lost the relative figures of the results obtained by the experiments made in 1886 and 1887. But Mr. Elfving, professor at the University of Helsingfors (Finland), to whom I had mentioned the results thus obtained, began once more to experiment with essence of turpentine, and I will here quote the results as he reported them to me in a letter which I have fortunately preserved:

"I have repeated and confirmed your experiments on August 30, 1888, from 8 A.M. to 4 P.M. with a clear sky. There were 53 per cent of the oxalic acid burnt above the water, and 39 per cent above a bath of essence of turpentine. The next day, which remained clear from 9 A.M. till noon, the figures were 47 per cent and 20 per cent for the same length of exposure. It is certain, therefore, that the presence of oxidizable substances in the air possibly diminishes the consuming power of the sun."

Mr. Elfving has confirmed this conclusion by the following experiment, which I have, in my turn, repeated and confirmed. It consists in sifting, so to speak, the rays of the sun through a solution of sulphate of quinine, which absorbs a part of the chemical radiations before they can react on the oxalic solution. Another sifting apparatus, of the same thickness, but consisting of pure water, furnishes a standard of comparison. The latter, rigorously, might be neglected, for the quantity of watery vapor or of liquid or solid water which the rays of the sun have traversed before reaching the level of the soil, exceeds by far the thickness of the supplementary screen of liquid; the absorption due to water, is, moreover, very feeble. In my experiments I suppressed this complication. Mr. Elfving used two glass bell jars with double walls, of which one contained water, the other a solution of sulphate of quinine. He wrote to me on June 17th:

"The light which has gone through a layer of water is five times more active than that which has traversed a solution of sulphate of quinine of quite the same depth. I shall continue my observations at the time of the solstice."

And on July 9th:

"I have again made an experiment with sulphate of quinine. On June 27th, while there were consumed in the open air during the whole day 87 per cent of the total amount of oxalic acid, and 78 per cent under a bell jar filled with water, the decomposition amounted only to 20 per cent under a precisely similar bell filled with a solution of sulphate of quinine."

Analogous results are obtained by comparing the effect of sifting solar rays through a solution of potassium bichromate, which by preference allows those radiations to pass which are least refrangible, with that of transmission through a solution of sulphate of copper which allows the most refrangible radiations to pass. All this proves that it is mainly the chemical radiations which are of importance, and that when these radiations are employed in oxidation, or more generally in the transformation of organic or even mineral substances in the air, they reach the surface of the soil much weakened.

Here is, therefore, a local cause of variations in the actinometric degree; a local and incidental cause, considering that it may be summed up thus: There may exist actinic clouds, clouds scarcely visible to the naked eye and not accessible to our senses, but the effect of which, at least as far as it can be measured by solutions of oxalic acid, exceeds by far, in intensity, that of the variations in brilliancy and obscurity produced by ordinary clouds. These clouds come and go, are no longer to-day where they were the day before; they dissolve, for they are, like other clouds, no sooner formed than they become subject to ceaseless causes of destruction. This explains very fully why the actinometric degree should vary so greatly from day to day and from one year to another. It may also be that we find here our explanation of the greater actinic power which spring has, in other words, that season during which the atmosphere is certainly poorest in organic substances.

Upon reaching this point we see new vistas open before us. It is well known that the turning green of the foliage and the production of chlorophyll may take place when the intensity of light is very feeble, as for instance in the back of a room lighted by one window, but that, under such circumstances, the chlorophyll does not begin to act and is not decomposed by carbonic acid. It requires a much stronger luminous intensity for the process of assimilation to begin. This phenomenon increases with intensity of light up to a certain maximum, differing in different plants; beyond this it decreases. Starting from this point, it is naturally suggested that those actinic clouds which we have just discovered, cannot be without influence on vegetation, since they modify so largely, although often invisibly, the strength of the chemical radiations, which is nearly, if not absolutely the only active element in the complex whole, which until now has been studied under the name of *Luminous Intensity*. And if again the plants themselves disperse into the air the materials which absorb the solar, chemical radiations, how can we avoid thinking that possibly the production of these odoriferous and oxidizable effluvia may be for the plant a means of protection?

To elucidate this subject fully, would require experiments which I have not the time to make. I have been satisfied with examining it under various aspects. Odorous and essential oils are not alone able to arrest the passage of chemical radiations. The surfaces of plants are, as is well known, frequently covered with a fatty or waxy layer, which is highly oxidizable. There are, besides, at all times fatty substances in the air, as is proved by the greasy feel of old dust deposited upon our furniture. What effect can these fatty substances exert upon the combustion of oxalic acid in the sunlight? If our ideas are correct, a slight layer of fatty matter should protect that acid against solar light.

INFLUENCE OF FATTY SUBSTANCES.

The presence of fatty matter on the surface of our test solution brings up a slight experimental difficulty. It is this, that solar oxidation of a fatty substance is always accompanied by a production of acid which raises the titre of the oxalic solution at the same time that the solar combustion lessens it. We must, therefore, either use a very small quantity of fatty matter so that it may barely form an imperceptible veil to cover the liquid, or, what is better still, we must spread it out in a transparent layer over a surface of glass interposed in the path of the luminous rays. Here are some experiments made in connection with this subject:

Exp.—On June 27, 1885, I exposed to the sun during six hours seven vessels of the same dimensions, containing each 10 c.c. of oxalic acid in half-decinormal solution. Two of these vessels, Nos. 1 and 2, had their walls clean. Vessel No. 3 had been rubbed with a weak solution of butter in sulphide of carbon, which left upon the sides, hardly tarnishing them, a greasy layer. Moreover, by virtue of a well-known phenomenon of superficial tension, the walls of the vessel have allowed an invisible layer of fatty matter to spread on the surface of the liquid. In order to separate this action as far as possible from that of the roughness of the walls, a fourth vessel is brought up to the same degree of opacity as No. 3, by rubbing it externally with chalk diffused in water. Finally, to increase the quantity of fatty matter present in the liquid, and also, in order to see the effect which a little opacity of the liquid may there produce, new vessels, Nos. 1^1, 2^1, and 3^1, have been prepared like the vessels Nos. 1, 2, and 3, simply adding to each two drops, in other words 5 milligrammes, of fatty matter.

These were the results:

	Combustion.
Vessel No. 1, clean sides	33 %
" " 2, " "	33 %
" " 3, dull sides, greasy surface	20 %
" " 4, " " (chalk)	32 %
" " 1^1, like 1, plus 2 drops of milk	16 %
" " 2^1, " 2, " " " "	17 %
" " 3^1, " 3, " " " "	17 %

Other experiments, made the following years, and the detailed reports of which have been lost, confirm these first results, and show that the fatty matter contained in a liquid or spread as an invisible layer over the surface, like that which covers the walls of a bell jar placed over the vessel containing oxalic acid, diminishes the actinic effect of the solar rays.

Finally, it is the same with many substances, more or less easily oxidizable, which also exert a protecting, or at least a retarding, effect upon the influence of the chemical radiations. Such is, for instance, alcohol.

Exp. On the 26th June, 1885, two vessels with 10 c. c. of an oxalic acid solution, containing $\frac{1}{15}$ equivalent per litre, gave me a combustion of 37 per cent, the same for both. Two other vessels, exactly alike, which have received an addition of 2.5 c. c. alcohol of 90 per cent, gave me only a combustion of 21 per cent.

Exp.—On September 11, 1888, two vessels with a solution of $\frac{1}{20}$ equivalent of oxalic acid, gave me identical combustions, rising as high as 10 per cent. They amounted only to 4 per cent in two like vessels, to which a few drops of oil of oranges had been added, so that the essential oil and the alcohol have acted similarly.

I have made numerous experiments with divers substances which were oxidizing or oxidizable, the details of which have been lost. In a general way I have found that the former increase the combustion of oxalic acid, while the others retard it.

But this rule is not always confirmed, on account of the intervention of what I have called in another paper phenomena of entanglement. These operate so that one oxidizable body may involve another in the same decomposition which it undergoes itself. But here we begin to stray away from the subject of this paper, which is the actinic study of the atmosphere. I am content, therefore, to draw from the great sum total of the results I have obtained the following conclusions: The nature and the proportion of the oxidizable elements which living nature scatters through the air, betray themselves in the solar combustion of oxalic acid, which is the more feeble on the surface of the solution the more the radiations have met with unstable elements to oxidize during their passage. The organic substances of the atmosphere are therefore a protection against too intense an action of the chemical rays at the surface of the soil, and the effect which they produce is not only measurable, but sometimes very great. In other words, we do not know what the chemical power of solar light may be at its entrance into the atmosphere, but on a level with the soil it is so impoverished that a thin layer of turpentine vapor, of sulphate of quinine, or of any oxidizable substance, suffices to destroy it almost completely.

This conclusion has, however, another side to be considered, which is, that the atmosphere must at every moment be the seat of combustions, such that, on the whole, all luminous radiations are utilized. I shall not insist here on the power and the importance of the phenomena of oxidation which take place in the atmosphere and at the level of the soil, nor upon the general effect which they have on sanitation over which they preside. I have published several memoirs on that subject,[1] to which I must be content to refer. I have there called attention to the power of the solar rays on microbes, first weakening and then killing them, a power which was first indicated, but incompletely proven, by Messrs. Downes and Blunt.[2] I have, moreover, studied the influence of the conditions of the medium on the resistance of germs. All that has been done since, has only confirmed the importance which I attached to light and to the chemical portion of the solar spectrum as principal agents in the hygiene of the globe.

INFLUENCE OF INCREASE OF LATITUDE.

This first problem, that of the possible influence exerted by oxidizable substances while in suspension in the atmosphere, having been sufficiently discussed in

---

[1] *Annales de Chimie et de Physique*, 6th S., vol. v., May, 1885, and *Comptes Rendus*, vol. c. and ci. *Annales de l'Institut Pasteur*, vol. i., p. 88.

[2] The conclusions of these scholars had been opposed by Tyndall and by Jamieson, so that when I took up the question anew, it had not yet met with a solution. It has found one to-day.

the statements just made, I found myself face to face, as Professor of Meteorology, with the following question:

It is an acknowledged fact, that the activity of the vegetative process in the northern parts of Europe is very great. The interval between sowing and harvesting, for spring wheat, lasts on an average 115 days in Alsace. According to M. Tisserand it amounts to only 133 days at Halsnö, in 59° 30′ N. latitude; and it is only 111 days at Skibbotten, in 69° 30′ N. latitude. It decreases therefore as we approach the pole; notwithstanding that the average temperature of the period of vegetation diminishes likewise with the increase of latitude.

This decrease in the number of days needed for vegetation, as we draw nearer the north pole, seems to be a general law. According to Arnell, barley requires 117 days to grow in Southern Sweden, 92 in Middle Sweden, and 89 in Lapland. It is true that these variations depend in part at least on the power which the plant has to adapt itself to external conditions, for if sown in our country the Norwegian grain grows more rapidly than ours, while our own native grain, carried to Norway, lags behind the acclimated variety. But this is not sufficient to explain all, and we must in the end always return, as a final analysis, to the influence of climate.

We may go even a little farther in our induction. According to Griesbach the increased rapidity in the development of plants cultivated at the extreme north does not affect the whole evolution of the plant, but only the period between germination and blooming. It applies, therefore, only to the green organs of the plant, and thus starts once more the question of light, which actually appears to be of greater importance than that of temperature. In fine, to return to the subject of our Memoir, the actinic influence of the solar rays seems to increase with the latitude.

To what is this increase due? This question is still open and to it I have tried to find an answer. The first point to determine was whether the solution of oxalic acid also showed such an increase of actinic effect?

It was on this account that I asked Mr. Elfving to assist me, whose interesting experiment I have mentioned above (page 17). I sent to him at Helsingfors an oxalic solution, and ten vessels exactly alike, such as I had used myself in France, in order to make sure that at least, and as far as possible, those experimental conditions which we could control should be as identical as they could be made.

Unfortunately there were other conditions which were entirely beyond our control. The ideal would have been attained with a series of days equally fine, occurring simultaneously in France and in Finland, and permitting us to make our observations under precisely the same circumstances. But there are obvious reasons why the weather could hardly ever be the same in France and in the Gulf of

Bothnia. When that vast mass of air, in relative repose, which I have named The Isle of Calms, rests over our part of the world and gives us fine weather, the equatorial current, which turns it northward, is over Sweden and Norway, to which it brings overcast skies and rains; when, on the other hand, the Isle of Calms rests over the north of Europe, we are in France subject to stormy disturbances which come to us through the Mediterranean or the Gulf of Gascony, or we are subject again to the return current, which, after having rounded the "Island," comes back to us in the shape of cold east and northeast winds. To find favorable coincidences in this grand atmospheric dance, we should need months of continued observations, which neither Mr. Elfving nor myself were in a condition to undertake.

In this difficulty we availed ourselves of the meaning of the word "fine day," as I have shown above (page 13), which is so uncertain as to its actinometric definition that every effort to make it absolute as to perfect equality of experimental conditions becomes rather illusory. We could be content, more modestly, with a first approximation; it was enough to compare the actinometric combustion of the finest days in the Gulf of Finland and in France, at the same time of the year.

Nor is this all. The length of the day is greater at the North than at the South during the period of vegetation, and the length of the insolation has, we all know, a direct influence on the relative quantum of combustion. Hence I requested Mr. Elfving to make every day two sets of experiments, one with vessels exposed to the sun from 8 A.M. to 4 P.M., like those which I was using in France, and the other with vessels left out from 8 A.M. till the setting of the sun.

Mr. Elfving made at Helsingfors between August 27th and September 4th, 1887, five series of experiments, which I cannot compare with those which I was making at the same time at the foot of the Puy-de-Dome, and the records of which have been lost. But I am fortunately able to compare them with those which I had begged M. Ch. Mascart to make at the same time near the seashore in the Channel. These may perhaps be better fitted for comparison with those made by Mr. Elfving, as both were made at maritime stations. All that I noted when I received them was that they gave much higher figures than those which I obtained at the same time on the bare table-land which carries the Puy-de-Dome.

In the first place, here is a table of the observations made in France; it is formed in the same way as those which have already been given in this Memoir.

ST. PIERRE LE PORT, 1887.

Date.		Combustion.	Remarks.
August	15	44	Clear weather till 10 o'clock P.M.; later cloudy.
"	16	38	Rain till 2 o'clock; later overcast.
"	17	31	Very clear from 11 till 3; afterwards cloudy.
"	18	23 %	Three-fourths cloudy till 10 A.M. Clear from 10 till 3 P.M.
"	19	33 %	Half overcast in the morning; then quite clear.
"	20	21 %	Half overcast all day long; a slight fog.
"	21	28 %	Slightly overcast in the morning; then clear
"	22	32 %	Slightly overcast in the morning; then clear.
"	23	36 %	Fine weather.
"	24	29 %	" "
"	25	42 %	Warm. Very close. Clear weather.
"	26	32 %	Covered in the morning and evening. Clear from 12 till 3 P.M.
"	27	23 %	Overcast. Rain from 10 till 11 A.M.
"	28	24	Unceasing rain.

Here again the solar combustion increases with the fine weather and diminishes when the sky is overcast or rain falls. Although the weather was on an average less fine than during the corresponding series of experiments cited before, the latter gives, on the average, higher results, a fact which confirms what we have already said concerning the actinometric differences of different years at the same epoch.

Here are now the experiments made by Mr. Elfving at the same time in 1887:

Helsingfors, latitude 60° 10′. Length of day, 14 hours. Height of the sun above the horizon at noon, about 38°.

Date.		Solar Combustion.	
		From 8 A.M. to 4 P.M.	All day long.
August	27	42 %	55 %
"	28	50 %	65 %
"	29	53 %	61 %
September	2	74 %	87 %
"	4	77 %	89 %

"The difference between the first three days and the two others is quite great; it arises, no doubt, from the fact that the atmosphere had been purified by heavy rains on August 30th and September 1st and 3d. In March, I had already observed this effect of rain." (M. ELFVING.)

The figures in the first column are on an average higher than those which correspond to them in the preceding report, and this superiority must be all the more striking, as by a mistake in our agreement the exposure to the sun lasted an hour longer in France than in Finland. The latter ought, therefore, to be somewhat increased, in order to make the comparison more just. We shall presently return to the results marked in the last column. Mr. Elfving had worked only during five days; the comparative experiments were therefore not numerous enough, and by a common understanding another beginning was made in 1888.

Here is the report of the experiments which I made in France, in the garden of the Agronomic Institute, during the months of May and June, 1888. My official duties prevented me from making them in an unbroken series, and, moreover, I had to leave out three observations during which a fierce wind suddenly sprang up and covered my vessels with a layer of dust.

PARIS. EXPOSURE FROM 8 A.M. TO 5 P.M.

Date.		Combustion.	Remarks.
May	12	46 %	A fine day. Fresh north wind.
"	13	29 %	Very fine day; rather warmer than the day before.
"	14	50 %	Cirrus in the morning. Very fine day.
"	15	23 %	Sky overcast. Barometer falls.
"	17	52 %	" South wind. Cirrus.
"	18	23 %	" " "
"	20	27 %	Quite a fine day. N. wind. Cirrus and alto-cumulus.
"	21	35 %	Sky overcast. Lighter in the evening. Fresh east winds.
"	26	43 %	g. g. clouds; fine at night. Fresh north wind.
"	27	30 %	Quite a fine day. g. g. Cirrus. Sudden storm.
June	1	33 %	Fine day. No wind.
"	2	55 %	Warm and stormy day.
	3	39 %	Very warm day. South wind.
	5	42 %	Warm and stormy day. Sky overcast.
	12	64 %	Fine day. A little air.

The correspondence between the degree of combustion and the state of the atmosphere is less striking in these observations, which were made in Paris, than in those made in the country, which is less surprising when we bear in mind the incessant heterogeneity and variability of the air in a large city. The influence of the spring season, however, to which reference was made before (page 14) is shown in the relative magnitude of the figures of combustion. The figure 64 %, dated on June 12th, is very exceptional.

Here follow next the results obtained almost simultaneously by Mr. Elfving at Helsingfors:

HELSINGFORS. EXPERIMENTS MADE IN 1888.

	Date		Solar Combustion.	
			From 8 A.M. to 4 P.M.	All day long
	May	19	50 %	— %
	"	21	47 %	58 %
	"	22	56 %	76 %
x	"	23	53 %	65 %
x	"	24	37 %	55 %
x	"	27	44 %	— %
	"	30	46 %	72 %
	"	31	51 %	72 %
	June	4	48 %	63 %
x	"	7	48 %	70 %
	"	8	%	74 %
	"	9	56 %	79 %
	"	10	57 %	77 %
	"	11	54 %	80 %

On the days marked with a cross (x), the sky was more or less overcast at Helsingfors. All the figures in the second column ought to be raised slightly, in order to make them fit to be compared with those in the preceding table, which correspond to an additional hour of exposure. It will be seen, however, that they are on an average higher, although none of them reach the exceptional figure of the 12th of June at Paris.

The conclusion is the same as that derived from the experiments of 1887. In order to add to its weight we recommenced another series in August and September. This time I installed myself on the Mont Dore, at a height of about 1100 metres, in a house some distance from that little village.

MONT DORE, 1888.

Date.		Combustion.	Remarks.
August	9	26 %	Cirrus in the morning, which increased towards evening.
"	10	19 %	Fine day.
"	11	18 %	" Sky slightly covered.
"	12	19 %	" " "
"	13	18 %	Cumulo-cirrus in the morning. Fine afternoon.
"	14	27 %	Fine day. Sky a little cloudy in the evening. South wind.
"	16	27 %	Very fine day. Atmosphere limpid. Cirrus in the evening.
"	17	—	Rain all day. No exposure.
"	18	—	Sky overcast, and rain.
"	19	22 %	Fine day. Cumulo-cirrus and cirrus.
"	20	15 %	Cirrus all day, especially in the evening. Barometer not falling.
"	31	15 %	Large white cumuli.

Date.	Combustion.	Remarks.
September 1	15 %	Same weather as day before.
" 2	10 %	Middling day.
" 3	24 %	Quite a fine day. Many cirri.
" 4	12 %	Middling day.
" 5	11 %	"
" 6	12 %	Quite a fine day. Some cumuli early.
" 7	11 %	Middling day.
" 10	11 %	Quite a fine day with a few clouds.
" 11	7 %	" " " "
" 12	18 %	Fine day, hot sun, a few cumuli.
" 13	25 %	Fine in the morning, middling later.
" 14	15 %	Fine day, very warm.
" 15	9 %	Very fine day, as yesterday.
" 16	4 %	Middling day. Warm and heavy.
" 17	29 %	Day divided between sun and clouds.
" 18	—	Dark day.
" 19	30 %	Superb day.
" 20	10 %	Sky fine early; covered in the evening.
" 21	17 %	Day rather finer than day before.
" 22	13 %	Quite fine in the morning. Cloudy at night.
" 26	15 %	Cumulus concealing about ¼ of sky.
" 27	25 %	Rather better than the day before.
" 28	49 %	Rather a dull day, but no clouds.

Between the 20th and 30th August there followed a long period of rain and overcast sky.

What strikes us in reading these figures is their smallness even on fine days. They are the smallest I have ever had to record in August and September, on an average, and this although the latter month was rather fine at Mont Dore during 1888; there is also to be noticed a great lack of agreement between the apparent character of the day and its actinometric character. Thus the very fine day of September 15th gave only a combustion of 9 per cent, when the slightly veiled day of September 28th gave a combustion of 49 per cent. This is a new confirmation of what has been stated before.

I partly attribute the very great want of agreement noticed at Mont Dore to the fact that this station is surrounded on all sides by pine woods which diffuse through the air a large quantity of terebinthine exhalations, so that the odor becomes striking. This explanation also agrees with the notions which I have suggested before. Nevertheless I admit that it would require very special comparative experiments to establish it firmly, and to draw from it the proper signification. We must be content, for the present, to remark that if our explanation is correct, it will also account, as a whole, for the want of agreement already mentioned. If the exhalations of essential oils are really able to arrest actinic radiations, the effect of what we call a fine day will be very variable according as it will succeed a period of rains which may have washed the atmosphere, as in the observations made by Mr. Elfving, or as it may come to us after a warm day or a period of great heat, which may have increased the invisible cloud of terebinthine vapors or other odorous essences. But, I repeat, all these points must be investigated directly, and this preliminary study, although it has continued for many years, has no other claim than that of suggesting new subjects for the study of the atmosphere.

Let us now return to the comparison of the effects which equal periods of exposure have in France and in Finland. The following are the results obtained by Mr. Elfving at Helsingfors, during the same period of the same year:

HELSINGFORS, 1888.

Date		Solar Combustion		Remarks
		From 8 A.M. to 4 P.M.	All day [illegible]	
August	22	56 %	66	Clear sky.
"	23	51 %	60 %	Almost clear
"	26	35 %	45	Cloudy.
"	27	56 %	75 %	Clear
"	28	50 %	68 %	Half-overcast.
"	29	55 %	71 %	Very clear sky from 9 A.M.
"	30	53 %	70 %	Very clear sky from 9 A.M. to 12.
"	31	39 %	—	" " " " "
September	2	49 %	59 %	Very clear sky.
"	3	49 %	67	" "
"	6	54 %		Almost clear.
"	8	40 %	—	Clear early, overcast afterwards
"	9	52 %	62	Very clear sky.
"	10	56	[illegible]	" "
"	11	59 %	—	" "
"	14	51 %	—	Clear sky.
"	15	46 %	—	"
"	16	51 %	—	"
"	17	51 %	—	"
"	18	42 %	—	Clouds.

The regularity is here greater than in France, and what is especially remarkable is the close resemblance in an actinometric sense of the days which are marked as "similar," in the column of "Remarks" (Aug. 29th and 30th, Sept. 2d and 3d, 14th, 15th, 16th, and 17th). But what is perhaps most striking in this table, when compared with that on page 26 is that the figures of solar combustion are notably higher than they were in France at Mont Dore, at the same time of the year. Still, Finland is very rich in resinous woods, and even if the station were less surrounded by them than at Mont Dore, the altitude is lower, which to some extent makes partial compensation. Besides, the higher figures obtained at Helsingfors, persist at the three positions of the French station: at Paris, on the coast of the Channel, and on the mountain of Puy-de-Dome.

There can, therefore, remain no possible doubt on this point: the actinic intensity of light in northern countries, close to the soil, is greater than in our temperate zone at the same hours of the day. It would no doubt be found still weaker if we approached more nearly to the equator. This conclusion was altogether unforeseen.

The fact once established, explanation becomes necessary. This greater activity of combustion which the air has in northern regions, might be ascribed to ozone, rendered more abundant there by the discharges which constitute the aurora borealis, and more active by the action of light. I have begun to study this subject, but my experiments, interrupted by winter and my return to Paris, are not yet completed, and I shall not be able to take them up again till next spring. I believe, however, that I may already say that ozone can have but a very secondary influence on the phenomenon, and that if light is more active within the same length of time at the north than in France, the reason is that it has lost fewer of its chemical radiations in passing through the atmosphere, because the latter is poorer in oxidizable substances. I know, of course, that there are in the north those pine forests, of which I have spoken before, and that perhaps, if Helsingfors were built in the heart of the woods, instead of being a large city on the sea-coast, the points of difference would be somewhat less. But there would always remain the fact that the quantities of vapor diffused through the air increase with the temperature, and that, for one and the same aspect of the fauna and the flora of the earth, the equatorial atmosphere will always be more heavily loaded than that of the temperate zones, which in its turn will again be more so than that of boreal regions.

Whatever finally the explanation of the fact may be, the important point is to show that it exists, and that there is a difference in light, so far as its *quality* is concerned, at the same hours of the day, at the north and in the heart of Europe. But this is not all. After having examined this question of quality, we have to look next at the question of *quantity*. The days which are useful to vegetation at the north are longer than with us—what now is the influence of the duration of light on the chemical phenomenon which serves us as a means of measurement? Is the effect thus produced proportionate to the length of exposure to the sun? Does it increase more or less slowly? Such are the first questions which we have to consider.

I believe they are new, because up to this day, both as regards meteorologic instruments and in theoretical speculations, it has always been held that the effect of illumination was, everything else being equal, proportional to its duration. We shall see that this is not so, and that the effect increases much more rapidly than the increase of time, so that all the notions which we entertain on this subject stand in need of revision.

INFLUENCE OF THE DURATION OF ILLUMINATION.

So far we have taken as a measure of the total actinic effect during the period of exposure, the sum total of the oxalic acid consumed. The conclusions which we have thus reached, subsist, whatever may be the law which connects the combustion with the actinic effect; it has been enough for us to expose, during the same length of time, solutions equally sensitive, in two different places and to proceed always by comparison.

But the law of the increase of actinic effect, with the time of insolation, does not the less merit attentive investigation. To begin, let us ask first, if the total effect of combustion, observed at the close of a day, upon a solution of oxalic acid exposed to the sun, represents the sum of the divers actinic effects produced at the different hours.

One way to answer the question is to expose in the morning, side by side, two vessels holding the same quantity of the same solution. One is to be examined at the end of the day, and this will give us the sum total of the effect. The other is to be examined at the end of an hour, and then to be replaced by another vessel like the first, but containing new liquid, to be likewise studied after another hour's exposure. In like manner, we shall renew the study at successive hours. If the actinic effects accumulate, without loss or encroachments in the liquid of the vessel which has been exposed to the sun all day long, the quantity of acid which we shall find has disappeared must equal the sum of the quantities of acid which have vanished in the vessels that were exposed for an hour each.

The experiment, repeated again and again, shows that it is never so. The sum of the quantities of acid burnt in the vessels which have been exposed each one hour only, is always insignificant in comparison with that consumed in a vessel which has spent the whole day in the sunlight. The difference varies from one day to another, and increases with the intensity of combustion. It decreases slightly if we carry the exposure of the successive vessels to two hours, and still more if we extend it to three or four hours, as should be expected. But, even if we divide a day of ten hours into two equal periods, one from 7 A.M. to noon, and the other from noon to 5 P.M., the sum total of acid consumed in the two vessels that correspond to the two periods of exposure sometimes does not exceed half the acid consumed in the vessel which spent ten hours in the sun. The combustion, therefore, does not begin as soon as the vessel is exposed to the light. There is a "lost time" at the beginning; two hours, three hours, are necessary for the solution to put itself in action. During this whole time the work is wholly interior and betrays itself by no diminution of the acidimetric titre.

This "dead time" at the beginning of the reaction should not surprise us. When we study the different reactions of chemistry, from this point of view, we become aware that there are few which begin immediately upon realization of the exterior conditions of production, even in cases when the energy which comes into play is altogether internal as regards the mixture. The formation of a precipitate of barium sulphate is not instantaneous; that of calcium sulphate, or of calcium tartrate, is still less so; a mixture of formate and of permanganate of potassium remains apparently inert for some seconds, after which begins an abundant, and, to some extent, an explosive liberation of carbonic acid, proceeding from the combustion of formic acid.

Here the heat produced by the reaction intervenes to increase its activity. We can say the same of the phenomenon which Bunsen and Roscoe discovered and investigated under the name of "photochemical induction," in the combination, in the sunlight, of chlorine and hydrogen. This reaction also requires a certain time to commence, but it accelerates afterwards, because it is exothermic. The same remark applies to the reduction of chloride or bromide of silver in the presence of an organic substance, which also shows a "dead time" at the beginning, and becomes more energetic afterwards. The same remark applies, moreover, to almost all photographic operations, whether we wish to obtain luminous impressions, to develop images, or to produce positive prints.

If we observe a "dead time" when the forces are internal and accelerating, it is not surprising that we should find a like one also in the solar combustion of oxalic acid, where the impulse is to come from without and where the reaction is so feebly exothermic. But this verification presents here an interest which it has not elsewhere, for we connect it intimately with the phenomena of sensibilization, which we discovered previously in the solutions of oxalic acid. In both cases a *molecular preparation* is evidently involved, the mechanism of which is still unknown to us, but which results in placing the molecule upon a kind of inclined plane, down which it may be made to roll by the slightest impulse. As a confirmation of this idea, I have ascertained that in fact the "dead time" at the beginning is less protracted with solutions which have been made sensitive, than with new solutions, so that if the latter do not undergo in the light of the sun, as we have seen before, the same degree of combustion as the others, it is partly because the "dead time" at the beginning is shorter. But I say "partly" because there is still another phenomenon. We shall see that combustion, once begun, does not go on with regular and equal steps, but is made to proceed faster and faster. In other words, everything goes on as if the sensitiveness were increasing during the oxidation. To put it still differently, the quantity of burnt oxalic acid, which amounts to little or next to nothing during the first moments of the exposure to the sun, starts out and increases, from that instant, quicker than time, so that there is no proportion between the length of the insolation and its consuming effects.

In order to take account of effect of insolation upon an oxalic solution, let us slightly modify the conditions of an experiment which I have just described. Let us expose in the morning a dozen similar vessels to the sun, and let us withdraw every other hour two of them, which will give us the sum total of combustion up to that moment. It will be easy by this means to ascertain the progress of combustion during the whole day. The following experiment I cite, not as being the most complete of those which I have made, but because it was performed with a solution of the same sensitiveness as that used in other experiments which I shall quote presently, so that all of them are comparable.

Exp.—On September 6, 1888, at 8.30 A.M., on Mont Dore, I exposed to the sun four vessels, which I withdrew at various intervals, and in which I measured the proportion of oxalic acid burnt.

	Solar Combustion %
After 2 hours	0 %
" 4 "	3 %
" 8 "	10 %
" 10 "	12 %

We see at the start the "dead time" of the beginning. We see, moreover, that from the fourth to the eighth hour, that is to say from 12.30 P.M. to 4.30 P.M., the combustion was twice as rapid as from 10.30 A.M. to noon, in spite of the gradual descent of the sun towards the horizon. During the last two hours, and notwithstanding the obliquity of the solar rays, which is already great at this time of the year, the combustion was still two thirds of what it had been between 10 A.M. and noon.

It is always the same, whether the total combustion be feeble, as it was at Mont Dore, or active, as I have at times found it in Paris. From the sum total of my results I think I may conclude that the progress of solar combustion does not remain constant during the whole of the day, and that instead of increasing towards noon, in order to decrease afterwards in proportion as the sun approaches the horizon, it, on the contrary, experiences a progressive acceleration which does not cease till the sun is near its setting.

Everything, then, goes on as if the sensitiveness which, as we have seen, a solution of oxalic acid attains if left to itself in darkness, were not by any means a maximum sensitiveness, and might be greatly increased in the light. I have in fact ascertained—and we shall presently see an example of it—that a recent solution of oxalic acid may be made very sensitive by a few hours' exposure to the sun, and so be brought up to the level of an old solution, or even beyond it. But then an unforeseen consequence appears: the sensitiveness acquired in darkness is persistent—might it not be perhaps the same with sensitiveness acquired in the light, so that the accelerating effect of a fine day might spread, as it were, in its totality, or at least in part, over the following day?

The following experiment proves in fact that a solution left for a whole day in the sun, and which has not been entirely oxidized, will retain for the next day a greater sensitiveness than another part of the same solution which was not previously insolated.

Exp.—There were exposed every day to the light four identical vessels, two of which were carefully examined at the close of each day, while the other two were left in reserve for the day following; on this day they were again exposed to the sun at the same time with the four new vessels of a second experiment. The total of combustion in the vessels which were exposed for two days was then compared with the sum of combustions in the vessels which were each exposed only one day. Some of the results which I thus obtained are as follows:

The day of September 2d, combustion 10 % } 34 % in all.
" " " " 3d, " 24 %
Both days together, 68 %.

The amount of combustion has therefore doubled. Here are the results of another experiment:

The day of September 4th, combustion 12 % } 23 % in all.
" " " " 5th, " 11 %
Both days together, " 38 %.

The difference points in the same direction as the preceding experiment; only it is not quite as great, because the two days, September 4th and 5th, were both quite indifferent days (page 28), whilst the day of September 3d in the first experiment was very fine.

To sum up, we see that the insolated vessel of the first experiment underwent on the second day a combustion of 68 − 10 = 58 per cent, while a new vessel suffered only an oxidization of 24 per cent. As to the second experiment, the corresponding figures are 26 per cent and 11 per cent; this shows that not only does the sensitiveness of the oxalic solution increase in consequence of insolation, but the gain continues during the night. Some experiments of the same kind, which I will not now explain in detail, prove that this excitation of sensitiveness by means of insolation, endures even to the second day after, in a solution which is kept in the dark after having been exposed for a day to the sun. It is only after three days, therefore, that traces of sensitiveness are no longer discernible. By that time, the insolated solution has nearly returned to the degree of sensitiveness which the mother liquid possessed, which seems thus to correspond to a kind of equilibrium. It is in fact remarkable that the different sensitive liquids which I have used in my long experiments and which were prepared at very different times, with the single precaution that they were not to be used before the lapse of several months, had all of them, at the moment when I used them, very nearly the same sensitiveness. It was on September 8th and 9th that I had to change my solutions at Mont Dore, and I availed myself of the fact that these two days were but indifferently fair, to interrupt my series and to compare again and again the old liquid with the new. The titre was always the same for both. Mr. Elfving compared likewise two solutions which I had sent him a year apart, and found in four days of experimenting the following corresponding figures for the old and the new:

			Old Solution.	New Solution.
1st	day,	combustion,	58 %	56 %
2d	"	"	52 %	51 %
3d	"	"	63 %	60 %
4th	"	"	42 %	35 %

The old solution was a little more sensitive, which is the usual rule. But the difference was trifling, and thus our former statement was confirmed (page 9). The oxalic solution, kept in diffused light, reaches a fairly constant sensitiveness in a few weeks, but this maximum, although stable, is not a *maximum maximorum*. It may be temporarily exalted in the sun, continue if the illumination continues, and return to its original level after some days of darkness.

In order to make this conclusion really valuable, we have to overcome one last objection. Might it not happen that the increase of combustion discovered on the second day in a vessel which had been insolated on the day before, might mean simply the suppression of the "dead time" at the beginning? Starting earlier, the combustion might better utilize the good hours of the day, and thus be enabled to go farther. A priori, the intervention of this cause does not seem to explain sufficiently the great difference observed. But it is safer to consult experience. It will be sufficient to cut the two days of observation by an intermediate examination and to discover the intensity of combustion during each one of the intervals. Thus it can easily be seen whether the vessels change at the same rate, after having recovered their "dead time," or whether the vessel which had been insolated on the previous day, still progresses more rapidly than its neighbor?

Exp.—On September 12, 1888, a fine day with a warm sun, and a few cumuli, there were exposed to the sun 4 vessels, Nos. 1, 2, 3, and 4.

Vessel 1 was examined

after 5 hours; combustion 10 per cent.

Vessel 2

after 9 hours; combustion 18 per cent.

Vessels 3 and 4 were put aside and exposed anew on the next day with two new vessels, Nos. 3′ and 4′. This day, the 13th, was very fine, with a few cirri in the morning. It changed a little for the worse towards evening.

Vessel 3′ was examined

after 5 hours; combustion 13 per cent.

Vessel 3

after 5 hours; combustion 44 per cent.

The difference is considerable and is certainly in part at least due to the suppression of the "dead time" in the vessel which was insolated on the day before. But this again is not all, for during the second half of the day, the insolated vessel kept up a much more rapid progress than the other, as the following figures clearly show:

Vessel 4′ examined after 9 hours; combustion 25 per cent.

Vessel 4 examined after 9 hours; combustion 62 per cent.

The acceleration in the solution which had been insolated on the day before, thus continued throughout the day, and while in the second half of the second day, the new liquid only showed an increase of $25 - 13 = 12$ per cent in its combustion, the liquid insolated the day before rose from 44 to 62, undergoing thus an increase of 18 per cent.

It will also be noticed that in the morning this same liquid had increased from $44 - 18 = 26$ per cent, while the new liquid experienced a combustion of only 13 per cent. Here has come in the double effect of suppression of "dead time" and that of the acceleration. The two solutions became a little more nearly equal towards evening, but the insolated solution continued its quicker progress.

Thus there can be no doubt that the insolation during the previous day continued its effects over the next day and the day after that. But this is not all. One fact, no less curious than the preceding, is that the sensitiveness due to the action of light, enables the solution to undergo in diffused light a combustion which is out of question as long as it has only its normal degree of sensibility, that is, the degree obtained by keeping for some weeks in a diffused light.

Exp. In August, 1889, at Noalhac near Aurillac (Cantal), at an altitude of about 700 metres, I prepared a solution of oxalic acid, part of which was left in a flask, exposed to a very feeble light, while another portion was exposed to the sun in a stoppered bottle. This was in order to see if the process of rendering the solution sensitive was necessarily accompanied by a process of combustion, or whether it could be accomplished without the latter. The experiment showed that the two effects are independent of each other. The solution contained in the closed flask had at its disposal only a very small quantity of dissolved oxygen, which it consumed, moreover, with but a slight diminution of its titre, but in one day of insolation it reached an intense sensitiveness, which was maintained for several days at the same rate by preserving it in a diffused light.

On August 30th, I exposed to the sun two vessels containing some of this insolated solution, and at the same time, two vessels of the same non-insolated preparation. The figures for solar combustion are:

18 and 19 per cent for the non-insolated, and
92 and 92 " " " insolated liquid.

The day was a very fine one; the flask with the insolated solution remained in the sun, but closed. On August 31st, two groups of two vessels each were prepared, one containing non-insolated, the other insolated solution. One of these groups was exposed to the sun, the other on a window-ledge, facing the north, where it received no light but that coming from the sky and dimmed somewhat by a slight dry fog. The figures found after 8 hours' exposure, for combustion in the sun and in diffused light, were the following:

Insolated liquid lost 63 per cent in the sun.
Non-insolated " " 21 " " " "
Insolated " " 19 " in diffused light.
Non-insolated " " 6 " " " "

The next day, September 1st, during a dark, threatening day, the same arrangement gave the following results:

Insolated liquid lost 50 per cent in the sun.
Non-insolated " " 13 " " " "
Insolated " " 6 " in diffused light.
Non-insolated " " 3 " " " "

Thus a previous insolation increases the rapidity of combustion, not only in direct light but also in diffused light. The experiment of September 2d shows, however, when compared with that of the day before, that this diffused light must have a certain intensity to make its effect measurable after some hours. But, viewed by itself, this experiment shows that even a dark day still has an accelerating effect upon a solution which has not seen the sky since the second day before.

The insolated liquid was from that moment kept in diffused light at the back of a room with but one window, facing the north. It was found that after a few days it had not sensibly changed in titre, but variation began to show itself at the end of a month. We thus see how here also, in spite of good conditions of preservation, the phenomena of slow combustion appear which have been observed since Wettstein in solutions of oxalic acid. Not insolated, this solution preserved in the same manner had remained much more stable, which shows that it is necessary to avoid exposure to light, even temporarily, or even in a carefully closed flask, of solutions of oxalic acid which are intended for processes of titration. The luminous impression, once received, persists and makes them much less stable—it continues, as we shall presently see, even after the liquid solution has been placed in darkness.

Exp.—Another experiment was begun identical with those that have just been described except that the flask which contained the insolated solution, sheltered from the air, was kept for three nights and two days in a cupboard of the laboratory before being distributed into vessels on September 6th. Unfortunately the day of the 6th was disturbed by cirri and cloudlets.
The insolated liquid lost 20 per cent in the sun,
Non-insolated liquid lost 7 per cent in the sun.
The oxidation in diffused light was insignificant.

The proportion of oxalic acid burnt in sunlight is, therefore, still, after 60 hours of obscurity, three times greater in the insolated solution than in the other. But the sensitiveness decreases afterwards and the difference soon ceases to be measurable after a day's exposure. We here meet again with that retrogradation which we have pointed out earlier, and which brings us back to normal sensitiveness.

I add, in order to close the subject, that this solar impression, which disappears slowly, is on the other hand produced very rapidly, and that, when investigating comparatively, with respect to the combustion which they undergo, the solution which I had exposed to the sun, in three flasks, and 1, 2 and 3 days, respectively, I have not been able to show that there was any essential difference between them!

I have left aside, in all which precedes, the question of the mechanism connected with both sensitization and combustion. The former goes on when the solution is sheltered from the air, and can take place only by a new arrangement of molecules. Combustion, on the other hand, takes place in contact with the air and possibly with the formation of ozone or of hydrogen peroxide. That is a question which must be investigated by itself. I purpose here only to put in evidence, as regards the constitution of the atmosphere, some properties and a variability of effects, not hitherto observed.

Metereological, Hygienic, and Agricultural Effects.

If we now return, with the results which we have obtained, to our investigation of the causes which provoke the rapid development of vegetation in the extreme northern regions, we see that those regions are superior to ours in a twofold aspect.

1. That cause which depends on the constitution of their atmosphere consists in this, that the absorption of the chemical radiations of solar light is there less great than with us. The actinic power at the level of the soil exceeds that which we have observed around ourselves at different hours of the day, and that in spite of a lower sun and a greater thickness of atmosphere, which the rays must traverse. These differences are due mainly to the fact that vegetation in the north sends into the air fewer oxidizable substances to form a screen.

2. The other point of superiority connected with the geographical situation consists in this, that in the extreme north, during the period of vegetation, the days are longer than in our temperate zones, and that the actinic power, at least so far as it may be measured by a solution of oxalic acid, increases more rapidly than the length of the day, and this out of all proportion. After a period of preparation, combustion begins, then accelerates so rapidly as to make up for time lost at the beginning, and finally, towards evening, reaches unusually high figures, such as are unknown to our regions. It is in this way that combustion has risen to

37 and 89 per cent on September 2 and 4, 1887.
79 and 80 per cent on September 9 and 11, 1888.
75 per cent on Aug. 27, 1888 at Helsingfors.

and this at a time when the highest figures, relatively to the same periods and with the same solutions, did not exceed 50 per cent and were even sometimes much lower in our country. In order to reach figures equal to those obtained in the Gulf of Finland, it was necessary for me in France to accumulate upon my vessels the radiation of two consecutive days. It may thus be said that, speaking generally, a day at the north is worth two of ours as regards actinic power.

Not only does the actinic effect of a fine day increase more rapidly than the length of the day itself, but it may actually spread itself over the next day, and the day after that, and thus make up, in some degree, for the absence of the sun. In like manner, a fine morning may render combustion more rapid even though the evening be dark and stormy. It is enough that the liquid shall have been made sensitive; and as this sensitization is the more rapid as the actinic intensity is greater, the atmospheric condition of northern countries favors them in this respect beyond us, and a new superiority is thus attained through the superposition and mutual emphasis of the other two causes.

Finally, the sensitiveness produced by a fine day continues for several days. A number of bad days, following each other, is consequently not a period of inertness and loss; it draws upon the store which was collected during fine weather. On the other hand, we have seen that the sensitiveness which was acquired in the sun, did not increase without limit, and that it reached quite rapidly a maximum beyond which it did not go. A succession of fine days, therefore does not develop actinic phenomena to an extreme. We here meet once more with the system of balancing which weakens great effects, increases small ones, and which has been pointed out with regard to so many other manifestations of the forces of nature.

Summing up the matter, then, it would seem that we have hitherto missed our way, in considering the chemical action of solar light as independent of locality and proportionate to time of isolation, or as furnished or measured by meteorological instruments. The first of these notions was purely instinctive and was suggested especially by the uniformity which was ascertained to exist at different points of the globe in so many other grand meteorological phenomena (such as the composition of the air, the average barometric elevation, the mean distribution of nebulosity, etc.) Instead of such a uniformity, we find, on the contrary, actinic climates, limited in point of surface, for they betray the local influence of the surface of the soil—limited also in point of duration, for they are due to two kinds of clouds which are subject, like the others, to the influences of place and season.

Misjudging thus local influences, only the first cause has been thought of, and all efforts had been directed towards measuring the duration of insolation. On this point, I think I have shown that the wrong way had been taken. The actinic force of a day is not the same for the same day, in different parts of the globe, and its effect increases more rapidly than its length; such is the principal lesson of this Memoir.

One step farther might be taken. We have just ascertained that in the solution of oxalic acid there takes place a kind of storing up of light, which shows itself in an increase of sensitiveness as regards phenomena of oxidation. Might not the oxygen which is present in the solution, or even that which is constantly dissolved there and transformed, might it not itself be rendered sensitive, and so be endowed with an oxidizing power which it could afterwards use in diffused light?

I have found nothing, while searching in this direction, with oxalic acid; this reagent, quite sensitive enough for the study of powerful actions, is not sensitive enough for such weak actions as that which I have just suggested. But I have been more successful with oxidizable substances of sharper reactions, so that the very smallest variations became measurable. This is the case with diastases; an almost infinitesimal quantity will produce very apparent effects, and it is, therefore, easy to trace their disappearance by oxidation in the liquids which contained them. With rennet especially the very smallest variations in quantity can be appreciated from corresponding variations in the time of coagulation of equal quantities of milk, so that this diastase is very convenient for study. By such means I found that it oxidized and disappeared in water which had been previously exposed to the sun, while it remained, if not quite intact, at least nearly so in the same water as freshly drawn from the hydrant. I also found that a glass flask exposed to the sun stored up on its walls enough chemical radiations to accelerate afterwards the oxidation of a solution of rennet, which was allowed to stand in the shade.

All these facts, upon which I do not insist because they go beyond the limits of this work, enlarge the field of those phenomena to which they apply. If isolated liquids and solids, may in certain cases, like our solutions of oxalic acid, acquire properties which they had not before, the phenomena of solar combustion may well extend below the surface, which has been directly illuminated, and assume in the general economy of the world an importance, no doubt as yet inferior to that of microscopic organisms, but certainly no longer to be neglected, as it has been heretofore.

Since I have entertained the views which I have developed in the preceding pages, I have investigated especially their agricultural and hygienic consequences.

As far as hygiene is concerned, I have shown more clearly I think than Messrs. Downes and Blunt that solar light kills the germs of microbes suspended in the air. I have proved, moreover, that this destruction was preceded by a veritable *attenuation.*

---

[1] *Annales de Chimie et de Physique*, 6th ser., vol. v., 1885.

I have ascertained since that this destruction and this attenuation go on in the superficial layers of the soil and even down to some depth. If, in the many attempts to count the microbes of the soil, it has so often been found that the number is less near the surface than at the depth of a few centimetres, we must attribute this result much rather to solar combustion than to desiccation. The sanitary action of oxygen, which is pursued and completed in the atmosphere, begins therefore, thanks to light, at the surface of the soil, and the healthiest countries are those in which the actinic power of the sun is greatest.

By a curious mechanism, which I have tried to make generally known, the solar action which neutralizes the microbes which it encounters, can act like them, and take their place. I have in fact shown in an extensive work [1] that the changes which carbohydrates undergo upon exposure to sunlight are exactly like those which they undergo under the action of ferments. Starting from the same point, these two modes of transformation, apparently so different, resemble each other not only in their variety and marvellous flexibility of conduct, but still more in their intermediary and final products.

Thus, invert sugar in alkaline solution, oxidized in sunlight, gives intermediary products which are colloidal and identical with humic acids, except that they are not nitrogenous. These black acids are afterwards consumed by light, exactly as we see in the bleaching of the black soil which the spade or the plow has turned up.

The extreme terms of the transformation of this sugar or of its humic derivatives are as numerous and as varied in solar combustion as when produced by the action of ferments. Thus, by contact with potash, or with soda, we obtain alcohol through an interior combustion which is identical with that produced during alcoholic fermentation. On the other hand, in the presence of baryta, no alcohol, but lactic acid is produced. In this there is analogy, not with alcoholic fermentation, but with lactic fermentation, and this analogy is all the closer since—as is recognized—there may be several lactic acids of different rotary power, which may be produced as well by the action of light as by that of fermentation.

This solar, lactic fermentation is accompanied by the production of acetic acid, as in the case of microbian fermentation. In other cases, butyric acid is formed, formic acid, oxalic acid—in short, all the ordinary residues of the ferment action. Finally, carbonic acid represents in all cases the extreme term of the change of organic matter into gas.

The luminous action, varying in quantity according to place and season, as the

---

[1] *Annales de l'Institut Agronomique*, vol. x., 1886.

different chapters of this Memoir have shown, may therefore differ in the quality of the effects which it produces. All these facts lend to the study of chemical radiation, an importance of the highest rank, and I shall consider myself very happy, if the first results contained in this paper shall lead men of science to new researches.

SUMMARY.

1. The oxidation of oxalic acid in a weak solution takes place mainly, and almost exclusively, under the influence of the chemical rays of solar light; it can, therefore, be used as an actinometric measure.

2. It depends on the concentration of the liquid, which for the best results should not exceed about three grammes per litre.

3. With an equal volume of solution, combustion decreases as depth increases; there is an absorption of chemical rays, although the liquid is and remains very transparent.

4. For equal depths of liquid, combustion is proportional to the surface, and consequently also to the volume.

5. It depends on the age of the solution, that is to say, of the time which has elapsed since preparation. As it grows older, an oxalic solution becomes more sensitive, and attains a certain maximum which is quite stable and quite regular. It is well to wait till this state of sensitiveness has been produced.

6. The daily combustion, such as is measured with sterilized liquids, varies from one day to another much more than any other meteorological phenomenon, and while subject to the influence of what we call "fine weather," and "overcast weather," it manifests very clearly other influences which are less visible.

7. It shows also the influence of the seasons, and manifestly exhibits a maximum in spring.

8. It is but feebly subject to the influence of altitude.

9. On the other hand, it betrays so strongly the presence of divers oxidizable essences or substances in the air, that we must consider local and daily variations as due to the presence in the atmosphere of actinic clouds, which are discoverable only by the reduction and absorption which they produce in the chemical radiations of sunlight.

10. The atmosphere of extreme northern regions is less absorbent than that of our temperate zones, and, consequently, at the same hours of the day, actinic radiation is more powerful, at the level of the soil, in the north than at the centre of Europe.

11. Northern countries add to this cause of superiority, which they owe to the constitution of their atmosphere, another, which is due to their geographical position, namely: that the actinic effect of the sun increases more rapidly than the duration of its presence above the horizon. The very long days of the north, during the period of vegetation, are, therefore, in their actinic effect, more active than an equal number of days in our temperate regions, and we can thus explain the particularly intense rate of the progress which vegetation makes in the vicinity of the polar circle.

12. This increase of sensitiveness which oxalic acid experiences in the sun, does not cease when the light begins to fade, and may continue several days. Hence follows a conclusion which may also be applied to our temperate regions: this is, that the actinic effect of a number of fine days in succession increases more rapidly than its duration, and also, that the effect of a fine morning is not lost by a dark and cloudy evening.

13. We must, therefore, give up the hope of finding, in the duration of a day or of solar action, a measure of its effects, and meteorological instruments, which accept such a proportionality, are to be rejected.

14. The importance of these actinic phenomena in the general economy of the world is great enough to make it necessary that we should approach the investigation by appropriate means.

SUPPLEMENT.

OBSERVATIONS MADE IN 1891 IN FRANCE AND ALGIERS.

Since sending my Memoir on Atmospheric Actinometry, I have been enabled by the courtesy of M. Gessard, Chief Pharmacist of the Military Hospital at Setif (Algeria), to make a number of combined observations in a temperate region and in a hot climate. It was interesting to discover whether we would meet here with the same differences as between the observations made in France and in Finland, that is to say, if for equal lengths of insolation the chemical activity of the solar rays would continue to diminish in proportion as we approach the equator, and as their calorific power increases.

For such a comparison the choice of the stations was of some importance. Setif is situated about eleven hundred metres above the level of the sea, on a buttress of the southern slope of the high mountains of the sea-coast, the chain of the Babers or the Bibans. Towards the south it overlooks from a height of two or three hundred metres an immense plain, which in its turn is bordered at a distance of 35 or 40 kilometres (22 to 25 miles) by a chain of not very high mountains, which cuts it off from another more extensive plain, the basin of the Hodna. Beyond this, separated again by an insignificant mountainous elevation, lies the Sahara and the desert climate, which makes its influence felt as far as the plain of Setif. This vast heating-centre south of the city frequently procures for the latter, towards evening, a fresh current of air from the north, and in ordinary times it stands on the boundary line where two contrary influences enter into direct conflict, the wind blowing from the coast and the high summits, and the burning wind from the desert. Thus Setif enjoys a relative freshness on certain days when the plain at its feet is given up to the full ardor of the sirocco, and when it even may happen that the cloud of dust, propelled by this wind, stopping at a distance of 15 or 20 kilos. from the town, screens the neighboring mountains at the very time when the atmosphere remains quite clear about Setif and the immediate surroundings.

The station which I have chosen in France for my comparative observations is also situated on the side of a slope, overlooking the plain of Vic-sur-Cère (Cantal), and 750 metres above the level of the sea. I might have gone higher, but I have already shown that the difference in altitude is of little importance. At all events it acted in the opposite sense to the phenomenon which I sought to verify. As a compensation, the climate of this station at Olmet is a temperate climate. The place lies on the line where the culture of the vine ceases and is in every respect equal to that of Fau, in the valley of Marmanhac, and of Noalhac, in the valley of Aurillac, where I had made my first observations.

Furthermore, the procedure of M. Gessard and myself was the same; we exposed, from 8 o'clock A.M. till 5 o'clock P.M., vessels containing the same solution, only, on account of the high temperature of Setif during the summer and of the evaporation caused by it, we had to pour into the vessels 20 cubic centimetres of oxalic acid, instead of 10, and place them, not upon wooden or stone supports, but upon the water of a great crystallizing pan. I need not say that at Olmet I followed the same practice. It is well known that the degree of solar combustion depends on the depth of the liquid, and this is the reason why the present series of experiments is not directly comparable with the preceding series. But it is sufficient for us that the experiments made in France and in Algeria should be comparable between themselves.

This being granted, I subjoin the results obtained by M. Gessard:

Date.	Solar Combustion.	Remarks.
July 2	12	
" 3	14	
" 4	12	Clouds.
" 5	13	Stormy weather. Sky covered at 3 o'clock.
" 6	16	Fewer clouds than on preceding days.
" 7	17	Clear weather. No dust.
" 8	62[1]	Cloudy at times. (See note below.)
" 9	18	Tempest. Dust. Sun obscured after noon.
" 11	40	Cloudy weather.
" 12	32	Fine weather.
" 13	22	Overcast weather; a few drops of rain.
" 15	25	Clouds, storms, dust repeatedly.
" 17	22	Fine weather. Hail-storm at 7 P.M.
" 18	22	The Southern mountain cannot be seen at 5 P.M.
" 19	24	No clouds. Very clear horizon.
" 20	22	Overcast from 2 to 4.30 P.M. Dust.
" 21	23	Overcast after noon. Downpour at 3 P.M.

In the following experiments, made in August and September, M. Gessard ascertained the direction of the wind and the temperature, as read on a thermometer

---

[1] One of the vessels was found to be submerged on this day, so that the result could not be correctly ascertained. The weather on this day did not essentially differ from that of the preceding and of the following days.

hanging in a northern exposure, against the wall of a house with lofty arcades, and consequently under a gallery formed by them. In the statements concerning the winds, the frequent violent changes of which we spoke at the beginning will be noticed.

Date		Solar combustion	Remarks	Temperature.			Winds (by the vane) at			
				Max.	Min.	Aver.	7.30	11	3	5
August	18	6	Clouds at noon. Overcast sky at 4. Rain at 4.30.	34.	15.2	31.5	W	W	N	SW
"	19	3	Quite a fine day. g. g. clouds at 2 o'clock.	30.2	14.	27.5	E	S	NNE	NNE
"	20	3	Sun rather overcast in the morning. Rain after 2 o'clock.	27.9	12.5	25.	SE	N	N	NE
"	21	3	Sun all day long and sky clear.	28.6	15.8	25.5	W	W	NW	N
"	22	8	The same.	31.1	17.5	28.5	W	W	N	NE
"	23	8	" "	32.6	18.6	30.	SW	W	S	SW
"	24	11	" "	33.2	17.2	31.5	SW	SW	S	SW
"	25	6	" "	31.4	17.	19.	SW	W	S	SW
"	26	8	Clouds in the afternoon.	32.6	17.8	29.5	SW	SW	S	SW
"	27	9	Clouds afternoon. Sun shines at 3 P.M.	31.8	16.2	29.5	W	W	NE	NE
"	28	8	Sun all day long.	31.3	16.3	28.5	W	SW	NNW	NNE
"	29	7	Same.	31.1	16.3	29.	SW	SW	SW	NE
"	30	7	"	31.6	18.6	30.	SW	SW	SW	NE
"	31	7	"	32.2	19.0	29.5	SE	SE	SE	SSE
September	8	9	Overcast. Much dust.	25.4	17.	29.5	E	S	SSE	S
"	19	10	Sun all day long	29.	15.6	20.5	SE	S	SSE	S
"	22	11	A few clouds all day long.	29.	14.8	27.	W	NW	W	N
"	23	11	Sun all day	29.4	17.7	26.5	W	NW	W	NW
"	24	11	Sun rather obscured, afternoon. Dust.	30.9	17.1	28	SW	SW	SW	SW
"	25	14	Overcast sun all day. Dust	30.8	17.	28.	S	SW	SW	S

When M. Gessard sent me the reports for August and September, he added what follows: "They seem to me to confirm the former. The combustions have not been more intense than in July. I notice, on the other hand, that during overcast weather they have not been inferior to those observed on days of full sunshine. The second fact which strikes me is this: that the quality of combustion should be maintained with such constancy in the two vessels under all circumstances. Thus, on the 11th September (I did not report it in the table), with a south wind blowing all day, raising the maximum temperature to 32° C., the contents of both vessels having evaporated, although they had been allowed to float upon the water, I had the curiosity to redissolve the residual acid and to test it: I found 8.4 c. c.

and 8.6 c. c., which corresponds to combustions of 36 per cent and 35 per cent. respectively.

It will be seen from all that has been said so far, that the daily actinometric combustions are quite as irregular in Algeria as in France, and have only a very remote connection with the external aspect of the sky and the clearness of the horizon. I have not been so fortunate as M. Gessard so far as the weather was concerned. The greater part of the month of August in the Cantal and a part of the month of September we had cloudy or rainy periods, and during this time observations were impossible. Availing myself of the fact that the method of comparison which we employed consists of a comparison of the finest days at the two stations, I shall here report only the figures noted down at Olmet during the rare times of fine weather.

Date.		Solar Combustion.	Remarks.
August	27	29 %	Fine day from beginning to end.
“	28	42 %	Fine weather, but rather heavy and stormy.
“	29	41 %	A fine day, although rather foggy.
“	30	35 %	A fine day, rather stormy. Some clouds.
“	31	41 %	A fine day. Some mist towards 4 o'clock in the west.
September	2	27 %	Clear in the morning ; rather foggy in the evening.
“	17	40 %	Quite a fine day in spite of g g. clouds. N. E. wind.
“	18	34 %	Cumulus covering ¼ of sky, all day long.
“	19	52 %	Less cumulus than the day before. Finer day.
“	20	60 %	A very fine day.
“	21	52 %	Rather stormy day.
“	27	28 %	A fine day ; few clouds.
“	29	23 %	An indifferent day.

Comparing this list with M. Gessard's we notice in the first place a coincidence between the days of August 27th, 28th, 29th, 30th, and 31st, which were either fine or very fine at Olmet and at Setif. Now if we compare the results of the daily combustion from 8 A.M. till 5 P.M. we find, respectively :

9, 8, 7, 7, and 7 for Setif ;
and 29, 42, 41, 35, and 31 for Olmet.

If we in like manner compare, leaving out the dates, the combustion on the finest days in France and in Algeria, we find again that it decreases with the latitude. This is the same conclusion to which we were led, when we compared the observations made in France and in Norway, and between the limits of the two stations at Helsingfors (lat. 60° 10'), and at Setif (lat. 36° 11'). This shows that the actinic effect of twilight during equal times of insolation goes on diminishing in proportion as we approach the equator and as the mean temperature rises.

It would be interesting to ascertain whether this law continues into the tropical regions. This is probable, but as yet is only a matter of conjecture. I have taken the proper steps to begin observations on this subject early next spring.

Whatever this extension may lead to, it is none the less unexpected to find that in our temperate regions, the most densely populated of the globe, the actinic effect of the sun is, so to speak, in the opposite direction to its calorific influence. The operation of this law on the flora cannot be doubted. But the future alone can tell us how this is brought about.

SMITHSONIAN CONTRIBUTIONS TO KNOWLEDGE.

— 1126 —

Hodgkins Fund.

A DETERMINATION OF THE RATIO (κ) OF THE SPECIFIC HEATS AT CONSTANT PRESSURE AND AT CONSTANT VOLUME FOR AIR, OXYGEN, CARBON-DIOXIDE, AND HYDROGEN

BY

O. LUMMER AND E. PRINGSHEIM

CITY OF WASHINGTON
PUBLISHED BY THE SMITHSONIAN INSTITUTION.
1898

The Knickerbocker Press, New York

SMITHSONIAN CONTRIBUTIONS TO KNOWLEDGE.

1126

Hodgkins Fund.

A DETERMINATION OF THE RATIO ($\varkappa$) OF THE SPECIFIC HEATS AT CONSTANT PRESSURE AND AT CONSTANT VOLUME FOR AIR, OXYGEN, CARBON-DIOXIDE, AND HYDROGEN.

BY

O. LUMMER AND E. PRINGSHEIM.

CITY OF WASHINGTON:
PUBLISHED BY THE SMITHSONIAN INSTITUTION.
1898.

ADVERTISEMENT.

The present memoir is the result of a series of investigations by Doctors O. Lummer and E. Pringsheim, of Charlottenburg, Germany, aided by a grant from the Hodgkins Fund of the Smithsonian Institution.

After a period of notable advance the kinetic theory of gases seems to have fallen into temporary abeyance, possibly from a fundamentally imperfect understanding of their behavior.

Progress in knowledge of this fundamental nature of gases may reasonably be looked for from interpretative researches on their thermal capacity, and the following paper may be regarded as a step in this direction.

Aside from its exceptional importance in thermodynamics, the specific heat ratio is of interest as affording a clue to the character of the molecule; and Messrs. Lummer and Pringsheim, using a new method, appear for the first time to have reached coincident results on the incoercible gases examined.

In accordance with the rule adopted by the Institution, the work has been referred for examination to a Committee consisting of Professor Doctor Friedr. Kohlrausch, President of the Physikalisch-Technische Reichsanstalt of Berlin, Doctor Carl Barus of Brown University, Providence, R. I., and Professor F. W. Clarke of Washington City; and, having been recommended for publication, the original memoir, submitted to the Institution in German by Doctors Lummer and Pringsheim, is herewith presented, translated into English by Doctor Barus, in the series of Contributions to Knowledge.

S. P. LANGLEY,

SECRETARY.

Smithsonian Institution,

Washington, June, 1898.

CONTENTS.

A DETERMINATION OF THE RATIO (κ) OF THE SPECIFIC HEATS AT CONSTANT PRESSURE AND AT CONSTANT VOLUME FOR AIR, OXYGEN, CARBON-DIOXIDE, AND HYDROGEN.

BY O. LUMMER AND E. PRINGSHEIM.

INTRODUCTORY.

The experiments detailed in the following pages are based on a method of research,[1] which in all its essential features we had carried through for air as far back as the year 1887. The data obtained in this original test were mutually accordant to within as little as $\frac{1}{4}$%, but their absolute value was decidedly too small, throughout.

The researches, however, were quite sufficient to convince us that the bolometric method of temperature measurement is well adapted for the *direct* determination of such increments of temperature as are met with in the adiabatic expansion of gases; but that the method, nevertheless, can be expected to lead to trustworthy results only when an extreme of sensitiveness and efficiency has been imparted to the bolometric thermometer. This must therefore be practically instantaneous in its registry (*i. e.*, free from inertia), and the effect of heat conducted either way through the terminals must be eliminated. It is to the latter source of error that we chiefly attribute the discrepancy in our earlier results.

In the meantime bolometric resistances[2] meeting every requirement had been successfully constructed. Thus it seemed reasonable to assume that in a repetition of the above experiments with the new bolometric material now available, the error due to terminal heat conduction might be reduced in any desirable degree. We were therefore fortunate in being able to repeat our work at the Physikalisch-Technische Reichsanstalt in consequence of a grant from the Hodgkins fund which

---

[1] *Verhandl. d. Physik. Ges. zu Berlin*, 1887, pp. 136–140.

[2] O. Lummer and F. Kurlbaum: *Wied. Ann.*, vol. xlvi., pp. 204–224, 1892; *Zeitschr. f. Instrumentenkunde*, vol. xii., pp. 81–89, 1892

was courteously placed at our disposal by the Smithsonian Institution in Washington. It gives us much pleasure again to tender to the Institution our grateful acknowledgments for the favors received.

The results of the present investigation were communicated by permission to the British Association at the Oxford meeting.[*] We purposely withheld the publication of the body of our work, however, inasmuch as we hoped to carry the experiments forward into regions of much higher temperature and to include these results, the preliminary preparations for which had long been completed, in a single memoir. In view of the technical difficulties encountered in the further development of our work, this plan was abandoned. It will take some time before the necessary experience for the construction of high-temperature baths of sufficient constancy is at hand.

I. THE METHOD IN PRINCIPLE.

The method used for the measurement of the specific-heat ratio of gases depends, in the present as in preceding investigations in the same direction, on the law of *adiabatic* expansion of the gas under treatment. For the case of a *perfect* gas expanding adiabatically from an initial pressure p_1 to a final pressure p_2, the ratio of absolute temperatures, T_1 and T_2, corresponding to p_1 and p_2, may be written ($T_1 > T_2$)

$$\frac{T_1}{T_2} = \left(\frac{p_1}{p_2}\right)^{\frac{\kappa-1}{\kappa}} \qquad (1)$$

where $\kappa = \frac{C}{c}$ is the ratio of the specific heats at constant pressure and at constant volume. From equation (1) κ is found as

$$\kappa = \frac{\log\frac{p_1}{p_2}}{\log\frac{p_1}{p_2} - \log\frac{T_1}{T_2}} \qquad . \qquad (2)$$

Hence κ may be computed if a perfect gas is permitted to expand adiabatically in such a way that p_1, p_2, T_1, and T_2 are all measurable. For the case of a gas compressed at the temperature T_1 as far as the pressure p_1, suddenly expanding to atmospheric pressure p_2, the three quantities p_1, p_2, T_1 are found with relative ease. The chief difficulty lies in finding the temperature T_2, or the final temperature of the gas which has been cooled by sudden expansion from p_1 to p_2; for the change of temperature from T_1 to T_2 must invariably occur in a very short time if the change of pressure is to be rapid enough to be compatible with the conditions of adiabatic expansion. On the other hand the cooled gas will not remain at the

[*] Report, British Association, Oxford, 1894.

temperature T_2 longer than an excessively brief interval, seeing that heat is continually poured into it from without.

II. The Method in Practice.

a. PLAN OF THE EXPERIMENTS.

To hold the charge of gas we made use of a large receiver of spun copper nearly spherical in form and about 90 litres' capacity.

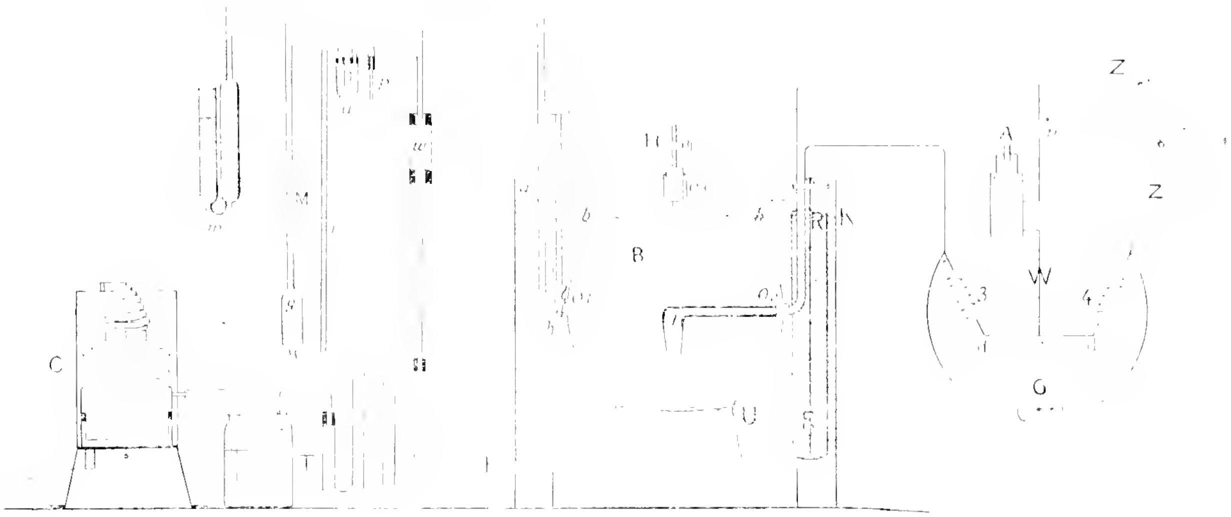


Figure 1.

This receiver B (fig. 1) contains three tubulated openings, one of which, shown laterally at O_1, may be closed with a stopcock h. This communicates in the manner seen in the figure with the manometers M and m, the drying apparatus T, and the compression pump C, by which the gas can be condensed in any necessary amount. If commercial oxygen, hydrogen, or carbon-dioxide is used, the gas may be tapped directly out of the high-pressure cylinders, through the drying train T into the receiver. The cock h is closed whenever the charge of gas is allowed to expand into the atmosphere.

The second lateral tubulure, O_2, is adapted to receive the bolometer strip s, which represents one branch (1) of the Wheatstone bridge W. The other branches (2, 3, 4) consist of suitably chosen resistance standards. For reasons relating to the heat-conduction discrepancy, the form given to the strip of the bolometer is as shown in fig. 2. The strip is cut from a piece of platinum-silver foil, in which the

Figure 2.

layer of silver is about ten times as thick as the coextensive platinum layer. In our definitive experiments the thickness of platinum foil used did not exceed

.00006 cm. With the aid of a suitable steel ruler and a thin sharp knife, we were able to cut a strip from the foil which between the rapidly narrowing end flaps *a* and *b* was but .02 cm. in breadth throughout a length of about 10 cm. After the end flaps (each about 4 cm. long and .5 cm. broad) had at their extreme edges been soldered to thick copper terminals, the middle of the strip was dipped in concentrated nitric acid to remove the silver from the platinum film to be used.

The resistance of the platinum bolometer strip etched off for a length of 7 cm. was about 80 ohms, while the resistance of the parts not freed from silver was computed as about .4 ohm, only .03 ohm of which makes up the total resistance of the flaps.

The third opening of the receiver is shown at O_3 and used as an avenue of efflux. Its diameter in the clear was 3 cm., and it was closed with a perforated rubber stopper, through which a wide glass stopcock *H* was inserted. Either by suddenly removing the rubber stopper, or in like manner wholly or partially opening the stopcock *H*, we had it in our power to vary the interval of expansion within a wide range.

A large zinc-lined wooden tank *K*, filled with water and surrounding the receiver served the purposes of a water bath. To compensate for the buoyancy of the receiver, sufficient counter pressure was applied through the perforated wooden yoke *b*, which on being forced down by the screw *a* held the receiver firmly down upon the annular tripod *C*. Two stirring appliances *R* were fitted to the diagonally opposite corners of the water bath. These consisted of zinc cylinders, open at both ends and containing an axial propeller-like rotating screw. Actuated by a small electromotor these screws were efficient in producing a flow of water in the zinc cylinders either from below upwards or in the reverse direction at pleasure. If the propelling screws within the cylinders rotate in contrary directions, a circulation of water in the bath will ensue from the surface downward near one of the stirrers, thence along the bottom to the opposite stirrer, which carrying the water aloft stimulates the return circulation along the surface. Small floating bodies like strips of paper gave evidence of the rate at which the current was moving.

b. MEASUREMENT OF TEMPERATURE.

To register the temperature of the water bath we used a calibrated thermometer graduated in tenth degrees. This was read off by a microscope of low power, provided with an ocular micrometer. Continually observing this thermometer, and adding small quantities either of cold or hot water according as the thermometer showed a leaning toward higher or lower temperatures, we succeeded in keeping the temperature of the water constant to about a hundredth of a degree.

frequently throughout a whole hour. Aside from this manipulation, the experiments were favorably circumstanced inasmuch as they were made in the subterranean chambers of the Reichsanstalt. On bringing the temperature into coincidence with that of the room, the observed changes would not exceed the mere fraction of a degree for hours.

Accurate measurement of temperature is of extreme importance in its bearing on the present experiments, since an error of but .02 C. in the datum for T, in the case of the pressure values actually employed, will affect the result by about 1 %. To facilitate the reading of the .01 C. required, all temperatures were so chosen as to make the mercury meniscus of the thermometer coincide very nearly with one of the division marks of the thermometer. After long practice we also learned to keep the temperature constant to .01 C. (by adding ice or hot water as occasion required and continued observation of the thermometer), even when the temperature of experiment lay considerably below that of the room. To be sure that the temperature was quite the same at all parts of the water bath, we made a special test in which, while the stirring device was in action, a sensitive thermometer was carried from place to place within the bath. Simultaneously, of course, temperature was kept constant in the lapse of time, at the single place of observation, by the means above set forth. The thermometer probe used in this test was a branch of one of Lummer and Kurlbaum's surface bolometers, carefully jacketed by a tight metallic case and appropriately insulated. The change of internal resistance experienced by this instrument gave us the necessary data for changes of temperature encountered during the excursions from place to place within the bath. These values, given on pages 18, 24, below, showed the variations of temperatures at any one place in the lapse of time, to exceed the differences of temperature for different positions within the bath at any given time, the bath being kept in action in the manner stated. We infer that

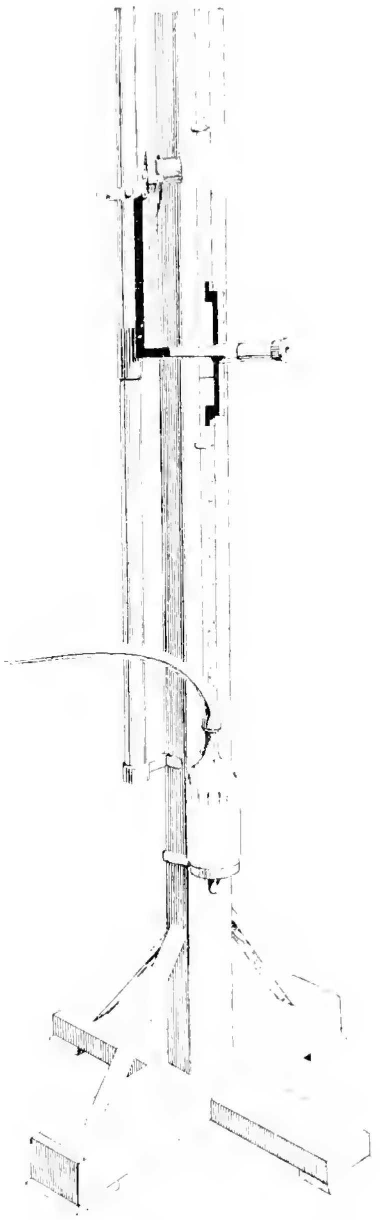


FIGURE 4.

the temperature throughout the whole bath must have been constant to at least .01° C.

c. MEASUREMENT OF PRESSURE.

In like manner the determination of the initial and final pressure of the experiment was pushed forward to a degree of nicety such as would not affect the γ values by more than 1 %. The final pressures were given by the barometer. We availed ourselves of Sprung's barograph as constructed by R. Fuess. The registry of this instrument is certainly correct to fractions of a millimetre, and an error of as much as .2 cm. in the value of the final pressure would have influenced the result by only 1 %. To be quite sure as to the identity of the final pressures with the atmospheric pressures for any given experiment, the efflux tubulure was kept open to the very end of the measurement, *i. e.*, until after the measurement of the temperature T_2 of the cooled gas.

The initial pressures or pressure excesses were registered both by a sulphuric acid manometer and by a mercury manometer of the construction shown in figures 3 and 4. The columns *m* (fig. 4) of the manometer were 4.5 cm. in internal diameter. The pressure tube of the mercury manometer *M* (fig. 4) was 1 cm. in diameter, with a reservoir *g* about 6 cm. in diameter. This instrument was chiefly used to measure pressure excesses during the course of the experiment, while the mercury manometer enabled us to reduce these pressures to their normal value in terms of the barometer. A simple microscope of low power, attached to a suitable slide on the sulphuric-acid manometer stand, enabled us to read off the position of the meniscus in terms of the attached scale. To obviate errors due to parallax, an incandescent mercury lamp was attached to the microscope carriage and moved with it. The scale being attached immediately behind the manometer tube, appeared enlarged when viewed through the part of the tube filled with acid. In this way the position of this meniscus could be read off at this manometer to about .02 cm., corresponding to about .0025 cm. of mercury. For decreasing pressures it was advisable to wait after each change of measurement, until the film of acid adhering to the sides of the tube had reentered the body of the liquid.

The open end of the sulphuric-acid manometer did not directly communicate with the air, but opened into it through a U-tube, *u* (fig. 4), containing calcic chloride and a capillary terminal *p*. In this way difficulties due to absorption of atmospheric moisture by the acid were avoided.

The mercury manometer naturally required much more precise reading than the other. Inasmuch as an error of .3 % in the determination of the pressure excess is equivalent to an error of 1 % in the result, it clearly follows that within this range of accuracy, pressure excesses of 3.3 cm., 6.6 cm., etc., must be read off within .01 cm., .02 cm., etc., respectively, along the mercury column observed.

To reduce the registry of the sulphuric-acid manometer to that of the mercury manometer we brought to bear on both the same pressure which had been observed during the course of a complete experiment; and for some time after its termination this pressure was maintained at the given value. Not until all pressure variations had fully subsided and permanent constancy of level was assured, did we proceed to the measurement of the equivalent mercury column. The telescope of the cathetometer was then alternately directed to the two meniscuses of the mercury manometer. In view of the large diameters of the tubes used, the middle parts of the terminal mercury surfaces were appreciably plane. Sharp lines of demarcation being desirable in the field of the cathetometer (preferably separating a dark shadow from a bright background), it was found expedient to illuminate the tubes of the manometer from behind. An incandescent lamp shining through a film of translucent tissue paper was therefore placed at such a level, that no light was reflected from either mercury meniscus into the cathetometer. Lamp and screen were movable up or down, so that the best illumination corresponding to any height of meniscus was attained. It is advisable to place the upper edge of the screen but very little above the mercury meniscus. At the same time the unavoidable specks of dust which float on the mercury surface are of much value in sighting. Our measurement of differences of level was correct to .01 cm. For an initial pressure of 3.3 cm. therefore, the value of $\varkappa$ obtained would not from this cause be discrepant by more than 1 %. A mercury thermometer suspended in the open tube of the mercury manometer showed its temperature. The excellent cathetometer used in these measurements was placed at our disposal by Mr. G. Hansemann, a courtesy for which we take pleasure in expressing our indebtedness.

d. MEASUREMENT OF THE FINAL TEMPERATURE, T_2.

Two distinct measurements are necessary to complete the determination of T_2. The decrement of resistance experienced by the bolometer strip while the pressure of the expanding gas falls from p_1 to p_2 is first to be found. Thereafter this electric datum is to be expressed in its equivalent of temperature.

1. Measurement of the initial pressure p_1, corresponding to the resistance increment w_1, w_2.

Suppose the initial conditions to be fully established, and let the bolometer strip be at the temperature T_1 of the gas, compressed as far as pressure p_1. Let the resistance of the strip be w_1. Suitably selecting the correlative resistances *2*, *3*, *4* of the Wheatstone bridge (fig. 1), the sliding contact may be so moved that the galvanometer is without current, indicating the usual balance of resistances. To be in correspondence with the approximate resistance (80 ohms) of the bolometer strip, the branch *2* consisted of a set of standards Z (given in full in fig. 5), the resistance of which could be made very nearly equal to that of the strip. The branches *3* and *4* contained coils suitably wound of standard wire, having about 75 ohms apiece. One end of each of these was connected with the bridge wire d.

The storage cell A, short-circuited through a resistance box, furnished the current. From two points of the box measuring currents of suitable magnitude could thence be tapped into the bridge. Care was taken to keep down the intensity of these currents, in order that appreciable heating of the bolometer strip would not have to be feared. Thus the galvanometer G when in adjustment showed no deflection, either on closing or on opening the circuit at the key n.

When the electrical or thermal condition has thus become stationary and the stopcock O_3 of the receiver is then suddenly opened, the gas will precipitately expand, cooling off both itself and the bolometer, and the galvanometer now shows a definite deflection. It is our problem to find the temperature T_2 of the strip at the instant when the *temperature depression of the gas is a maximum*, by availing ourselves of the electrical registry w_2. Let us assume in the first place that the temperature of the strip and that of the surrounding gas are at all times identical. Instead of considering the initial pressure p_1 given, to find the resistance decrement $w_1 - w_2$ corresponding to the pressure decrement $p_1 - p_2$, let us preferably adopt an inverse method in the following way: Start with a given resistance decrement $w_1 - w_2$; then by trial and error continually change the initial pressure p_1 until the resistance w_2 of the bolometer strip exactly corresponds to the maximum temperature depression of the gas. No doubt this is a somewhat cumbersome method, but it has the advantage that the galvanometer is used with the needle in the zero position only. It is at least practicable in the definite and final measurements, after the approximate values of the correlated quantities $p_1 - p_2$ and $w_1 - w_2$ are already known.

The approximate values referred to can be found either by computing backwards from known values of κ, or by the following direct procedure. At the gas pressure p_1 and temperature T_1 let the bridge be adjusted. Then let the resistance of the standards Z be reduced from W_1 to any suitable value W_2. The bridge is thereby thrown out of adjustment and the galvanometer needle will show a deflection. For convenience in designation let the direction of this deflection be called

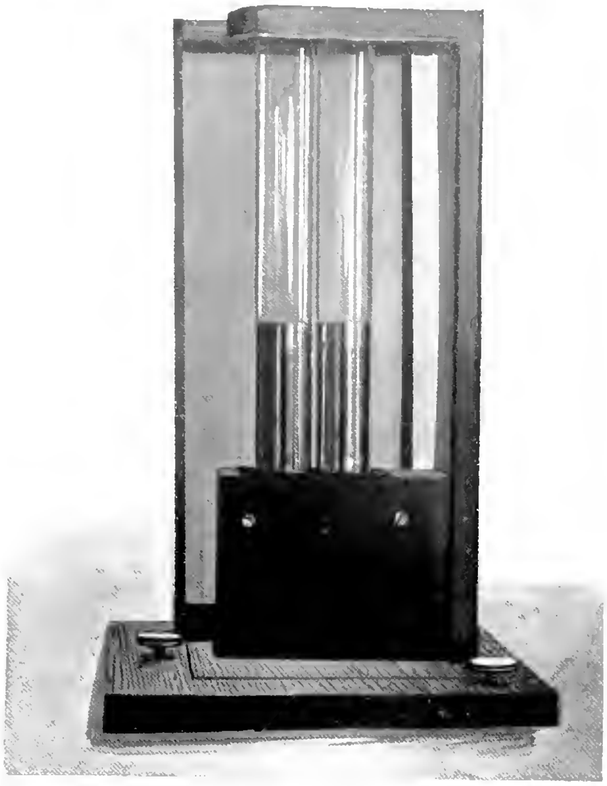


FIGURE 3

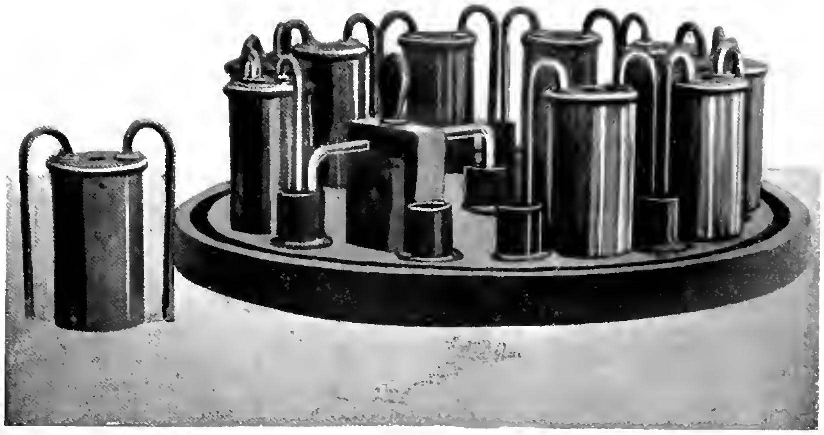


FIGURE 5

positive or negative according as the resistance in Z is larger or smaller than the equilibrium value. When the deflection due to the changed resistance in Z has become permanent, let the receiver be opened and note the effect of expansion on the galvanometer needle. Then according as the arbitrary change of resistance at Z is too large or too small, the needle will move beyond its normal position of equilibrium, or it will stop and return before reaching it from the new position of equilibrium. Owing to the inertia of the needle such results are not very accurate, and they are in large measure dependent on the rate of efflux of the gas. A rather insensitive galvanometer (or one made so by proper shunting) is necessary in these trials because of the relatively great resistance decrements encountered.

If it be granted that the temperature of the gas is always identical with that of the bolometer strip, and that furthermore the maximum of cooling coincides in date with the maximum elongation of the needle, then in addition to furnishing approximate values for w_1-w_2 and p_1-p_2, the experiments throw light also on the time consumed by the gas in passing to its lowest temperature.

Guided by this introductory work we were able to avail ourselves of the following much more accurate method without unduly sacrificing time. Let the pressure p_1 (known approximately from the preceding experiments) be established, and let the bridge be adjusted for the temperature T_1. The approximate value w_1-w_2 corresponding to p_1 being given, let the current be broken and the resistance of the standards Z be lowered from W_1 to W_2, without change in the position of the sliding contact c. While the bridge is thus thrown out of adjustment and the current broken, the gas is allowed to expand, but the current[1] is to be made by closing the key n of the bridge only after the bolometer has reached its minimum resistance.

After some practice it was always possible to so change the initial pressure by small amounts and so vary the estimated period of expansion, that the needle of the galvanometer remained quite at rest[2] for some time after making the current.

When the correct pressure p_1 has been found, this value may easily be checked, since for initial pressures either slightly less or slightly greater than the true value the galvanometer will show positive or negative deflections, respectively; and thus the datum p_1 can be enclosed between very narrow limits.

---

[1] It was found preferable to close the current in the battery circuit, not in the galvanometer circuit, in order to obviate errors arising from the presence of thermoelectric currents in the bridge. No temporary thermocurrents arise during the efflux of the gas, as we proved by special efflux experiments made for a circuit open at n. The galvanometer needle remained quite at rest.

[2] We owe this method ("Einspringmethode") to Dr. Kurlbaum, who took part with us in the original experiments in 1885.

The galvanometer used in these experiments must obviously be provided with a needle which will follow the changes of current in the bridge as quickly as possible. Hence we specially constructed a small galvanometer on the model of Lord Kelvin's instruments. The mirror was suspended from a quartz fibre 5 cm. in length, and carried on its rear face a sufficient number of small lamellar magnets. Deflections were read off with scale and telescope placed at a distance of about 200 cm. from the galvanometer.

To guard against the effect of external magnetic disturbances on the galvanometer, we enclosed it in a double envelope of soft iron. The walls of this chamber were 2·5 cm. in total thickness of solid iron, and were perforated by only a small opening suitable for observing the mirror. Two astasizing magnets were specially provided, one of them placed above the galvanometer on a plate with leveling screws, the other lying on the galvanometer bracket. The latter was additionally useful as a directing magnet. The period of the needle in the final experiments was about 4 seconds, so that a single throw was completed in 2 seconds.

We estimated the period of expansion ("Einspringzeit"), *i. e.*, the time which is to elapse between opening the receiver and closing the galvanometer-circuit, by the beats of a metronome, and, after some practice, found it fully vouched for to a fraction of a second. This interval is dependent on the size of the efflux pipe.

2. *Reduction of the resistance increment, w_1-w_2, to degrees of temperature.*

Having found the resistance w_2 corresponding to the instant of maximum temperature depression, we next proceeded with the measurement of T_1-T_2, the temperature equivalent of w_1-w_2. For this purpose, the Wheatstone bridge was first put into balance for the temperature T_1 of the bolometer strip, without, however, compressing the gas. Tests were applied to ascertain whether or not the strip resistance was still w_1 as required. Thereafter the resistance at the standards, Z, was changed to W_2, and a corresponding depression produced, from without, in the temperature of the water bath (and therefore also of the strip), until the bridge again gave evidence of a balance by reason of absence of current in the galvanometer. This condition was maintained for some time, throughout the whole of which the needle showed no deflection on closing the bridge circuit. The temperature of the bath was now read off and considered identical with the temperature T_2 sought. The datum was corroborated by returning again to the initial temperature T and noting whether w_1 had simultaneously regained its original value.

The advantages which we claim for the present method of reducing w_1-w_2 to T_1-T_2 are not far to seek: In the first place the experiments take but little time, while in the second almost all the corrections which are usually to be applied in resistance measurement are here insignificant, even when temperature increments of .01 C. are in question. For neither w_1 nor w_2 nor their differences need be known in absolute value. The position of the sliding bridge contact, c, alone requires careful attention. This, together with the resistance standards Z in branch 2 of the bridge, including the necessary terminal and connecting wires, must be the same and similarly circumstanced during temperature measurements, as during the actual measurements relative to changes of gas pressure.

Our resistance standards were made of manganine wire. Thick copper terminals and yokes, dipping into large mercury troughs, enabled us to connect the individual units of Z at pleasure. All the connection pieces were stout and of copper wire. Hence changes of temperature in the laboratory were quite without influence on the resistance measurement.

III.—SYSTEMATIC ERRORS.

Before proceeding to a report of the experimental data, we will endeavor to form some estimate as to the effect of systematic errors on the results. The chief assumption in the present and all preceding and similar methods is fundamental: Even supposing the intrinsic equation for the perfect gas to be fully applicable to the actual phenomena, what assurance have we that the expansion obtained is truly *adiabatic?* Rigorously considered, none; for heat will certainly gain access into the interior of the gas. This heat enters partly by conduction or convection, partly by radiation, and its influence on the results will be such as to make the values found for $\varkappa$ smaller than the true values. The influx of heat due to conduction comes partly from the walls of the receiver, partly by direct metallic conduction from the terminals and flaps of the bolometer strip. The former source of discrepancy occurs uniformly in all experiments in which measurements are made relative to an expanding gas. It is just in this respect that the present procedure for $\varkappa$ measurement has distinct advantages over all earlier methods; for these determined T_2 indirectly, by the aid of a special pressure measurement; and therefore the total heat conducted inwards from the walls of the receiver must have entered the results as an error. In our experiments, however, the bolometer strip is suspended in the centre of a large sphere and that part only of this heat can be effective which moves as far as the bolometer through the concentric layers of gas. In virtue of the low order of heat conduction in gases, the time in which heat can reach the centre is so long an interval, in spite of convection, that appreciable rise of temperature at the bolometer cannot occur until the expansion is complete and T_2 fully measured. The superiority of the present method of attack is evidenced, for instance, by results which show all resistance changes in the bolometer to be independent of the time of efflux, within time limits as broad as 2 to 8 seconds, in the case of air. True, in the best of the earlier experiments, the heat influx from conduction from the walls of the vessel is of serious moment only for the better conducting gases, since the receivers used were all of large capacity. *Röntgen*, however, openly acknowledges that the value of κ for hydrogen found in his experiments must be considerably below its real value. We therefore refer to it as conclusive evidence in favor of our method, that, at variance with the results of all earlier investigators, our method actually gives us a larger κ-value for hydrogen than for air.

Neither can the heat which enters by metallic conduction along the electrical terminals of the bolometer adjustment have produced any serious rise of temperature—certainly not in that part of the gas immediately around the strip. The thin film of pure platinum by which the measurements are virtually made, is free from silver and quite distant from the walls of the receiver. It is, moreover, placed *below* the levels of the terminals, so that true conduction heat only and not convection heat can reach it. For this reason the bolometer temperature remains constant even for several seconds after the completed expansion of air.

Regarding the heat imparted by the bolometer to the gas, the following inferences may be drawn. We have intimated that the measuring current was always reduced to so small a value as not appreciably to change the temperature of the bolometer strip. Hence we may abstract from the Joule heat set free within the film altogether. Similarly the heat which the bolometer strip gives up to the expanding gas is negligibly small: the thermal capacity of the strip, in view of the dimensions stated, is only about .000 007 gram calories. This is about equivalent to the thermal capacity of $\frac{1}{40}$ cm^3 of air. Similarly the heat removed from the silver-covered parts of the bolometer is without moment, for these cool very rapidly.

Thus it happens that at least those regions of the gas which immediately surround the etched part of the platinum strip may be regarded as screened from all heat conduction. They therefore expand quite adiabatically.

We have now to consider the question in what degree the temperature Z_2 of the gas after expansion, coincides with the actually measured minimum temperature of the bolometer strip. Since the temperature of the bolometer is constant for several seconds during the observation of Z_2, it follows that the bolometer temperature can only differ from that of the gas if there is a permanent flow of heat into the strip. In such a case a stationary distribution of temperature is conceivable, in which the bolometer would impart heat to the gas at the same rate in which it receives it. We can but acknowledge that there must be accession of heat in the bolometer from the following three sources: (1) as the result of electric current in the strip (this, as we have already seen, being negligible); (2) as due to conduction through the terminals; (3) as due to direct *radiation* impinging upon the strip from the walls of the receiver.

To treat the second case first: the heat received by the strip from the thick terminals may be approximately computed,—at least with reference to the error resulting. We will assume for this purpose that the terminals retain their initial temperature during the whole interval of expansion. Let the bolometer strip be a thin straight conductor, one end of which is kept permanently at the temperature ϑ_0 of the terminals, while the surrounding air is at the temperature ϑ_1. Let x be the distance of any point of the strip from the terminal end at temperature ϑ_0, and let ϑ be the temperature at this point at the time t. Hence by Fourier's equation of the temperature distribution in an infinitely long rod subject to radiation

$$\frac{\partial \vartheta}{\partial t} = a^2 \frac{\partial^2 \vartheta}{\partial x^2} - f^2 \left(\vartheta - \vartheta_1\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

wherein

$$a^2 = \frac{k}{c\,u},\text{ and } f^2 = \frac{h\,u}{c\,u\,q}.$$

and k denotes the coefficient of internal heat conduction.
h, the coefficient of external heat conduction.
c, the specific heat of the strip.
u, its density.
q, the area of a right section.
u, the circumference of a right section.

But the thickness, d, of the strip is negligibly small as compared with its breadth: therefore

$$\frac{u}{q} = \frac{2}{d}.$$

At the close of the expansion the thermal distribution is stationary along the wire as observation has shown. Hence $\frac{\partial \vartheta}{\partial t} = 0$, and equation (3) becomes

$$a^2 \frac{\partial^2 \vartheta}{\partial x^2} = f^2 (\vartheta - \vartheta_1) \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

If for $x = 0$, the temperature of the strip, we put $\vartheta = \vartheta_0$, and for $x = \infty$, we put $\vartheta = \vartheta_1$, the integral of equation (4) is

$$\vartheta - \vartheta_1 = (\vartheta_0 - \vartheta_1)\, e^{-x.f/a} \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

where $\frac{f}{a} = \sqrt{\frac{h}{k} \cdot \frac{2}{d}}$.

The following values may be assumed for the middle or etched part of the platinum strip:

$k = 10,$ $a = 21,$
$h = .003,$[1] $d = .0006,$
$c = .03,$

all quantities being here given in terms of milligrammes, millimetres, and seconds. Thus f/a is very nearly 1 and we obtain

$$\vartheta - \vartheta_1 = \left(\vartheta_0 - \vartheta_1\right) e^{-x} \quad \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Hence when the gas cools down as far as $\vartheta_0 - \vartheta_1 = 15°$ C., we find for

$x = 0.1$ cm $\vartheta - \vartheta_1 = 6°$ C.,
$x = 0.5$ cm $\vartheta - \vartheta_1 = .1°$ C.

If, therefore, the very thin silver-free platinum film were soldered directly to the stout copper terminals, a fall of temperature would be manifest at the ends of the platinum strip, the influence of which would be far from negligible in its bearing on T_2.

In view of the interposition of the gradually narrowing or arrow-shaped flap of platinum and silver between the terminals and the effective bolometer strip, the distribution of temperature is materially changed. For the flap in question the constants may be estimated as follows:

$k = 109,$
$h = .003,$
$c = .06,$
$a = 10.5,$
$d = .0066,$

all taken, as before, with reference to milligrammes, millimetres, and seconds, while h is entered unfavorably with a value decidedly large. In this case the quotient f/a is found by computation to be .09, and the temperature distribution for $\vartheta_0 - \vartheta_1 = 15°$ is now such that at a distance of 3 cm., the increment is but 1° C. The effect of using the end flaps of silver is thus a reduction of temperature from the terminals to the strip, fast enough to quite wipe out any serious discrepancy due to unequal temperature in the strips.

In view of the good conduction of electricity by the silver flaps, furthermore, the change of resistance due to change of temperature is equally inappreciable. Thus any marked discrepancy due to conduction of heat along the terminals to the

---

[1] This number has been obtained for thick rods of iron and German silver. We were obliged to enter it, not having found any special value for platinum. Clearly the quantity h cannot in any real case be a constant. It must increase very rapidly with the decreasing diameter of a given rod. Thus the value above assumed is considerably too small. For very thin rods Cardani finds $h = .06$ (Nuov. Cim., [3], vol. 30, pp. 33–67, 1891). If a larger value for h than the above is put into the equations, the results obtained would be more *favorable* to our argument than those given in the text. Thus if $h = .06$, and $x = 0.1$ cm., $\vartheta - \vartheta_1 = 14°$.

bolometer strip seems to have been effectually excluded in the form of experiment stated.[1]

We may also use the Fourier equation to find in what degree the platinum strip coincides with or follows the temperature of the gas. For simplicity we will assume that the gas temperature sinks from its original value (ϑ_0), at a constant rate in the lapse of time. In other words, put

$$\vartheta_1 = \vartheta_0 - b\,t \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

If now we neglect the heat flux from the ends of the bolometer strip toward the middle,

$$\frac{\partial^2 \vartheta}{\partial x^2} = 0,$$

and $\vartheta = \vartheta_0$ for $t = 0$. The integral of the general equation (3) thus becomes

$$\vartheta - \vartheta_1 = \frac{b}{f^2}\left(1 - e^{-f^2 t}\right) \ldots\ldots\ldots\ldots\ldots (8)$$

which for $t = \infty$ takes the simpler form

$$\vartheta - \vartheta_1 = \frac{b}{f^2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

The difference ($\vartheta - \vartheta_1$) between the temperature (ϑ) of the bolometer strip and the temperature (ϑ_1) of the air has therefore a maximum value of b/f^2. For the platinum measuring strip (silver removed), the above constants show $f^2 = 15$. Hence the bolometer will coincide in temperature with the air after about 1/15th second. However, since b has been taken very decidedly too small, the real case is correspondingly more favorable. With this deduction our observations agree; for the bolometer reached the stationary state immediately after the noise due to outrush of gas on expansion had subsided.

The last of our sources of error, viz., internal radiation, remains to be discussed. By this agency the bolometer permanently receives heat from the environment, since the walls of the receiver B retain their initial temperature T_1. But this heat, which is proportional to $T_1 - T_2$, may be computed only if the values of the emission and absorption coefficients of the reciprocating bodies were known. In the absence of satisfactory data for these quantities we made an endeavor to determine the effect of radiation experimentally.

With this end in view, we covered the silver-free part of the bolometer strip, galvanically, with platinum black,[2] and then repeated the expansion experiments

---

[1] If with the same constants and in the same manner the fall of temperature be computed for our original device of a bolometric spiral of silver wire, .004 cm. in diameter, the results are such as fully to account for the difference between our earlier values and the present.

[2] According to the recipe given by Lummer and Kurlbaum, *cf. Verh. der Physik. Gesell.*, Berlin, June 14, 1895.

with the blackened strip so obtained. The high absorptive power of platinum black led us to anticipate an increased temperature difference between the bolometer strip and the air, since this difference, due to the influx of radiant heat from the walls of the receiver, would more appreciably affect the black strip than the bright strip of the usual experiments. Indeed the temperature differences severally encountered should be in the ratio of the absorptions in the two cases. We made a special measurement of the relative absorption of bright platinum and platinum covered in the manner in question, by exposing two surface bolometers, one of which contained the bright platinum foil and the other the platinum-blacked foil, to the radiations of warm water in a copper vessel.[1] These investigations showed that platinum black absorbs the radiations from a copper surface for the temperature interval of 100° C. to 30° C., nearly fifteen times more powerfully than bright platinum. Hence as the change of κ, due to radiation, is now a small quantity, it suffices to deduct the κ value computed by equation (1) for a blackened bolometer strip from the value obtained under otherwise like conditions but with the bright bolometer strip, to divide this difference by 14, and eventually to add the correction so found to all κ values corresponding to uncovered bright platinum foil. This correction is in fact so small that we deemed it sufficient to determine it for air only, and to apply it without further change to the values for the other gases.

IV.—OBSERVATIONS.

a. AIR.

We will premiss the present section by communicating a few tables taken at random from our journal of observations, in order to afford an insight into the general character and the accuracy of our results.

As an example showing the consistency of the results in relation to velocity of efflux, we may cite the pressure measurements for *air* made on the 12th of June, 1893. For an interval of expansion ("Einspringzeit") of 12 seconds for the case of the smallest, and of 2 seconds for the largest efflux opening, the data contained in the two following tables were respectively obtained. The first column in each shows the numbers read off on the scale of the sulphuric acid manometer[2] directly. In the second column + shows that the pressure was too large, − that it was too small, while ± denotes a correct pressure value. The third column contains data for the position of the sliding contact on the Wheatstone bridge, and the fourth

---

[1] We wish in this place again to thank Mr Kurlbaum for his active participation in these preliminary experiments.

[2] The numbers refer to an arbitrary scale, and do not show the height of the column of acid at once. To find the pressure in centimetres of H_2SO_4, they must be increased by about 26. *Cf.* data for comparison in table, pages 20, 22.

the temperatures read off on the mercury thermometers. Throughout this temperature measurement the balancing resistance W_1 inserted at Z was

$$70 + 10 + 2^* + 1 + .2 + .2^* + .1 + .5 + 2,$$

of which 2 ohms were inserted before opening the receiver; hence $W_1 - W_2 = 2$ ohms.

The following results were therefore found on July 12, 1893, 12$^{\text{sec.}}$ being the period of efflux:

EFFLUX TIME 12$^{\text{SEC}}$; JUNE 12, 1893.

Manometer.	Pressure.	Bridge.	Temperature.[1]
Mark 25.05	—	598	14.63° C.
25.12	—	594	14.61
25.22	±	595	14.62
25.35	+	596	14.63
25.27	+	597	14.64
25.20	±	597	14.63
25.20	—	598	14.63
25.28	+	598	14.63
25.25	+	597	14.63

These data show that 25.23 cm. is the correct value at the pressure manometer, since 25.20 cm. is obviously low and 25.25 cm. too high.

The data found on the same day for the smallest efflux time of 2 seconds are similarly detailed as follows:

EFFLUX TIME 2$^{\text{SEC}}$; JUNE 12, 1893.

Manometer.	Pressure.	Bridge.	Temperature.
Mark 25.25	+	597	14.63° C.
25.21	+	597	14.63
25.17	+	597	14.64
25.08	+	597	14.63
24.96	—	597	14.63
25.00	±	596	14.63
25.04	+	596	14.63

To accord with this table, 25.00 must be considered as the pressure value most nearly correct; and indeed the galvanometer needle during this observation remained absolutely at rest for several seconds after expansion. The pressures corresponding to 12$^{\text{sec.}}$ and to 2$^{\text{sec.}}$ of efflux time, differed on that date only by .23 cm. of sulphuric acid or by .023 cm. of mercury. True, the expansion can no longer be considered adiabatic when the efflux time is as large as 12 seconds, and yet this large variation of the experiment does not change the κ value sought, by more

---

[1] All the temperatures given are corrected values.

than the equivalent of the pressure difference, or in consideration of the Z_1 values applicable, by more than .2 %.

A third complete measurement corresponding to 6sec of efflux, gave us 25.03 cm. as the correct pressure value at the sulphuricacid manometer.

The agreement between the reduced values of observations made under like conditions on different days was equally satisfactory.

The temperature measurements corresponding to the experiments to which the above tables apply showed for the resistance W_2 at Z,

$$W_2 = 72 + 10 + 2^* + 1 + .2 + .2^* + .1 + 5.$$

that there was a balance in the Wheatstone bridge for the temperatures contained in the following table. This table, moreover, gives a good exhibit of the constancy of temperature in the water bath, here definitely below the temperature of the room.

Temperature	Time
8.02° C.	11 46
8.01	11 55
8.00	12 5
8.00	12 10
8.00	12 15
8.00	12 20
8.00	12 25

Thus the temperature of the air imprisoned at a pressure excess of 25.00 cm., falls during adiabatic expansion from 14.63° C. to exactly 8.00° C.

The pressure comparisons made on June 13 and belonging to the given example are among the following data, where the temperature of the mercury was 18° C. Owing to motion of the mercury columns in the tubes an even number of observations is made for one limb and an uneven number for the other.

	Position in the Sulphuric Acid Manometer	Mercury Manometer.	
		Upper Limb.	Lower Limb.
	25.15		8.76
1		15.32	8.77
		15.32	
	25.15		8.78
	25.15 [cm., H_2SO_4] =	6.55 [cm., Hg.]	
	25.08		8.79
2		15.30	8.79
	25.10	15.28	8.79
	25.09 [cm., H_2SO_4] =	6.50 [cm., Hg.]	

Hence

Division mark 25.00 H_2SO_4, = 6.47 cm., Hg. at 18° C.
" " 25.00 H_2SO_4, = 6.45 cm., Hg. at 0° C.
Initial temperature T_1 = 272.4[1] + 14.63 = 287.03,
Final temperature T_2 = 272.4 + 8.00 = 280.40.
The barometer height was found to be 75.97 cm. of Hg.

Thus we find

Initial pressure : p_1 = 75.97 + 6.45 = 82.42 cm.,
Final pressure : p_2 = 75.97 cm.,

whence

$$\kappa = \frac{\log p_1 - \log p_2}{\log p_1 - \log p_2 - (\log T_1 - \log T_2)} = 1.4021$$

The following tables are to show in what degree observations made on different days, but under like conditions, agree with each other.

EFFLUX TIME 5^{SEC} ; JUNE 13, 1893, 2^H P.M.

Manometer.	Pressure.	Bridge.	Temperature.
Mark 25.12	+	593	14.63° C.
24.93	—	593	14.64
25.10	+	590	14.63
25.05	+	591	14.63
24.95	—	591	14.63

The barometric height for the day was 76.01 cm., and the value of κ computed for 25.00 at the acid manometer becomes

$$\kappa = 1.4019$$

when the pressure comparison cited above is inserted.

The following table was obtained on the morning of the same day, the barometric height being 76.06 cm. Hg.

EFFLUX TIME 2^{SEC} ; JUNE 13, 1893, 12^H M.

Manometer.	Pressure.	Bridge.	Temperature.
Mark 25.02	—	586	14.61° C.
25.17	+	594	14.64
25.12	+	597	14.63
25.07	+	593	14.63
25.10	+	595	14.63

The same pressure, 25.07, at the acid manometer was obtained for an efflux time of 6 seconds, while the needle of the galvanometer remained motionless for 8 seconds. Availing ourselves of the above pressure measurement we thus obtain

$$\kappa = 1.4012.$$

---

[1] The reasons for preferring − 272.4° C. to − 273° C. as the position of the absolute zero of temperature will be given on page 25.

Several series of experiments which after a long interval of inactivity were obtained with a new sulphuric-acid manometer and a more accurate cathetometer are now to be given. The first series of experiments was conducted on March 13, 1894, under conditions of low barometric height, 74.42 cm., and for a relatively low temperature, 11.91° C., of the water bath. At this temperature the balancing resistance in the Wheatstone bridge at Z was

$$W'_1 = 70 + 10 + 2 + 1 + 2^* + .2,$$

of which $2^* + .2$ ohms were inserted before opening the charged receiver, March 13, 1894.

Manometer	Pressure	Bridge.	Temperature.
Mark 13.4	—	580	11.91° C.
15.2	+	580	11.91
13.55	—	580	11.91
14.02	—	580	11.91
14.40	+	580	11.91
14.50	+	580	11.91
14.22		580	11.91
14.20		580	11.91
14.40	+	580	11.91

The pressure value corresponding to the division 14.21 on the acid manometer was therefore considered correct. Its value was found from the following pressure comparison made when the temperature of the mercury was 20° C.

Sulphuric-Acid Manometer.	Mercury Manometer.	
	Lower Limb.	Upper Limb.
14.30	8.078 cm.	15.20 cm.
	8.080	15.20
	8.076	15.21
	8.075	15.205
14.25	8.085	15.200
	8.088	15.208
	8.088	15.204
14.23	8.085	15.200
	8.081	15.210
	8.099	15.202
	8.099	15.198
	8.101	15.200
14.20	8.095	15.197
	8.096	15.198
	8.104	15.198
14.18	8.099	———
14.20	8.090	15.190
	8.097	15.190
	8.090	15.202
	8.088	15.190
14.18	8.090	———

The mean value of all these data shows that the division mark 11.21 on the acid manometer corresponds to 7.105 cm. of Hg.

The temperature, Z_2, corresponding to the resistance standards at Z.

$$W_2 = 70 + 10 + 2 + 1,$$

and the position 589 of the sliding contact of the bridge, were deduced from the following data observed on the 10th of February:

Temperature.	Bridge.	Time.
4.31° C.	522	$1^h\ 0^m$
4.31	522	1 5
4.30	522	1 10
4.31	522	1 15
4.31	522	$1^h\ 50^m$
4.31	522	1 55
4.31	522	2 0
4.89	646	$2^h\ 10^m$

From these data we find by interpolation that the temperature 4.64° C corresponds to the position 589 of the sliding contact. Hence the present result is

$$\gamma = 1.3989.$$

Another series of experiments was made on March 16, 1894, when the barometer stood at 75.24 cm. Hg., and the temperature of the water bath was 16.41 C. The resistance standards inserted at Z in the bridge were

$$W_1 = 70 + 10 + 5 + 1 + .5 + .2.$$
$$W_2 = 70 + 10 + 2 + 1.$$

Manometer.	Pressure.	Bridge.	Temperature.
51.15	−	489	16.42° C.
51.45	−	486	16.42
52.25	+	487	16.41
51.55	−	487	16.41
51.88	+	487	16.41
51.70		487	16.41
51.62	−	487	16.41

The correct pressure was taken as the equivalent of division mark 51.70. How closely the corresponding mercury pressure has been found will be seen in the following pressure comparisons made on successive days:

MAY 9, 1894

Sulphuric Acid Manometer	Mercury Manometer	
	Lower Limb	Upper Limb
51.75	6.396	18.761
	6.395	18.757
	6.398	18.758
	6.400	18.756
	6.398	18.755
	6.399	18.755

[illegible] [mm. H_2SO_4] = [illegible] mm. Hg]

MAY 25, 1894. NO. 1

Sulphuric Acid Manometer	Mercury Manometer	
	Lower Limb	Upper Limb
51.75		17.185
	4.826	17.185
51.70	4.828	17.187
51.69	4.83	17.186
51.70	4.832	17.187
51.69		

[illegible] [mm. H_2SO_4] = [illegible] mm. Hg]

MAY 25, 1894. NO. 2

Sulphuric Acid Manometer	Mercury Manometer	
	Lower Limb	Upper Limb
51.70		17.186
51.71	4.832	17.186
51.7	4.833	17.185

[illegible] [mm. H_2SO_4] = [illegible] mm. Hg]

The temperature T_2 (1.11°), corresponding to the resistance W_2, was determined in a way similar to the method given above. These data therefore show

$$k = 1.4012$$

b. HYDROGEN.

In conclusion we will communicate a similar series of results for hydrogen, selecting data found for three different pressures. The same bolometer strip subserved the purposes of measurement as in the preceding experiments. The resistance at Z was at the initial temperature:

$$W = 75 \ldots$$ [illegible]

and at the final temperature:

$$W = 75 \ldots$$ [illegible]

In the case of hydrogen the period of efflux for corresponding apertures is much smaller than for the other gases.

[illegible]

Manometer	Pressure	Bridge	Temperature
51.00	[illegible]	[illegible]	16.[illegible] C
53.00	[illegible]	601	16.01
51.90	[illegible]	599	15.99
51.40	[illegible]	[illegible]	16.01
51.60	[illegible]	601	16.01
51.65	[illegible]	602	16.[illegible]2
51.55	[illegible]	[illegible]	16.01
51.65	[illegible]	603	16.02

EFFLUX TIME [illegible]

Manometer	Pressure	Bridge	Temperature
51.54	[illegible]	603	16.01
51.20	[illegible]	[illegible]	[illegible]
51.65	[illegible]	[illegible]	16.01

In spite of the shortness of the efflux time (¼ second), the galvanometer needle at the pressure of 51.54 remained quite at rest for *two* (2) seconds. In the following series of experiments all quantities except the position of the sliding contact on the bridge and the initial temperature are exactly the same as in the preceding series; but we operated with a larger efflux opening.

EFFLUX TIME ¼ [illegible]

Manometer	Pressure	Bridge	Temperature
65.00	[illegible]	[illegible]	17.3[illegible] C
63.50	[illegible]	[illegible]	[illegible]
64.20	[illegible]	[illegible]	[illegible]
64.00	[illegible]	[illegible]	[illegible]
63.55	[illegible]	[illegible]	[illegible]
63.95	[illegible]	[illegible]	[illegible]
63.65	[illegible]	[illegible]	[illegible]
63.75	[illegible]	[illegible]	[illegible]
64.00	[illegible]	[illegible]	[illegible]

In the following experiments for a smaller pressure excess, the change of resistance amounted to 3.1 ohm. The largest efflux opening was made use of.

EFFLUX TIME [illegible]; APRIL 28, 1894.

Manometer	Pressure	Bridge	Thermometer
36.00	[illegible]	530	17.31 C.
34.10	[illegible]	532	"
35.20	[illegible]	"	"
36.00	[illegible]	"	"
35.50	[illegible]	"	"
35.70	[illegible]	"	"
35.35	[illegible]	"	"

The period of quiescence of the galvanometer needle proved at the pressure 35.50 to be quite one second.

We may remark that the observer at the galvanometer was not instructed as to the height of the pressure excess which the second observer produced. The same observer simultaneously kept the temperature of the water bath at the desired value.

c. TEMPERATURE DISTRIBUTION IN THE WATER BATH.

Finally we wish to give a brief summary of the bolometric measurements made relative to the distribution of temperature within the water bath (*cf.* page 5). The mean temperature of the bath in the lapse of time was kept constant in the manner specified above, to the degree given in the first column of the following table. The second column shows the deflection of the galvanometer needle in scale parts, obtained for suitable resistance ratios in the respective branches of the Wheatstone bridge. The third column contains the time of observation. We adduce three series of observations: in the first and third the bolometer was near the surface of the water in the bath, while in the second it was near the bottom.

Temperature.	Deflection.	Time.	Bolometer.
15.70 C.	105.0	1ʰ 17′	above
15.70	104.0	1 22	
15.7	104.0	1 27	
15.70	103.0	1 32	
15.70	104.0	1ʰ 37′	below
15.70	105.0	1 42	
15.69	103.0	1 47	
15.70	106.5	1ʰ 53′	above
15.70	105.5	1 58	

The sensitiveness of the method is particularly seen in the following table of collateral data.

Temperature	Deflection	[illegible]	1
15.60° C.	53.[illegible]	[illegible]	above
15.60	54.[illegible]	[illegible]	
15.60	54.0	2 15	

V. —RESULTS.

Equation (1) which is made the basis of the present experiments applies for perfect gases, the intrinsic equation of which is of the form due to Mariotte and Gay Lussac:

$$pv = RT,$$

where p is the pressure corresponding to the volume v at the absolute temperature T, and R is a constant. For air, oxygen, and hydrogen this equation is admissible, provided the zero point of the absolute scale of temperature be located in conformity with the properties of the gases. This is done if the absolute temperature T is computed from the temperature t in degrees centigrade by the formula

$$T = \frac{1}{\alpha} + t,$$

in which α is the coefficient of expansion of the gas in question. We may remark that the effect of this difference of α for the different gases in question is usually of little significance.

We made the computation in the same way for carbon-dioxide, although the departure from the laws appertaining to perfect gases is appreciable for this body, or at least is larger than for the other gases. The values for α and $\frac{1}{\alpha}$ used in the present paper[1] are as follows:

	α.	$1/\alpha$.
Air	.0036706	272.4
Oxygen	.0036743	272.2
Hydrogen	.0036613	273.1
Carbon-dioxide	.003690	270.3

a. AIR.

The air was taken directly from the atmosphere in the room and successively passed through concentrated sulphuric acid, a drying tube containing calcic chloride

---

[1] The values for $\varkappa$ communicated at the Oxford meeting of the British Association were found for $1/\alpha = 273$. Hence these results will differ slightly from the present series.

and a wad of absorbent cotton w (fig. 1). Two series of experiments were made: one consisting of 5 determinations in June, 1893; a second series of 6 determinations in February and March, 1894. In the first of these the pressure measurements at the mercury manometer were read off on a cathetometer of only moderate accuracy. The fine cathetometer of Mr. Hansemann was not available until we reached the second series.

In the following tables T_1 and T_2 are the absolute values of the initial and final temperatures, p_1 and p_2 the corresponding pressures of the gas before and after expansion, in cm. of mercury. $\varkappa$ denotes the ratio of the two specific heats, and D the variation of each value from the mean.

Date.	T_1.	T_2.	p_1.	p_2.	$\varkappa$.	D.
6, 6, 93	287.02	280.30	82.85	76.32	1.3980	−.0024
12, 6, 93	287.03	280.42	82.42	75.07	1.4021	+.0017
13, 6, 93	287.03	280.40	82.53	76.06	1.4012	+.0008
13, 6, 93	287.03	280.41	82.46	76.01	1.4019	+.0015
16, 6, 93	288.91	276.66	88.09	76.10	1.3988	−.0016

Mean: $\varkappa = 1.4004$.

Date.	T_1.	T_2.	p_1.	p_2.	$\varkappa$.	D.
9, 2, 94	284.21	276.72	82.28	75.12	1.3996	−.0008
12, 2, 94	289.71	276.46	87.390	74.15	1.4016	+.0012
16, 2, 94	289.63	284.04	81.583	76.78	1.4009	+.0005
16, 2, 94	289.63	279.72	80.753	76.80	1.4000	−.0004
13, 3, 94	284.31	277.[illegible]4	81.50	73.42	1.3989	−.0015
16, 3, 94	288.81	276.54	87.554	75.24	1.4012	+.0008

Mean: $\varkappa = 1.4004$.

The mean values of $\varkappa$ of both series happen exactly to coincide.

The mean value ($\varkappa$) for data obtained with a platinum-blacked bolometer strip was

$$\varkappa = 1.3783.$$

Hence the correction for the radiation discrepancy is

$$\frac{1.4004 - 1.3783}{11} = .0021.$$

The final result for air is therefore

$$\varkappa = 1.4025$$

b. OXYGEN.

Commercial oxygen obtained from Dr. Elkan in Berlin was used. The method of experiment did not differ from that detailed for air. The results are as follows:

Date.	T_1.	T_2.	p_1.	p_2.	κ.	D.
12, 4, 94	288.71	275.46	89.462	75.80	1.3952	— .0004
12, 4, 94	288.71	282.07	82.291	75.80	1.3948	— .0008
13, 4, 94	289.21	275.01	89.713	75.71	1.3963	.0007
13, 4, 94	280.21	279.25	85.694	75.75	1.3969	+ .0013
13, 4, 94	284.71	275.76	84.793	75.75	1.3950	— .0006

Mean $\kappa = 1.3956$.
Correction for radiation + .0021.
Final value (corrected), $\kappa = 1.3977$.

c. CARBON-DIOXIDE.

The gas was obtained from a cylinder of commercial, liquid carbon-dioxide. Hence it was passed through the drying train into the copper receiver for experiment.

Date.	T_1.	T_2.	p_1.	p_2.	κ.	D.
19, 4, 94	288.01	277.08	89.477	75.54	1.2961	— .0013
19, 4, 94	288.01	280.36	84.998	75.56	1.2965	— .0009
19, 4, 94	280.71	277.41	79.677	75.68	1.2987	+ .0013
19, 4, 94	280.71	274.11	83.986	75.72	1.2983	— .0009

Mean $\kappa = 1.2974$.
Correction for radiation + .0021.
Final value (corrected), $\kappa = 1.2995$.

d. HYDROGEN.

Commercial hydrogen obtained from Dr. Elkan in Berlin was passed through a solution of permanganate of potash and thereafter treated in the manner specified for air.

Date.	T_1.	T_2.	p_1.	p_2.	κ.	D.
24, 4, 94	285.32	276.35	84.617	75.75	1.4064	+ .0001
26, 4, 94	289.02	276.72	87.930	75.64	1.4062	— .0001
28, 4, 94	290.32	276.47	89.463	75.46	1.4056	— .0007
28, 4, 94	290.32	279.99	85.527	75.46	1.4070	+ .0007

Mean $\kappa = 1.4063$
Correction for radiation + .0021.
Final value (corrected), $\kappa = 1.4084$.

CONCLUSION.

We have already anticipated that the values for κ obtained with the new bolometer would be *larger* than the corresponding data obtained in 1887 by the use of a silver wire .001 cm. thick for bolometric purposes. This anticipation has been quite borne out by the experiments, showing that the discrepancy due to heat conducted inward from the terminals had seriously affected our earlier results.

A summary of the different experiments made for evaluating κ is given by A. Winkelmann in his *Handbuch der Physik*, 1895, vol. ii., pp. 381, 382, covering the ground up to 1895. Furthermore, the *Journal de Physique*, 1895 (3), vol. iv., pp. 163–165, contains an historical and critical review[1] of the subject as to methods and observations, by M. G. Maneuvrier. We do not therefore think it advisable to reproduce these bibliographies here, in which, to our knowledge, only the experiments of J. Webster Low[2] seem to have been overlooked. On the other hand, a comparison of our results with those of earlier observers in the form of a table such as is given at the end of this paper, will conduce to an intelligent survey of the present aspect of the subject. All correlative results were obtained by methods different from ours.

The researches of Röntgen and of Paquet are based on the well-known method of Clément and Desormes.

The values of Kayser, Wüllner, and J. Webster Low are computed from data for the velocity of sound. The first two of these observers made use of Kundt's method, while Low reached his results through the interferential method for the velocity of sound waves devised by Quincke. Maneuvrier's method is the following: A given mass of gas is compressed *adiabatically*, and the increase of pressure produced determined. The change of pressure due to an equal but *isothermal* change of volume is easily computed from known laws. If both volume decrements be small, the ratio of the pressure increments is very nearly equal to the ratio of the specific heats. Hence κ may be found from the data for the adiabatic volume reduction.

All data given in the following table refer to ordinary atmospheric temperatures.

---

[1] In this review, as well as in another paper (*Journal de Physique*, 1895 (3), vol. iv, pp. 368–373), M. Maneuvrier devotes a large space to a criticism of [illegible] and to the results of the present investigation, so far as they were given in the brief summary contained in the Reports of the Oxford meeting of the British Association. We do not deem it desirable to go into particulars, for the points raised by M. Maneuvrier are all met by the [illegible] published [illegible] so far as they are matter-of-fact and not merely controversial.

[2] J. Webster Low, *Wied. Ann.*, vol. lii., pp. 641–663, 1894.

TABLE OF COMPARATIVE VALUES OF k.

Observer.	Air	Oxygen.	Carbon-Dioxide.	Hydrogen.
Röntgen, 1873	1.4053	——	1.3052	1.3852
Kayser, 1877	1.4106	——	——	—
Wüllner, 1878	1.405	——	1.3054	—
Paquet, 1885	1.4038	——	——	—
J. Webster Low, 1894	1.3968	——	1.291	——
Lummer and Pringsheim, 1894	1.4025	1.3977	1.2995	1.4084
Manoevrier, 1895	1.3925	——	1.298	1.384

Physikalisch-Technische Reichsanstalt,
Charlottenburg, Germany,
October, 1897.

SMITHSONIAN CONTRIBUTIONS TO KNOWLEDGE
1309

Hodgkins Fund

EXPERIMENTS WITH IONIZED AIR

BY

CARL BARUS

HAZARD PROFESSOR OF PHYSICS AT BROWN UNIVERSITY

CITY OF WASHINGTON
PUBLISHED BY THE SMITHSONIAN INSTITUTION
1901

The Knickerbocker Press, New York

SMITHSONIAN CONTRIBUTIONS TO KNOWLEDGE

1309

Hodgkins Fund

EXPERIMENTS WITH IONIZED AIR

BY

CARL BARUS

HAZARD PROFESSOR OF PHYSICS AT BROWN UNIVERSITY

CITY OF WASHINGTON
PUBLISHED BY THE SMITHSONIAN INSTITUTION
1901

Commission to whom this memoir has been referred:

WILDER D. BANCROFT,
EDGAR F. SMITH.

ADVERTISEMENT.

The present memoir, describing experiments with ionized air, is the result of a series of investigations by Professor Barus which were carried on from 1893 to 1895, under aid from Mr. Clarence King and Doctor Alexander Graham Bell, and later continued under a grant from the Smithsonian Institution.

This research is tributary to an investigation of the colors of cloudy condensation. Lord Rayleigh's famous theory, if applied, would stop at the deep reds of the first order terminating in opaque, whereas in the laboratory experiments, exceptionally brilliant colors extending almost into the third order of Newton's series may be produced.

It is thus essential as a preliminary step to investigate appropriate means for the production of nuclei, to determine their number per cubic centimetre, their velocity, their association with ionization, the effect of the presence of an electric field, etc. This is the general trend of the work of the present volume though the experiments have a special interest apart from their ulterior purposes.

The endeavor is made with the aid of the condensation tube (which proves to be unique in its adaptation to the present ends) to show that the nucleus has a specific velocity of its own, and that this is retained even in the absence of an electric field. The application of this principle to plate, to tubular, and to spherical condensers leads in every case, and in spite of the variation of method, to an order of values as to the number of particles in action, agreeing with the data obtained by other investigators from different experiments and theoretically different points of view.

In accordance with the rule adopted by the Smithsonian Institution the work has been submitted for examination to a Committee consisting of Professor Wilder D. Bancroft, of Cornell University, and Professor Edgar F. Smith, of the University of Pennsylvania, and having been recommended for publication, it is herewith presented in the series of *Contributions to Knowledge.*

S. P. LANGLEY,
SECRETARY.

Smithsonian Institution,
Washington, June, 1901.

PREFACE.

The present researches are a continuation of the work begun in 1893, while I held a professorship of meteorology in the United States Weather Bureau, and completed in 1895 in a private laboratory, whose facilities and maintenance I owed to the generosity of Mr. Clarence King and Prof. Alexander Graham Bell. For reasons of no moment here, the work was abruptly discontinued at a very promising stage of progress and I have had no opportunities to return to it since.

In the meantime the whole subject underwent an astounding transformation, due to the discovery of the X-rays and the brilliant achievements reached with these new means, chiefly at the University of Cambridge, by Prof. J. J. Thomson and his pupils.

It was therefore with great pleasure that I welcomed an invitation from the Secretary of the Smithsonian Institution, empowering me to begin the work anew, along lines but little cultivated with this end in view by the other physicists.

The present work, as a glance at the following pages will show, has been laborious throughout, and the interpretations difficult and precarious. If the steam jet is to be used as an instrument of research, the evidence is of the nature of color criteria, unsatisfactory at best. The ionizer chiefly used, though admirable in all other respects, has shown a degree of subtle variability, for which I was, at the outset, altogether unprepared. It was essential, therefore, that the results reached, to be warrantable, should be looked at from many points of view, and this has given rise to a greater variety in the chapters than was originally planned. The peculiar value of the steam jet in spite of all disadvantages, remains: it is a non-electrical instrument giving evidence with a direct bearing on obscure electrical processes; and from this point of view I believe that extensive work with it is eventually bound to be fruitful.

In work so alive and well known as that to which the following pages are tributary, I have thought it unnecessary to enter into a full bibliography.[1] Most of it has issued from the Cavendish Laboratory (Thomson, C. T. R. Wilson, Rutherford, Townsend, Zeleny, H. A. Wilson, McClelland, and others; to whom

---

[1] Cf. E. Merritt: *Science*, xii, pp. 41–48, 98–104, 1900; H. Becquerel: *Nature*, lxiii, pp. 396-398, 1901; N. E. Dorsey: *U. S. Monthly Weather Review*, Sept., 1900; above all, the monographs in the *Rapports présentés au Congrès International de Physique*, Paris, 1900, vol. iii, by Becquerel, Curie, J. J. Thomson, Villari, and Villard.

we must add Bidwell, Chattock, Beattie, Russel, Smithells, and Dawson), and the papers will be found without difficulty by consulting recent numbers of the *Philosophical Magazine*. Moreover, Prof. Merritt, M. Becquerel, and others have given historical accounts of other phases of it.

I may say in concluding, that condensationally, Kelvin's nuclei and Aitken's "dust" have not yet been quite superseded. The use of these somewhat antiquated terms is therefore not merely dictated by convenience. Their appearance is in a measure inevitable. To employ them interchangeably with "ion," would, in a research like the present, be hazardous.

C. B.

TABLE OF CONTENTS.

CHAPTER I.

CHAPTER II.

CHAPTER III.

CHAPTER IV.

Transmission through Air.

Transmission through Solid Media.

Ionization by other Dust Producers.

CHAPTER V.

CHAPTER VI.

LIST OF FIGURES.

CHAPTER I.

CHAPTER II.

CHAPTER III.

CHAPTER IV.

CHAPTER V.

CHAPTER VI.

EXPERIMENTS WITH IONIZED AIR.

By Carl Barus,

HAZARD PROFESSOR OF PHYSICS AT BROWN UNIVERSITY.

CHAPTER I.

PRELIMINARY EXPERIMENTS.

1. *Color tube.*—The apparatus for the observation of the colors of the cloudy condensation of water vapor in air will be briefly called the color tube or the steam tube, as convenience suggests. In most of my earlier experiments it did not differ essentially from the form devised after long trial in my previous papers[1] on the subject. It will be necessary, however, to insert a short description here, as otherwise the account of many of the experiments given below would be unintelligible. So too the condition under which steam-jet criteria are admissible will have to be succinctly stated.

The tube and appurtenances are shown in figures 1, 2, 3, and 4, the tube itself in the first figure. Steam enters the tube AA directly by the jet j, screwed into it near the bottom. Air is supplied through C, which is of the same diameter as AA, and B is the efflux. Sky light, L, transmitted through the tube by means of the adjustable mirror M, and the window a, is observed through the inclined plate g. Here a difficulty presents itself, inasmuch as g at once clouds over; but I eventually overcame this by moistening the inside of g with a solution of caustic potash applied with a sponge probang through B. In this way a clear field is again obtained for some time at least, after which the moistening must be renewed. The inclined position of g makes the whole window easily accessible, and a special hole closed by a cork may be cut in the elbow for inserting the probang when B is otherwise engaged. Other tubulures have special purposes, to be shown and stated below. The windows are suitably secured between rubber gaskets held in place by flanges and bolts.

The observer faces the plate g symmetrically and looks down the color tube

---

[1] Cf. *Condensation of Atmospheric Moisture,* Bulletin No. 12, U. S. Weather Bureau, Washington, 1895, pp. 1–104.

AA, while a screen cuts off all extraneous light. With this apparatus a brilliant field of color is obtained, so that minute differences may be detected, and I thus investigated the scale given below between the intense oranges of the first order

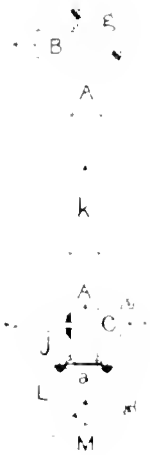


Fig. 1

Fig. 2

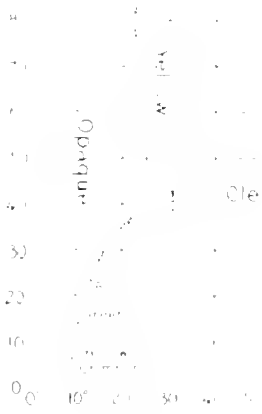


Fig. 7

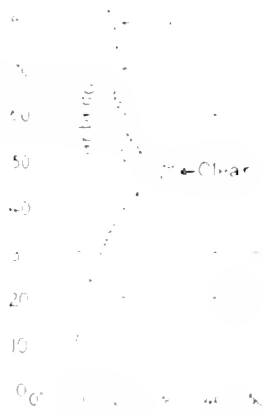
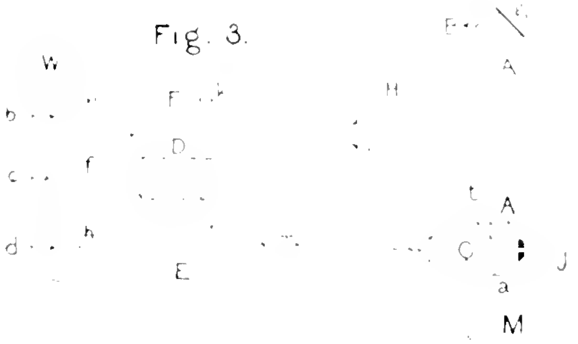


Fig. 8

Fig. 3.



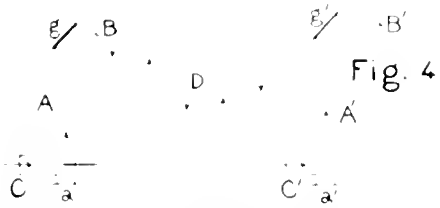
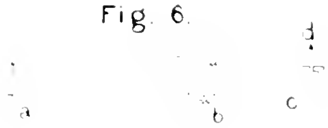


Fig. 4

Fig. 6.



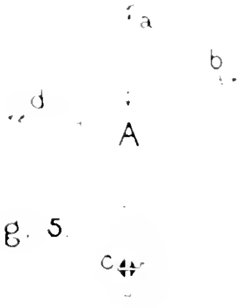


Fig. 5.

Fig. 1. Color Tube, Sectional Elevation. Scale [illegible]. Fig. 2. Differential Color Tube. Fig. 3. Color Tube with Filter Pipe. Fig. 4. Color Tubes in Series. Fig. 5. Steam Box or [illegible]. Fig. 6. Nozzle of Steam Jet. Scale [illegible]. Figs. 7, 8. Charts, showing the Margins of the C[illegible] Field at Different Temperatures and Pressures, for Atmospheric Air.

and the final greens of the second order, after which the colors are too faint for recognition. In the latter case, since low-pressure steam must be employed, an advantage is secured by drilling two or more holes in the jet *j*. Figure 1 shows that the tubes slide into the snugly fitting envelope k, and the system may therefore be shortened for observing very intense colors, or lengthened for faint colors. Either end of AA may be rotated.

Color tests are as a rule more satisfactory for quantitative work if some fiducial field is at hand for comparison. Figure 2 therefore consists of two color tubes, identical in every respect and admitting of an independent use of both eyes. Sky light is introduced by the mirrors M and M'. The observer looks down into both windows, g and g', at once. The two tubes may be connected rigidly by the double bridge, and supported from a stout rod, n. If the jets are identical and communicate with the same steam box, the colors seen by both eyes should be identical. This state of things is found by trial. Supposing, therefore, the right tube is left without interference, the other tube may be manipulated in various ways. In all such cases the two tubes are connected in multiple, as it were. But if the jet be removed from $A'A'$, and the discharge from AA, after passing through a suitable length of wide tube, be eventually passed through $A'A'$, without further interference, the two tubes are in series. This adjustment is shown in figure 4 and leads to interesting application of the apparatus.

On reviewing the earlier experience it appears that the adjustment of air and steam which secures the clearest field must be made as nicely as the adjustment of air and gas in a Bunsen burner. Otherwise the colors are either dull or faint, quite apart from temperature or pressure conditions. Often the efflux may be stimulated to advantage by an auxiliary ventillating tube at B, containing its own jet, without interfering with the color tube itself. Whenever possible it is preferable to take the air entering C from a room heated nearly equally throughout. In cases where this is not possible, the train represented in figure 3 is useful. Here a, g, are the windows of the color tube AA, j the jet, and M the mirror. B is the efflux tube for mixed steam and air, C the influx tube, showing the thermometer, t, in place. The air entering C is taken from the outside atmosphere, the three influx tubes, E, D, F, passing through the window frame, W. Valves are inserted in each of these tubes, as at e, f, h, so that the quantity of air passing through each of them may be regulated or quite shut off. In winter when the valves are open, the air rushes through the tubes with considerable velocity, even when the jet j is not in action. This velocity increases with the steam pressure actuating the jet. Under no circumstances must the valves be so far closed that there is not free influx of air at C. The tube E is clear, and the air passing through it has the temperature of the atmosphere. The tube D discharges into E and is provided with a drum containing a coil of thin lead pipe. About 20 turns of pipe, each about 5 cm. in diameter, and a drum about 35 cm. long and 10 cm. in diameter, are more than sufficient. In winter time steam is passed through the lead pipe; hence by suitably regulating the valves h and f, the air flowing through C may be kept at any desirable temperature, since temperatures between 9° and 10°, only, are needed for the present purposes. In summer time, chilled brine or an expanding gas would be similarly serviceable.

The auxiliary tube,, also F discharges into E, and is useful for increasing the "dust" contents of air entering C, with the aid of a "duster" at k, and a variety of similar purposes. It is to be noted that the tubes E, D, F, must all pass out of the room. If, for instance, b opened into the room (often very desirable), then if the jet is only slightly in action or not at all, cold air will pass into C and D and out at b, as well as at B, into the room. The flow of dusty air would therefore be irregular. An advantage is secured in making the common tube C long, so that the air may be well mixed before impinging upon the jet. At best, however, air dusted in this way is but an inferior substitute for good room air, and the results show more fluctuation.

2. *Jet.*—A jet of almost any kind, with a smooth round hole about 1 millimeter, is satisfactory. It may be conveniently shaped from lead pipe. When the variations of color phenomena are to be quantitatively studied it is desirable to make the jet as shown in figure 6. Here ab is a brass tube about 10 cm. long and 1 cm. in diameter, the end b of which is threaded both on the outside and inside, so that a thin-walled nipple, c, closed at the outer end, may be inserted. Into the top of c a hole, d, is smoothly drilled. The outer thread at b is useful in screwing the jet to the color tube, in to the centre of which c projects. The open end a of the jet is connected with the tube b of the steam box, figure 5, by a union.

The jet may either be fed with pure steam or with compressed air supersaturated with aqueous vapor. When steam is used alone, it must be available in large quantity at a pressure up to one atmosphere or more. This pressure may then be reduced by an ordinary steam-cock. To dry the steam it is conveniently passed into a cylindrical box, A, figure 5, called a separator, through the vertical pipe a, surmounted by the cock specified. It is conveyed to the jet by a lateral pipe, b. The water which collects is discharged through c, and a pipe, d, communicates with an open mercury monometer for the measurement of pressure. The separator should be made of gas-fitters' appurtenances and suitably jacketed.

3. *Available color sequences.* The next question to be preliminarily disposed of is the succession of colors. I will arrange them in table 1, stating briefly how they were obtained and placing the colors where I think they belong. I will also add Quincke's[1] revision of the colors of Newton's rings, as quoted by Kohlrausch,[2] for comparison. Kiessling's[3] results need some explanation. His first series of colors is produced by compressing surcharged, suitably dusted air, and then allowing it to expand suddenly to atmospheric pressure. The experiment being made in a glass sphere illuminated by sunlight, the colors are observed in the axis of illumination. The succeeding series are obtained by aid of an exhaust pump. They are less easily located relatively to Newton's scale (see last columns) than Kiessling's first series, which is intensely brilliant. Aitken,[4] who exhausts long tubes, gets a wider range of colors, running, as I interpreted them, from the first

---

[1] Quincke: *Pogg. Ann.*, CXXIX, p. 18[illegible], 1866.

[2] Kohlrausch: *Leitfaden*, 5th edition, p. 34[illegible].

[3] Kiessling: *Dämmerungserscheinungen*, p. 14[illegible], 1888; Hamburg, L. Voss.

[4] Aitken: *Trans. Roy. Soc. Edin.*, XXXV, part I, 1888; *ibid.*, XXXVII, part I, No. 3, 1892; *Proc. Roy. Soc. Edin.*, XVI, p. 135, 1889 (containing full descriptions); *ibid.*, XVIII, p. 259, 1890–

into the third order. Von Helmholtz[1] saw all his colors in the successive regions of an open steam jet, and reasonably inferred that the remote and cooler parts contain the larger particles. Aitken's jets play into tubes.

In my own work, most of the colors from the browns of the first order to the crimsons of the second could be produced in the tube, figure 1, by simply decreasing the pressure under which the steam issues from about 80 cm. of mercury to zero, if the ingoing air is not too hot or cold. A much better method, however, consists in using a copious steam efflux at very low pressure excess, and adding uniformly dusted air in the necessary amounts at C, as will be instanced below.

TABLE I.—SHOWING THE SUCCESSION OF COLORS.

[Data of the last column for air, white light, and normal incidence.]

By exhaustion.			Experiments with jets					Colors of Newton's interferences.	Thickness of plate of air in millimeters.
Kiessling, 1884.		Aitken, 1892.	Helmholtz, 1887.	Aitken, 1892.	Barus, 1892.	Remarks.			
					White.			White.	.000,020
		Pale yellow.		Yellow.	Yellow.			Yellow white.	.000,048
							Jet of continually decreasing intensity of flow from the top to the bottom of this series of colors.	Brown white.	.000,079
	(Second, third, and fourth series.)	Slightly reddish.			Orange.	Efflux violent.		Yellow brown.	.000,109
				Brown.	Brown.			Brown.	.000,117
					Opaque.	Efflux noisy.		Red.	.000,129
(First series.)	Pale purple.			Opaque.	Opaque.			Carmine.	.000,133
					Opaque.			Dark-red brown.	.000,137
Pale lilac.					Dark violet.	Efflux intense.		Dark violet.	.000,140
Pale blue violet.					Indigo.			Indigo.	.000,153
		Blue.	Blue.	Blue.	Blue.			Blue.	.000,166
Light blue.	Stone gray.				Gray blue.			Gray blue.	.000,215
Blue green.					Blue green.			Blue green.	.000,252
Emerald green.	Olive green.	Green.	Green.	Green.	Green.			Pale green.	.000,268
								Yellow green.	.000,275
Yellow green.	Yellow green.								
					Green yellow.			Yellow green.	.000,282
								Green yellow.	.000,287
Green yellow.								Yellow.	.000,294
Light orange.	Bronze yellow.	Yellow.	Yellow.		Straw yellow.			Orange.	.000,332
	Orange.							Brown orange.	.000,364
Dark orange.		Brown.			Muddy brown.			Light carmine.	.000,374
Pale scarlet.				Pale crimson. (Uncertain.)				Purple.	.000,413
Pale purple.		Purple.	Purple.		Pale purple.			Violet purple.	.000,421
					Pale violet purple.			Violet.	.000,433
								Indigo.	.000,455
		Blue.	Blue.		Pale violet.	Jet nearly shut off.		Dark blue.	.000,474
					Pale indigo.			Green blue.	.000,499
		Green.			Faint green.			Green.	.000,550
		Yellow.			Faint yellow green.	Long tube.		Yellow green.	.000,564
								Dull yellow.	.000,575
					Beyond recognition.				

Between the brown and dark violet of the colors of the first order, there is an opaque region. Sometimes the brown takes on a reddish hue and sometimes the violet appears purplish: but the opaque region of indefinable color remains. Indeed, it is a characteristic landmark in the color territory. Being absent in exhaustion it is to be interpreted with regard to the researches of Osborne Reynolds,[2] on the flow of liquids in pipes. Reynolds found that a colored jet passing through

---

91 ; *Nature*, XXXVII, p. 428, 1888 ; *ibid.*, XLI, p. 394, 1890 ; *ibid.*, XLIV, p. 279, 1891 ; *ibid.*, XLV, p. 299, 1892, and elsewhere : *Proc. Roy. Soc. Edin.*, LI, p. 425, *et seq.*, 1892.

[1] R. v. Helmholtz : *Wied. Ann.*, XXVII, p. 508, 1886 ; *ibid.* XXXII, p. 1, 1887.

[2] Reynolds: *Phil. Trans.*, London, III, p. 935, 1883.

clear water remains uniformly filamentary, so long as a certain critical velocity of efflux is not exceeded. After this the jet breaks up suddenly and violently into eddies. But as applied to the steam jet, this reason is not quite adequate; for if the intensity of the latter is still further increased, magnificent browns and oranges appear beyond the opaque. To account for opacity it is thus essential to inquire into the relation of color to size of particle at the point where color is extinguished.

4. *The boundaries of the opaque region.* The final subject to which attention must here be directed is the relation of the color obtained from a given influx of nearly pure air, its temperature, and the pressure actuating the steam jet. I append two illustrative charts, figures 7 and 8, from my earlier paper. In these the abscissas indicate the temperature (in degrees centigrade) of the air entering the color tube at *C*, figure 1, or in other words, the registry of the thermometer *t*, figure 3. The ordinates show the pressure in centimeters of mercury under which the steam is forced out of the jet. Points of the curve between 0 and 10 centimeters then show the corresponding values of air temperature and steam pressure at which the dark violet of the first order merges into opaque. The points of the curve lying quite above 10 cm. (this datum depends on many factors) show the condition at which the brown yellows of the first order just emerge from opaque. Curves indicating the approximate loci are drawn through the points.

Below 9°, therefore, the field is opaque at all pressures. Above 9°, the pressure at which the blue changes to opaque rapidly increases with increasing temperature; and the pressure at which brown yellow changes to opaque decreases from an enormous value, and at even a more rapid rate, as temperature increases. Both loci curving at a retarded rate, eventually reach a common asymptote at, say, 11 cm., the temperature being indefinitely high. At the same time the colors which were very intense at the lower temperature gradually become fainter and the opaque zone more translucent, until at about 40° of air temperature (depending on the size of the nozzle) the field is quite clear and without color. The escaping steam is gaseous and not visibly condensed. When temperature decreases again from 40°, faint white yellow is the first color to appear, showing that the particles here must be the smallest of the whole series. At 35° the change from faint yellowish tones to faint white blues, when pressure is made to vary suitably from larger to smaller values, is quite marked. There is no opaque demarcation, however, but rather a mixture of colors, for the field is scarcely impervious to light above 30°.

For all temperatures and pressures lying to the left of the two curves, figures 7 and 8, the field is opaque, and it sends off a kind of cusp to penetrate into the higher temperatures. There is a characteristic difference between the two margins; for whereas the yellow opaque after a sharp inflection shoots up almost vertically, blue opaque shows a regular curvature throughout into lower temperatures than the other. At about 15° I have inscribed the successive position of the chief colors. This cannot be nearly so well done as the location of the opaque margin; but the contour of the color curves is surmised from the line for blue opaque. Similarly above the yellow opaque line, a family of browns, oranges, and yellows might be located. When the dust contents are increased, the cusp of the opaque region approaches the abscissa, and hence the color loci will be successively more crowded together.

In the chart, figure 7, only a single air tube (*d*, fig. 3) was available. The air was heated to about 40° by the circulating steam in the drum. This was then shut off and the temperature and pressure at which the colors disappeared noted on cooling. The mercury thermometer is scarcely sensitive enough for such observations, and the temperatures of the diagram are probably too high. The observations of figure 8 were obtained with the apparatus shown in figure 3. There is greater certainty near the cusp, which is higher. The cardinal features of the phenomenon are, however, the same in both charts.

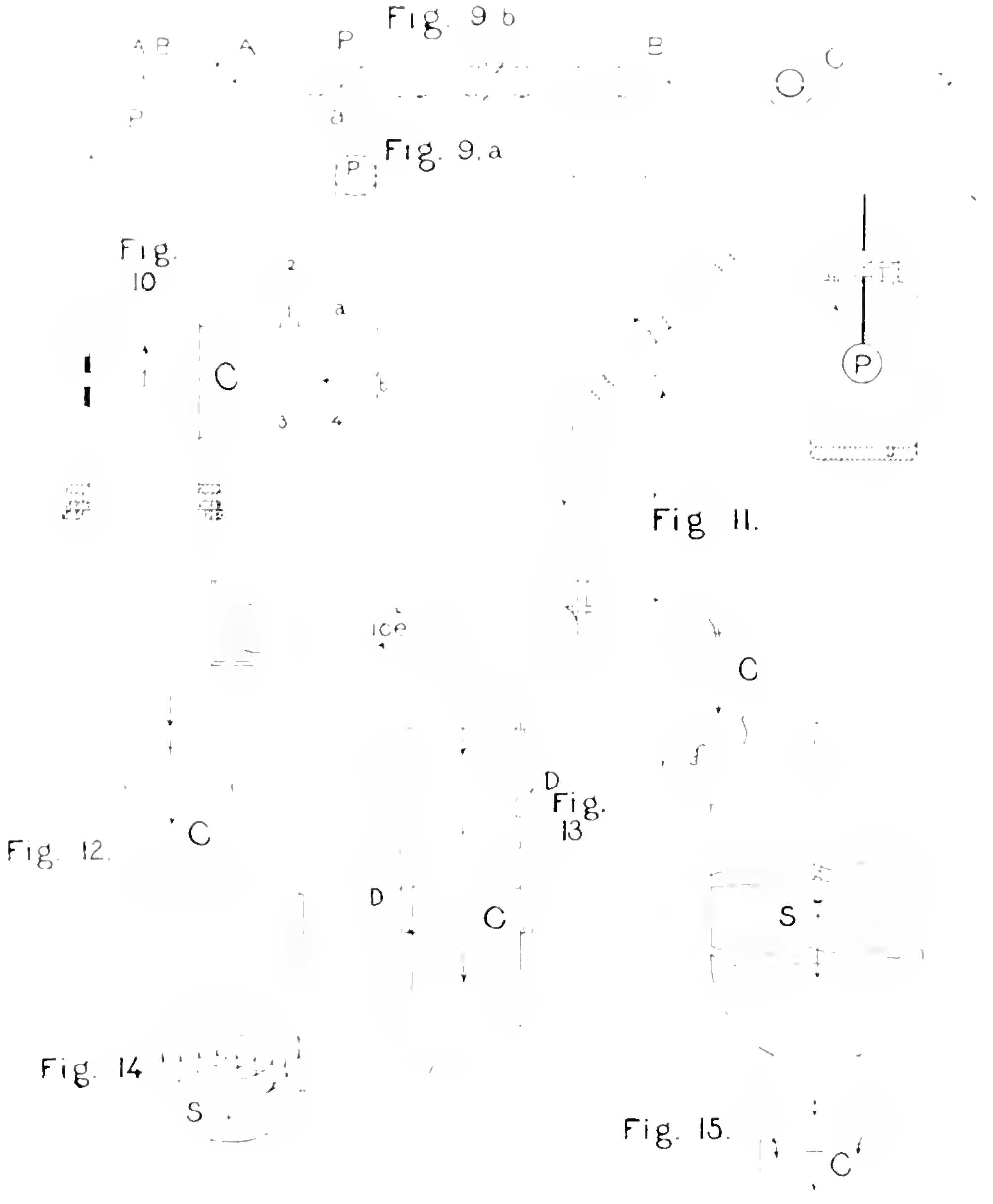
All colors are cleared and become fainter on opening the bottom window of the color tube. The opaque margin as a whole shifts to the left, indicating the occurrence of lower temperatures. Thus at about 16°:

Pressure of blue:	Pressure of yellow:
Open, 33 cm.	Open, 45 cm.
Closed, 25 cm.	Closed, above 100 cm.

The jet is sensitive to about one inch above the hole. No effect is produced by introducing dusty air two or more centimeters above it. When it is merely a question of producing opaque condensation without regard to color, a wide jet supplied copiously with steam at a vanishing pressure excess, is useful. Thus a flat lava tip is very sensitive under these conditions.

5. *Ionizers and "dust" producers.*—The most convenient and generally efficient "dust" producer which I have found is phosphorus at a temperature somewhere between 20° and 30°. Thin discs, *P*, of it may be enclosed between pieces of wire gauze, about as large as a dime, and mounted on a stem, as in figure 9 *a*. When not in use, this duster is as usual submerged in water, to be thoroughly dried by squeezing it between folds of bibulous paper prior to the next experiment. It lasts indefinitely, since it is only the glow visible in the dark which is effective, while the noxious smoke which sometimes shows itself at higher temperatures is without a condensation-producing tendency. A better source of dust particles is made, as in figure 9 *b*, by inserting strips of wire gauze soldered together at points *a*, about an inch or less apart, and holding discs of phosphorus *P*, in the intervening spaces, into a wide tube, *A B*. This is drawn to a finer end at *C*, where a stopcock may be placed. When not in use the strips are withdrawn and dropped into water.

If the end *A* is placed near the mouth of the color tube (*C*, figure 1) and the narrow end is open, sufficient air traverses the tube to produce a color depending on the degree to which the end is open. It is far better, however, to send a definite current through the tube from an aspirator controlled by a screw stop-cock like those attached to oxygen cylinders. In such a case any desirable color of cloudy condensation may be maintained in the tube for an indefinite length of time, assuming that the steam jet is equally constant. No diffusion is observable when the cock is closed. Even when phosphorus is contained in the bottom of a bottle, it is not liable to diffuse out of the mouth in sufficient quantity to color



[illegible] Scale [illegible] Sensitive Point, etc., of the Steam Jet. [illegible] Figs. 12, 13, 15. Electrical (High Potential) [illegible]

the jet. To be effective the dust must therefore be conveyed into the tube by convection.

The tube is to be from 6 to 12 inches long or longer, depending on the velocity of the current of air to be passed through it. If the current is too rapid, the phosphorus is apparently chilled or oxydized too highly, so that the air which escapes is now as ineffective as from a tube with too slow a current or a closed tube. A somewhat similar difficulty is encountered on using the color tube with a pellicle of phosphorus. If this is put too near the jet it will not color it. So an X-ray tube too near the jet is neutral. A certain volume for growth of nuclei is apparently needed. If the pellicle, figure 9*a*, is approached through *C*, figure 10, toward the jet or removed from it, blue flashes appear between relatively clear fields. In position *a*, to take another instance, there is permanent coloring due to phosphorus dust slowly entering *C* around the edge. At *b*, the color effect is apt to be absent. The result is unchanged even for a tube, *C*, two feet long. Placed in a lateral tubulure as at (1), the phosphorus pellicle is ineffective, whereas if at (2), (3), or (4), the field is markedly colored. In like manner in using the multiple tube method for graduation, the place of insertion of the mouths of the tubes of the form *AB*, figure 9, made a difference in the color effect obtained, cæt. par.

6.—Aspirating air at the rate of several liters per minute over sulphur at 300 did not produce perceptible darkening, although ignited sulphur is very effective. Ignited phosphorus, even when passing oxide visibly into the color tube, is without action. Glass tubes when heated high enough to show the sodium flame on the outside throw an abundance of nuclei into the air current passing through them to the color tube. Other tubes (metallic) are also liable to volatilize sodium vapor under like circumstances, if not quite recently cleaned. In such a case a change of color from yellow to blue through opaque occurs as the tube cools. The phenomenon is complicated by the efflux of hot air.

7.—For concentrated sulphuric acid, a Wulff's bottle is a convenient apparatus for producing the nuclei, the air being bubbled through it as shown in figure 11. Coal gas as a convection agent is even more effective. Phosphorus, *P*, may also be used in this way, but less efficiently.

8.—Washing the air charged with nuclei has but little effect, if any. Heat, however, seems to exert a tendency to dissociate them. In the apparatus shown, figure 11, the nuclei from the Wulff's bottle were passed through a hot tube, thereafter cooled down in a spiral of lead tubing surrounded by crushed ice, then discharged into the color tube *C*. On examination the hot metallic tube showed a violet-opaque, the cold tube a blue-gray color when the dust was discharged into the color tube, indicating more dust in the first instance. After the removal of the phosphorus from the bottle no color was observed, proving the tube to have been clean at the given temperature. The red-hot metallic tube gave a blue color, however.

9.—Clean hot copper surfaces removed out of the reducing flame darkened the tube instantaneously, while the oxide coats were forming. As I failed to get the same result with iron, it is probable that ions were carried out of the flame in temporary combination with the metal. Sodium (oxidizing) is without effect.

10.—If air is aspirated through ammonium polysulphide considerable pressure is needed to produce a colored field. It colors markedly while the liquid is evaporating from a wet stopper, for instance. Coal gas is itself but slightly charged with nuclei; if bubbled through the polysulphide, however, the latter becomes intensely color producing though opaques are rare. It is a striking feature of this experiment, that the air of a room when tested with the color tube remains permanently fouled for hours afterwards. In all these instances an unstable sulphur compound is apparently preserved from oxidation, and this nucleus is permanently present in coal gas.

11. It is well to note that such volatile chemicals as camphor, camphor monobromide, naphthalene, benzoic acid, phenol, toluol, amylbenzoate, diphenylamine, etc., like sal ammoniac, produce no color effect unless they are charred. Some of these are electrolytes. With ammonic chloride it is even possible to clear the blue field due to phosphorus, by passing its emanation with a definite amount of the smoke of the former into the color tube. The phosphorus nuclei seem thus to be absorbed by the particles of sal ammoniac and the condensation effect of the former is destroyed. This result seems to me to be of considerable importance.

If coal gas is passed through the phosphorus tube, figure 9*b*, the field is all but cleared after an initial puff of color. There is, however, a residual faint tint due to the coal gas alone. The phosphorus at once becomes active again when air is blown through the tube.

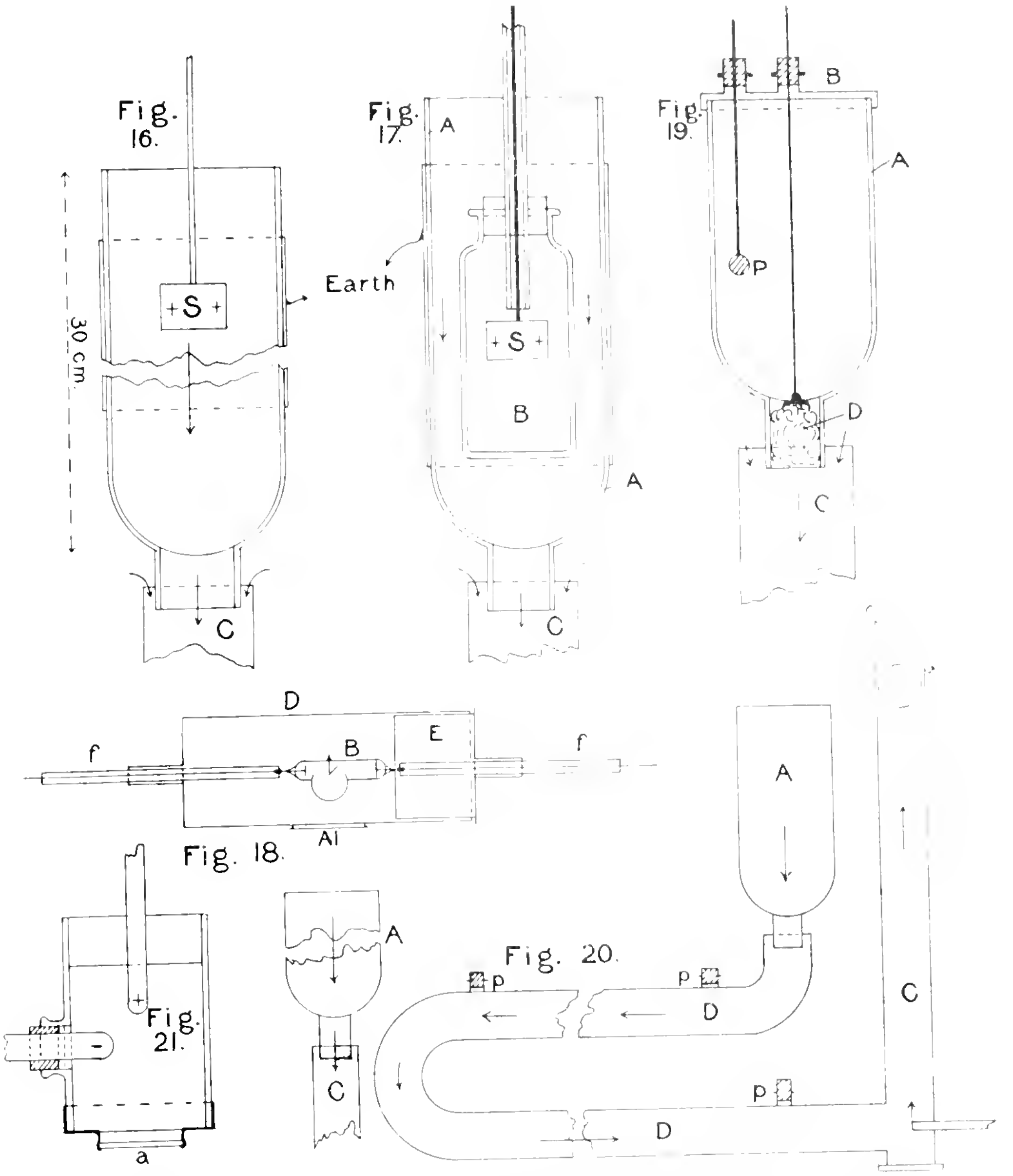
12. *Electrical ionizers.*—The prime conductor of a Holtz machine placed near the mouth of the color tube is without effect. When a needle is added, however, the coloration becomes intense. Hence the brush or glow is a powerful dust producer. Air passed through the cylindrical shell of a tubular condenser is not active without sparks. If the air is dust laden it is not appreciably affected by the condenser.

A gauze condenser surmounting the color tube *C*, as in figure 12, shows intense action corresponding to the continual leakage. If enclosed by a close-fitting glass jacket, *DD*, figure 13, its effectiveness is nearly destroyed, probably because the leakage runs down the glass or the lines of force terminate in it. In these experiments a spark at the machine clears the field completely, so that the color surges with the potential. If the upper condenser plate is a spiral brush of fine wire gauze, *S*, figure 14, the color effect continues for a distance of even 20 centimeters between the plates, the machine now giving one-inch sparks. Similarly ½ inch sparks on the machine give like color results for ½ inch distances between the plates.

More effective than a narrow jacket is a wide bell jar, as shown in figure 15. Here ½ inch sparks on the machine darken the field when the condenser plates are 20 or even 30 centimeters apart. Reversal of polarity showed no definite results. Darkness now continues during sparking at the machine, and it takes about 30 seconds to empty the vessel after the electric machine is switched out. Here and elsewhere a maximum darkening effect seems to correspond to a definite spark length. Very high potentials probably develop brushes along the electric conductors, as the presence of an electric wind not playing into the tube *C*, clears the field.

13. The electric duster is further increased in efficiency by the spiral brush *S* and radial condenser arrangement of figure 16. In the dark the influx into the color tube *C* passes through the radial glow and becomes a tremendously strong dust producer, even with small sparks on the machine.

This arrangement loses but little of its activity when the brush *S* is enclosed in a glass bottle, *B*, figure 17, where the well-insulated terminals are sealed in place by a plug of paraffine. The whole is placed within the wide vessel *A*, with



FIGS. 16, 17.—COMPLETED ELECTRICAL IONIZERS. SCALE $\frac{1}{6}$. FIG. 18.—X-RAY IONIZER. SCALE $\frac{1}{10}$. FIG. 19. APPARATUS FOR TESTING THE PERSISTENCE OF NUCLEI. SCALE $\frac{1}{6}$. FIG. 20.—LONG TUBES (60 FEET), FOR TESTING PERSISTENCE. SCALE $\frac{1}{10}$. FIG. 21.—ULTRA-VIOLET IONIZER. SCALE $\frac{1}{2}$.

an external condenser surface added and put to earth. The neck of *A* dips into the influx pipe *C* of the color tube. In the dark, radial streamers of great beauty pass between the vessels, *A* and *B*. All brushes are within the outer vessel and the effect is not changed by a coating of paraffine, the glass being 3–4 millims. thick.

14. *X ray duster.* This experiment suggested the efficient method of adjusting an X ray duster, as the X ray tube did not easily react on the naked jet. The plan, in other words, is to ionize the air within a spacious bell jar, by X-light, and then to carry the nuclei so produced into the color tube C by convection. In figure 18 (drawn to a smaller scale), B is the X ray tube (Bowdoin pattern), enclosed in a cylindrical box of tin plate, D, with a removable lid, E, and an aluminum window at M. The terminals ff are enclosed in glass tubes filled with paraffine, and their exposed ends 52 inches apart to avoid brush action on the color tube C. The tube radiates through the window into the bell jar A, and may even be placed over 18 inches above its mouth. The action of this dust producer is intense, and the field opaque when the current passes. Phosphorus placed within the cylinder D is quite ineffective, showing that no direct leakage occurs out of it. The usual experiments may be made. A tin plate screen between the window and jar cuts off all rays, an aluminum screen almost none. The steam pressure of the jet may be reduced until steam just passes.

15. *Persistence of nuclei.* The same method may be modified to test the persistence of nuclei, particularly in the case of phosphorus. The apparatus is shown in figure 19, consisting of the large bell jar, A, closed loosely by the lid B, so as to admit of a circulation through the jar when the cotton plug D is removed. The contents then discharge into the color tube C. P is the globule of phosphorus on a wire stem, which, like the plug, can be inserted into A and withdrawn easily through stoppered tubulures in the lid.

With the valve open and P in place, the field is always opaque, a test which was made throughout the experiments. The following results indicate the coloring power of the contents of the jar at different times after the phosphorus was suddenly removed. Removal of the lid showed a blue color lasting fifteen seconds.

Time after removing	Color in tube.	Duration (time to empty the vessel).
15 sec.	opaque.	10 sec.
30 "	dark blue-gray blue	10 "
60 "	smoky brown.	—
[30 "	opaque-blue.	15 "]
60 "	smoky blue-gray	10 "
120 "	flash of darkness.	——
150 "	gray-green flash when	——
180 " (lid wadded).	lid is removed.	——
20 "	opaque to blue.	——
180 "	flash of darkness.	—

These data show that even after three minutes enough dust is left to make an impression on the color tube C. The apparent decay, however, is marked, and even during the time taken in emptying the vessel (10–15 sec.), the attenuation is apparent. Colors so produced, moreover, are not clear.

16. *Coefficient of decay.* Taken in connection with the results of the next chapter, the present experiments admit of a preliminary estimate bearing on the

size of the particles. Let n be the number per cubic centimeter. Then the rate of decay is $-(dn/dt)=k'n^2$, where k' is a constant. Hence $1/n_2 - 1/n_1 = k' (t_2-t_1)$, for any two given observations. Now if the number of particles entering the color tube per second is N, and V the inflowing volume of gas per second carrying them, $N = Vn$. At the two times of observation therefore, $1/n_2 = V/N_2$ and $1/n_1 = V/N_1$. Hence, $V(1/N_2 - 1/N_1) = k'(t_2 - t_1)$. The colors seen in the color tube at the times t_1 and t_2 correspond by the next chapter to different volumes, V_1 and V_2, of similarly dusted air, per second. Thus if N be the number of dust particles here and n the common concentration of each of the two volumes specified, $N_1 = V_1 n$ and $N_2 = V_2 n$, where N_1 and N_2 must have the same value as above. Hence $(V/n)(1/V_2 - 1/V_1) = k'(t_2-t_1)$. Here V, the convection volume flowing out of the vessel per second, may be estimated from the time taken to empty it, or otherwise determined. Thus, $n = (V/V_2 - V/V_1)/k'(t_2 - t_1)$. Supposing that k' were known from other sources, the value of n would follow, this being the number of particles per cubic centimeter for nearly saturated air; or vice versa. The following is a rough measurement.

The equation may be put in the form, $k' n_0^2 / n_0 = (V/V_2 - V/V_2)/(t_2-t_1)$, which states the number decaying per cubic centim., per second relatively to the total number present.

The only datum of the preceding table available here is marked by a bracket. Hence,

$t_2 = 60$ sec.	opaque-blue.
$t_1 = 30$ sec.	blue-gray.

The volume of the bell jar was 2690 cubic centims. The time to empty it is 10–15 seconds, by the table. Hence, $V = 210$ cub. cm. / sec. $= 12.6$ liters / min. In the next chapter the data are roughly for

blue-opaque,	2. lit./min. $= V_1$
blue-gray,	.7 lit./min. $= V_2$

Thus $k' n_0^2 / n_0 = (18 - 6.3) / 30 = .4$, that is $\frac{1}{10}$ of the ions per cubic centim. mutually destroy each other per second, in the saturated region. If $n_0 = 4 \times 10^4$, $k' = .000010$.

These results are naturally uncertain from the character of the measurements, which in the above table are mere estimates. So also the times of emptying the vessel are not sharp values. The experiment is chiefly interesting from a theoretical point of view but does not lend itself for accurate measurement. Apart from this it will be argued in Chapter III *et seq.* that k' may be ignored if each ion is endowed with a velocity k of its own. In such a case the loss of ions results from their absorption at the walls of the bell jar. In other words, ions wander out of the interior of the jar in all directions to eventually impinge on the walls where they are destroyed. It is in this sense that I understand the action of cotton and other filters, these being a means of increasing the absorbing surface enormously.

17. *Persistence of nuclei in long tubes.*— Experiments with a similar bearing

may be made by passing dust-laden air through considerable lengths of wide tubing. Drain pipe made of tin plate is admirable for this purpose, one end being left open and the other joining the color tube. This is shown in figure 20, at *D*, if the vessel *A* is removed. Stoppered holes, *p*, at different distances apart admit the phosphorus particle. The following results were found with tubes 2 inches in diameter and as much as 60 feet long. The draft in the influx tube being actuated by the jet depends on the steam pressure. It may be reduced by opening the bottom of the tube *C*. The first series of values were found with a pellicle of phosphorus placed in the tube at different distances, *D*, from the jet.

Distance from jet.	Color.	Jet pressure.	Lower window of color tube.
54 feet	green.	6 cm.	1/3 open.
48 "	opaque-blue	6 "	1/2 "
38 "	opaque.	6 "	1/2 "
54 "	blue-gray.	3 "	1/3 "
48 "	blue-violet.	3 "	1/2 "
38 "	just opaque.	3 "	1/2 "
54 "	blue-gray.	3.5 cm.	Removed.
48 "	blue.	"	"
38 "	blue.	"	"
6 "	opaque.	"	"

The persistence of dust nuclei is thus again a question of minutes, for in the time of transfer through these long tubes at the slowest velocities obtainable (lower window of color tube opened for this reason), the color effect still survives, though with diminished vigor.

The work was afterwards repeated, with extremely small steam pressures but relatively wide jets (½ inch), introducing an abundant flow of steam nearly at atmospheric pressure. The time of passage through the tubes and the duration of the color due to an instantaneous introduction of the phosphorus pellicle at the far end were also noted. Mixture and diffusion occur during the passage. The tube lengths were 54 to 60 feet.

(1) Flash at far end lasts 1[illegible] seconds at near end.

(2)

Time of passage.	Color.
3[illegible] sec.	Not changed perceptibly.
65 sec.	Darkness (opaque field) intense.
45–75 sec., diam. jet .45 cm.	Phosphorus inserted in far end a few seconds only. Effect prolonged at near end as shown.
60–90 sec., diam. jet .75 cm.	

Thus the increased supply of low-pressure steam (wide jet) has much enhanced the sensitiveness of the apparatus, though color, as such, no longer appears. The time of passage obtained in this way (90 seconds in the maximum) is below that of the preceding experiments with bell jars. The gradual lengthening of the dust-laden column of air is due to the eddying mixture in passage.

18. *Persistence of X-ray nuclei in long tubes.*—With the addition of the vessel *A*, figure 20, and the adjustment of figure 18, the former arrangement was

used to test the persistence of X-ray dust in the pipes D. The results are as follows, the time of transfer being found by the phosphorus pellicle.

Z, Tube length.	Color.	Time of transfer.
15 feet.	Blue field ($Z = o$) cleared to green.	–
34 "	" " " " " yel.-green.	15 sec.
54 "	" " " " " "	20 "

The jet being of the usual pattern, it will be seen that dust due to phosphorus and to the X-rays is about equally persistent, being supposedly of the same nature in both instances, namely, ionized air. The dusting activity of phosphorus is here far stronger, however, as the colors show.

19. *Differential experiments with long tubes.*—A few tests with the differential apparatus, figures 2 and 4, may here be referred to, the connecting pipe, D, being about 50 feet long. If the near tube, (I) or A, is opaque (steam at high pressure), the far tube, (II) or A', shows a gray field not quite opaque. The dust producer (P), active in (I), will not be so in (II). If the latter be supplied with its own jet, phosphorus will again color the field. If the tube length is 34 feet the result is not materially changed. For 14 feet of tube length both become opaque, but no color is seen in (II), only a less degree of darkness. For 5 feet of tube length, the colors are the same in both apparatus, but muddy and dull in the second. Yellow brown in (I) becomes opaque in (II). No congested tube will produce the yellows of the first order, nor any colors brilliantly. The distribution of particles has become irregular as to size. A stimulated draft would be needed.

20. *Ultraviolet ionizers.*—Results with ultraviolet light failed in all instances except with the wide vessel, which was not tried. Sparks of a Holtz machine screened by a quartz window showed no darkening of the tube, wherever applied. The sparking apparatus is given in figure 21, the terminals being of zinc and the window, a, of quartz.

CHAPTER II.

THE COLORS OF THE STEAM JET, AS RELATED TO THE NUMBER OF NUCLEI IN REACTION.

1. *Preliminary.* After these preliminary experiments on the efficiency of the jet, it seemed advisable to make a first attempt to find the relation of the color of the cloudy condensation to the degree of saturation of the ionized air producing it. Qualitative experiments for this purpose are easily devised, but in the absence of direct knowledge of the nature of the condensational activity of phosphorus, and of the behavior of the steam jet in relation thereto, interpretation is necessarily difficult. Thus, for example, if the air currents passing over phosphorus are either too swift or too slow they both give a colorless field, as has already been instanced. If the temperature is too low or too high, similar results appear; whether the condensation is due to nuclei or to chemical or electrical reactions is not definitely disposed of; etc.

2. *Apparatus.*—The apparatus used in this work is given in figure 1. C is the color tube provided with a lateral elbow, C', open above and either side about 18 inches long. Into the top of this dips the phosphorus tube P, so that the charged efflux may be carried down by the current in C'. P has the usual form as given in Chapter I, figure 9*b*, above. It is about 1 cm. in diameter and 20 cm. long, and contains phosphorus strips stretched along the axis. A definite volume of air per second is passed through P by aid of the aspirator train V, M. V is a large flask of 8 litres capacity, graduated on the side S. Water is added from or removed to the bucket M, which can be raised or lowered by the pulley p. The air from V passes the stopcock E, a pin valve of fine workmanship, and by opening this more or less the color in C can be regulated to a nicety. A dessicator, D, removes superfluous moisture. I did not find this appurtenance essential, though it clearly must prolong the life of the ionizer in P. In this respect alone, moreover, it is unadvisable to draw the air backward, through the phosphorus tube, into V.

A seconds watch was at hand to measure the rate of influx of water into the volumeter V, and therefore the rate of efflux of air out of V, through P, into C' and C. The elbow was supposed to insure mixture.

This original apparatus has an obvious error in design, since the pressure of the air in V varies as M is more or less raised above the water level in V. Air is at first introduced at slightly higher pressure and relatively greater volume than at the end of the experiment. The effect on the color of the tube was not marked, but it was thought best to obviate it as follows. Retaining V with the new cock at *b* (not shown) leading to the phosphorus train as above, the influx canal of *V* was modified by the addition of a lateral tube, *h*, with the wide stopcock at *c*, and a small one at *d* communicating with the out-side air. The bucket was replaced by an enormous Mariotte flask, *M*, of copper, having the tube *if*, within and an outlet at *g*, joined by half-inch rubber hose to *c*. The pulley at *p* is in action as before. When the apparatus is in operation, the water pressure on *V* is equivalent to the difference of level between *d* and *f*. Hence the head is constant, *c* and *d* being closed during influx. The gauge *U*, measures variations of this pressure. At the end of the experiment, *c* and *d* are opened and *M* lowered, insuring rapid flow when the stopper or valve at *v* is removed.

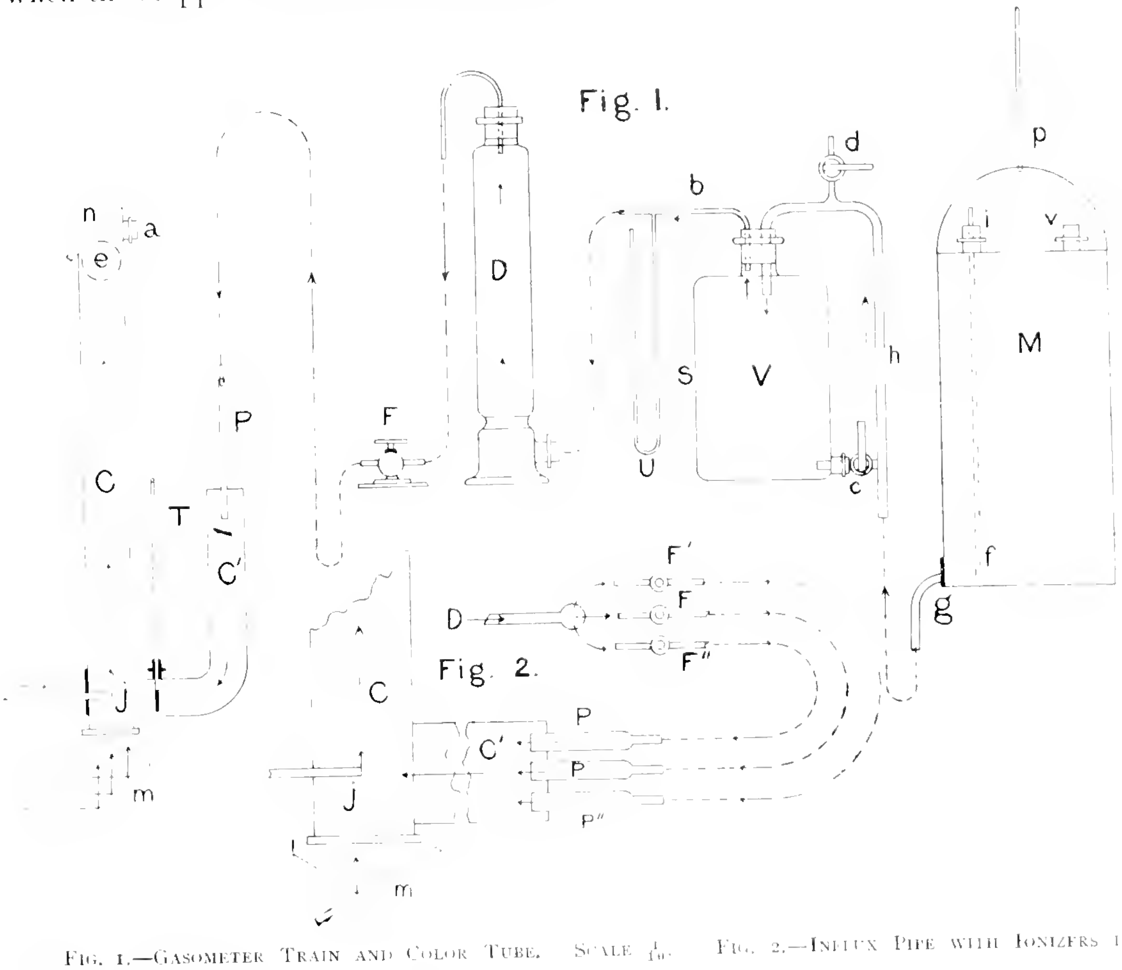


FIG. 1.—GASOMETER TRAIN AND COLOR TUBE. SCALE $\frac{1}{10}$. FIG. 2.—INFLUX PIPE WITH IONIZERS IN MULTIPLE. SCALE $\frac{1}{4}$.

In figure 2, three phosphorus tubes are used at once for purposes to be explained below.

3. *Results.*—In making the observations, it was customary to observe the thermometer *T*, for the temperature θ, and the steam gauge for the pressure, *p*, at the jet. The volume *V*, of air flowing per minute out of the gasometer, was next taken when the given color stated was clearly seen throughout the dust discharge into *C'*. All these results are given in the following table 1, where the volume

per minute necessary to produce the full blue of the first order is put equal to one unit. The volume ratio for all the other colors is then the equivalent, in the same scale, of the numbers of particles necessary to produce them, provided that the air passing through the phosphorus ionizer is discharged in the same state of saturation, and there is no other variation of the steam jet and color tube during the experiment. The table also gives the volume in litres per minute in case of each standard blue taken. As this datum is on the average of the order of .5 liters/min., the tabulated volumes V are in a general way about twice the absolute mean volumes. The use of the standard blue for reference is unavoidable, so long as the precise conditions under which phosphorus emanates are not understood.

The reciprocal of the volume ratio V will vary as the bulk of the steam globule produced, supposing that the supersaturation which precedes condensation has remained constant. Thus there must be no change in the pressure of the steam jet or in the temperature of its environment. The cube root of the reciprocal of the volume ratio might then be called the diameter of the particle. It will be shown below, however, that variations of θ and p are not of the importance which one would attach to them at the outset.

The table consists of 4 parts of which the first is preliminary, the second at a relatively high room temperature, promoting the occurrence of the browns of the first order but giving very faint tints of the second order. The third part at relatively low room temperature (θ) favors the second order of colors but terminates in opaque of the first order. In the fourth part the air was taken from the outside of the room and warmed in the steam drum. The last part is incidental.

TABLE I.

Each part of this table contains successive series of data obtained on different days, as a rule. In all there are 23 series.

TABLE I, PART I, PRELIMINARY—COLOR AND RELATIVE NUMBER OF PARTICLES. BLUE = "1." RELATIVE BULK AND DIAMETER.

Color	Volume Ratio, Number.	Bulk	Diameter	p.	θ.	Series No.
Dark Violet.	2.72	.367	.72	11 cm.	23	1
Blue.	.98	1.02	1.00	10	23	
Blue-Green.	.52	1.92	1.24	10	23	
Yellow Green	.26	3.85	1.57	10	23	
Violet-Blue	1.66	.602	.84	9.5	23	
Blue Green.	.84	1.19	1.06	9	23	
Opaque-Violet	2.02	.5	.79	9	24	
Blue Green.	.62	1.61	1.17	9	24	
Opaque	2.3	.43	.76	7	24	2
Blue.	1.	1.0	1.0	6.5	24	
Green	.72	1.39	1.11	6.5	24	
Yellow-Green	.44	2.27	1.32	6.5	24	

PART I.—*Continued.*

Color.	Volume Ratio, Number.	Bulk.	Diameter.		θ.	Series No.
Dark Violet	1.40	.71	.89	7.5 cm.	25	3
Blue	.86	1.16	1.05	7.0		
Green-Yellow	.29	3.45	1.51	7.5		
Pale Purple	.11	9.10	2.09	8.0		
Green	.60	1.67	1.19	7.5		
Blue	1.00	1.00	1.00	6.0		
Dark Violet	1.70	.59	.84	—		
Pale Purple	.29	3.45	1.51	4.0		
Violet-Blue	1.30	.77	.92	7.5 cm.	25	4
Opaque	2.20	.45	.77	7.5		
Green	.54	1.72	1.20	8.0		
Pale Purple	.14	7.10	1.92	8.1		
Pale Purple	.25	4.00	1.59	1.5 cm.	24	5
Pale Yellow	.33	3.03	1.45	1.0		
Blue-Green	.67	1.49	1.14	1.0		
Dark Violet	1.30	.77	.92	1.0		
Opaque	1.60	.62	.85	1.0		
Pale Purple	.25	4.00	1.59	1.5 cm.	26	6
Yellow-Green	.37	2.70	1.39	1.5		
Blue-Green	.75	1.33	1.10	1.5		
Dark Violet	1.40	.71	.89	1.5		
Opaque	2.50	.40	.74	1.5		
Pale Purple	.25	4.00	1.59	1.5		
Pale Yellow	.50	2.00	1.26	1.5		
Blue-Green	.62	1.60	1.17	1.5		
Dark Blue	1.00	1.00	1.00	1.5		
Dark Violet	1.60	.62	.85	1.5		

PART II.—COLORS AT RELATIVELY HIGH TEMPERATURES.

Yellow-Green	.43	2.35	1.32	2.5 cm.	28	7
Blue (.40 $\frac{L}{m} = 1$)	1.00	1.00	1.00	"	"	
Violet	1.60	.62	.85	"	"	
Yellow (muddy)	9.00	.11	.48	"	"	
Yellow-Green	.35	2.86	1.42	3.5	29	7
Blue-Green	.54	1.85	1.23	"	"	
Blue (.43 $\frac{L}{m} = 1$)	1.00	1.00	1.00	"	"	
Violet	1.90	.53	.81	"	"	
Yellow (muddy)	8.10	.12	.49	"	"	
Pale Yellow	.27	3.70	1.55	4.0 cm.	29	8
Yellow-Green	.36	2.78	1.41	"	"	
Blue Green	.27	3.70	1.55	4.5 cm.	"	
Blue (.48 $\frac{L}{m}$) = 1.	1.20	1.00	1.00	"	"	
Violet	1.40	.71	.89	"	"	
Violet-Opaque	2.25	.45	.76	"	"	
Yellow-Opaque	4.25	.24	.62	"	"	

PART II (*continued*).

	[illegible] Number	Ions.	Diameter		t°.	Series No.
[illegible] Purple-Yellow	.22	4.54	1.66	4.5 cm.	29	9
Green-Yellow	.45	2.22	1.31	"	"	
Blue-Green	.55	1.82	1.22	"	"	
Blue (.45 = 1)	1.00	1.00	1.00	"	"	
Violet	1.62	.62	.85	5	"	
Opaque Violet	2.25	.44	.76	"	"	
Yellow	8.75	.11	.49	"	"	
Blue-Green	.50	2.00	1.26	"	"	
Green-Yellow	.27	3.70	1.55	2.5 cm.	31	10
Blue (.55 = 1)	1.00	1.00	1.00	"	"	
Opaque-Violet	1.85	.54	.81	"	"	
Opaque-Yellow	3.45	.29	.66	"	"	
Green	.44	2.27	1.32	"	"	
Yellow-Green	.44	2.27	1.31	4.5 cm.	29	11
Blue Green	.44	2.27	1.31	"	"	
Blue (.45 = 1)	.89	1.12	1.04	"	"	
Violet	1.55	.65	.87	"	"	
Dark Blue	1.07	.93	.98	"	"	
Yellow Opaque	4.60	.22	.60	"	"	
Blue (.5 = 1)	.94	1.06	1.02	8 cm.	30	12
Violet	1.9	.53	.81	9	"	
Opaque-Yellow	4.00	.25	.63	8	"	
Yellow-White	10.50	.09	.45	7	"	
Green	.56	1.79	1.21	4 cm.	29	13
Blue (.45 = 1)	1.10	.91	.97	"	"	
Violet	1.38	.72	.90	"	"	
Yellow	8.4	.12	.50	"	"	
Purple-Yellow	.20	5.00	1.71	7 cm.	29	14
Blue-Green	.80	1.25	1.08	7	"	
Dark Blue	1.1	.91	.97	5.5	"	
Opaque Violet	1.90	.53	.81	"	"	
Blue (.5 = 1)	1.00	1.00	1.00	5	"	
Violet	2.20	.45	.77	"	"	

PART III.—LOWER ROOM TEMPERATURES.

Faint Purple	.13	7.69	1.97	9 cm.	21	15
Green-Yellow	.40	2.50	1.36	"	"	
Blue Green	.86	1.16	1.05	"	"	
Dark Blue	1.20	.83	.94	"	"	
Dark Violet	1.47	.68	.88	"	"	
Faint Purple	.58	1.72	1.20	6 cm.	21	16
Yellow-Green	.86	1.16	1.05	"	"	
Blue Green	1.00	1.00	1.00	"	"	
Blue Violet	1.30	.77	.92	"	"	
Opaque	1.43	.70	.89	"	"	
Blue Violet	1.3	.77	.92	6.5	21.5	
Blue (.35 = 1)	1.0	1.00	1.0	"	"	
Blue Green	.86	1.16	1.05	"	"	
Purple Yellow	.43	2.33	1.33	6	22	
Pale Violet	.34	2.94	1.43	"	"	
Dark Blue	1.10	.91	.97	"	"	

PART III.—*Continued.*

Color.	Volume Ratio, Number.	Bulk.	Diameter.	p.	θ	Series No.
Pale Violet	.34	2.94	1.43	5 cm.	22	17
Yellow-Purple	.48	2.08	1.28	"	"	
Yellow-Green	.60	1.67	1.19	"	"	
Blue....................	.87	1.15	1.05	"	"	
Dark Violet	1.27	.79	.92	"	"	
Blue (.38 $\frac{L}{m} = 1$)..........	1.00	1.00	1.00	"	"	
Blue-Gray	1.00	1.00	1.00	"	"	
Blue-Green	.74	1.35	1.11	"	"	
Faint Yellow	.53	1.89	1.23	"	"	
Faint Purple.............	.42	2.38	1.33	"	"	
Pale Violet	.32	3.12	1.46	"	"	
Whitish Indigo...........	.19	5.26	1.74	"	"	
Faint Purple.............	.40	2.50	1.36	3 cm.	24	18
Yellow-Green	.50	2.00	1.26	"	"	
Blue	.90	1.11	1.04	4	15	
Violet..	1.30	.77	.92	4.5	"	
Blue (.50 $\frac{l}{m} = 1$)	1.00	1.00	1.00	4	"	
Blue-Gray...............	.70	1.43	1.13	5	"	
Pale Yellow	.40	2.50	1.36	5.5	"	
Faint Purple.............	.20	5.00	1.71	5	"	

PART IV.—COLD AIR TAKEN FROM OUTSIDE THE HOUSE AND WARMED.

Color.	Volume Ratio, Number.	Bulk.	Diameter.	p.	θ	Series No.
Faint Purple	.45	2.22	1.30	4 cm.	19.5	19
Green	.70	1.43	1.13	"	"	
Blue (1.00 $\frac{L}{m} = 1$).........	1.00	1.00	1.00	"	"	
Faint Purple	.47	2.13	1.29	5 cm.	18.5	
Purple-Yellow	.47	2.13	1.29	4.5	"	
Yellow	.59	1.69	1.19	"	"	
Yellow-Green	.67	1.49	1.14	4	"	
Blue-Green	.80	1.25	1.08	"	"	
Blue (.75 $\frac{L}{m} = 1$).........	1.07	.93	.98	"	"	
Violet	1.60	.62	.85	"	"	
Blue	.94	1.06	1.02	3	18	
Green	.71	1.41	1.12	"	"	
Faint Yellow.............	.55	1.82	1.22	2.5 cm.	17.5	20
Green	.83	1.20	1.06	"	"	
Blue (.60 $\frac{l}{m} = 1$)..........	1.00	1.00	1.00	"	"	
Violet	1.33	.75	.91	"	"	
Blue	1.00	1.00	1.00	5.5	"	
Green	.67	1.49	1.14	4	"	
Faint Purple............	.50	2.00	1.26	"	"	
Faint Purple-Yellow.....	.29	3.45	1.51	6.5 cm.	26.5	21
Green-Yellow	.43	2.33	1.33	"	"	
Blue-Green	.76	1.32	1.10	"	25	
Blue (.70 $\frac{L}{m} = 1$)....	—	—	—	—	—	
Violet-Blue.......	1.29	.77	.92	"	"	
Opaque-Violet	1.57	.64	.86	"	"	
Opaque-Yellow	4.40	.23	.62	"	"	

PART IV. SUPPLEMENTARY DATA.

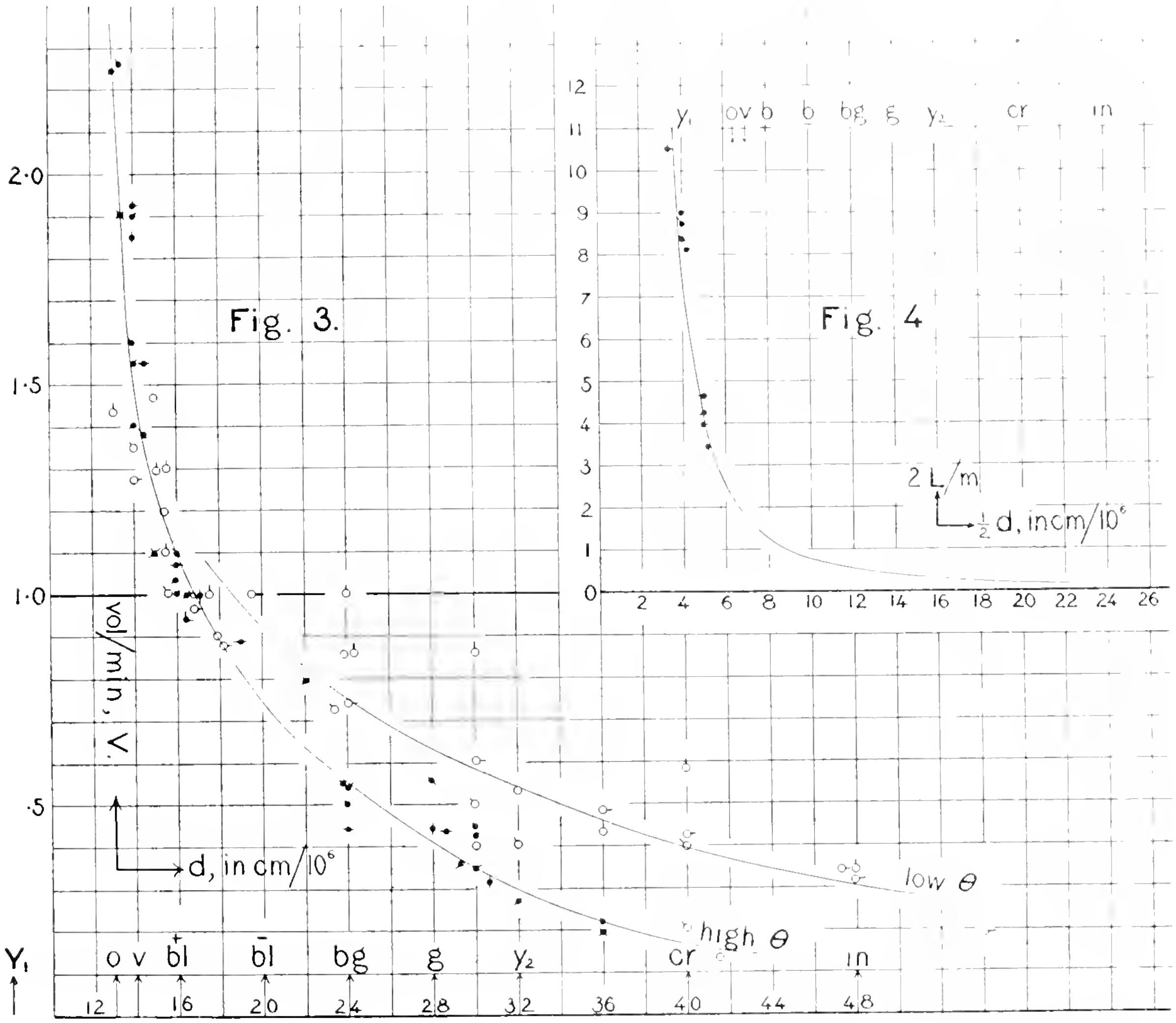
	[illegible]	Ball.	Diameter	*p.*	*h.*	Series No.
[illegible]	.24	4.17	1.61	5 cm.	24	22
Yellow	.52	1.92	1.24			
Green	.52	1.92	1.24			
Light Blue	.80	1.25	1.08			
Dark Blue (.5 = 1)	1.00	1.00	1.00			
Violet	1.60	.62	.85			
Opaque	2.80	.36	.71			
Pale Violet	.30	3.33	1.49	5 cm.	27	23
Green-Yellow	.39	2.56	1.37			
Blue Green	.40	2.50	1.36			
Light Blue	.65	1.54	1.15			
Blue (.57 = 1)	1.00	1.00	1.00			
Violet	1.27	.79	.93			
Dark Violet	1.46	.68	.88			
Dull Yellow	4.75	.21	.60			

4. *Results Charted.*—Some of these data are given in the accompanying charts, figures 3 and 4, and the attempt is made to distinguish the different series by different forms of dots. Part 2, made under the most favorable conditions and giving the best results, is marked by full dots; part 3 by open dots.

In the construction of these data, the volumes per minute (on the average about twice the actual number of liters min.) of saturated phosphorus emanation are made the ordinates, corresponding to the colors given by the abscissas. To have a scale in the latter case I took the thickness *d*, of air plates giving, on normal incidence and transmitted light, the identical color in case of Newton's interferences. In figure 3 the data are on a large scale, but reach only as far as opaque. In figure 4 the whole curve and remaining data are constructed on a smaller scale, *L m*, denoting liters per minute. The two curves of figure 3 refer respectively to lower and higher temperatures θ, or to the 2d and 3d parts of table I. The latter is decidedly the better, showing some definiteness of a locus, quasi-hyperbolic in character. The low-temperature data are diffuse, due, I think, to the weak and variable ionizing activity of phosphorus at low temperatures. During the long period of observation there must have been some corrosion of the jet. This is probably one of the chief reasons why the dust contents (lit. min.), corresponding to the standard blue, vary. In the second place, the air of the room does not retain a fixed degree of purity.

5. *Discussion.* In consulting these charts for practical purposes, curves obtained in joining points of the same kind should alone be used, as the reasons for the differences between the series are naturally very complicated. In spite of all care bestowed on the observations, they are insufficient to suggest the form of locus with certainty. Their usefulness will therefore be confined to testing the theory of the phenomenon when such a theory is forthcoming. In a general way the locus, beginning with opaque and extending toward the right into the fainter second

order of colors, is horizontally asymptotic with its concavity upward. Toward the left of opaque the browns of the first order make a very rapid ascent, suggesting a vertical asymptote. If one is led to infer that the latter are due to the scattering of fine particles set forth in Rayleigh's dynamics of the blue sky, whereas the others are diffractions or interferences (Clausius) of the more nearly regular kind (*i. e.*, cases where the particles or vesicles are large enough to be subject to the ordinary optical laws), the continuity of curve from either side of opaque is baffling.



FIGS. 3, 4.—CHARTS SHOWING THE RELATION OF THE RELATIVE NUMBER OF PARTICLES (DUST CONTENTS) TO THE COLOR PRODUCED, EXPRESSED IN THICKNESSES (AIR) OF NEWTON'S INTERFERENCE PLATES.

There is further difficulty in making a comparison of the data as a whole, seeing that one arbitrary element must enter the work even if the jet action and the ionizing intensity of the phosphorus remain constant; for the velocity of the current of air entering the color tube at C'' for a given jet, varies with the form and dimensions (resistance to flow) of the influx tube. The dust density which actually reaches the jet is determined by a ratio of the volume of the air inflowing at C', and due to the action of the steam jet, and the volume of the charged air inflowing from P, determined by the pressure of the aspirator. In this respect also must the apparatus be left unaltered if the data are to be comparable. Hence, when the air is taken from without the room in winter, the rush of air through the color tube

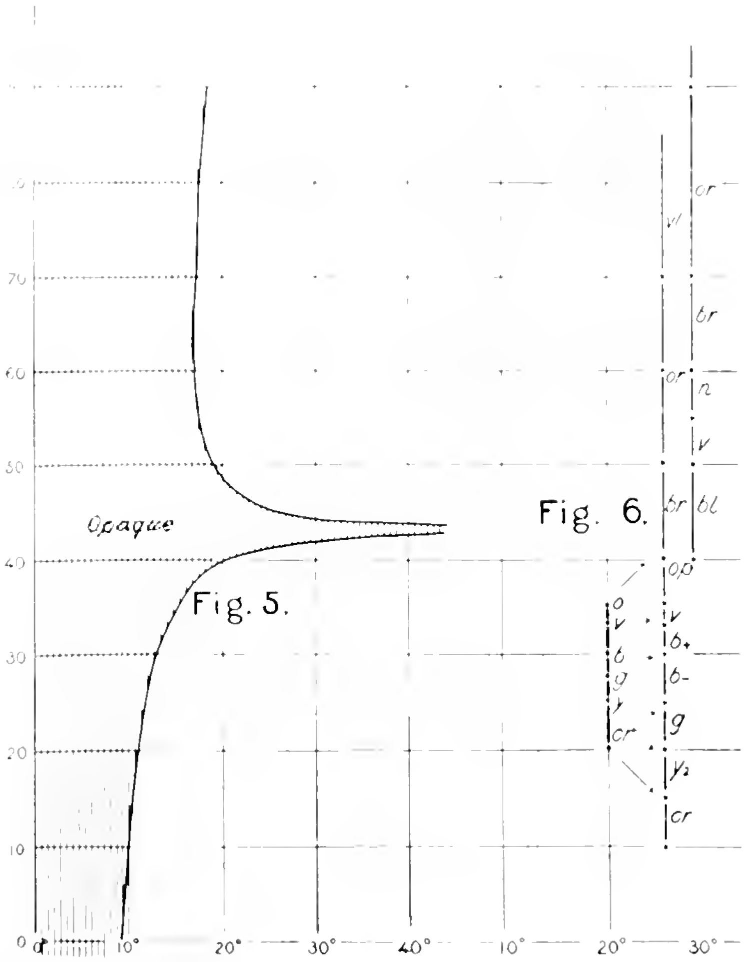


FIG. 5.—CHART SHOWING MARGINS OF THE OPAQUE FIELD IN TERMS OF AIR TEMPERATURE AND STEAM PRESSURE. FIG. 6.—CHART SHOWING MARGINS OF THE COLORED FIELDS IN TERMS OF TEMPERATURE AND PRESSURE.

will be increased by the natural draught under which the air enters. As a result, the dust content is diluted, cæt. par. This discrepancy is quite observable, and the colors show an uncertainty and flicker, due to bad mixture. Hence these results are discarded in the chart. Again, the difference between a warm and a colder room implies a difference in the ionizing activity of phosphorus.

6. *Color Margins and Distribution.*—In endeavoring to find the effect of temperature and pressure on the distribution of color in question, the diagram worked

out in Chapter I. (§4) should be recalled, as shown in the foregoing figure 5. The pressure temperature locus, which determines the margin of the opaque zone, is here fully given, and it is probable that the colors must lie along parallel loci. In my earlier memoir I found the equation $\theta = A\,10^{CP/(p-B)^m}$, where $A = 9$, $C = .013$, $m = .35$, $B = 43$, expressed the opaque margin pretty well, and this has been drawn in the diagram. B is the height of the asymptote and $(p-B)$ to be taken numerically.

In the following table 2, I have added some special results for the position of the color curves in question, obtained from direct experiments made at different temperatures. These agree with the view stated pretty well, but are not as decisive as one would wish, possibly because the actual temperature at which the reaction takes place is not given by the thermometer. The peculiar feature is the distribution of colors at 27°–28°, as seen in the chart, figure 6. All attempts to clear up these discrepancies have thus far failed.

TABLE 2.—VARIATION OF COLOR WITH STEAM PRESSURE IN THE ABSENCE OF ARTIFICIAL DUST.

Color.	Pressure.	Color.	Pressure.	Color.	Pressure.
Yellow	70 cm.	White-Yellow	100–95 cm.	Opaque	35 cm.
Brown-Yellow	40–50	Orange	90–70	Violet	33
Opaque	40	Brown	65–60	Blue	30
Violet	33–35	Violet	55–50	Gray-Blue	27
Blue	30	Blue	50–40	Faint Yellow	25
Blue-Green	28–25			Faint Purple	25–20
Faint Yellow	15–20	30°		21°	
Purple	10				
Violet	....				
White	....				
Temp. 27 –28°					

7. *Effect of Steam Pressure.*—The following table 3 gives data bearing on the practical question as to how far pressure is to be kept constant in work like the present. The unlooked for independence of the color obtained, considered as subject to the pressure actuating the steam jet, is very striking. Persistence of color throughout wide variations of pressure (much wider than are incident to the investigations below) is the rule. The observation is capable of two explanations: either the influx of air keeps pace with the additional steam supplied by the jet when the pressure rises, or the color criterion is not a sensitive one, showing indistinguishable gradations for large variations of dust contents, etc. Probably both reasons apply. In the table L/m denotes the number of liters per minute of air passed over phosphorus to produce the full blue in question.

TABLE 3.—DUST REQUIRED AT DIFFERENT PRESSURES TO PRODUCE A GIVEN COLOR (BLUE) AT A GIVEN TEMPERATURE, 21°.

[illegible]	Z	Temp.	Pressure	Remarks
B[illegible]	45	21	18 cm	Field remains at about the same color while pressure, at constant dust contents and temperature, varies from nearly zero to 25 cm
[illegible]	50	21	18 cm.	
[illegible]	"	"	5 cm	
B[illegible]	"	"	25.	
Blue	....	25	0 cm.	Field remains blue from 30 cm. as far down in pressure as steam supply is available. Depth of color changes with quantity of steam.
Blue	....	"	25 cm.	
Blue	....	"	35 cm.	
Violet-Opaque	....	"	33	

8. *Effect of Air Temperature.*—Corresponding to the preceding experiments in which pressure is the only variable, a correlative series of experiments was made in which the temperature *θ* of the inflowing air was alone permitted to change. For this purpose air was taken from without and heated in the steam drum *D*, figure 3, Chapter I. The results are summarized in the following tables, 4 and 5, and are remarkable inasmuch as no certain effect of temperature could be discerned within the limits employed.

These remarks, it will be seen on consulting the tables, refer to the colors of the first order, chiefly to the blues, and in this respect are in accord with the two curves in the chart, figure 3, which merge into each other in the blue region. For the colors of the second order, however, as the curve shows, the effect of temperature is not negligible. More dust is required, cæt. par., at low temperatures than at higher temperatures, a result which goes hand in hand with the presumably greater supersaturation at the lower temperatures of the inflowing air.

TABLE 4.—DUST REQUIRED AT DIFFERENT TEMPERATURES TO PRODUCE A GIVEN COLOR (BLUE), AT THE GIVEN PRESSURE, 5 CM.

Color.	Z %.	Temp.	Pressure.	Color.	Z %.	Temp.	Pressure.
[illegible]	.60	15	5.5 cm	Faint Indigo	.00		5
Blue Opaque	.75	22°	"	Blue	.80		"
Faint Purple	.00	17	5	Dark Blue	1.00		"
Dull Blue	.65	"	"	White	.00	21	5 cm
Blue	.7	"	6	Blue	.9[illegible]	"	"
Green-Yellow	[illegible]	16	5	Dark Blue	1.10	"	"
Blue	.65	"	"	White		24	5
Yellow Green		17	5	Blue	1.15	"	"
Blue	.65	"	"				
Faint Purple	.50	18	5				
Blue	.90	"	"				

TABLE 5.—VARIATION OF COLOR WITH TEMPERATURE AT A GIVEN PRESSURE.

Color.	L/m.	Pressure.	Temperature.	Remarks.
Blue	......	6	23°	The blues remain blue from 15° to 28°, as nearly as can be seen; above they are bright, clear violet-like; below (at low temperature) dull and grayish At 15° the field is yellow-green without phosphorus dust.[1] Changes of tint occur at once with motion of the valves of the influx pipes.
Blue-Violet, faint	......	6	26 to 28°	
Blue Gray (muddy)	.	6	20 to 15	
Blue	......	6	15	Opaque condensation.
Blue	......	6	to 30°	Colorless. The blue field persists through 15° to 30°, as above.
Blue	......	4 cm.	26 to 40°	Color runs through dull blue, clear blue, violet blue, colorless, as temperature continually rises. Falling temperature reverses the order.
Blue	......	5.5 cm.	26° to 35°	Same results.
Opaque	......	......	......	Opaque runs through smokiness to clear with increasing temperature, but it does not become violet or yellow. The results throughout are a mere blanching or a thickening of tint, without producing color differences available for discrimination.

---

[1] At 15 change of pressure up to 6 cm. produced indigo, purple, yellow, yellow-green.

9. *Corroborative Method of Graduation.*—I shall now describe a totally different method of graduating the color tube, already referred to in connection with figure 2 (§ 2). Here *C* is the color tube with its jet *j*, mirror *m*, and influx pipe *C'*. Instead of a single tube, two or more ionizers, *P*, *P'*, *P''*, are used simultaneously, each of them being charged with phosphorus and controlled by the independent stop-cocks *F*, *F'*, *F''*. The air needed comes from the above gasometer train, and after passing through the desiccator *D*, branches into three independent currents. Obviously the air supply at *D* must be in excess.

The method of using this apparatus is evident; colors are compared by summation and difference. Thus if the colors for each tube separately as well as for the tubes conjointly are known, and if one of the colors is defined in terms of the dust content needed to produce it (Blue = 1 for instance), then as many equations may be obtained as there are colors. The method is thus very similar to the correction of a set of weights, etc.

In table 6 I have inserted a number of such results, p and θ, being the steam pressure and air temperature constant within the required limits. I have also added the data obtainable from the chart, figure 3, using the lower curve as this is the more definite. *B* denotes blue; *G*, green; *V*, violet; *O*, opaque; *Y*, yellow; *Cr*, crimson.

TABLE 6.—COLORS COMPARED IN RELATION TO DUST NEEDED, BY SUMMATION OR BY DIFFERENCE.

No. of tubes.	Color of each.	Combined color.	From chart.	p	s
2	Green	Violet	B +	10.7	23
2	Yellow	Green	BG		
2	Yellow	Green	BG	8.5	20
2	Violet	Straw yellow	Yl. 2	7.5	26
3	Green	Blue +	B +	8.5	24
2	Green	Blue —	B —	8.5	24
3	Purple, n.	Green	G	8.5	24
3	Blue —	Violet	V +	8.5	24
3	Yellow	Blue —	B	8.5	24
3	Blue — Yellow Green	Violet	V		
3	Green	Blue +	B +	12.5	21
2	Blue —	Violet	V	13.0	21
2	Blue + Green	Violet	V	7.0	21
3	Green Blue — Violet	Opaque	O	8.5	24
3	Green Green Blue +	Opaque	O	8.5	24

The difficulty with this method, though beautiful in principal, is the large error introduced at each color discrimination. Thus in an equation with three tubes there will be four terms and four corresponding discrepancies for the colors. I did not, therefore, pursue the method further, merely noting its general agreement with the data of the chart, figure 3.

10. *Modified color tube.*—The color tube, as above used, has two grave disadvantages, inasmuch as in the first place the quantity of steam issuing at a given pressure cannot be easily varied, and in the second place, the manner in which the dust is brought into the jet is not easily understood. One is not sure that the whole of the dust is actually brought to bear in producing condensation when the charged air comes in contact with the jet from without, as at *CC'*, figure 1. Again the colors of higher order are best seen at relatively low temperatures and pressures, but require a large volume of steam if they are not to be too faint for recognition. First order colors require almost the opposite conditions, etc. Many of these desiderata are met in the following device, figure 7, for axial influx, which has the further advantage of making the jet more easily accessible; for the saturation of colors, even of higher orders, is now such that the lower window and lateral influx pipe of the color tube, figure 1, Chapter I, may be dispensed with.

The jet, figure 7, is annular in patern, the bullet-shaped body, *A*, being a hollow conoid about 5 cm. long and about .9 cm. in diameter internally, provided with a lateral tubulure, *T*, for the influx of steam from the steam box. The body being open above and below receives the hollow spindle *BC* axially, the latter being secured in any position by the snugly fitting screw at *C*. The top of the spindle *B* is ground into the upper aperture of the body like an ordinary screw valve, so that steam may be quite shut off or supplied in any reasonable volume at any pressure by turning the head of the spindle. The bottom of the spindle receives the T-tube *GEF*, the joint being ground so as to admit of rotation of the spindle around the tube. Air charged with nuclei is conveyed through this tube, entering at *F* and coming from the identical gasometer train and phosphorus tube already described.

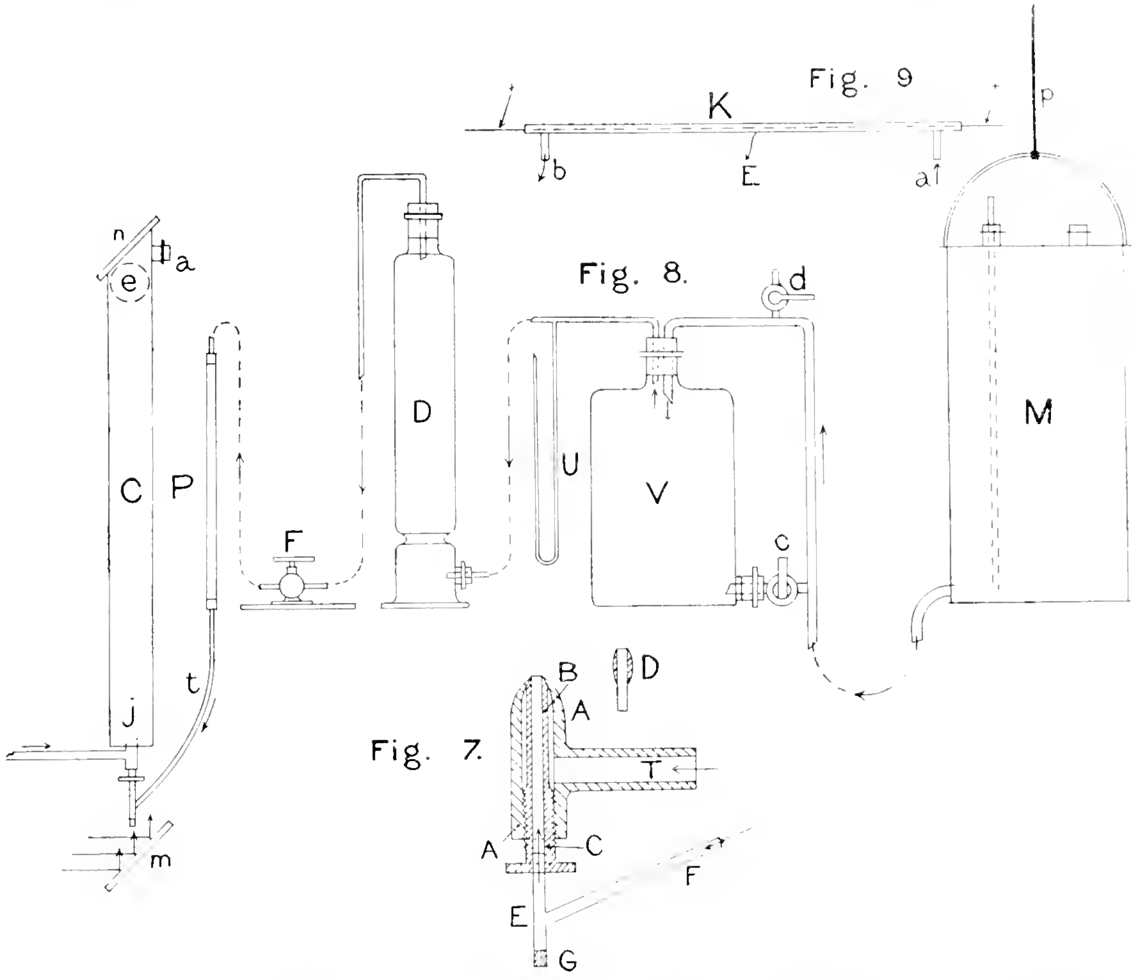


Fig. 7.—Adjustable Nozzle for Steam Jet. Scale ½. Fig. 8.—Gasometer Train and Modified Color Tube. Fig. 9.—Tubular Condenser for Ionized Gases.

To obviate the danger of steam entering the tube, *EF*, and quenching the ionizer, a hollow nozzle, *D*, is ground into the top of the spindle and removable at pleasure. This introduces the dust at 1 cm. above the annular opening in the jet, where the pressure excess is smaller. The nozzle does not otherwise interfere with the action. Should water enter the tube *E*, it may be removed by opening the stopper *G*.

The color tube as now modified is shown at *C*, figure 8, the jet playing directly into the open end of the tube, which is telescoped (not shown) so that the lower section may be raised to facilitate access to the jet. The mirror for illumination is at m, n being the observation window cleared through a, and e the escape steam pipe.

The bottom of the spindle is joined by a thin tube, t, called *absorption* tube, about 1 millimeter in diameter to the phosphorus ionizer, P, which here consists of a tube about 30 cm. long and 1 cm. in diameter, charged in the manner described above. F is the screw stopcock, D the desiccator, U the pressure gauge, V the volume flask, M the large Mariotte flask.

Figure 9 is a slender tubular condenser by which the absorption tube t may be replaced for correlative electrical measurements. See Chapter 5.

11. *Results.*—In table 7, I have given several series of results obtained at different times. Different absorption tubes at t were used, and hence the results can only be compared by putting the volume of charged air producing the standard blue equal to one unit. Variations between the series necessarily remain, because it is impossible to select the same shade of blue from a continuous series. The pressure of the steam jet is given under p; θ is the air temperature, and δP the pressure excess in the volume flask in cm. of mercury. Reduction to standard pressure and temperature is superfluous.

TABLE 7.—COLOR AND RELATIVE NUMBER OF PARTICLES IN CASE OF NEW JET (AXIAL INFLUX). "BLUE" = 1

Color.	Vol. Min.	p, θ, δP	Remarks.	Color.	Vol. Min.	p, θ, δP	Remarks.
		cm. °C.		Green	.48	$p = 9.5$ cm	Blue requires 1.25 liters per minute.
Cr.-Gr.	.30	$p=5.5$–6.5	Long absorption tube.	Blue —	.72	$\theta = 26$	
Vl-Cr.	45	$\theta = 27$° C.		Blue +	1.00		
Green	70	$\delta P=5.5$ cm.		Violet +	1.40		
Blue —	83		Blue + requires 2.2 liters per minute.	Crimson	.10	$p = 7.5$	Blue requires 1.5 liters per minute.
Blue —	.95			Yellow	.21	$\theta = 26$	
Violet	1.87			Green	.52		
Blue +	1.10			Green-Bl.	.66		
Blue —	.95			Blue —	.83		
Green	.78			Blue +	1.00		
Crimson	.28	$p = 5.8$	Short, thin absorption tube.	Crimson	.17	p 7.5	Blue requires 1.75 liters per minute.
Yellow	.38	$\theta = 25.4$		Vl.-Cr.	.26	θ 25	
Green	.53	$\delta P = 5.5$ cm.	Blue requires 1.5 liters per minute.	Vl Gr.	.37		
Gr.-Bl.	.69			Green	.51		
Blue	.83			Blue-Gr.	.53		
Blue +	1.00			Blue —	.77		
Violet +	1.25			Blue +	1.00		

These observations are constructed in the chart figure 10, by representing as abscissas the thicknesses of air-plates which would give the same color by Newton's interferences for normal incidence and transmitted light, as no better method is immediately available. The ordinates are the volumes per minute of charged air producing the same color in the tube. The curves are taken directly from the chart, figure 3.

12. *Discussion.*—To turn first to table 7, it is seen that whereas in the earlier work the dust contents needed to produce a blue field was but .5 liter per minute on the average, the requirements here are as high as 2 lit./min. and not below 1.2 lit./min. On the average even three times as much dust is needed. This is a disadvantage of the present form of jet, inasmuch as the law of absorption in the tube *t*, Fig. 9, has now a fundamental bearing on the data obtained from the apparatus, which will in many cases outweigh the convenience of stronger colors of the second order. The jet, moreover, is not available for the capture of atmospheric nuclei. Different purposes will therefore be subserved by the two forms of jet.

If these series of observations are examined individually as far as blue, they will be found to lie on a line with somewhat less concavity upward than was the case above. Their regularity, even for color criteria, is not as great as would be anticipated, particularly in the region of the second order (right end of curve). As the observations were taken on different days, it seems to me that the state of the atmosphere must impress itself upon these measurements, as the effect of atmospheric nuclei would be largest on the right where the supply of artificial nuclei is smallest.

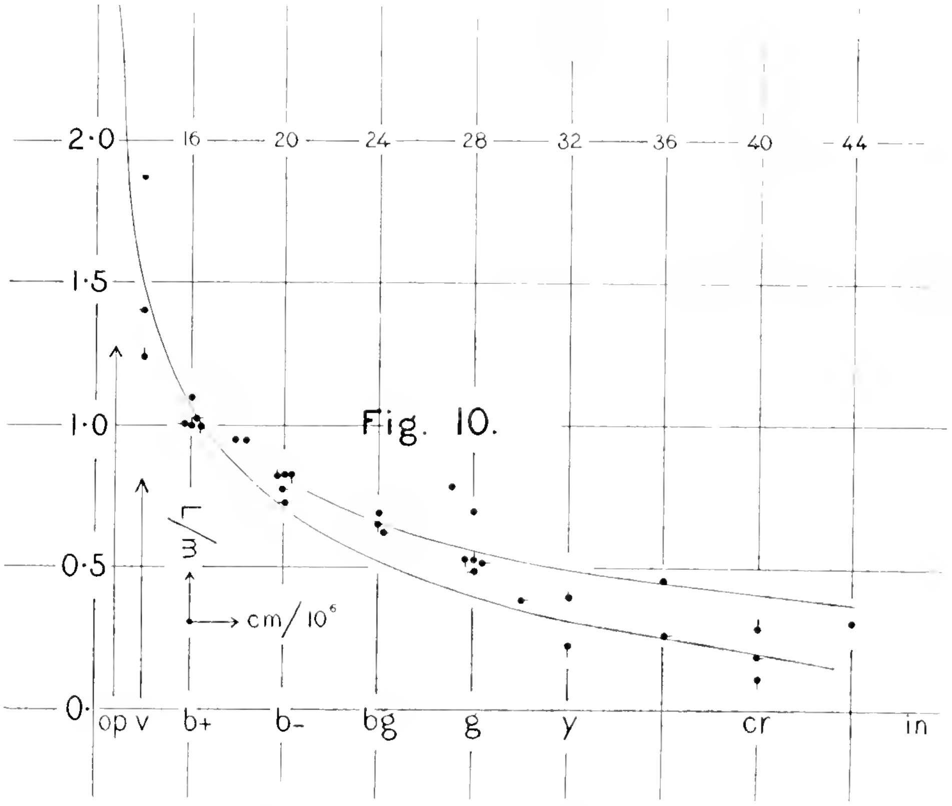


FIG. 10.—CHART OBTAINED WITH NEW JET CORRESPONDING TO FIGURES 3 AND 4.

Compared with the preceding results (figure 3), the present series of data lie quite within the same margins of values. Indeed, the results with the jet dusted in the great variety of ways from without, the nuclei being borne into the jet on a convection current often traversing many feet to meet it, and the results here, when the active dust is at once introduced into the jet from within, are indistinguishable on the whole, provided the same color value (blue = 1) be given to one of the colors. The absolute volumes of charged air (liters/min.) evoking the color may in different experiments vary over threefold. The reason for this, the absorption of the tube *t*, figure 9, will appear in the next chapter.

CHAPTER III.

TRANSMISSION OF THE IONIZED EMANATION OF PHOSPHORUS THROUGH AIR IN THE ABSENCE OF AN ELECTRIC FIELD.

1. *Introductory.*—For reasons of both theoretical and practical import, it is next necessary to ascertain the precise conditions under which the phosphorus nucleus vanishes on passing through tubes at a definite velocity; or in general on being retained in any vessel or put in contact with any barrier in a definite way, for a definite time. The experiments of the present paper thus relate to the absorption[1] of condensation producing atmospheric nuclei by surfaces or by suspended particles. They show, I think, that such absorption takes place as though each nucleus of a nearly saturated region travelled in the entire absence of an electric field, with a velocity of about 3 millims. per second; or if it be put roughly that $\frac{1}{3}$ of the total number travel in a given cardinal direction, as though each nucleus had a velocity of about a centim. per second.

Fig. 1.

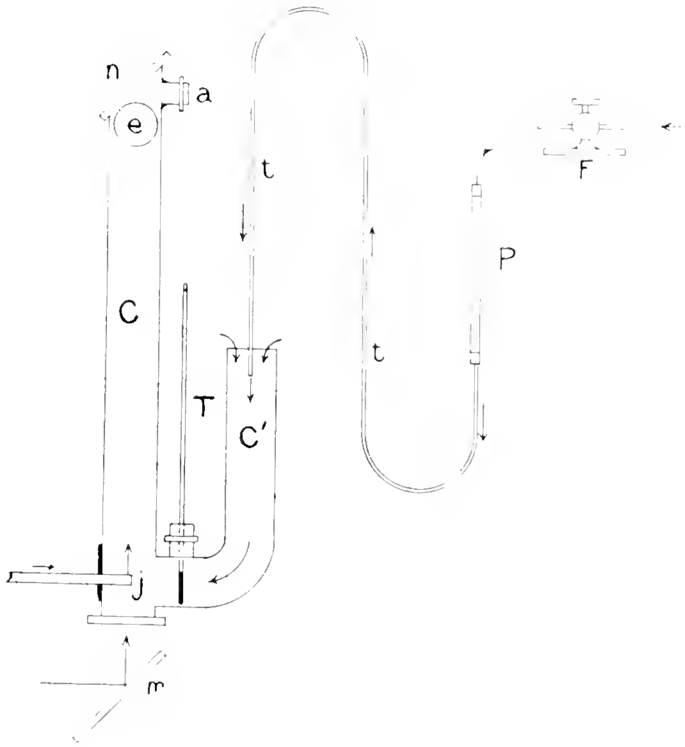


FIG. 1.—COLOR TUBE AND ABSORPTION TUBE. SCALE $\frac{1}{10}$.

---

[1] Cf. *Phil. Magazine*, (6), vol. II., p. 40, 1901; *Am. Journ. Sci.*, (4), xi., p. 237, 1901; *Science*, xi., p. 1, 1900.

2. *Method and Apparatus.*—The method of experimentation has been indicated in the preceding chapter, and is based on color criteria obtainable with the steam jet. Here I need only recall that a current of moderately dry air is furnished by a gasometer train (Mariotte flask, volume flask, pressure gauge, dessicator) terminating in the fine screw stopcock *F*, figure 1. On opening the latter, this passes through the phosphorus tube *P* (containing pellets of phosphorus between strips of wire gauze), where it is highly charged with the ionized emanation. This saturated air is conveyed into the color tube *CC'* (old pattern of which *j* is the simple jet), through the absorption tube *t*, of the length, diameter, and material to be examined. The tube *t* is sealed into *P*, while the other end dips slightly into the lateral influx pipe *C'*, of the color tube. The arrangement of *C'* (length, etc.), has very little, if any, effect on the results, as was pointed out in my last paper. The draft due to *j* is sufficient to capture all the nuclei from the open end of the absorption tube *t*, and the whole of it is impressed on the jet.

3. *Results for thin tubes.*—To illustrate the method of work the chief data for each tube are given in the following table. Other results are briefly summarized or expressed in the chart. Length, *x*, and radius, *r*, refers to the absorption tubing employed. The volume (*V* liters per minute) of charged air passing through *P* is the amount needed to produce a definite color (full blue) in the field of the color tube *C*. The velocity of the air current through *t* is given under *v* in centims. per second. The constant *k*, in the final column, is the absorption velocity, computed from the equation $k = 2.65\,(V/rx)\ln(V/V_0)$, where V_0 is the volume in liters per minute giving the identical blue color when the absorption tube *t* is removed, and the phosphorus tube conveys its contents directly into *C*. The other data (*p*, the pressure of the steam issuing from the jet, always low, and *θ*, the temperature of the air at influx, measured by the thermometer *T*), are of little immediate interest. Their variations are not important.

In most cases, many observations (often four or five) were made for each tube length, *x*, in each series given, the difficulty being to select the same standard blue. The table contains only the mean values.

TABLE 1.—ABSORPTION OF PHOSPHORUS DUST IN TUBES. GRAY RUBBER. DIAMETER, $2r = .64$ cm. $p = 4$ cm $\theta = 26$

x Length	V Vol. time.	v	k.	Computed. V.	 x
cm.	L./min.	cm./sec.	cm./sec.	L./min.	cm.
0	.7	—			
125	3.1	161			
205	4.7	244			
455	6.5	345		.60	0
	.8		28	1.0	15
	.5			2.00	71
75	2.1	111		3.00	142
125	2.8	147		4.00	222
205	5.2	271		5.00	309
455	6.9	366		7.00	504

TABLE 1 (*Continued*).—ABSORPTION OF PHOSPHORUS DUST IN TUBES. BROWN (PURE) RUBBER. DIAMETER, .35 cm. $p = 5-7$ cm. $\theta = 24°$.

Length.	Vol./time.	v.	k.	Computed.	
				V.	x.
cm.	L/min.	cm/sec.	cm/sec.	L/min.	cm.
0	.5	—			
50	1.3	236			
100	1.7	306			
150	2.2	385		.60	00
200	2.6	465		1.00	25
250	3.3	577		2.00	112
300	4.2	735	.32	3.00	228
0	.7	—		4.00	356
50	1.5	268		5.00	500
100	1.9	341			
150	2.3	396			
200	2.8	498			
250	3.1	546			
300	3.5	620			
0	.6	—			

TABLE 1 (*Continued*).—ABSORPTION OF PHOSPHORUS DUST IN TUBES. LEAD. DIAMETER, .63 cm. $p = 4-5$ cm. $\theta = 27°$.

Length.	Vol./time.	v.	k.	Computed.	
				V.	x.
cm.	L/min.	cm/sec.	cm/sec.	L/min.	cm.
0	.5	—			
100	2.3	125			
200	4.2	224			
300	4.6	246			
400	4.7	249		.60	00
0	.8	—	.25	1.00	18
0	.5	—		2.00	80
34	1.2	65		3.00	162
68	2.0	107		4.00	256
100	2.6	137		5.00	355
200	3.8	203			
300	4.3	230			
0	.6	—			

TABLE 1 (*Continued*).—ABSORPTION OF PHOSPHORUS DUST IN TUBES. LEAD. DIAMETER, .32 cm. $p = 8-10$ cm. $\theta = 27°$.

Length.	Vol./time.	v.	k.	Computed.	
				V.	x.
cm.	L/sec.	cm/sec.	cm/sec.	L/sec.	cm.
0	.7	—	—	.60	00
50	1.4	276	.30	1.00	30
100	1.7	346		1.50	78
				2.00	136
150	2.0	411		2.50	202

TABLE 1 (*Continued*).—ABSORPTION OF PHOSPHORUS DUST IN TUBES. GLASS. DIAMETER, .20–.32 cm. $p = 7–10$ cm. $\theta = 27$.

Length x.	Volume V.	[illegible]	[illegible]	Computed. V.	Computed. x.
cm.	L. sec.	cm. sec.	cm. sec.	L. sec.	cm.
[illegible]	.8	—		.60	00
5	1.2	297	.27	1.00	37
10	1.4	302		1.50	95
15	1.9	482		2.00	166
[illegible]	.8	—		2.50	247

A brief summary of the chief results is appended for reference.

TABLE 2.—ABSORPTION OF PHOSPHORUS DUST IN TUBES.

Tube of	Diameter.	Range of Lengths, x.	Jet Press, p.	Influx Air, θ.	Range[1] of V.	Range[2] of v.	Mean[2] k.
Gray rubber	.64 cm.	0–455 cm.	4 cm.	26	.7–7.0	40–360	.28
Pure rubber	.35 "	0–300 "	6 "	24	.5–4.2	80–740	.32
Lead	.63 "	0–300 "	5 "	27	.5–4.6	30–250	.25
Lead	.32 "	0–150 "	9 "	27	.7–2.0	140–410	.30
Glass	.29 "	0–150 "	8 "	27	.8–2.0	200–480	.27

These results are entered in the chart, figure 3, with greater fulness, where the abscissas are the lengths of the absorption tubes in centims., the ordinates the volumes (liters) per minute producing the fiducial blue. The curves drawn through the points are computed from the theory presently to be given. For the wider tubes and greater lengths, the higher volumes sometimes show a break in the curve (cf. lead), meaning, I think, that the phosphorus ionizer is being overtaxed by the quantity of charged air demanded.

In view of the difficulty[3] of observing subject to color criteria, the widely different values of the velocity with which the ionized air traversed the absorption tubes, the high velocities employed, and the marked difference of material (conducting and insulating) which makes up the absorbing walls, the proximity of the values of k is particularly noteworthy. No relation to diameter is apparent. In case of glass, of impure gray rubber, of pure brown rubber, and of lead, this velocity k, so far as observation warrants, is the same.

4. *Results for wide tubes.*—In contrast with these results with tubes of relatively small bore, I shall now add data for wide tubes. These were 5 centims. in diameter (2-inch drain-pipe of tin plate) and they may be regarded as direct prolongations of the influx pipe, C, of the color tube. The arrangement is shown in Chapter I., figure 20. The air passing through these tubes is moved by the suction of the steam jet and is independent of the ionizing current through the gasometer. The velocity of the air current through the tubes (often 50 feet long) was about 100 centims.

[1] liters min. [2] cm. sec. [3] Adding to this the variable ionizing intensity of phosphorus.

per second and was determined by the time it takes the dust, suddenly injected into one end of the tube, to show itself at the other end by coloring the steam jet. The phosphorus emanation (V' liters per minute) was introduced into the current at distances 150 and 1500 centims., respectively, from the jet, as the data show. The table gives the series chronologically. The velocity is here computed from $k = (rv/2\,(x-x'))\ \ln\,(V'/V'')$, where the volumes V' and V'' correspond to the tube lengths x and x'.

TABLE 3.—ABSORPTION OF PHOSPHORUS DUST IN TUBES. TIN DRAIN-PIPE. DIAMETER 5 cm. $p = 4$ cm. $\theta = 28°$.

	Length.	Volume/time.	v.	k.
	cm.	L./min.	cm./sec.	cm./sec.
Blue-opaque	150	.95	(100)	(.05)
“ “	1500	2.00		
Blue	1500	2.24		
“	150	1.40		
Blue-green	150	.70	(100)	.05
Blue	150	1.10		.06
Blue-opaque	150	1.05		.06
Blue-Green	1500	1.15		
Blue	1500	2.00		
Dark Blue	1500	2.00		
Blue	1500	.77	(100)	0.01
$\theta = 26°$ $p = 8.5$ cm.	150	.67		
	1500	.65		
	150	.70		
Blue	150	.73	(100)	.02
$\theta = 26°$ $p = 11$ cm.	1500	.90		
Violet	1500[1]	1.40	(100)	
$\theta = 26°$ $p = 5$ cm.	150[2]	.60		.08
Blue	1500[3]	.80	(100)	
$\theta = 26°$ $p = 5$ cm.	150	.70		.01
Violet	1500[4]	1.60	(100)	
$\theta = 26°$ $p = 5$ cm.	150	.60		.09

These results have also been constructed in the chart, figure 3, on the same scale as the other curves, the data selected being those showing the maximum effect of length. In fact, they are liable to be very variable, as the colors for the long tubes become dull and are unsuitable for sharp comparisons. One may state that more dust is required for long than for short tubes, but that the difference is a relatively vanishing quantity and out of all proportion with the data for small tubes. The difference between the present and the preceding experiments with tubes is this, that whereas in the latter case (small bore) the saturated air is conveyed in the undiluted condition through the tubes, in the case of wide tubes (5 cm.) the saturated dust is necessarily diluted on being introduced into the tube having its own independent current of air. The present series shows the remarkable preservative tendency of this operation of dilution and points out a reason for the constancy of behavior of the color tube itself, after the nuclei have once been captured.

[1] Opaque at 150 cm. [2] Green-yellow at 1500 cm. [3] At 150 cm., violet. [4] Opaque at 150 cm.

5. [illegible] *hypotheses.* In the endeavor to frame at least a working hypotheses for these phenomena, two possible occurrences are prominent: the first of these is the decay of the particle so far as its activity in producing condensation is concerned. This may be due to growth and loss of charge, to the action of ordinary dust particles floating in the air, or any similar cause whatever. It constitutes a loss *within* the ionized medium itself. The second relates to the motion of the ionized particle, whether stimulated by an electric field, or a diffusion gradient, or not, occurring in the latter case as a mere ionic velocity. Since electric field is absent, it would at the outset be natural to treat the motion as a case of diffusion and due to a concentration gradient. It seems hardly probable, however, that in a swift-moving, turbulent current of air, diffusion can be recognized. I have therefore thought it best to regard the nucleus as moving with a definite velocity *k*, independent of direction and (for a given class of experiments) independent of concentration. So circumstanced the swarm of nuclei are transferred by the air current. As the nucleus impinges upon but does not rebound from a barrier, *k* may still be regarded as an external diffusion coefficient, corresponding to the constant in Newton's law of cooling.

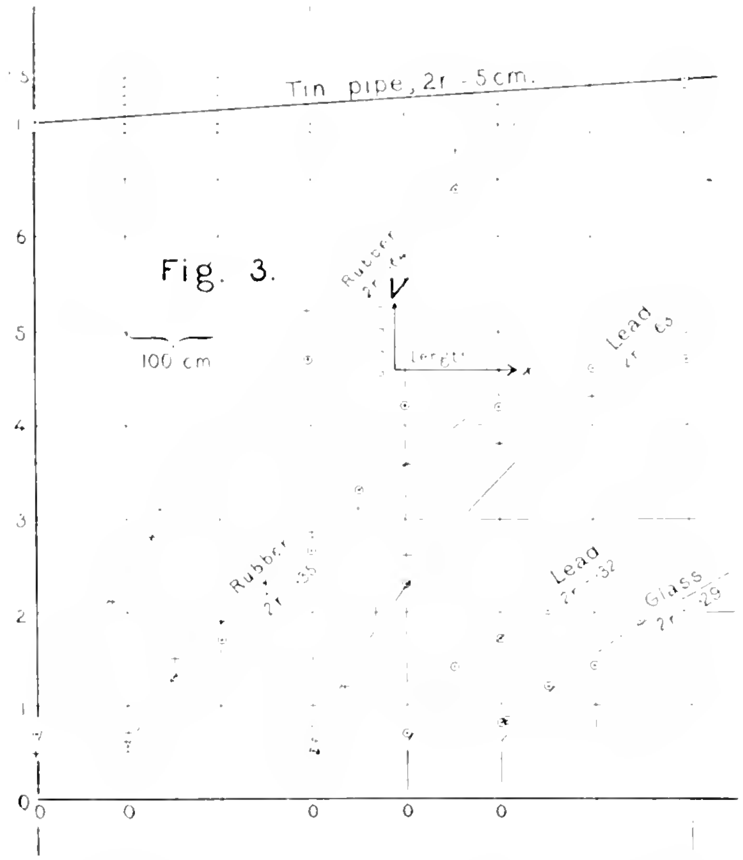


FIG. 3.—CHART SHOWING THE RELATIVE NUMBER OF PARTICLES (ORDINATES, [illegible] IN LITERS PER MINUTE NEEDED TO PRODUCE FULL [illegible]) FOR DIFFERENT LENGTHS (ABSCISSAS) AND DIAMETERS OF THE ABSORPTION TUBE.

6. *Computation for saturated emanation.*—Let dx, figure 2, be the thickness of an infinitesimal right section of the absorption tube of radius r, traversed at velocity v by an air current charged with nuclei. Let n be the number per cubic centim., and k the number absorbed per square centim. per second, if $n = 1$. Hence k is the absorption velocity discussed. If, as in cases considered elsewhere, the absorption tube were a condenser with the field acting radially outward (Chapter V.), k would be replaced by $UeE/(R_2 - R_1)$, where e is the equivalent charge of an electron, U the velocity of the ions relatively to each other, $E/(R_2 - R_1)$ the potential gradient, R_1 being the axial and R_2 the circumferential radius of the condenser. I mention this here for future reference.

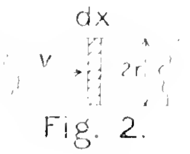


Fig. 2.—Diagram.

Let k' be the number of particles decaying by mutual destruction, etc., per cubic centim. per second, if $n = 1$, so that $k'n^2$ is the number vanishing for the density of distribution n.

Hence the number of particles accumulating per second in the element is $-\pi r^2 v(dn/dx)dx$; the number absorbed per second by the walls of the tube, $kn 2\pi r dx$; the number decaying per second within the element, $k'n^2 \pi r^2 dx$. Thus $-(v/k')(dn/dx) = 2kn/k'r + n^2$. This equation is integrable in finite form, and putting n_0 as the concentration at x_0, the equation becomes $n = 2kn_0/(\epsilon^{2k(x-x_0)/rv}(2k + k'rn_0) - k'rn_0)$. The direct discussion of this equation is cumbersome. Its bearing on the present results is best shown by evaluating the two special cases in which $k' = 0$, and $k = 0$, respectively. The former case is incompatible with the observations and may be dismissed. See § 9.

7. *Case of absorption without decay.*—Let, then, $k' = 0$, so that decay within the element from any causes whatever is absent.[1] The only loss of nuclei is at the surface of the absorption tube. Hence, $n = n_0 \epsilon^{-2kx/rv}$, if n_0 is the concentration at $x_0 = 0$, i. e., in the absence of the absorption tube. But $v = 1000V/60\pi r^2$, if V liters per minute produce the velocity v centims./sec. Hence, $n = n_0 \epsilon^{-krx/2.65V}$. The total number of nuclei injected into the color tube is thus nV. Let these produce the fiducial clear blue field. In the same manner let $n'V'$ nuclei produce the same field when the dimensions of the absorption tube are r' and x', and the air passing V' liters per minute. Then, since $nV = n'V'$, $V\epsilon^{-krx/2.65V} = V'\epsilon^{-kr'x'/2.65V'}$. If V_0 be the volume per minute when the tube length is $x' = 0$ and the field the identical blue,

$$k = 2.65(V/rx)\ln(V/V_0),$$

an equation from which the value of k, the velocity of the nucleus, is computed at once in cm./sec., supposing decay (k') to be a vanishing quantity.

Waiving the more refined methods of the kinetic theory of gases, if but $\frac{1}{3}$ of all the nuclei wander in a given direction, the term expressing absorption of the wall of the tube in the differential equation would be $k(n/3)2\pi r dx$, or $k/3$ replaces k. Hence the data in the above tables should be increased threefold to meet this point of view, as stated in the first paragraph of this paper.

---

[1] More generally the decay is compensated by the production of new ions within the region by collisions, etc.

The value of k is given for each series in the tables, computed from three points of the observational data corresponding to $x = 0$ and the maximum and mean lengths. It will be noticed that $V' = .60$ liter/min is nearly the same for all the absorption tubes, as it should be for initially saturated air, and has been so taken. From the value of k found for each tube I then computed the corresponding curves, these being given in the last columns of table 1. The computed curves are constructed in the chart, figure 3, to show the distribution of the observations with respect to them. The agreement is throughout surprisingly good; it would be impossible to get a better interpretation of the observations in view of the difficulty of color experiments. If we compare the nuclear velocities k, with the radii of the absorption tubes, with which they were obtained, we find that they vary for the wide tubes (gray rubber and lead) as much as for the narrower tubes (lead, pure rubber, and glass). Hence k must be regarded independent of r, and the variations found are observational errors.

I conclude, therefore, that the proposition which considers decay (k') to be relatively and virtually negligible and the absorption effect of the tubes of velocity k, or an ionic velocity $3k$, to be real, is one of great probability. The whole ionized region is under volume expanding stress, much like an osmotic pressure.

8. *Computation for diluted emanation.* The case of the wide tubes of tin plate ($2r = 5$ cm.) is different in character, for here the different lengths correspond to different initial densities, n_x and $n_{x'}$, while the radius of the tube and the velocity of the air current are the same. One may assume that the initial densities are to each other as the liters per minute (V) of air saturated with phosphorus emanation put into the tube at distances x and x' from the jet. Thus $n_x/n_{x'} = V/V'$, and therefore $k = (rr'/2(x - x'))\ln(V/V')$. Since $rr'/2(x - x')$ is about .093, the volume ratio V/V' should be between 15 and 20. The observed values rarely exceed 2, often falling much below this. The coefficients k are thus too small as compared with the preceding set.

It is interesting to compare the degree of dilution here with the above cases. The volume of saturated air added rarely exceeded 1 or 2 liters/min. The volume of air traversing the tube and due to the jet is 120 liters/min. The dilution is thus from 50 to over 100. The above cases of dilution with narrow tubes would be given by $n/n_0 = e$ [illegible], while in the tube. Otherwise, since $nV = n'V'$ for a given color, the chart gives n/n_0 at once. The range of values does not exceed 11 (gray rubber), the other maxima being 7 (lead, rubber), 4 (lead, glass), terminating with 1. Hence the orders of dilution in the two experiments are very different.

The results for the tin tube are naturally much less certain because the colors become dull after the dust has passed through great lengths (50 ft.) of tube, or they flicker, and because x is not easily found. Still the preservative qualities of dilution are undeniable, and my observations again lead me to disbelieve that diffusion within this wide, eddying current (tested), can be in question. Ignoring it, it seems most probable to conclude with others (J. J. Thomson, Rutherford, Townsend) that new ions are being continually reproduced by collisions. From the present experiments with wide tubes it would then follow, that when the ionized air is markedly diluted, the new ions produced are in excess of the old. From this one may argue that their velocity must diminish. Admitting the delicate nature of this speculation, it is certain, unless I have misunderstood the observations with wide tubes, slow currents, and weak ionization, k here in all my experiments has never exceeded $\frac{1}{5}$ and often fallen below $\frac{1}{10}$ of the very definite values for small bore tubes, swift air currents, and nearly saturated ionization.

9. *Case of decay without absorption.*—It will be interesting to contrast with this, the second special case in which $k=0$, and k' is alone significant. Here, in brief, the diminution of nuclei is due to decay while sojourning in the tube. If in the narrow tubes the destruction of nuclei were merely the result of decay due to their mutual reaction, then the time of their sojourn within the tubes, *i. e.*, $(x-x_0)/v$, should be of paramount importance, apart from the diameter of the tubes. The differential equation for this case becomes on integration, $1/n - 1/n_0 = (k'/v)(x - x_0)$, or $n/n_0 = 1/(1+k'n_0\,(x/v))$, if n_0 corresponds to $x_0 = 0$. Since $v = 1000\,V/\pi 60 r^2 = 5.30\,V/r^2$, and since $nV = n_0 V_0$,

$$k' = \frac{V-V_0}{x}\,\frac{5.30}{V_0 n_0}\,\frac{V}{r^2},$$

so that k' cannot be found absolutely in this way.

Moreover since for a given tube of radius, r, the ratio $(V-V_0)/x$ is very nearly constant for the larger values of V, k' varies nearly as V and is not therefore a constant. The equation for k' may be otherwise written $k'=((V-V_0)/x)\,(v/n_0 V_0)$, so that ($k'n^2$ being the number of particles decaying per cubic centimeter per second) k' varies with the velocity of the ionized air current through the absorption tube, roughly speaking.

I conclude that an explanation in terms of decay alone is inapplicable, and even with modifications inferior to the explanation ($k'=0$) given above.

CHAPTER IV.

THE TRANSMISSION OF THE IONIZED EXHALATIONS OF PHOSPHORUS THROUGH AIR AND OTHER MEDIA, IN THE PRESENCE OF AN ELECTRIC FIELD.

TRANSMISSION THROUGH AIR.

1. *Object and plan.*—The experiments of the present chapter[1] are made with an electrical method. They relate to the apparant decay of the ionization produced by phosphorus, in the lapse of time, for fixed distances apart of the condenser plates: to the transmission of the ionization through layers of air and other media and barriers. They are thus preliminary to the subsequent experiments, in which the condenser and the color tube are combined and the coincident effects interpreted. I hope moreover to decide whether a form of radiation from phosphorus is presumable or whether the case is merely that of an ionized gas exhaled by the slowly oxidizing body. I shall venture to treat the results in a simple and direct manner, in order to present them more consistently with my earlier chapter on the same subject, in which the attempt was made to arrive at the ion velocity of the phosphorus emanation by a non-electrical method and therefore in the absence of an electrical field. Finally I want in particular to ascertain whether by giving less prominence to the decay of ions by mutual destruction within the element of volume, or otherwise, the phenomena may not be equally well explained.

2. *Apparatus and method.*—To turn first to the behavior of phosphorus in contributing in the lapse of time to the discharge of a simple air condenser whose plates are at fixed distances apart, the following experiments were made: In figure 1, B_2 is a water battery of 48 volts, permanently charging the quadrants of an Elliott electrometer, one of which is always earthed and controlled by the switch, S_2. B_1 is a storage battery (20 cells suffice) one pole of which is kept earthed as determined by the switch S_1, to be closed momentarily on charging. The other terminal charges the two condensers in parallel, M, N, in the electrometer and C, P, for the ionization experiment. The plates M and P are also permanently earthed. N communicates in the usual manner with the needle of the

---

[1] *Science*, XI, p. 231, 1900; XIII, p. 501, 1901; *Physical Review*, X, p. 257, 1900; and the current numbers of the *Phil. Mag.* The ionization of the phosphorus emanation was known to Matteucci and has been studied since by Naccari. It was rediscovered by Bidwell (*Nature*, Dec., p. 212, 1893). Cf. *Nature*, LV, pp. 6, 125, 155, 1897; also XLIX, p. 363, 1894. I believe I was the first to point out its remarkable activity in producing condensation, and the substance is specially interesting to me because of this property. Cf. *Bulletin* No. 12, U. S. Weather Bureau, Washington, 1895.

electrometer, which is thus at the same potential as the plate C. P is a phosphorus grid, consisting of two sheets of wire gauze placed close together facing each other, so that between them discs of phosphorus may be secured. As the air has free access to P on all sides, the medium between C and P is heavily charged with phosphorus "dust." The essential precautions to be preserved in work of this kind have been given elsewhere. Barriers are placed for examination between C and P, quite out of contact with the former plate.

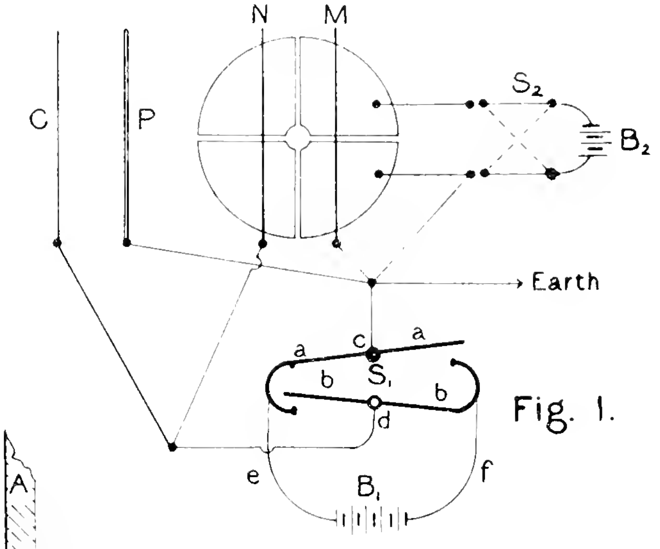


Fig. 1.

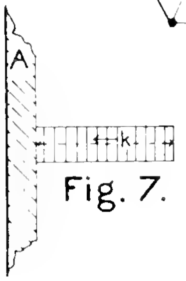


Fig. 7.

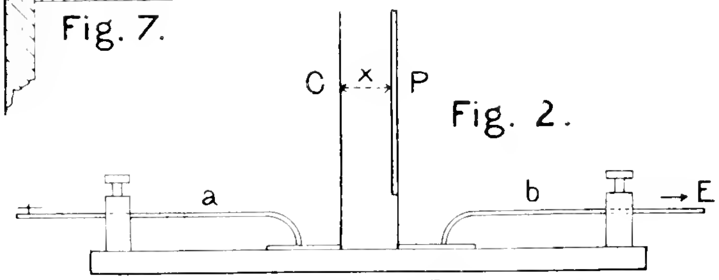


Fig. 2.

FIG. 1.—DIAGRAM OF THE CONDENSER AND THE ELECTROMETER IN PARALLEL. FIG. 2.—SECTIONAL ELEVATION OF THE CONDENSER. SCALE, 1/6. FIG. 7.—DIAGRAM.

The arrangement of condenser selected is thus essentially one in which the air at P is saturated with phosphorus emanation at all times. On passing from P to C this saturation is reduced, depending on the distance apart of the plates. The actual form of the condenser is shown in figure 2, where B is a hard rubber base on which the plates C, P, are supported on metallic feet at a distance x apart. They are secured by spring terminals, a, b, adjusted by clamp screws. The charging key has been drawn in diagram in figure 1, where a, b, are parallel insulated metallic rods, trunnioned at c, d, and there put to earth and connected with the condensers, respectively. The terminals of the charging circuit are e and f. The levers are either top heavy or controlled by springs to the effect that contact with one side or the other is always made unless broken by special adjustment. It is frequently difficult to keep these keys free from leakage, so that simple devices are sometimes to be preferred.

3. *Computation.*—The computation of the present results of discharge may be made in the usual way. The curves are obviously nearly exponential. In other words, initially, $-dV = cV\,dt$, dV being the loss of potential in the time dt when the potential difference of the plates is V, and c being a constant. Thus cV is proportional to the current flowing between the plates and $V = V_0\,\varepsilon^{-ct}$. The constant c occurring in this equation has for the present either the meaning of

$(dV/dt)/V$ or $-(dQ/dt)/Q$, where Q is the charge of the one condenser plate, the other being kept at zero. The justification of this equation is at hand: Let n be the number of ions available, e the average charge of each, U their relative velocity, x the distance apart of the condenser plates of area A, for the potential difference V. Then $-(dQ/dt) = U(V/x)ne = -C(dV/dt)$, where C is the capacity of the condensers conjointly, (dQ/dt) being the current, all taken per square cm. Hence, if for brevity $A/Cx = 1$, $-(dV/dt)/V = Une = c$. It will be convenient to express the data in terms of common logarithms, wherefore $c = -\log\varepsilon\,(dV/dt)/V$ will be given and $V = V_0 10^{-c't}$, and $c' = Une\log_{10}\varepsilon = c\log\varepsilon$.

4. *Data as to ageing of the ionizer.*—The first question at issue, is the behavior of phosphorus itself, the object being to throw light on its persistence as an ionizing agent in the lapse of time, change of temperature, etc. The following tables show results. The leakage of the condenser was observed in the lapse of time, the apparatus being charged at successive intervals but not otherwise interfered with. The constant c' (varying with n the number of ions per cubic centim.) was found for each two minutes after charging. Plate distances of 1 and 3 centims. occur in the tables.

TABLE 1.—DECAY OF IONIZING ACTIVITY OF PHOSPHORUS.

Distance apart of plates.	Time t.		Diff. of potential V.	$c' = Une\log\varepsilon$	Distance apart of plates	Time t.		Diff. of potential V.	$c' = Une\log\varepsilon$.
cm.	h.	m.	volts.		cm.	h.	m.	volts.	
1	10	19.5	39.0	.39	3	2	44	35.6	.081
		20	22.0				44.5	32.4	
		20.5	14.0				45	29.4	
		21	10.0				45.5	26.8	
1	10	25	39.0	.39	3	2	55	35.4	.078
		25.5	22.0				55.5	32.6	
		26	14.0				56	29.6	
		26.5	10.0				56.5	27.0	
1	10	36	39.0	.37	3	3	16.5	35.4	.086
		36.5	22.0				17	33.0	
		37	14.8				17.5	29.4	
		37.5	10.8				18	26.8	
1	10	46	39.0	.34	3	3	47.5	35.4	.078
		46.5	23.0				48	32.6	
		47	16.0				48.5	29.6	
		47.5	11.6				49	27.2	
1	10	59	38.0	.35	3	4	18	35.4	.078
		59.5	23.0				18.5	32.6	
		60	15.0				19	29.6	
		60.5	11.2				19.5	27.2	
1	11	27	38.0	.34	3	4	45.5	35.4	.070
		27.5	23.0				46	32.6	
		28	15.6				46.5	30.0	
		28.5	11.4				47	27.6	
1	12	.0	35.4	.33	3	5	22	35.4	.080
(Plates readjusted.)		.5	22.8				22.5	32.1	
		1	15.8				23	29.4	
		1.5	11.2				23.5	27.0	

These data are summarized in the following table, for the three series of results in hand. The limit of sensitiveness of the electrometer was about equivalent to $\delta c'=.002$. The largest values of c' observed were of the order of .500.

TABLE 2.—SUMMARY. DECAY OF IONIZING ACTIVITY OF PHOSPHORUS.

Distance apart of plates.	Time.		$c'= nUe\log\varepsilon$.
cm.	h.	m.	
1	10	20	.39
		26	.39
		37	.37
		47	.34
		60	.35
	11	28	.34
	12	1	.33
3	11	39	.095
		58	.083
	12	15	.066
		33	.096
		40	.080
		57	.093
3	2	45	.081
		56	.078
	3	17	.086
	3	48	.078
	4	18	.078
	4	46	.070
	5	23	.080

The first of these series (see figure 3) shows a decrease of conduction from .39 to .33 within two hours, such as would naturally be associated with the waning ionizing power of phosphorus. The succeeding series show similar fluctuations, but the conduction of the condenser is retained intact after two or even three hours of exposure. It is improbable, therefore, that the number of ions ($c'=nUe(A/cx)\log\varepsilon$) is supplied at a diminishing rate in the lapse of time by the phosphorus; it is much more probable that fluctuations of temperature and like incidental causes account for the difference. In the first series the decrease of c' is most marked, being .0007 per minute while the value .0009 occurs in instances below. Thus in the 15 minutes or less (usually less than 5 minutes) which outlasts the time of a single series of observations, appreciable diminution of the ionizing potency of the source cannot be inferred apart from the environment.

5. *Effect of temperature.*—The effect to be ascribed to temperature is much more serious. I made the following observations (table 3) with the same condenser, endeavoring to obtain the temperature discrepancy by varying the temperature of the room. The observations for $c'=Une(A/Cx)\log\varepsilon$, were completed in the usual way, all being satisfactory. Unfortunately the temperature of the air between the plates is not identical with the superficial temperature of the phosphorus itself, and it is upon the latter that the ionizing effect depends. Hence the data as constructed in the curves, figure 4, show curious lag phenomena. The observations are difficult, as drafts of air if but slightly too warm, are liable to kindle the phosphorus. Different parts of the grid often respond unequally. In a cold room (about 9°) phosphorus is nearly inert. It then rises rapidly to the large ionizing value between 20° and 30°; but experiments like the present merely emphasize the need of a room of constant temperature. The relation itself is elusive and yet to be found.

TABLE 3.—EFFECT OF TEMPERATURE ON THE IONIZING ACTIVITY OF PHOSPHORUS. DIFF. POTENTIAL, 60 VOLTS. DISTANCE APART OF PLATES, 3 cm.

Remarks.	Temp.		Time.	Remarks.	Temp.		Time.
Temperature of cooled room rising from 10	20.6	.040	11 h. 21 m.	(Air)	11	.002	10 h. 14 m.
	24.0	.124	27 m.	Phosphorous grid cold, temperature rising	9.3	.005	10 h. 21 m.
	25.0	.090	32 m.		8.9	.002	26 m.
(Air)	20	.003	—		9.3	.022	45 m.
					9.4	.070	49 m.
					9.6	.107	11 h. 3 m.
Temp. falling	12.5	.101	11 h. 53 m.		9.2	.100	39 m.
	10.3	.026	12 h. 9 m.		18.4	.272	12 h. 4 m.
Temp. rising	10.3	.067	14 m.		19.0	.219	23 m.
	13.1	.115	19 m.		20.0	.200	47 m.
	17.8	.101	25 m.				
	22.3	.138	50 m.				
	23.2	.146	1 h. 15 m.				

TABLE 4.—LEAKAGE OF CONDENSER DUE TO PHOSPHORUS EMANATION.

Absorbent Medium.	Distance apart.	Time		Observed Potential Difference.	Computed Potential Difference.	
		Date.	t			
Air	4 cm.	10 h. 0 m.	0 m.	40.0 volts.		.0007
		10	10	39.0		
		15	15	39.0		
		20	20	38.6		
Air saturated with phosphoric dust	4 cm.	10 h. 27 m.	0 m.	39 volts.	39 volts.	.0360
		28	1	35	36	
		29	2	32	33	
		30	3	29	31	
		31	4	27	28	
		32	5	25	26	
		33	6	23	24	
		34	7	21	22	
		35	8	20	20	
		36	9	19	19	
		37	10	17	17	
		38	11	16	16	
		39	12	16	15	
		40	13	15	13	
		46	19	13	—	
		51	24	13		
		57	30	9		

6. *Fall of potential in the lapse of time.* After these preliminaries the leakage of the condenser in the course of time when the air space is ionized by phosphorus is next to be considered. The method was essentially like the preceding except that longer intervals of time were given to each set of observations. Table 4 shows the leakage through the condenser C, P, figure 2, when the plates are 4 cm. apart, a relatively large distance. The exponential character of the law ($V' = V\,10^{-c't}$) is obvious from the chart, figure 5, but the leakage is throughout faster than can be

reproduced by a simple geometric progression. This might plausibly be ascribed to the waning activity of the phosphorus itself, for c' is necessarily a quantity decreasing in the lapse of time with the number of particles per cub. cm. supplied. Compatibly with the direct experiments just discussed, however, the cause is probably incidental.

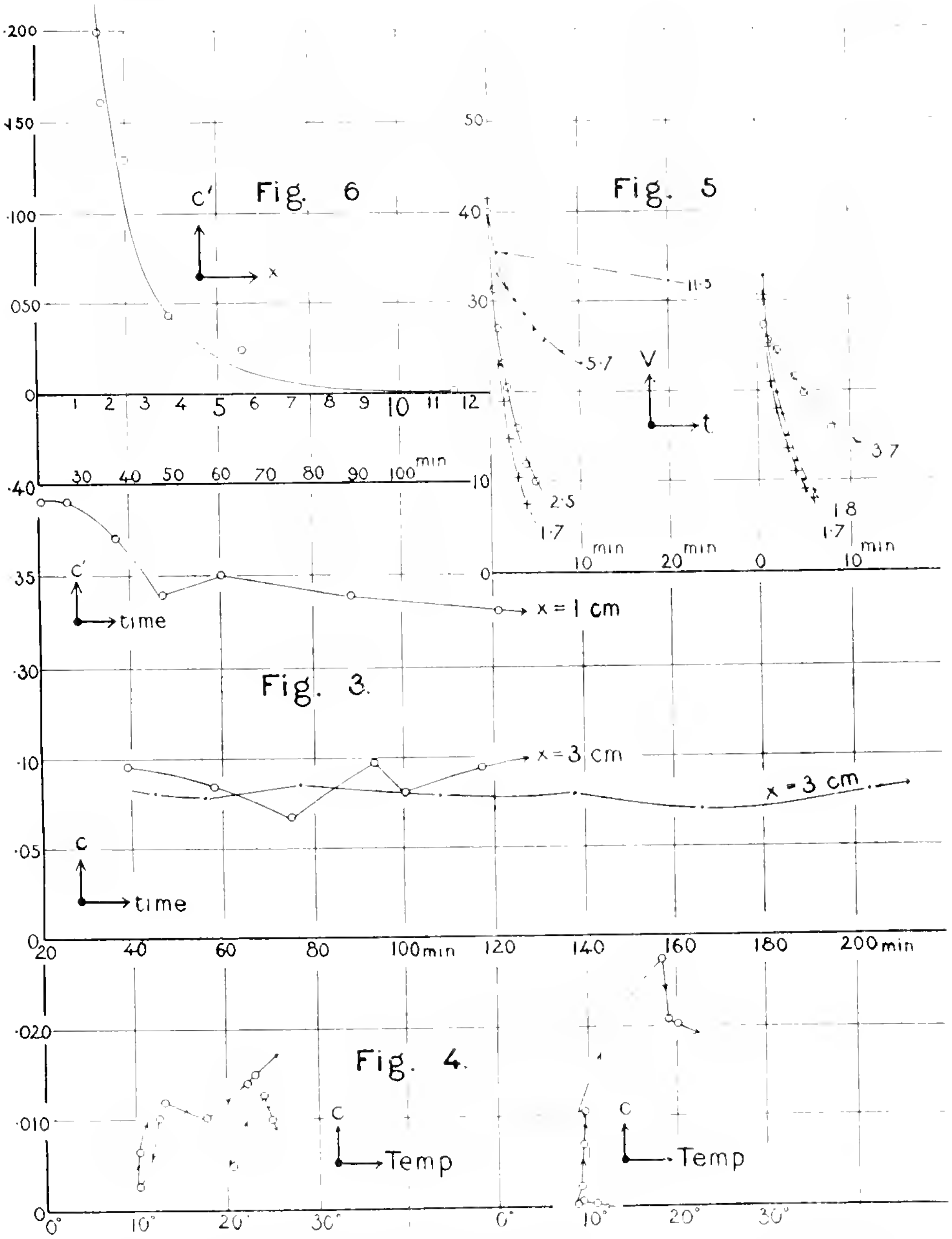


Fig. 3.—Chart showing the Ageing of the Ionizer. Fig. 4.—Chart Showing the Effect of Temperature on the Activity of the Ionizer. Fig. 5.—Fall of Potential in the Lapse of Time for Different Distances of the Condenser Plates. Fig. 6.—Computed Curve and Observed Values of $c = -(dV/dt)/V\log e$, for Different Distances apart, x, of the Condenser Plates.

TABLE 5.—SHOWING THE INSUFFICIENCY OF A SIMPLE GEOMETRIC PROGRESSION.

	[illegible]	[illegible]	$\delta V/\delta t$	Mean V	Mean t		$c = (\delta V/\delta t)/V$	C
d = 3 cm.	4	.0374	.0023	.0327	10 h.	31 m.	.071	.0374
	5	348	18	312		32	59	370
	6	331	24	254		34	93	387
	7	309	20	222		36	93	393
	8	280						384
	9	275						406
	12	177						346
	15	136						340
d = 4 cm	10	.0076	.0005	.0059	11 h.	51 m.	.085	.0076
	13	55	3	45			60	73
	17	42						73
	21	35						87
d = 1.7	1.2	.205	.039	.191	11 h.	18 m.	.20	
	2.0	.176	29	.183		19	.16	
	2.7	.162						
5.7	3.0	.0234	.0022	.0207		21	.11	
	4.0	230	26	192		22	.14	
	5.5	179						
	7.0	153						
2.5	1.2	.125	.015	.120		31	.12	
	2.0	.114	07	.120		32	.06	
	2.7	.115						
1.8	1.7	.136	.021	.117	12 h.	2 m.	.18	
	2.5	.118	17	.103		3	.17	
	3.5	.099						
	4.2	.088						
3.7	3.0	.0335	.0028	.0307		13	.09	
	5.0	279	21	287		14	.07	
	7.5	240						
1.7	1.7	.145	.026	.125		25	.21	
	2.5	.119	.019	.105		26	.18	
	3.2	.106						
	4.0	.091						

7. *Insufficiency of the equation of leakage.*—As I have not made up my mind as to a satisfactory explanation I give above an exhibit of the inadequacy of the simple geometric equation. Let the observations be separated into two halves and the constant c be computed from corresponding members V, t, and V', t', of the two series. The values c and t of table 5 show the datum so obtained and the mean-

time for which it holds. If the process is repeated to get the ratio of increments δc and δt of the values just found, the rates $\delta c/\delta t$ of the table follow. These are practically constant in the same series but differ widely in successive series, i. e., varying with c'. Let the mean c' of each ratio be found as in the table. Then if $\delta c'/\delta t$ be computed, a result is obtained which though not fully independent of c' is restricted to narrow limits. Thus in place of the above equation there follows (per unit of e, A, and x, as above) a double exponential law,

$$V_0 = V_0 \varepsilon^{-N\varepsilon^{-\gamma T}/Ca},$$

expressing that some independent cause has for the time T been decreasing the number of particles at the rate γ. If c corresponds to C as n corresponds to N, $C/c = 10^{\gamma T \log e}$. The last column shows the values of C found in this way. Compared with c they are constant enough to plausibly suggest some independent cause of decay attributable to the source.

8. *Effect of distance between condenser plates.*—I come now to the main purpose of the present paper, namely, to find and to explain the decrease of the leakage, c', of the condenser when the plates are separated. This is equivalent to finding the change of n, the number of particles per cubic centim. with the distance between the condenser plates. The farther away the ions move normally from the condenser plate the fewer will have survived, whether this be due to mutual destruction or other decay or to the escape of particles laterally out of the condenser.

Table 6 gives the distance apart, x, of the condenser plates, the current time (date), and the interval, t, elapsed since charging, together with the voltages, V (potential difference of the condenser), corresponding. The constant c' is computed from $V = V_0 10^{-c't}$, for the time, t, given in minutes. The last column contains the values, V, computed from c'. The fall of potential for the different distances, x, is shown in the chart, figure 5.

TABLE 6.—RATES OF DISCHARGE FOR DIFFERENT DISTANCES BETWEEN PARALLEL PLATES, WHEN ONE PLATE (GRATING) IS THE SOURCE OF PHOSPHORUS EMANATION. PLATES 14 CM. SQUARE. $V = V_0 10^{-c't}$.

x, Distance apart.	Time.		t	V Observed Potential Difference.	c'	Calculated Potential Difference.
cm.	h.	m.	min.	volts.		volts.
1.7	11	17.0	.0	——		(38.0)
		17.5	.5	30.0	.200	30.2
		18.0	1.0	23.0		24.0
		18.5	1.5	18.8		19.0
		19.0	2.0	14.8		15.1
		20.0	3.0	10.2		9.5
		21.0	4.0	7.4		6.0

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	Observed Potential Difference.		Calculated Potential Difference.
		m	mm	volts.		volts.
	11	18	0	—	.023	
		19	1.	33.		33.0
		20.	2	31.4		31.3
		21.	3.	30.0		29.8
		22	4	28.4		28.0
		23	5.	26.6		26.8
		24	6.	25.4		25.3
		26	8	24.4		22.8
		28	10.	23.0		20.5
5		30	0	—	.120	(35.8)
		30.5	.5	31.4		31.1
		31	1.0	27.0		27.2
		31.5	1.5	23.2		23.6
		32	2.	20.4		20.6
		33	3.	16.0		15.7
		34.	4	12.0		11.9
		35.	5	10.0		8.9
11.5	14	37	0	—	.0023	(35.6)
		38	1.	35.4		35.4
		39.	2.	35.2		35.3
		43	6	34.6		34.4
		48.	11.	33.6		33.5
		52.	15.	33.0		33.0
		57	20	32.0		32.1
1.8	12		0	—	.130	(37.6)
		5	.5	32.4		32.4
		1	1.	26.6		27.8
		2	2.	19.4		20.7
		2.5	2.5	17.0		17.8
		3	3.	14.8		15.3
		4	4	11.8		11.3
		5.	5	9.8		8.4
		6	6	8.4		6.3
1.7	12	10	0		.033	28.1
		10.5	.5	27.6		27.2
		11	1	26.4		26.0
		12.	2	24.4		21.4
		14	4	21.2		20.8
		15	5	19.4		19.3
		18	8.	16.6		15.3
		21	11.	14.4		12.1
1	12	23	0	—	.140	35.7
		23.5	.5	30.4		30.4
		24	1.	24.6		25.9
		24.5	1.5	20.6		22.0
		25	2.	17.6		18.8
		26	3.	13.2		13.6
		27	4	10.8		9.8
		28.	5	8.8		7.1
		29	6	7.6		5.2

To interpret the above results I will suppose as a first trial, that $e' = e'_0 10^{-ax}$, where $e' = nUe(A/ex)\log_\epsilon$ as given above. The following table is a summary of completed series of experiments computed in this way, the value of e' in the 3d column being taken at once from the preceding table 6. It will be noticed, however, that the value of e' at $x = 1.7$ cm. has fallen off considerably during the course of the experiment. Its probable value at the successive times and $x = 1.7$ is given under e''. For any values of x, the observed value, e', is then to be referred to the value e'' ($x = 1.7$ cm.), corrected for the apparent decreased intensity of the phosphoric ionization above referred to. These computed values e'' are given in table 7, as well as the values e' (column 5) reduced in terms of them.

TABLE 7.—TRANSMISSION OF THE PHOSPHORUS EMANATION IN AIR. SUMMARY. $e' = e'_0 10^{-ax}$; $a = .25$; $e'\lambda / e_0\lambda_0 = n/n_0$.

Distance apart, x.	Mean Time.	e' Directly Computed from $I' = I'_0 10^{-at}$.	e'' Contemporaneous[1] Values for $x = 1.7$.	e' Corrected (obs.).	e' Corrected (computed).	10^{-ax}
1.7 cm.	11 h. 18 m.	.200	.200	.200	.200	.376
5.7	22	.023	.106	.024	.020	.038
2.5	32	.120	.187	.128	.126	.237
11.5	43	.002	.178	.002	.001	.001
1.8	12 h. 3 m.	.130	.160	.162	.188	.355
3.7	14	.033	.150	.044	.064	.119
1.7	25	.140	.140	.200	.200	.376

[1] The time correction is made linearly. At $x = 1.7$ cm. the value e' fell from .20 to .14 in 67 minutes; i. e., .0009 per minute. This result is referred to above in relation to tables 1 and 2.

Table 7 deduces the mean value of a to be .25, whence it follows that at $1/a = 4$ cm. the value e' is but 1/10 of the original number. Similar ratios, $e'/e'_0 = 10^{-ax}$, are given in the last column. For $x = 1$ cm., .5 cm., .1 cm., the relative numbers are .56, .75, .94, showing how rapidly the saturation is reduced even close to the phosphorus grid.

9. *Another computation.*—The above table exhibits the character of the phenomena, fairly well. From another point of view I also tested the equation $e' = e'_0 / (1 + bx)$. I have given the constants so obtained in the following table, 8. The equation $1/e' - 1/e'_0 = bx/e'_0$, where $b/e'_0 = 8.8$ is closely in accord with the observations, but the result for small values of e' is absurd, as e'_0 is negative. Inasmuch as the errors in the last two tables are cumulative, better results than this are not to be expected, seeing that the reason for the apparent decay specified has not been made out. Taking the observations at their face value, preference would have to be given to the exponential first discussed.

Neither of these expressions however can be expected to represent the case fully, for in both differential equations all allowance for those particles which escape laterally from between the plates is left out. The term ignored may be much more than a correction; indeed I shall presently show that by introducing it and disregarding the mutual destruction of the ions altogether, one obtains a much better explanation of these data than by either of the preceding methods.

TABLE [illegible].—SUMMARY [illegible] (1 + [illegible]); [illegible] n/n_0 [illegible] = .150; b = .88.

		Corrected Observed.	Corrected Computed.
1.7	.201	.200	.201
1.8	.130	.162	.172
2.5	.120	.128	.083
3.7	.033	.044	.044
5.7	.023	.024	.025
11.8	.012	.012	.011

10. *Working hypothesis.* It will be seen in the next chapter that the current removes a relatively insignificant number of particles. Hence in the condenser, figure 2, the loss of ions is due either to their mutual destruction or decay in the space x between the plates, or to their escape laterally out of this space into the surrounding atmosphere.

Let n be the number of particles per cubic centim. at a distance x from the phosphorus grid, P, figure 2. Let A be the area of the condenser of air space x, and let ax be the circumferential area terminating in the edges of the condenser (mantle of the cylinder of air). Let k be the absorption velocity of the ions in the absence of an electric field, when passing from a saturated region either into free air or normally to an absorbing surface. Thus k is the number lost under these conditions, per square centim. per second, when $n = 1$. Let $k'n^2$ be the number decaying per cubic centim. per second. Then the accumulation in the air plate Adx will be, per second, $-(dn/dx)Akdx - ankdx$; the decay in the element will be, per second, $k'n^2Adx$; and when the flow is stationary $dn/dt = 0$; whence $-(dn/dx) = an/A + k'n^2/k$. If n_0 be the value of n at $x = 0$, the position of the phosphorus plate, P, figure 2, this equation admits of integration in finite form leading to $n = n_0(a/A)/((a/A + n_0k'/k)e^{ax/A} - n_0k'/k)$. If $k' = 0$, the decay within the element is ignored and the equation takes the simple form $n_0 = ne^{ax/A}$, which is specially interesting as n is independent of the absorption velocity also, depending for a given n and x merely on the circumferential area, ax, and the base area A of the cylinder of air space between the plates.

Thus far no reference has been made to the electric field. With the velocity, k, moreover, it would not be practicable to approach the question of electric conduction at once, for the other variables, n and e, remain undetermined in relation thereto. If n were found by Aitken's method of nuclear condensation, e would then be deducible by methods presently to be indicated; but I have not yet done this.

11. *Electrical considerations introduced.* Suppose, however, in order to estimate in how far the present argument is tenable, that the number $n = n_0e^{-ax/A}$ just found, is a correct value: The question is put whether this number is in reasonable accord with the usual theory of electrolytic conduction. In other words, let the condenser be charged, remembering that the additional contribution of ions from this cause is insignificant. Let V be the potential difference at the time t.

Then if C is the effective capacity of the condenser, U the relative velocity of the ions to each other, e the charge of each,—

$$-(dV/dt) = AUVn_x e/Cx = AUVn_0 e/Cx\varepsilon^{ax}$$

when the above value of n is inserted.

Now in the data of table 7 the leakage of the condenser was computed as $V = {}_0V10^{-c't}$, which when substituted in the last equation gives on reduction $c' = (AUn_0 e/C \ln 10)\,(1/x\varepsilon^{ax})$, remembering that c' refers to minutes.

12. *Constants Computed.*—This equation may now be tested with the corrected values (corrected for loss of potency of the ionizer in the lapse of time) of c' in table 7 as related to x, figure 6, the distance apart of the plates. These computations are made in the following table by choosing the constant $K = AUn_0 e/C \ln 10$) so that the first observations ($c' = .200$ and $x = 1.7$) coincide. There is no smoothing.

TABLE 9.—VALUE OF $K = \frac{AUn_0 e}{C \ln 10}$; $-(dV/dt)/V = c' \ln 10$; $c' = \frac{K}{x\varepsilon^{ax}}$.

Plates.	Distance apart, x.	Observed leakage per min., c'.	Computed c'.	$\frac{AUn_0 e}{C \ln 10}$
	cm			
$A = 132^{\text{cm}}$	1.7	.200	.200	.634
$a = 46^{\text{cm}}$	1.8	.162	.182	
$a/A = .35$	2.5	.128	.101	
	3.7	.044	.044	
	5.7	.024	.013	
	11.5	.002	.001	

The curve so computed is shown on the chart, figure 6, and the observations are inserted with reference to it. It will be seen that the coincidence is surprisingly good, far superior to the cases of tables 7 and 8, lending to the new equation deduced a degree of probability which becomes enhanced when viewed in connection with the similar result of my last chapter.

13. *Number of ions in the saturated emanation.*—It is even possible to make an approach toward computing the constant n_0. If, conformably with c', the value of K be taken relative to minutes instead of seconds, the equation becomes $K = 26\ AUn_0 e/C$. Now if the velocity of the ions produced by phosphorus is like that of the other gases, U is of the order (say) of 1 centim. per sec. (Thomson, Rutherford, Townsend, Chattock), and e of the order of $7/10^{10}$ electrostatic units or 2.4×10^{-19} coulombs (Thomson). The ratio of areas in my condenser was .35, the area $A = 132$ cm^2, the capacity, C, estimated at 60 centims. or $.7 \times 10^{-10}$ farads. Finally the value of K found in the last table is $K = .634$. Thus the initial saturation, or the number of ions $n_0 = .634 \times .7 \times 10^{-10}/26 \times 132 \times 1 \times 2.4 \times 10^{-19} = 5.5 \times 10^4$. Hence if *all* the ions which reach and are absorbed by the condenser plates actually convey charge, less than 10^5 and more than 10^4 ions per cubic centim. occur in the saturated emanation contiguous to the surface of the phosphorus grid.

If the emanation of phosphorus is ionized air, $U = 1.5$ cm/sec (Thomson, Rutherford, Chattock) and $n_0 = 3.6 \times 10^4$, agreeing very well with J. J. Thomson's 4×10^4 as the number of ions in air ionized to saturation by the X-rays.

14. *Electrolytic mechanism.* If, instead of $U = 1$ cm/sec for the field of 1 volt per centim., the absorption velocity found in the preceding chapter as $3k = .9$ cm (approximately) were taken, the number n_0 would be of about the same order. In such a case however, from the implied absence of an electric field, a special mechanism of electrolysis is in question. The following is the point of view taken:

Let k (replacing $3k$) be the ion velocity of the phosphoric "dust" particle, normally to a charged wall, A, figure 7. The prism of charged air, figure 7, which reaches A will, for any appreciable length in the direction of k, be at an average potential zero, and its successive layers will on the average show no charge, although saturated with the ionized agency stated. Considered non-statistically, however, the individual sections at molecular distances apart must convey immensely different charges successively, the distribution of charge or of potential on successive sections following a law something like Maxwell's, for instance, in the kinetic theory of gases. To deal with the problem in this broad form would make it needlessly cumbersome, without conducing to the present purposes. It seems possible to obviate the question of distribution somewhat as follows:

Suppose the distribution of potential in the direction k is enormously variable, as compared with the potential of A, in such a way as to give preference neither to positive nor to negative values. A will lose charge if its potential is instantaneously greater than that of the section which meets it; it will receive charge in the opposite case. A at potential zero, therefore, neither receives nor loses charge, since the number of sections reaching A carry equal and opposed charges in like distribution. If the charge on A is positive, there must be fewer layers which impart charge to A, and more layers which withdraw it than in the preceding case, since the average charge on the layers is still zero. Thus A will be discharged in the lapse of time and this more rapidly as its potential gradient, V/x, is higher. Precisely the reverse will happen if A is negatively charged. Hence to avoid the law of distribution specified, I suppose that the charge per square centim. on A is relatively so small, that if it is increased n times, there will be n times more layers to discharge it under like conditions than in the initial case. In other words, I regard the charge on A small enough to correspond to a linear element of the law of distribution of charges along the length of the prism, k. The rate of discharge of A is then taken proportional to V/x.

If n is the total number of ions per cubic centim., and e proportional to the average charge (positive or negative) carried by each, $Akne$ is the total quantity of free electricity of both kinds promiscuously carried to A per second. Thus kne is the equivalent of conductivity. The rate of discharge of A is thus $-dQ/dt = (V/x)Akne$ where the constant of proportionality is contained in e. The potential of the charged plate of area, A, the other being earthed, is therefore $V = V_0 e^{-Aknet/Cx}$ in the lapse of time after charging to the initial potential, V_0, V being the capacity of the condenser.

The conveyance of charge into the ionized region would be similarly explained, virtually in the way of Clausius. Through any interface in the ionized region two such prisms may be imagined travelling in opposite directions. They travel to and from a boundary. The motion of the prism k is an abstraction, but if I accentuate it here, I do so because in the present investigation with phosphorus it may run closely parallel to the actual state of things. When the phosphorus grid is placed on a smooth, clean surface, the position of the discs is soon marked by apparent grease spots due to deliquescing phosphoric oxide which has diffused across. Virtually therefore an outgoing current originating in the phosphorus is continually kept up, whether electricity is demonstrably conveyed or not.

To summarize: Instead of operating with the velocity $U(V/x)$, I have used the constant absorption velocity, k, found in the absence of an electric field.[1] Thereafter I have endeavored to account for the inevitable factor V/x, or dV/dx, by associating it with the conditions of discharge of the plate, A.

The only other explanation which I can suggest would be an hypothesis whereby the ions in certain cases like the present are released out of nuclei by the presence of a field. In fact, this is, bluntly, about the drift of the computations in the above paragraphs, 8 and 9.

TRANSMISSION THROUGH SOLID MEDIA.

15. *Method.*—The remainder of the chapter will be devoted to a number of promiscuous experiments. I shall endeavor to ascertain whether the ionized particles exhaled by phosphorus are accompanied by some form of obscure radiation, or whether the reaction is restricted to an oxidation the products of which at first escape in gaseous form. This is best done by placing barriers of thin material between the plates of the condenser, care being taken to prevent the nuclei from passing around the barrier, yet allowing sufficient space for access of air. It was my plan to fold sheets box-like around the phosphorus grid, kept at potential zero, so that escape around the edge would require a passage of 8–10 centims. to reach the other plate. This suffices, and the plates may then be placed quite closely together on opposite sides of the barrier. Energetic action is secured at a distance apart of about 1 centim.

16. *Results.*—The results are given in the following tables, which will be intelligible at once, remembering that $V = V_0 10^{-ct}$, so that c varies as $-(dV/dt)/V$. The insulation of the condenser itself (absence of leakage when the phosphorus grid is replaced by an ordinary plate) was frequently tested, often with the barriers in place.

---

[1] Remembering that k is to be replaced by $3k$, if but $\frac{1}{3}$ of all the ions travel in a given cardinal direction, roughly speaking.

TABLE [illegible].—TRANSMISSION OF PHOSPHORUS DUST THROUGH BARRIERS [illegible] VALUES OF APPARENT TRANSMISSION [illegible]

[illegible]	Time		Observed Potential Difference.		Barrier.	Time.		Observed Potential Difference.	
	h.	m.	volts			h.	m.	volts.	
[illegible], .150 [illegible] thick		[illegible]	[illegible]		Same repeated	6	3	37.0	.072
		1	37 [illegible]				4	32.0	
		2	34 [illegible]				5	27.2	
		4	34.4				6	22.4	
		6	34.						
[illegible]			39.6		Insulation (with paper)		12	38.4	0[illegible]2
		4	39.4				1[illegible]	37.6	
							14	37.4	
							16	37.2	
Celluloid, .024 cm. thick		[illegible]	37		None				5
		1	36.6						
		2	37.[illegible]						
		4	36.8						
		8	36.4		Insulation (with paper)	1	25	41.2	0[illegible]1
							28	40.8	
							35	4[illegible].2	
Celluloid removed			3[illegible]			12	5	35.0	
		1	2[illegible]						
					Writing paper, [illegible]1 cm. thick		15	41.[illegible]	[illegible]
Tissue paper, [illegible]3 cm. thick, two sheets	5	29	34.4	.092			16	4[illegible].6	
		3[illegible]	27.2				23	39.6	
		31	22.4				27	39	
		32	18						
					Same (dust blown out)		29	40.0	[illegible]1
Insulation		34	37.7	[illegible]			32	39.8	
		3[illegible]	37.[illegible]				35	39.6	
Aluminum, [illegible]3 cm. thick, holes 1.5 cm. apart		41	37[illegible]	[illegible]3	Paper barrier off		27	4[illegible]	500
		43	37.6				27.5	24.0	
		45	36.8				28	12.0	
		47	36.4				28.5	8.[illegible]	
Aluminum, [illegible]3 cm. thick, [illegible] cm. [illegible]		5[illegible]	36.[illegible]	.01	Aluminum, large sheet, [illegible]3 cm. thick		43	4[illegible]	0.[illegible]2
		51	36.4				45	4[illegible]	
		53	35.[illegible]				47	39.6	
		55	35.2				49	39.4	
Writing paper, [illegible]1 cm. thick	5	59	36[illegible]	.71	Same, air space in front of grid.		50	39.[illegible]	.002
		6[illegible]	3[illegible].6				52	39.6	
		61	3[illegible]				55	38.0	
		62	22.[illegible]				58	37.4	

Probably leakage around the edge of foil.

Barrier.	Time.	V Observed Potential Difference.	c	Barrier.	Time.	V Observed Potential Difference	c
Writing paper, air space in front of grid.	1 4	40.6	000	Same, paper bridging loosely between plates (conduction)	49	36.0	.023
	7	40.6			50	34.4	
	9	40.6			51	32.4	
	11	40.6			52	30.8	
Tissue paper, .003 cm. thick, two sheets	14	40.4	.018	Filter paper, .020 cm. thick	6 1	31.6	.011
	15	38.0			2	31.0	
	16	36.8			3	30.0	
	17	35.2			4	29.4	
Same	—	—	.011	Same (larger sheet), .020 cm. thick	11	37.4	.008
					12	38.8	
					13	34.2	
Insulation (with paper)	5 26	38.0	.002		14	33.4	
	31	37.4					
				Tissue paper, .003 cm. thick, two sheets	20	37.2	.007
Writing paper, .010 cm. thick	34	35.0	.002		21	36.6	
	35	34.8			22	36.0	
	36	34.6			23	35.6	
	37	34.4					
Same, with air space in front of grid.	39	32.8	.001				
	40	32.6					
	42	32.6					
	43	32.6					

TABLE 11.—SUMMARY. TRANSMISSION OF PHOSPHORUS DUST THROUGH BARRIERS. PLATES ABOUT 1 cm. APART.

Barrier.	Thickness.	c	Date.	Barrier.	Thickness.	c	Date.
Tissue paper	.006 cm.	.092	Feb. 3,	Aluminum	.003 cm.	.003	Feb. 4, A.M.
" "	.006	.018	4, A.M.	Another sample		.002	P.M.
" "	.006	.007	4, P.M.				
				Celluloid	.024 cm.	.000	
Writing paper	.010 cm.	.072	Feb. 3				
" "	.010	.002	4, A.M.	None	—	.5	—
" "		.002	4, P.M.				
				Insulation		.002	—
Filter paper	.020 cm.	.011	Feb. 4, A.M.				
Another sample	.020	.008	4, P.M.				

The last table, 11, is a brief summary of the results. Porous and tissue paper transmit the emanation in small quantity, depending on circumstances not easily made out. Usually not more than a few per cent. of the emanation will pass even under favorable conditions. The large values found for writing and tissue papers were not again obtained in many subsequent experiments except in a single instance. They may be errors, though careful inspection of the results revealed none. It is also possible that the emanation from phosphorus may be different in quality under qualitatively different circumstances apart from intensity.

The general result obtained is thus definitely against any obscure radiation. The emanation passes with great difficulty and loss in quasi-gaseous form even through very thin porous barriers. It is stopped by impervious media, however thin. Oiled tissue paper cuts off the ions unconditionally. Negative leakages are sometimes observed with such barriers as celluloid, due no doubt to static charges produced by friction. One is also easily misled by conduction.

17. *Effect of temperature, etc.* It was thought that temperature might possibly have some discriminating influence on the charge in relation to its tendency to pass through paper. The following experiments were made at low temperatures with this quest in view.

TABLE 12. TRANSMISSION AT LOW TEMPERATURES, $\theta = -12°$.

Barrier.	Time.	Observed Potential Difference.	[illegible]	Barrier.	Time.	Observed Potential Difference.	[illegible]
	h. m.				h. m.		
None. P. removed.	3 43	54.0	.001	Writing paper, .01 cm thick.	58	55.5	.007
	44	54.0			59	54.6	
					60	53.7	
					61	53.1	
None P. in place. −12°.	45	55.5	.181				
	46	34.2					
	47	22.8		Writing paper P. removed (Insulation.)	4 14	55.5	.000
	48	15.6			15	55.5	
					16	55.5	
					17	55.5	

No effect is detected.

The following experiments, table 13, show curious incipient permeabilities[1] decreasing in the lapse of time, afterwards to be regained. The large values for tissue paper and larger values for filter paper ($e' = .05$ to $.06$) have thus again been obtained under trustworthy conditions. Change of the sign of the charge is without effect.

---

[1] In recent experiments I have demonstrated the penetrating potency of moist phosphorus emanations.

TABLE 13.—PROMISCUOUS RESULTS WITH BARRIERS.

Barrier.	Time.			Barrier.	Time.		
	h.	m.			h.	m.	
Fresh tissue, double.	10	4	.084	Filter paper.	10	56	.053
" " plates apart.		9	.057	" " plates apart.		61	.055
" " later.		31	.067				
" " oppos. charge.		38	.066				
" " later.[1]	11	21	.005	Double tissue paper.			
" " plate scoured.[2]		48	.010	Charge ±	3	32	.044
				" ∓		37	.051
				" ±		42	.048
Writing paper.	10	50	.002	" ∓		46	.050
Fool's-cap.	11	14	.003	" ±	4	10	.047

IONIZATION IN OTHER DUST PRODUCERS.

18. *Concentrated sulphuric acid.*—In conclusion I will briefly advert to a few endeavors to detect ionization in other dust producers. The method consists in blowing dust-laden air between the plates of the condensers, the current entering the center of the earthed plate and escaping at the edges. Thus 86,000 cubic centims. of air, bubbled through concentrated sulphuric acid in about 6 minutes, produced an electric leakage equivalent to but $c' = .0005$, while the leakage of the condenser before the experiment was $c' = .0010$. Hence the effect is increased insulation to the exclusion of all ionization. The same air current tested in the color tube gave an intensely opaque field, showing a condensation producing potency of high order.

19. *Ammonic polysulphide.*—Ammonic polysulphide tested in like manner gave similarly negative results. About 80,000 cubic centims., passed in five minutes through the condenser, showed no leakage whatever, whereas the insulation leakage was originally equivalent to $c' = .0006$. In this case, however, the current produced only just perceptible darkening of the field of the color tube, evidencing therefore but slight tendency to produce condensation. The effect of this reagent on the color tube is in general very fleeting. When evaporating from the stopper of a bottle it is very active, but only momentarily, as a rule. If, however, the current of air is replaced by a current of coal gas (which is itself somewhat dust-laden, as appears when the test is made with the color tube), the effect is much more persistent. Indeed if the air of a large room is rendered impure in this way, it reacts on the color tube for a longer interval than under any easily producible conditions which I have found. The fleeting nuclei from ammonium polysulphide seem therefore much more stable when preserved out of contact with an oxydizing medium like air, and the same is true of sulphuric acid in a measure, and for sulphur itself. The data follow in table 14. It should be noted that coal gas bearing the very active nuclei is just as inactive electrically as air

---

[1] Increasing c' to .010.

[2] No effect.

TABLE 14. NON-IONIZATION OF DUST FROM CONC. SULPHURIC ACID AND AMMONIUM POLYSULPHIDE.

Remarks.	Time.		Volts.		Remarks.	Time.		Volts.	[illegible]
	h.	m.				h.	m.		
85,7[illegible] cub. centim. of air bubbled through sulphuric acid.		21	36.4	.0005	Coal gas.	11	35	39.0	.000
		23	36.4				36	38.7	
		25	36.2				37	38.7	
		27	36.2				38	38.7	
Insulation.				.0010	Coal gas bubbled through ammonium polysulphide.	2	52	37.5	.001
							53	37.2	
							54	37.2	
8[illegible] cub. centim. of air bubbled through ammonic sulphide.		45	35.6	.0000			55	36.9	
		47	35.6						
		49	35.6						
		50	35.6		Coal gas bubbled through sulphuric acid.	4	17	38.1	.000
							18	37.8	
							19	37.8	
							20	37.8	
Insulation.				.0006					
					Air.	4	13	37.4	.001
Air	11	32	39.0	.000			14	37.4	
		33	39.0				15	37.1	
		34	39.0				16	37.1	
		35	39.0						

I conclude, therefore, that neither Kelvin's nuclei nor Aitken's "dust" particles have yet been downed by the wily ion. I admit that an electric field may sometimes stress ions out of them, leaving the nuclei to do the condensation.

CHAPTER V.

SIMULTANEOUS ELECTRIC AND VOLUMETRIC GRADUATION OF THE COLOR TUBE.

1. *The problem stated.*—After graduating the color tube in terms of the volume influx per second of air saturated with phosphorus emanation, it is next necessary to investigate corresponding data for the degree of ionization of air as related to the color effect. Indeed both graduations may be made simultaneously by passing a known volume of saturated air per second through a suitably constructed tubular condenser, and observing coincident values of the electrical leakage of the latter and the color of the enclosed steam jet. Clearly the colors of the tube will each correspond to a definite electrical current passing through the condenser. Moreover, while the volumetric equivalent of a given color is dependent on the degree of saturation of the phosphorus emanation conveyed by the current of air, the electric equivalent should be independent of it. The final graduation cannot at once be carried out, however; for in the case of the color tube constructed and used as below, the nuclei are injected into the air current maintained by the steam jet. An arbitrary element is thus introduced, and the results will only be comparable when all observations refer to a tube the action of which has been left quite undisturbed. True, there seems to be no objection to putting a vane anemometer into the influx pipe (enlarged) of the color tube, in which case the arbitrary factor would be specified; and other methods of eliminating the factor will be indicated, but the data following refer to the earlier methods of experiment.

2. *Apparatus.*—In figure 1, *CC'* is the color tube, with the jet *j*, the thermometer *T*, and the influx pipe *C'*, bent for convenience. *KL* is the tubular condenser, consisting as shown in detail in figure 2, of a brass tube *d*, .6 centim. in internal diameter and effectively 50 centims. long, surrounding a steel rod *a*, .318 centim. in diameter, coaxially. Rod and tube are separated symmetrically throughout by the short hard-rubber tubes, *b*, at each end, fitting over the rod and within the tube, snugly. Thus the cylindrical shell (air space) is but .141 centim. thick and 50 centim. long, and the condenser is adapted to bring to bear a high potential gradient (the shell of air being as thin as admissible in consideration of flexure) along a considerable length of air column conveying phosphorus nuclei. The outside of the condenser (figure 1) is permanently put to earth, while the rod inside is in metallic connection with the electrometer needle, as suggested in the figure at *E*. A suitable key is added (see figure 1, Chapter IV., at *S* 1) in order to conveniently charge the rod. Upwards of 300 volts were applied. Notwithstanding its slender dimensions, no difficulty attended the use of the condenser.

The air from a gasometer train after passing the desiccator (*D*) and the stopcock *F* is charged with nuclei by the ionizer *P*, containing pellets of phosphorus between strips of wire gauze. It then traverses the condenser *LK*, and thence enters the color tube. The gasometer has already been described (figure 1, Chapter II.), where *M* is a large Mariotte flask, *V* the volume flask, *U* the pressure gauge, *D* the desiccator.

3. *Method and results.* The method of observation was as follows: the two sets of data to be obtained, viz., the readings at the volume flask and at the electrometer, were taken in consecutive minutes, the stopcock *F* having been previously adjusted to show any desired color in the steam tube. From observations at 15 seconds apart at the gasometer flask, I obtained two sets of results for the discharge of air per second, the pressure of the jet (*p*), the temperature of the inflowing air (*ϑ*, by the thermometer *T* in the figure), the pressure of the air in *V* and its temperature.

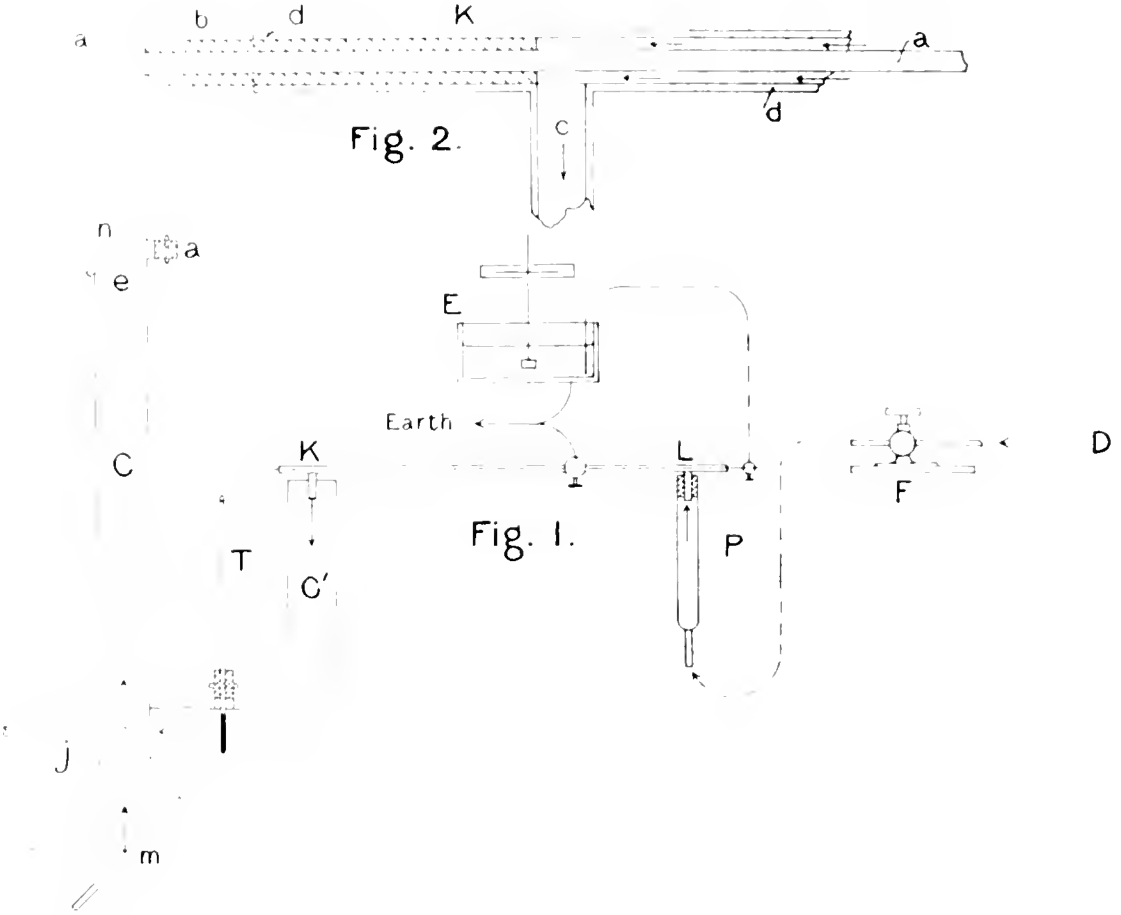


FIG. 1.—DISPOSITION OF COLOR TUBE, CONDENSER, ELECTROMETER, AND GASOMETER TRAIN. SCALE $\frac{1}{10}$.
FIG. 2.—TUBULAR CONDENSER SLIGHTLY ENLARGED.

Meanwhile the condenser had been charged to its full potential, and after breaking the charging circuit, the leakage of the electrometer was observed each 15 seconds. This furnished two sets of data for the initial electric current.

The experiments with the train of apparatus described usually progressed smoothly. The data are given in table 1, which is divided into three parts, referring respectively to the steam jet, the gasometer (volume conveyed per minute, V, being the essential datum), and the electrometer. It was thought superfluous to reduce the air volumes to normal conditions as the fluctuations of pressure (pressure excess, p) and temperature (θ) are relatively insignificant in view of the variability of the ionizer. For the steam jet, the pressure, p, and temperature, θ, are also practically constant (See Chapter II). Relatively to the electrometer series, the two initial potential differences, E, are given as obtained immediately after, and 15 seconds after charging. These are needed in the reductions. The potential in these experiments usually begins with about 40 volts. The table also contains the value of E/E', for observations half a minute apart, two of these being available for each color as specified. The current was computed as follows: For a very short time after charging the fall of potential is appreciably logarithmic. Hence, $E/E' = 10^{-x(t-t')}$ may be assumed, where E and E' are the potential differences at the times t and t', in minutes, and x a constant for a given color in the tube. Hence $-C(dE/dt) = CEx \ln 10 = i$, if C is the aggregate capacity of the electrometer and the condenser, and i the current flowing radially through it. Since $\log (E/E') = -x(t-t')$, or $-x = \delta \log E/\delta t$, the table furnishes these data with E, to compute i relatively, and it was thought superfluous to supply the factor $(C \ln 10)/60$, sharply. Its estimated value is about 230/60, as the combined capacity of the electrometer (60 cm.) and the condenser (39 cm.) is about 99 cm., roughly. This would make $C = 1.1/10^{10}$ farads and the factor $(C \ln 10)/60 = 4.2/10^{12}$. The table shows a few of the values of i, in amperes.

TABLE 1.—COINCIDENT REGISTRY OF THE GASOMETER, ELECTROMETER, AND COLOR TUBE.

Steam Jet.			Gasometer.			Electrometer.			
Color.	p, θ		p, θ		V litres/min.	E	E/E'	$x = -\frac{\delta \log E}{\delta t}$	$i \times 10^{12}$
Blue+	6.0 cm.	29	5.4	30	2.70	39.0 volts	.72	.2852 $\frac{1}{\min}$	48 amperes
					2.40	33.3	.68	.3348	—
Bl.-Bl. Gr.	6.5	29	5.8	30	1.20	40.0	.83	.1616	28
					1.20	36.8	.82	.1722	—
Green	6.5	29	5.9	30	.90	40.0	.88	.1108	19
					1.00	37.8	.87	.1208	—
YI	6.5	29	5.9	30	.50	40.0	.92	.0722	12
					.50	38.4	.92	.0722	—
YI′-Op.[1]	6.5	29	5.0	30	3.60	40.0	.64	.3874	66
					3.80	32.0	.55	.5195	—
Violet+	6.5		5.5		2.30	40.0	.75	.2496	42
					2.30	35.2	.73	.2732	—
Blue?	—	29	5.8		1.26	40.0	.88	.1108	19
					1.30	36.8	.84	.1512	—
Blue	6.5		5.6		1.90	40.0	.80	.1926	33
					1.80	36.2	.78	.2156	—

[1] Yellow marked YI′ is of the 1st order, the other, YI, of the second.

[illegible]				Gasometer.			Electrometer.		
	δ			δ	[illegible]	E	E'/E	log E/E'	$i \times 10^{13}$
B. —	6.5	29	5.9	30	1.20	40.0	.86	.1308	22
					1.00	37.4	.86	1308	—
Green	6.7	29	5.8		.92	40.0	.89	.1010	17
					.86	38.1	.87	.1208	
Yellow	—	–	5.9		.66	40.3	.91	.0818	14
					.70	38.4	.92	.0722	–
Faint Gr		–	5.9		.46	40.6	.95	.0444	8
					.40	39.4	.94	.0536	—
Green		–	5.9	30	.76	40.6	.92	.0914	16
					.70	37.8	.91	.0818	
Blue[1]	5.5	21	5.6	21	1.40	39.6	.84	.1512	26
					1.40	36.3	.82	.1722	-
Violet	7.5		5.5		2.30	38.9	.78	.2156	36
					2.40	35.3	.74	.2614	
Opaque	6.0	21	5.1		2.30	39.6	.73	.2732	46
					2.30	33.7	.72	.2852	—
Green	6.0		5.8		.90	39.6	.87	.1208	21
					.80	36.6	.87	.1208	-
Bl. Gr.	6.0	21	5.8		1.10	39.6	.83	.1616	27
					1.10	36.0	.85	.1410	—
Yl-Green	6.0		5.8		.50	39.6	.93	.0628	11
					.50	38.0	.93	.0628	—
Blue	5.5	21	5.5	21	1.80	39.6	.83	.1616	28
					1.80	36.0	.82	.1722	—
Viol.-Op.[2]	.5	25	5.0	24	3.40	39.8	—	——	—
					3.40	35.7	—	——	—
Blue	.6		5.3		2.60	39.8	.64	.3874	66
					2.30	32.3	.60	.4434	
Blue—	.8	25	5.6		1.60	39.8	.74	.2614	44
					1.50	34.0	.72	.2852	—
Green	1.0		5.7		1.00	39.8	.82	.1722	29
					1.00	36.4	.82	.1722	—
Yellow	1.0	25	5.9		.56	39.8	.88	.1108	19
					.60	37.4	.88	.1108	—
Gr.	.9	25	5.9		.40	39.8	.92	.0722	12
					.44	38.1	.93	.0628	–
Indigo	—		5.9		.00	39.8	1.00	.0000	00
					.00	39.8	1.00	.0000	—
Blue +	–		5.4		2.30	39.8	.70	.3096	53
					2.30	34.0	.65	.3740	—
Opaque	—		—	24	3.60	39.8	.60	.4434	75
						31.3	.52	.5678	—

In the chart, figure 3, I have constructed $c = 60\, i/EC \ln 10$, which in view of the nearly constant initial potential differences E, varies as the current i, in its dependence on V. The linear character is apparent. The colors (Y, yellow, $B+$, dark blue, $B-$, light blue, G, green, O, opaque) are inserted.

4. *Effect of presence or absence of electric field.*—The effect of the presence or absence of this electrical current on the color tube is quite inappreciable, no change of tint or suggestion of change occurring on charging the condenser. I gave the

---

[1] Initial field yellowish.

[2] Initial field bluish. Less steam taken.

question an additional and specially severe test as follows, showing that only an insignificant part of the nuclei present take part in the convection of electricity radially across the condenser.

The question is as yet an open one, whether, after all, the condensation may not be promoted by a distinct set of nuclei from those which convey the electric current. The two, however, must in the same series be produced proportionally to each other, the nuclei being later stages of growth or clusters of ions, or produced in other ways one from another, for instance. The factor may vary in different series.

The observations were made by looking down the color tube, figure 1, through the window *n*, after adjustment had been made at *F* for a given color and then alternately charging and discharging the condenser. For potential differences of 60, 150, and 300 volts and for all available colors, not a trace of color fluctuation in the steam tube was to be observed, due to charge or discharge. A slight turn at *F* immediately changes the tint.

Fig. 3.

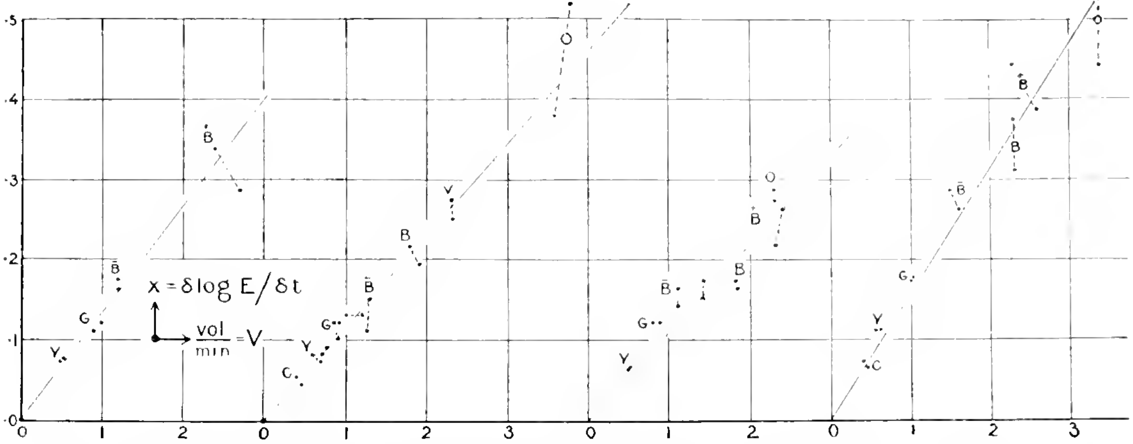


FIG. 3.—SIMULTANEOUS VALUES OF THE ELECTRIC CONDUCTION, AND VOLUMES PER MINUTE OF THE NEARLY SATURATED EMANATION TRAVERSING THE CONDENSER.

The result admits of quantitative expression. From the chart it appears that color differences of .06 lit/min (blue = 1) can certainly be detected. This amounts in the blue region to 6% of the total number of nuclei entering. The potential gradient was 300/.141 = 2100 volts/centim. Hence even in this strong field the total number of nuclei is still overwhelmingly large as compared with the number conveying current, unless different nuclei discharge the divers functions.

5. *Remarks on the observations.*—On the other hand, however, the current varies with the number of nuclei present, no matter how small the relative quantity actually promoting electric conduction. This is well shown in the chart, figure 3; also in figure 4, which both graphically reproduce table 1. The radial electrical currents or their equivalents, *x*, are given as ordinates, the corresponding volumes per minute (*V*) of the air passing longitudinally through the condenser, as abscissas. The relation of saturated volumes per minute longitudinally, and coulombs per second radially is thus apparent for the 2d and 4th series.

The curves, figure 3, contain all the data in hand, the different series of observations being distinguished by lines in different positions. Each series conforms pretty closely to a straight line, but these lines *differ in inclination* for the different series. The colors corresponding to the observations are also added in a suggestive way. Their real positions are not the same in all series, electrically, but they are so volumetrically.

The two most nearly satisfactory series of observations are given in the chart, figure 4. The curve is in both instances clearly linear. It is noteworthy that the colors referred to volumes of charged air per minute (abscissas, V) are again in agreement, whereas the electrometer data referred to the same color[1] differ. Some variation of the constant of the electrometer, if in question, would have shown itself in the initial potentials; but these (about 40 volts) are nearly constant.

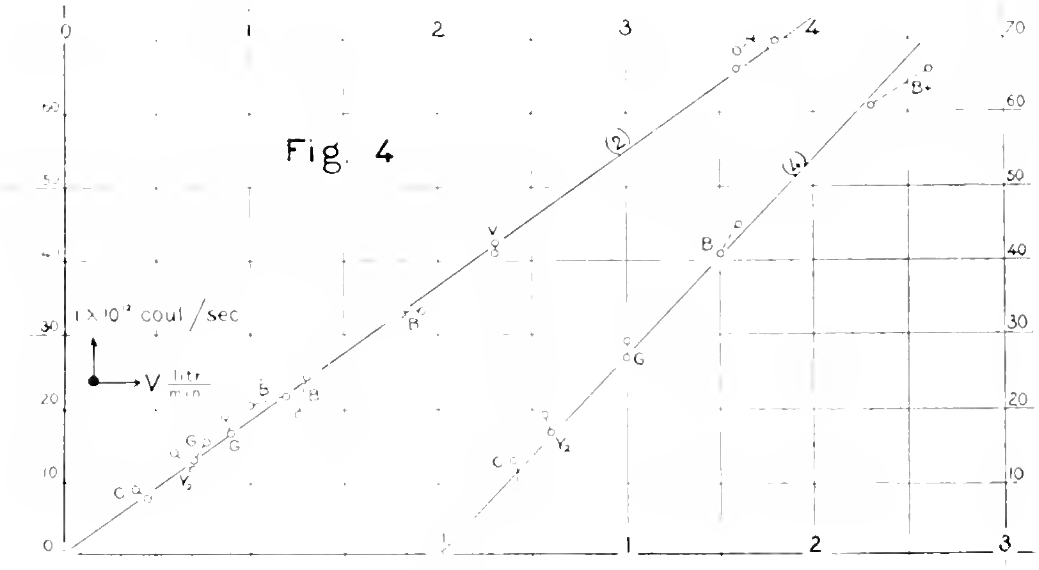


FIG. 4.—SIMULTANEOUS COULOMBS PER SECOND (RADIALLY) AND VOLUMES OF THE SATURATED PHOSPHORUS EMANATION PER MINUTE (LONGITUDINALLY) TRAVERSING THE CONDENSER.

6. *Working hypothesis.*—I shall next endeavor to account in some theoretical way for the observations just described, seeing that the data as a whole are very satisfactory when the inherent difficulties (fluctuating ionizer, color criteria, etc., as repeatedly detailed) are taken into consideration. The method pursued will be alike in principle to that already applied to tubes in the absence of an electric field in Chapter III. The complete equation is to be deduced and the numerical reasonableness is then to be tested when the decay of the ions within the ionized region is ignored.

Let k be the absorption velocity, so that kn particles are absorbed per second per square centim. by any barrier, n being the number of particles per cubic centim. As usual if but 1/3 of the particles travel in any given cardinal direction, k is to be replaced by $3k$. Let $k'n^2$ particles decay within a cubic centimeter per

---

[1] Elsewhere I shall show that the degree of desiccation of the phosphorus nucleus will account for the difference of slope.

second, as the result of mutual destruction[1] or otherwise. Let v be the longitudinal velocity of the current of air within the tube conveying the emanation through the condenser, eventually to discharge it into the color tube. Finally let r_1 and r_2 be the internal and external radii of the condenser. Consider the element of volume between the two right sections of the condenser, dl, apart. The accumulation within the element is $-\pi(r_2^2-r_1^2)\,v\,(dn/dl)\,dl$; the loss by decay within the element is per second $k'n^2\pi(r_2^2-r_1^2)\,dl$; the absorption at the walls (internal and external) of the element is per second $kn2\pi(r_2+r_1)\,dl$. Hence in the stationary condition, $-v(dn/dl)=k'n^2+2nk/(r_2-r_1)$. This equation is integrable in finite form. To determine the constant of integration let n_0 be the saturation at the right section l_0 of the condenser. Then

$$2kn_0/n=(2k+k'n_0(r_2-r_1))\varepsilon^{2k(l-l_0)/v(r_2-r_1)}-k'n_0(r_2-r_1),$$

an equation containing n in terms of the variable l and the parameters, k, k', n_0, v, r_1, r_2, l_0. If $r_1=0$ and $r_2=r$, the equation in Chapter III. is again deduced.

7. *Decay ignored.*—I will now continue in the manner usual in this memoir and write $k'=0$. Then $n=n_0/\varepsilon^{2k(l-l_0)/v(r_2-r_1)}$, where n_0 is the number of particles at the right section l_0 of the condenser, and n the number at l. Thus n depends essentially on k and is not, as in the preceding and following chapters, independent of it. Moreover k is to be replaced by $3k$ as already intimated, the latter being nearly identical in numerical value with U of the next paragraph.

8. *Effect of an electric field.*—Supposing this number of particles to be actually conveying electric current, or, from a different point of view, supposing that one ion is separated in case of the phosphorus emanation from each of these nuclei by the stress of the electric field, the current may be found as usual. Or the other theory developed in my last paper may be applied, remembering that the effect of the presence or absence of the electric field on the number of nuclei is inappreciable as demonstrated by the color tube.

Let E be the difference of potential of the faces of the condenser (potential of the inner rod since the metallic envelope is continually earthed), U the velocity of the positive ions relative to the negative ions in the unit field, Q the charge of the condenser, C its capacity. Then the charge per second at the element dl is $2\pi\,EUne\,(r_2+r_1)\,dl/(r_2-r_1)$ in consequence of radial conduction across the ionized air space. The total loss of charge per second is $dQ/dt=CdE/dt$, whence

$$\frac{2\pi Ue(r_2+r_1)}{C(r_2-r_1)}\int_{l_0}^{l} n\,dl=-\frac{dE/dt}{E}.$$

If now the value of $n=n_0\,\varepsilon^{-2k(l-l_0)/v(r_2-r_1)}$ just found for $k'=0$ is inserted and the integration completed, the result will be

$$-(dE/dt)/E=\frac{\pi(r_2+r_1)vUen_0}{k\,C}\left(1-\varepsilon^{-2k(l-l_0)/v(r_2-r_1)}\right).$$

It is next necessary to evaluate the velocity v (cm/sec) in terms of the volume V (litres/minute), taken out of the gasometer and passed through the condenser into the color tube. Since $V\,1000/60=\pi(r_2^2-r_1^2)\,v$, the datum V if inserted into the last equation reduces it eventually to,

---

[1] Note that if decay is absent, ions may be supposed to be separated out of the nuclei by the stress of an electric field and not to occur in the absence of the field.

$$-(dE/dt)/E = \frac{6.7\,Ue}{n_0}(1-\varepsilon^{-.376\,k\,(l-l_0)/(r_2+r_1)V})$$

$$\text{or}\ -(dE/dt)/E = KV(1-\varepsilon^{-L/V}),\ \text{where}\ K = 16.7\,Ue\,n_0/kC(r_2-r_1)$$

$$\text{and}\ L = .376\,k\,(l-l_0)\,(r_2+r_1).$$

9. *Numerical comparison.*—Case of $U = k$.—Instead of computing the current $C(dE/dt)$, I have considered it preferable to deduce

$$-(dE/dt)/E = -\ln 10\,\delta(\log E)/\delta t = \ln 10\,x/60,$$

in paragraph 4, table 1, seeing that x there is referred to minutes: for this result is almost at once given by the observations. Thus $x = KV(1-\varepsilon^{-L/V}) \times 60 \times \log \varepsilon$. On consulting the chart, figure 3, however, x/V is seen to be constant in one and the same series, to the extent in which the observations are trustworthy. Hence finally $x/V = 26\,K(1-\varepsilon^{-L/V})$ is the convenient quantity[1] for a general survey.

Moreover it will at the outset be expedient to assume $U = k$, for the saturated emanation, where U, the ion velocity in the unit field, may be taken as 1.5 centim./sec, and where k is equivalent to $3k$, admitting roughly that $n/3$ ions travel in a given cardinal direction. In my second paper $k = .9$ cm/sec was directly found in the absence of an electric field for the emanation *not* quite saturated however. In my first paper I gave experimental evidence showing that k may be looked upon as decreasing with the degree of saturation n. Indeed it will appear presently that if $U = k$, it makes little difference within certain limits what its absolute value is: for in such a case it practically vanishes from the equation. Thus either of the values given for U and for k will suffice for the discussion, and in the absence of detailed knowledge as to the nature of the phosphorus emanation, whether ionized air or not, the stated premise is a convenience.

Hence the following values make up the constants K and L:

$U = k = 1.5$ cm/sec, $r_2 - r_1 = .14$ cm, $l - l_0 = 50$ cm,

$E = 10$ volts, $r_2 + r_1 = .46$ cm, $C = 1.1 \times 10^{-10}$ farads,

$e = 2.3 \times 10^{-20}$ (J. J. Thomson).

$n_0 = 4 \times 10^4$ (J. J. Thomson; together these values follow also from the present series of experiments, but from different hypotheses). Thus

$$26\,K = 434 \times 16.7 \times 2.3 \times 10^{-20} \times 4 \times 10^4 / 1.1 \times 10^{-10} \times .14 = .260,$$

since $U = k$ cancels out;

$$L = .376 \times 1.5 \times 50 \times .46 = 13.0.$$

The following table is thus computed from $x/V = 26\,K(1-\varepsilon^{-L/V})$:

V	1	2	3	4	5	litres/minute
$x/V =$	$.26 \times 1.00$	$.26 \times 1.00$	$.26 \times .99$	$.26 \times .96$	$.26 \times .93$	
	$= .26$	$= .26$	$= .257$	$= .250$	$= .242$	

Hence *within the limits of observation* ($V < 4$ litres/min), x/V *is appreciably linear*, compatibly with the evidence of the four series contained in the chart, figure 3.

10. *Slopes of the loci.*—The slope, x/V, of the computed values is, however, in every case definitely above the slopes found by experiment, which as taken from the chart are.

---

[1] $26\,K = 434\,Uen_0/kC(r_2-r_1)$. The electric conductions, x, might have been left referring to minutes, like the volumes V, but for convenience in other computations.

Series 1, $x/V = .13$, Series 3, $x/V = .10$,
Series 2, $x/V = .12$, Series 4, $x/V = .16$.

Quantitatively, therefore, the assumption $U = k$ makes the computed data of x/V from 1.6 to 2.6 times too large. To improve this result one would thus have to write $U < k$. Now since there is evidence in my second paper that k decreases as the degree of dilution increases, and since k when experimentally ($U < k$) found comes out smaller than the value assumed for U, this inference is not tenable, k being simply the absorption velocity for the average concentration in the tube. Again $U > k$, though presumable from the earlier work, is strongly negatived here.

Moreover the variability of the slopes x/V, observed for the different series, 1 to 4, clearly with an inherent cause since the slope for a given series is determinate, is additional evidence in this direction.

In a color tube left entirely without disturbance, the color must depend on Vn, the total number of nuclei entrapped. Thus the color may be reckoned as $Vn = Vn_0 \varepsilon^{-kV}$. The same color should appear if $Vn = V'n' =$ const., if the saturation decreases as the volume supplied increases. The ratio of the electric current in the condenser or preferably the conduction, x, of the ionized medium to the color constant is thus $x/Vn = 434\,Ue\,(\varepsilon^{kV} - 1)/Ck(r_2 - r_1)$, which is independent of the initial saturation n_0 but varies with V. Thus, although two volumes, V and V', produce the same color ($Vn = V'n'$), they will nevertheless correspond to different conductions, x. Hence the variable slopes of figure 3 for the different series. There, is however, an outstanding difficulty requiring further observation for singularly enough the volumes alone appear to determine the colors in the chart rather than the quantities Vn.

Solid conductions and other leakages were not found in the tests made, in quantity to be menacing.

11. *The number of particles.*—The probable explanation of the discrepancy (leaving the ratio U/k in abeyance) is that the value $n_0 = 4 \times 10^{10}$ inserted is too large; for the emanation within the condenser is not saturated to begin with. It enters and leaves unavoidably from a certain length of influx tubulure, *c* in figure 2, insuring absorption at the outset. Unfortunately my notes do not supply the details of adjustment, as I did not suspect their importance at the time. But if they did the loss at the elbow at both ends of the condenser would remain as a vague but definite cause of ion dissipation.

On the other hand the value of n_0 which the observations demand is easily computed from the observed values of $x/V = 26K$, nearly, and from these very satisfactory inferences may be drawn.

Solving therefore,

$$n_0 = \frac{(x/V)kC(r_2 - r_1)}{434\,Ue},$$

where as before $U = k$ may be assumed for orientation.

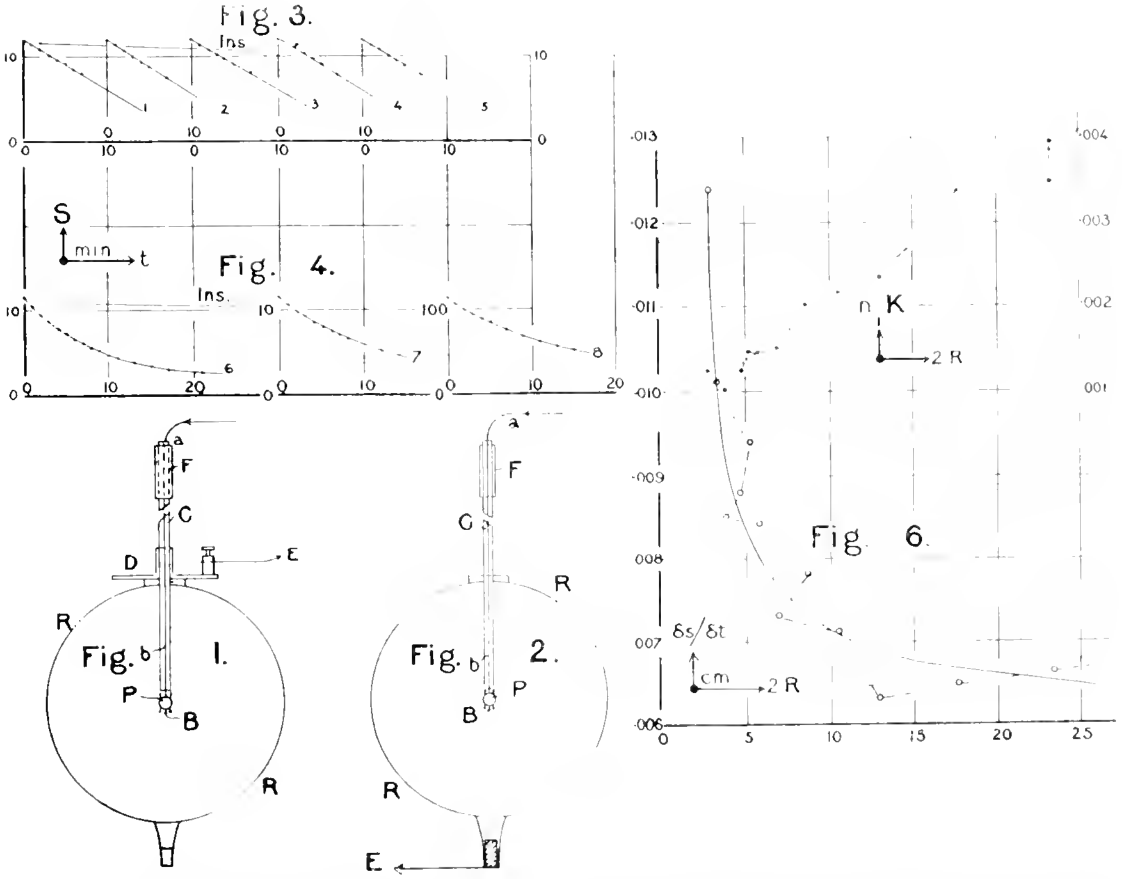
The extreme values of x/V experimentally obtained were, $x/V = .10$ in series 3, and $x/V = .16$ in series 4. Hence the values $n_0 = 1.5 \times 10^4$ and $n_0 = 2.4 \times 10^4$ are computed for these extremes. Recalling that 4×10^4 is the number of particles per cubic centim. inferred for complete saturation, and that n_0 is the number at the initial section of the condenser contiguous to the hard-rubber plug, where many ions must already have vanished by absorption. I hold the value of n_0 stated to be in reasonable accord with the theory sketched in §§ 6–8 and throughout the course of the present chapters.

12. *Origin of k.* With me the belief is gradually gaining ground, and will be further qualified in my next chapter with spherical condensers, that the absorption velocity k is a constant, irrespective of dilution, and that the evidence to the contrary obtained in my second paper with very wide absorption tubes (2 inches in diameter) must be otherwise interpreted. These results were at the outset not very satisfactory, and one may reach other conclusions than the immediate ones there stated. In speculating on the origin of k, considered as a nuclear constant one is confronted with this question: If the nucleus is larger than the molecule, as I believe it is, it will with increasing size be more liable to the bombardment of a number of molecules at the same time, promiscuously in all directions, whereas the molecules themselves collide singly; therefore, how large must a nucleus be made in order that the molecular velocity of, say, 485 meters second may sink to the value of only about 1 centimeter second both as the result of increased inertia and of the increasingly unfavorable conditions of bombardment?

CHAPTER VI.

THE BEHAVIOR OF THE IONIZED PHOSPHORUS EMANATION AS THE DIELECTRIC IN SPHERICAL CONDENSERS.

1.—In the preceding chapters it was assumed that the conditions could be so chosen (swift air currents, highly active ionizer, etc.), that the decay of the ionization might be temporarily disregarded. Such an assumption is naturally precarious, and the following series of experiments are planned with particular reference to the factor ignored. Accordingly a closed spherical condenser was installed, with its outer surface put to earth and its inner (concentric) surface, always very small, in



Figs. 1, 2.—Spherical Condensers. Figs. 3 to 15.—Charts Showing Successive Electrometer Deflections (*s*), and their Derivatives, in the Lapse of Time (*t*), for Different Radii (*R*) of the Condensers. $Kn_1 = Kd(\log V)/dt$.

contact with the charged electrometer. The intervening space was suitably ionized by a small piece of phosphorus, about as large as a split pea, suspended at the center. From such a condenser no ions can escape; it therefore offers greater theoretical simplicity than the plate condenser as discussed in Chapter IV., while the two discriminating variables, radius R and voltage V, may be changed at will. Practically, however, the experiments are very difficult not only because of the baffling irregularity of the ionizer, but because it is not easy to lead a charge to or from the center, without conduction. Nevertheless the results as a whole show, I think, that decay due to the mutual destruction of ions is virtually absent in the saturated emanation, and that increased dilution effectively generates new ions.

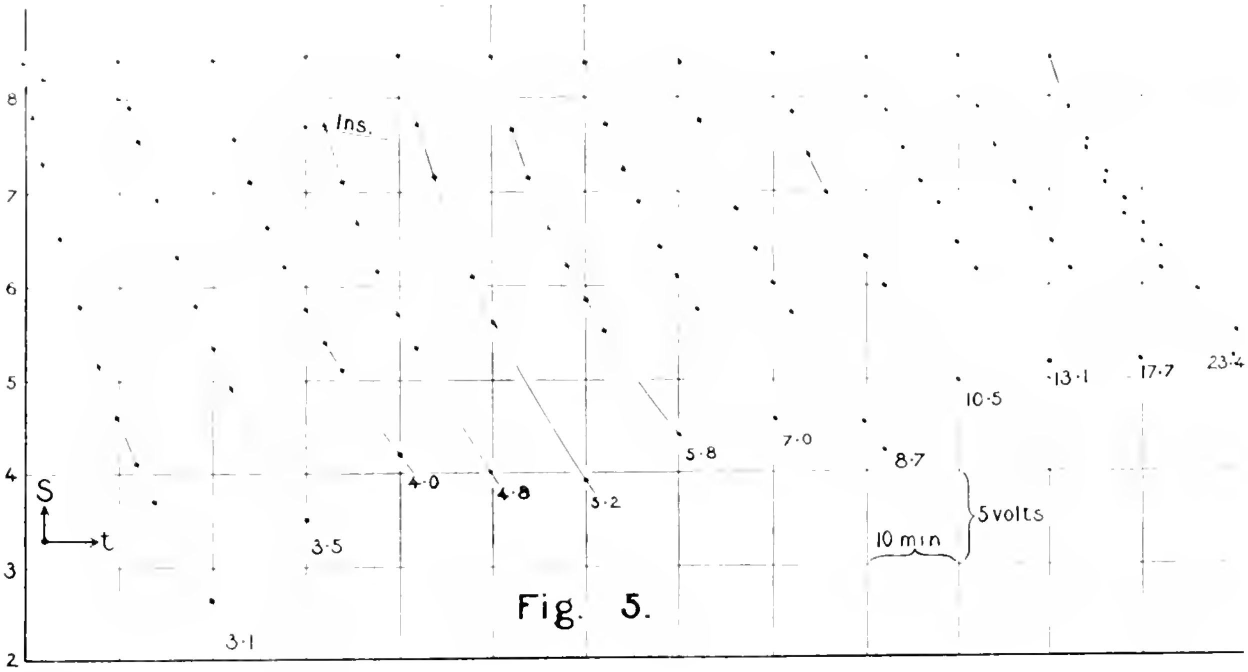


Fig. 5.

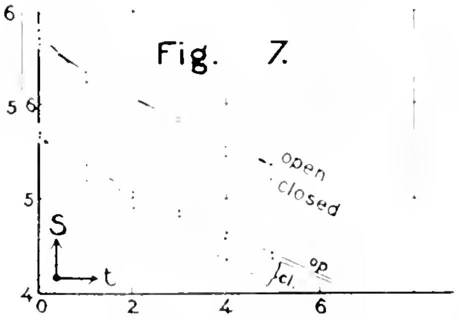


Fig. 7.

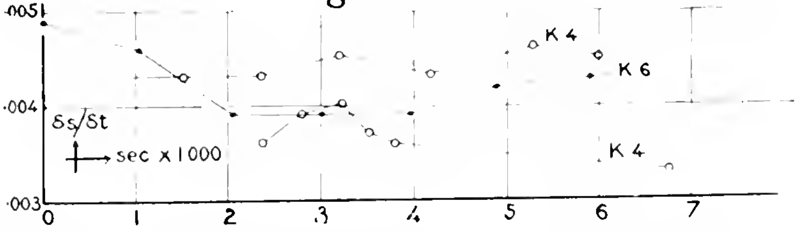


Fig. 9.

FIGS. 5, 7, 9.—CHARTS SHOWING SUCCESSIVE ELECTROMETER DEFLECTIONS (S), AND THEIR DERIVATIVES, IN THE LAPSE OF TIME (t), FOR DIFFERENT RADII (R) OF THE CONDENSERS. $Kn_1 = K'a \log V/R$.

2. *Apparatus.* A series of König's resonators seemed very suitable for the present purposes, since they were at hand in a large range of diameters, and figure 1 shows the original adjustment. R is the brass resonator; B the curl of wire making the inner surface of the condenser, and supporting the piece of phosphorus

P; C is an insulating glass tube 30 centims. long, through which the charge is conveyed by the wire ab, to be dissipated in the condenser. The tube C is grasped by the hard-rubber sheath F. B is thus in contact with the electrometer, and the capacity of the latter (about 90 cm.) is always large as compared with the condenser (negligible here and less than 1 cm. in the experiments below). D is a perforated copper plate closing the condenser and putting it to earth at E.

3. *Introductory observations.*—The early experiments made with this apparatus (Resonator, K6, diameter $2R=8.6$) are given in figure 3, and they seemed to indicate a linear relation of potential and time at least within the first 7 minutes. This constant current was not appreciably modified by stopping the lower tubulure of the resonator with cotton (removed stopper, curve 5), nor after vigorously airing it out (2, 4); neither is there any marked change of current even after 30 minutes (2, 3). The figure also shows the degree of insulation ("Ins.") attained. The currents (rates) expressed in scale parts and seconds would here be .01.

This interesting result was not, however, borne out by longer periods of observation (20 minutes), as shown in figure 4. Marked curvature is now in evidence which does not seem referable to conduction leakage. Moreover the conduction decreases in succeeding curves, apparently indicating a diminution of the ionization due to the phosphorus. The initial rates or currents are, roughly, .015, .013, .012, respectively, for the same condenser. Possibly the activity of phosphorus may be quenched by its own emanation in the lapse of time, but the discrepancy is liable to be thermal.

A systematic series of experiments was now carried through with receivers ranging in diameter from $2R=3$ to $2R=23$ centims., as detailed in table 1 and by the charts figures 5 and 6. In all cases of figure 5, time (t) in minutes is the abscissa, and the corresponding potential in scale parts (s) of the electrometer, (roughly, 8.4 sc. pts. are 40 volts), is the ordinate. The mean rate $\delta s/\delta t$ is computed in the table for the first 5 minutes of observation, using readings made about one minute apart. This curve is drawn in figure 6 where the abscissas are diameters, $2R$, in centims. The same chart contains in its upper part the dependence of the quantity $\delta(\log V)/R\delta t$ on diameter, to be discussed below. In figure 5 the insulation ("Ins.") of the apparatus is shown.

TABLE 1.—ELECTRIC LEAKAGE OF SPHERICAL CONDENSERS.

No. Diameter, D Tempt. θ	Time t	Deflection s	Rates: $\delta s/\delta t$ and $n_1K=K\delta(\log V)/\delta t$	No. Diameter, etc.	Time t	Deflection s	Rates: $\delta s/\delta t$ and $n_1K=K\delta(\log V)/\delta t$
K 00	0 m.	8.40	.0145	K 20	15 m	8.40	.0120
$D=3.0$ cm.	1	7.30	120	$D=3.4$ cm.	16	7.55	097
	2	6.50	106		17	6.90	86
$\theta=29.2$	3	5.80			18	6.30	
	4	5.15			19	5.80	
	5	4.60	.00134		20	5.35	.00117
	6	4.10	126		21	4.90	108
	7	3.70	125		22	4.50	104
	10	2.65			25	3.50	

[illegible]	[illegible]	[illegible]	[illegible]
K [illegible]	[illegible] m	8.[illegible]	[illegible]
D = [illegible]		7.65	81
		7.4	75
	[illegible]	6.[illegible]	
	3	6.[illegible]	
	5	5.75	113
	6	5.4[illegible]	98
	7	5.1	99
	1	4.2[illegible]	
K 13	45	8.45	[illegible]
D = 4.7 cm.	6	7.70	86
	7	7.4	78
	[illegible]	6.65	.0088
	9	6.15	136
	[illegible]	5.7[illegible]	128
	1	5.35	123
	55	4.00	
K 12	59	8.45	.0106
D = 5.1 cm.	6[illegible]	7.70	89
	1	7.15	86
	2		
	3	6.15	.00158
	4	5.60	143
	5	5.15	150
	9	3.9	
K 1[illegible]	73	8.45	[illegible]3
D = 5.7 cm	4	7.05	81
	5	——	69
θ = 20	6	6.60	
	7	6.25	[illegible]169
	8	5.85	144
	9	5.50	133
	83	4.4[illegible]	
K [illegible]	86	8.45	[illegible]83
D = 6.9 cm.	7	7.7[illegible]	72
	8	7.25	64
	9	6.9	
	[illegible]	6.4[illegible]	
	1	6.1	164
	[illegible]	5.75	154
	6	4.6	144
[illegible]	9[illegible]	8.4	[illegible]9
D = [illegible] cm	[illegible]	7.7[illegible]	75
	1		69
	[illegible]	6.8	

[illegible]	Time t	Deflection	Rates [illegible]
K 6 [illegible]	3 m	6.40	
	4	6.[illegible]	219
	5	5.70	198
	9	4.55	196
K 5	113	8.50	.0083
D = 1[illegible]4 cm	4	7.85	69
θ = 29[illegible]	5	7.40	61
	6	7.00	
	7	——	.00243
	8	6.3[illegible]	217
	9	6.[illegible]0	204
	123	5.00	
K 4	127	8.45	[illegible]75
D = 13.[illegible] cm	8	7.87	57
	9	7.45	56
	13[illegible]	7.10	
	1	6.85	
	2	6.45	[illegible]272
	3	6.15	218
	7	5.15	225
K 3	142	8.45	.0075
D = 17.6 cm.	3	7.90	61
	4	7.50	58
	5	7.10	
	6	6.80	
	7	6.45	.00369
	8	6.15	318
	152	5.20	320
K 2	157	8.45	.0075
D = 23.3 cm	8	7.90	64
	9	7.45	56
θ = 28.6	160	7.10	
	1	6.75	
	2	6.45	.00491
	3	6.15	444
	7	5.20	4[illegible]7
K 2	168	8.45	.0069
(Repeated)	9	7.90	56
	170	7.55	50
	1	7.2[illegible]	
	2	6.90	
	3	6.65	.00452
	4	6.4	383
	176	5.95	358

The results of figure 6 are surprisingly irregular, seeing that some pains was taken with the work, but they map out a graph of an exponential character to which different interpretations may be given. Either there is a decided falling off of the ionizing potency of phosphorus, or the ions are subject to a potential or a concentration gradient, or they destroy each other in the lapse of time. These cases will be discussed at length below. It will be noted that the room was quite warm, nearly 30° C. at the place of experiment. This may account for the remarkably large conductions ($\delta s/\delta t$) obtained in these experiments, as compared with the data below. The difference between positive and negative charges was not tested.

4. *Modified apparatus.*—Before continuing the work it seemed advisable to make trials to secure more perfect insulation. It was found to be nearly perfect without the condenser (current $i=.0010$ sc. p.), but uncertain when the condenser was installed ($i=.0010$, $.0005$, $.0002$). This is often too near the data themselves (for K 6, $i=.0060$ in extreme cases of smallness); but, since the currents are derived from differences, the effect of the leak is reduced. No means were found for removing it perfectly (paraffine, rubber, etc., were tried in succession with no advantage), and a dry, clean glass stem C, figure 1, held in place by a wide hard-rubber sheath F, seemed the best remedy.

Experiments were then tried to ascertain the difference between a condenser closed as above and one left open for the stem to pass through, as shown in figure 2. Here the wire and plug attachment puts the outer surface to earth at E. The closed condenser always introduced the larger leakage as shown for instance in the graphs[1] figure 7 for the given condenser K 6. Care was also to be taken to avoid friction in manipulating the stem C.

5. *New observations.*—Conformably with the experience gained the condenser in the following experiments is left open above, as seen in figure 2, and is put to earth at E by a brass plug wedged into the neck. The tube C terminating in the ball of phosphorus is kept clean and dry, and extends to 30 centims. above the condenser. Unfortunately there is some escape of ions around the neck, and the access of air here is a menace, but there seems to be no way out of the dilemma.

To estimate the loss of ionizing activity of the phosphorus pellicle, one of the condensers (K 6 and K 4, respectively) was treated as a standard and observations were made upon this before and after each of the observations of the other condensers. Table 2 and the corresponding curves, figure 8, are obtained in this way. The scheme adopted limited all observations to an interval of 5 minutes. Readings were taken per minute, and by dividing them into 2 parts the rates $\delta s/\delta t$ were obtained linearly from data 3 minutes apart. The table also contains other constants to be discussed below. In figure 8 the numerals attached to the curves show the number of the condenser and the order of measurement.

Curiously K 6 shows a linear diminution of potential or constant current, while in the other cases the currents usually fall off. Again, the values of $\delta s/\delta t$ for K 6

---

[1] Curves marked "closed" were obtained before and after the curve marked "open." This eliminates the fluctuations of the ionizer.

[illegible] ELECTRIC LEAKAGE OF SPHERICAL CONDENSERS. V_0 = 40 VOLTS

	[illegible]		[illegible]	$\delta/\delta t$ Rate	Mean $\delta/\delta t$ Mean time. Corrected $\delta/\delta t$	$n_1 K$ $K\delta \log V/\delta t$
	[illegible]	sec	cm	cm/sec		
[illegible]	35		6.50	[illegible]45	[illegible]45	—
		66	6.3[illegible]		—	
E.	55		6.6[illegible]	[illegible]50	.00400	.00153
D [illegible]		60	6.30	.0050		161
3		120	6.00	.0047	[illegible]	159
[illegible]		180	5.7[illegible]			
		240	5.40		.0050	
		300	5.15			
K.	3		6.65	.0075	[illegible]687	.00082
D = 3[illegible] cm		60	6.15	.0060		82
		120	5.70	.0062	540	77
[illegible] m		180	5.30			
		240	4.90		[illegible]724	
		300	4.60			
K 6	12	0	6.65	.0047	.00462	[illegible]142
D [illegible] cm		60	6.40	.0047		140
		120	6.10	.0044	1020	146
0.3[illegible] cm.		180	5.80		—	
		240	5.55			
		300	5.3[illegible]			
K 3	[illegible]	0	6.65	[illegible]25	.00222	.00140
D 17.6 cm		60	6.45	[illegible]22		136
		120	6.30	[illegible]19	1560	122
[illegible]		180	6.20			
		240	6.05		.00264	
		300	5.95			
L.	[illegible]		6.60	.0039	[illegible]300	.00117
D 8.6 cm		60	6.40	.0039		121
		120	6.15	.0039	2040	124
0.3[illegible]		180	5.9[illegible]		—	
		240	5.70			
		300	5.45			
E.	37	[illegible]	6.6[illegible]	.0078	[illegible]668	.00086
D [illegible]		[illegible]	6.[illegible]5	.0064		77
		[illegible]	5.6[illegible]	.0058	2520	75
[illegible]		[illegible]	5.[illegible]			
		[illegible]	4.9[illegible]			
		3[illegible]	4.55		.00[illegible]55	

No., diameter, etc.	t Time		δ Deflection	$\delta/\delta t$ Rate	Mean $\delta/\delta t$ Mean time. Corrected $\delta/\delta t$	$\frac{n_1 k}{K\delta}(\log I)/\delta t$
	min.	sec.	cm.	cm. sec.		
K 6	45	0	6.60	.0039	.00390	.00116
D=8.6 cm.		60	6.35	.0039		122
		120	6.10	.0039	3200	127
9.3 v/cm.		180	5.90			
		240	5.65		—	
		300	5.40			
K 3	53	0	6.55	.0019	.00168	.00116
D=17.6 cm.		60	6.40	.0017		103
		120	6.30	.0014	3480	86
4.5 v/cm.		180	6.20			
		240	6.10		.00216	
		300	6.05			
K 6	1	0	6.65	.0036	.00390	.00104
D=8.6 cm.		60	6.45	.0039		120
		120	6.25	.0042	3960	132
9.3 v/cm.		180	6.00			
		240	5.75		—	
		300	5.50			
K 17	9	0	6.60	.0056	.00500	.00077
D=3.9 cm.		60	6.20	.0047		69
		120	5.90	.0047	4440″	73
20.5 v/cm.		180	5.60			
		240	5.35		.00615	
		300	5.05			
K 6	16	0	6.60	.0039	.00418	.00116
D=8.6 cm.		60	6.40	.0042		78
		120	6.20	.0044	4860″	144
9.3 v/cm.		180	5.90			
		240	5.65		—	
		300	5.40			
K 2	24	0	6.55	.0019	.00178	.00156
D=23.3 cm.		60	6.40	.0017		136
		120	6.30	.0017	5340″	137
3.4 v/cm.		180	6.20			
		240	6.10			
		300	6.00			
K 6	33	0	6.55	.0042	.00428	.00127
D=8.6 cm.		60	6.30	.0042		132
		120	6.10	.0044	5880″	146
9.3 v/cm.		180	5.80			
		240	5.55		.00212	
		300	5.30			
Insulation	41	0	6.60	.00083	.00057	—
		120	6.50	.00031		
		960	6.30		—	

in the lapse of time, figure 9, first show a decrease (.0049 to .0039), thereafter a constant variation, finally actually an increase (.0039 to .0043). Hence the factors which determine the activity of phosphorus are extremely complicated. Moreover, if the observations for the other condensers are corrected by the results for K 6 (see table 2, column 5), by putting the current for the latter .0050 throughout, the new values show worse agreement than the original values. It follows from this that the method of correction proposed is not available except as a suggestion and that the discrepancies to be eliminated are not regular but temporary fluctuations.

TABLE 3. ELECTRIC LEAKAGE OF SPHERICAL CONDENSERS. $V_0 = 40$ VOLTS.

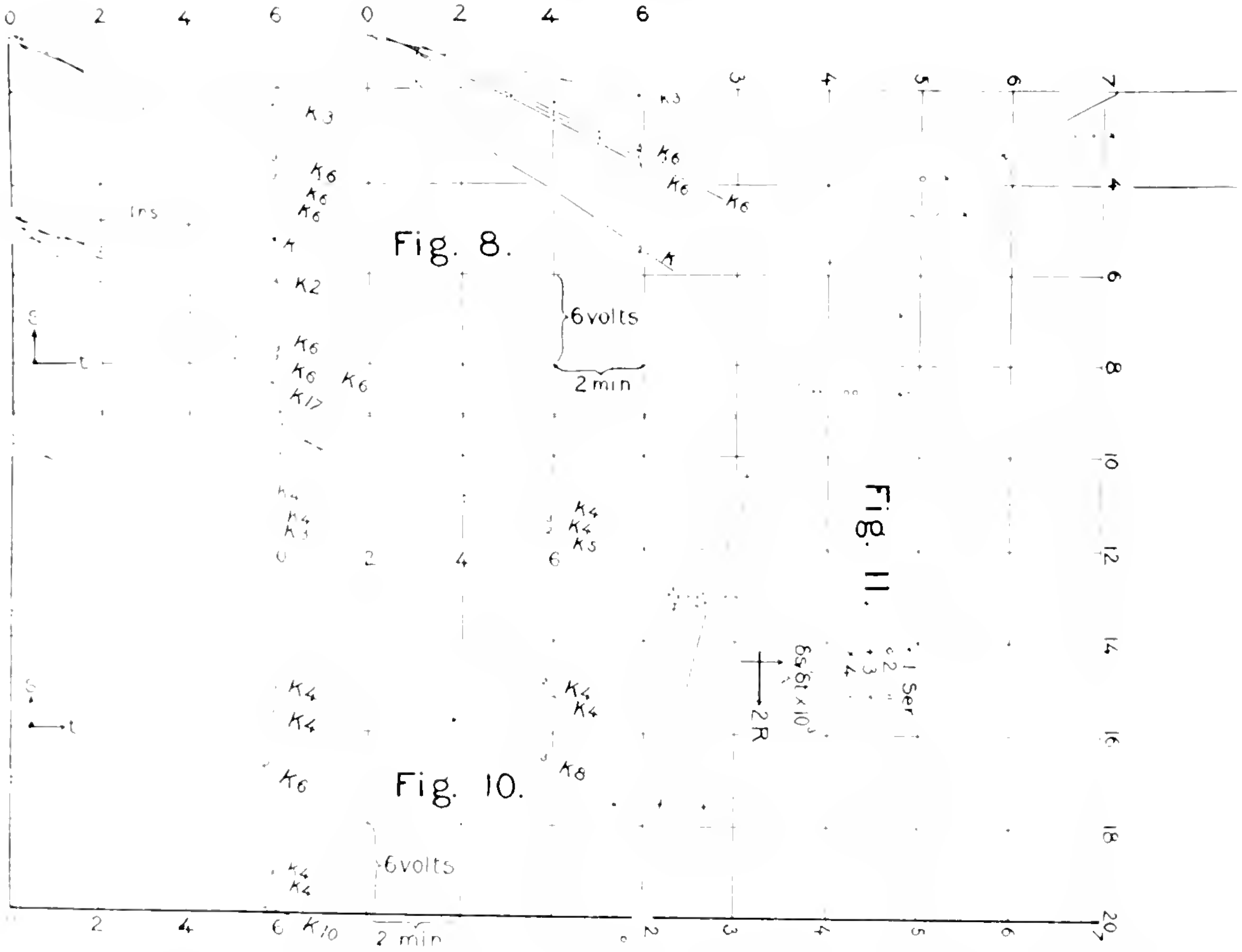
No., Diameter, etc.	Time t		Deflection δ	Rate $\delta/\delta t$	Mean $\delta/\delta t$	$K\delta(\log V)/\delta t$ $n_1 K$
	min.	sec.				
K 1	24	00	7.10	.0028	.00230	.00115
$D = 13.0$ cm.		60	6.90	22		094
		120	6.75	19		083
6.2 [illegible] $\alpha = 24.4$		180	6.60			
		240	6.50			
		300	6.40			
K 3	31	00	7.20	.0033	.00267	.00186
$D = 17.6$ cm.		60	6.90	22		127
		120	6.75	25		147
4.5 [illegible] m.		180	6.60			
		240	6.50			
		300	6.30			
K 4	38	00	7.30	.0025	.00230	.00099
$D = 13$ [illegible] cm.		60	7.15	22		91
		120	7.00	22		92
6.2 [illegible] cm.		180	6.85			
		240	6.7[illegible]			
		300	6.60			
K 5	46	00	7.30	.0036	.00306	.00117
$D =$ [illegible] cm.		60	7.00	28		093
		120	6.85	28		096
7.7 [illegible]		180	6.65			
		240	6.50			
		300	6.45			
K [illegible]	53	[illegible]	7.25	.0031	.00250	.00123
$D = 13$ [illegible] cm.		60	7.00	22		092
		120	6.85	22		094
[illegible] cm.		180	6.70			
		240	6.60			
		300	6.45			

No., diameter, etc.	Time t.		Deflection s.	Rate $\delta s/\delta t$	Mean $\delta s/\delta t$	[illegible]
	min.	sec.				
K 6	61	00	7.30	.0053	.00480	.00145
$D = 8.6$ cm.		60	6.95	47		136
		120	6.60	44		134
9.3 *v/cm.*		180	6.35			
		240	6.10			
		300	5.80			
K 4	68	00	7.30	.0022	.00230	.00088
$D = 13.0$ cm.		60	7.15	22		090
		120	7.05	25		103
6.2 *v/cm.*		180	6.90			
		240	6.75			
		300	6.60			
K 8	78	00	7.30	.0050	.00480	.00109
$D = 6.9$ cm.		60	7.00	50		115
		120	6.70	44		106
11.5 *v/cm.*		180	6.40			
		240	6.10			
		300	5.90			
K 4	86	00	7.45	.0025	.00260	.00098
$D = 13.0$ cm.		60	7.30	25		099
		120	7.15	28		113
6.2 *v/cm.*		180	7.00			
		240	6.85			
		300	6.65			
K 10	93	00	7.40	.0041	.00400	.00078
$D = 5.7$ cm.		60	7.10	39		71
		120	6.85	36		68
14 *v/cm.*		180	6.60			
		240	6.40			
		300	6.20			
K 4	100	00	7.35	.0022	.00250	.00087
$D = 13.0$ cm.		60	7.25	25		100
		120	7.10	28		114
6.2 *v/cm.*		180	6.95			
		240	6.80			
		300	6.60			

6. *Further data.*—Moreover, the data of this table are uniformly smaller, scarcely $\frac{1}{2}$ or $\frac{1}{3}$ of the values of table 1, due possibly to the lower temperature of the present case. They are insufficiently definite to suggest the form of the locus. New observations were therefore needed and were made in the same way, with the results given in table 3. The condenser was slightly modified, consisting in this case of a sphere of wire gauze about 1 centim. in diameter, containing a much

large piece of phosphorus than above. The larger condenser, K 4, is now the standard, admitting of easier adjustment. The graphs, figure 10, throw additional light on the results. Numerals on the curves show the order of measurement, etc. Figure 9 shows the fluctuations of the standard, K 4, displaced .002 in ordinate.

In table 4 the ionizing activity of phosphorus is exhibited when the condenser, K 4, is left quite without interference. A remarkable rise and fall is, as usual, apparent, without discernible cause. The curve is given in figure 9, displaced .001 in ordinate. After this, the other condensers are again tested with the object of securing sufficient data to at least roughly suggest the form of the locus.



FIGS. [illegible]—CHART SHOWING SUCCESSIVE ELECTROMETER DEFLECTIONS (s), AND THEIR DERIVATIVES, IN THE [illegible] OF DIFFERENT RADII (R) OF THE CONDENSERS. $Kn_1 = K\delta(\log V)/\delta t$.

7. *Summary.* In view of the fact that the ionizing potency of phosphorus sometimes increases and at other times decreases, as it were, incidentally and subject to arbitrary conditions not easily made out, I have in the following table, 5, summarized the uncorrected values of the currents, $\delta s/\delta t$, preferably to the corrected values. The former, as has been stated, usually show greater regularity than the latter, upon which the fluctuations of the standard condensers have been imposed.

TABLE 4.—ELECTRIC LEAKAGE OF SPHERICAL CONDENSERS. *V* = 40 VOLTS

No. Diameter, etc.	Time *t*.		Deflection *s*.	Rate $\delta s/\delta t$.	Mean $\delta s/\delta t$.	[illegible]	Remarks.
	min.	sec.					
K 4 *D* = 13.0 cm. 6.2 *v/cm.* θ = 25.0°	40	00	7.65	.0026	.00260	.00106	First five series without disturbing the condenser, consecutively.
		60	7.45	25		098	
		120	7.30	25		103	
		180	7.15				
		240	7.00				
		300	6.85				
K 4	46	00	7.70	.0028	.00290	.00115	
		60	.55	31		114	
		120	.40	28		109	
		180	.20				
		240	.00				
		300	6.90				
K 4	53	00	7.85	.0031	.00300	.00114	
		60	.60	28		106	
		120	.45	31		120	
		180	.30				
		240	.10				
		300	6.90				
K 4	58	00	7.75	.0028	.00270	.00104	
		60	7.55	25		096	
		120	7.40	28		109	
		180	7.25				
		240	7.10				
		300	6.90				
K 4 *D* = 13.0 cm. 6.2 *v/cm.*	64	00	7.75	.0028	.00260	.00104	
		60	7.60	28		106	
		120	7.40	22		087	
		180	7.25				
		240	7.10				
		300	7.00				
K 14 *D* = 4.7 cm. 17 *v/cm.*	15	00	7.60	.0050	.00490	.00072	
		60	.30	47		70	
		120	.00	50		79	
		180	6.70				
		240	.45				
		300	.10				
K 14 *D* = 4.7 cm. Repeated	21	00	7.75	.0050	.00547	.00087	
		60	.40	58		87	
		120	.05	56		87	
		180	6.65				
		240	.35				
		300	.05				

No.	[illegible]		[illegible]	Reading [illegible]	Mean [illegible]	[illegible]	Remarks
	m.	sec.					
K 17	30		7.60	.0056	.00539	.00066	
D = 3.0 cm.		60	.25	5		62	
24 [illegible] cm.		120	6.95	53		65	
		180	.65				
		240	.35				
		300	.2				
K 2	37	0	7.65	.0058	.00590	.00066	
D = 3.4 cm.		60	.30	61		67	
23.5 [illegible] cm.		120	6.95	58		67	
		180	.60				
		240	.20				
		300	5.90				
K [illegible]	45		7.70	.0075	.00713	.00070	
D = 3.0 cm.		60	.20	72		72	
27.7 [illegible] cm.		120	6.8	67		70	
		180	6.35				
		240	5.90				
		300	5.60				
K 4	52	0	7.7	.0022	.0023	.00083	
D = 13.0 cm.		60	7.55	22		85	
6.2 [illegible] cm.		120	7.45	25		98	
		180	7.30				
		240	7.15				
		300	7.0				

TABLE 5.—SUMMARY OF THE INITIAL CURRENTS.

No., etc.		t	D [illegible] $2R$	δ [illegible]
K [illegible]	First series	27.0	3.0	.0069
				67
K 6			8.6	49
				46
				39
				39
				39
				[illegible]
				17
K 3			17.6	
K 17	Second series		3.9	.005[illegible]
K 6			8.6	42
				43
K 2			23.3	1[illegible]
K 1	Third series	24.4	5.7	.004
K [illegible]			6.9	45
K 6			8.6	45
				31
K [illegible]			17.4	

No., etc.		t.	D [illegible] $2R$.	δ [illegible]
K 4	Third series		13	.0024
				26
				23
				25
				23
				23
K 3			17.6	27
K [illegible]	Fourth series	25.[illegible]	3.0	.0071
K 2			3.4	59
				53
				55
K 17			3.9	40
K 14			4.7	23
				26
K 4			13.0	27
				30
				29
				26

The values so found are then constructed in the chart, figure 11. It appears at once that the data as a whole, though investigated with care, still fail to lend themselves for the nice discernment of the nature of the locus in a relation of current, $\delta s/\delta t$, to the diameter $2R$ of the condenser. The results even of a single series are not smooth. Indeed the exceptional positions of the results for the standard condensers, those of K 6 being abnormally high while those of K 4 are low, is perplexing and has led me to suppose that some occult cause of variation has been left undiscovered. The relation suggested is really sinuous. One is almost tempted to infer that each condenser behaves as an individual, a conclusion for which I am unable to assign adequate reasons. The curve which has been put through the observations was computed from $(dV/dt)_0(R+a)=A$, in the way presently to be explained.[1] The observations are in accord with it, in so far as they show an increase of current at an accelerated rate as diameter decreases.

8. *Working hypothesis.*—The attempt must now be made to derive some theoretical conclusions from the experiments detailed in the above paragraphs. As before let n be the number of particles or ions per cubic centim., so that n is the concentration or density of distribution of the phosphorus emanation. Let k be the "absorption" velocity of the ion as defined in Chapter III., treated in the first instance as independent of the potential, and of the concentration gradients. Let k' be the coefficient of decay, so that $k'n^2$ is the number of ions vanishing per cubic centim., per second. Finally, let R be the external radius of the condenser, and C its effective capacity including that of the electrometer.

With regard to the electrical currents, let V be the potential at a distance r from the center of the condenser whose external face is put to earth. Let U be the aggregate velocity of the ions in the unit electric field and e the charge of each.

In all cases the observations are made when the flux is stationary, so that $dn/dt=0$, throughout for any shell. Moreover as shown above, the effect of a potential gradient is but a negligible contribution to the number of ions which are absorbed by the outer surface of the condenser.

To begin with the simplest cases, if the motion of the ion is entirely independent of dV/dr and n, the accumulation in an elementary shell at a distance r from the center will be $4\pi k d(r^2 n)/dr.dr$, per second; the decay per second, $k'n^2 4\pi r^2 dr$. Hence $d(r^2 n)/dr=(k'/k).n^2 r^2$, or, if A is a constant, $1/n=r((k'/k)+Ar)$. In the absence of decay, $1/A=nr^2$, so that A is the reciprocal of the concentration n_1, at a distance 1 from the center. If conduction were promoted solely by the ions which reach the external shell kept at $V=0$, since the charge in this shell is per square centim., $e\,dR/[R(k'/k+AR)]$, and its time of discharge dR/k, $\therefore dV/dt=4\pi\, keR/(k'/k+AR)$. In the absence of decay, $k'=0$, and $dV/dt=4\pi ken_1/C$, where n_1, as stated, holds for $r=1$. This case in which $dV/dt=\delta s/\delta t=$ const., independent of the radius of the condenser, is effectually excluded by the observations as given in figure 11. If, however, k decreases with concentration, for which there is some evidence in Chapter III., the case is still open.

If k' is not zero, $dV/dt=(4\pi ke/C)[1/(k'/kR+A)]$, so that the current

---

[1] V is potential difference equivalent to s; A and a are constants.

increases with R which is not admissible. Neither of these cases is open to comparison and they are thus without immediate interest. They may be treated in a different manner, as already set forth in Chapter IV., by introducing the ion velocity in the unit field V, in place of the absorption velocity k, and they then become suggestive. If $1/A$ is replaced by n_1, the number of ions per cubic centimeter at a distance of 1 centim. from the center, the above concentration n at a distance r may be written, $n_1/n = r[(k'/k)n_1(1-r)+r]$. If decay is ignored, the number $n = n_1/r^2$, as is otherwise clear, is independent of k also.

Now if the electric conduction is determined by the number of ions which reach the external shell $(r = R)$, $-dQ/dt = -C dV/dt = 4\pi R^2 v(V/R)ne$. It is understood that this number is not appreciably modified by the occurrence of the field so that when decay is absent $(k' = 0)$, $n = n_1/R^2$, as above deduced. Hence, $-(dV/dt)/V = -d(\ln V)/dt = 4\pi ev n_1/CR$. Here the first member is equivalent to $-d(\ln s)/dt$, and is obtainable from the observations directly, $4\pi ev/C$ is a constant, n_1 expresses the apparent waning intensity of the phosphoric source of ionization, and R is the external radius of the condenser. The equation, therefore, admits of being tested. The integral of the equation found for the potential gradient becomes $V = V_0 e^{-4\pi evn_1 t/CR}$, which is compatible with the data of tables 1–4. In these tables I have therefore inserted the quantity, $n_1K = (4\pi ev/C)n_1$, computed from $-(dV/dt)/V.R$ for each pair of values of s and t, usually 3 minutes or 180 seconds apart. The values n_1K are given in terms of common logarithms and seconds. Hence $Rd(\ln V)/dt = 2.3\, n_1K$.

9. *Comparison of data.* The values so found, *i.e.*, $n_1K = -Rd(\log V)/dt$, are shown graphically in figure 12, as ordinates[1] in terms of R as abscissas. Besides the data of tables 2, 3, 4, I have added those of table 1 taken from figure 6. The curve here is apparently sinuous due to the abnormally high values of K 6, and the abnormally low values of K 4, alluded to, both of which remain unexplained. In the absence of these there would be a rise of n_1K, of a gradual character with increasing radius. Since in n_1K, K is constant, this means that relatively more ions n_1 are available at the larger radii of the condensers, corresponding to weaker fields, than for smaller radii and correspondingly stronger fields. But as there is no reason for excluding K 4 and K 6, and no suggestion for the occurrence of the sinuous curve obtained, n_1K must be regarded as increasing rapidly from the values for condensers of small radii, $r = 2$ centim., but reaching a practically constant result after the radius 4 centim. has been surpassed. On the whole therefore, the data, so far as investigation has been possible, agree with the remarks made in §1, that the evidence in case of dilution is rather in favor of an increased number of ions and that an occurrence of decay is not manifest. This means more generally that whereas in the saturated emanation the ions are produced at the same rate at which they decay, so that n is constant, in the diluted emanation at a distance from the center $(n = n_1/r^2)$, the production is in excess of the decay and conduction relatively too great.

Another method of treating n_1K is to refer it to strength of field. This, how-

---

[1] Common logarithms and seconds are used, R being as usual in cm

ever, may be done more advantageously after the data of the next section, in which R is constant and V variable, have been similarly brought forward. The values for table 1, in which for higher temperatures and remarkably stronger ionization, the values n, K show a practically linear and relatively rapid increase with R, must be left without comment. Cf. figure 6.

10. *Case of diffusion.*—The next case with a bearing on the present results and deserving a statement is that of diffusion. Since but a small part of the ions are utilized as electrical carriers, as repeatedly evidenced, the effect of current may be neglected. This facilitates integration.

The motion is now subject to the concentration gradient dn/dr, and a new constant is thus needed. Let a be the number of particles flowing across a square centim. per second when the gradient (dn/dr) is a unit. Thus $a(dn/dr)/n$ is the velocity of the flux. If influx into the spherical element, $dr.d\omega$, be positive, the accumulation within the element is, per second at a given instant, $ard^2(rn)/dr^2.drd\omega$. The decay in the same element is $k'n^2drd\omega$. Hence, if the effect of current is neglected, $d^2(rn)/dr^2 = k'n^2/ar$. This equation is not integrable in finite form, being virtually $y'' = by^2/r$. It is equivalent to the series

$$y = C + C'(r-a) + b(C^2/2a)(r-a)^2 + b(C/3a^2)(aC' - C/2)(r-a)^3 + \ldots\ldots$$

where C and C', a and b are constants. Thus if $a = r$

$$n = C/r + C'(r-R)/r + bC^2(r-R)^2/2Rr + bC(RC' - C/2)(r-R)^3/3R^2r + \ldots\ldots$$

If at $r = R$ the concentration n vanishes, or $n = 0$, then $C = 0$ and

$$n = C'(r-R)/r + bC^2(r-R)^2/2Rr + b(R^2C' - (C - RC')^2)(r-R)^3/2\times 3R^2r + \ldots\ldots$$

Hence, very near the surface the gradient is $dn/dr = C'R/r^2$, and at the surface $dn/dr = C'/R$, so that C' is negative. Thus $a4\pi R^2C'/R = 4\pi aC'R$ is the number of particles available per second, at the boundary, increasing with R, while aC'/nR is their velocity, decreasing with R.

If all particles were here used to carry electric current (dQ/dt), $dQ/dt = CdV/dt = 4\pi aC'Re$, where C' is negative. Hence the current would be greater as R increases and constant as to time which is not compatible with the observations as a whole. Thus e must be an average charge and a function of V/R, so that the case does not admit of immediate numerical computation and is therefore of minor interest in promoting the present inquiry.

In the preceding instance the effect of current is ignored. If this is not done and the presence of current is a destruction of particles in each shell, the conditions are as follows. The accumulation per second in the shell of radius r will be $4\pi ard^2(rn)/dr^2.dr$, the decay per second $k'n^24\pi r^2dr$, the number per second destroyed by the current $C(dV/dt)e.dr/R$. Thus

$$d^2(rn)/dr^2 = k'r^2n^2/ar + C(dV/dt)/4\pi eaRr$$

or simply $y'' = (k'y + k'')/r$. The integral if obtained in a way similar to the above gives

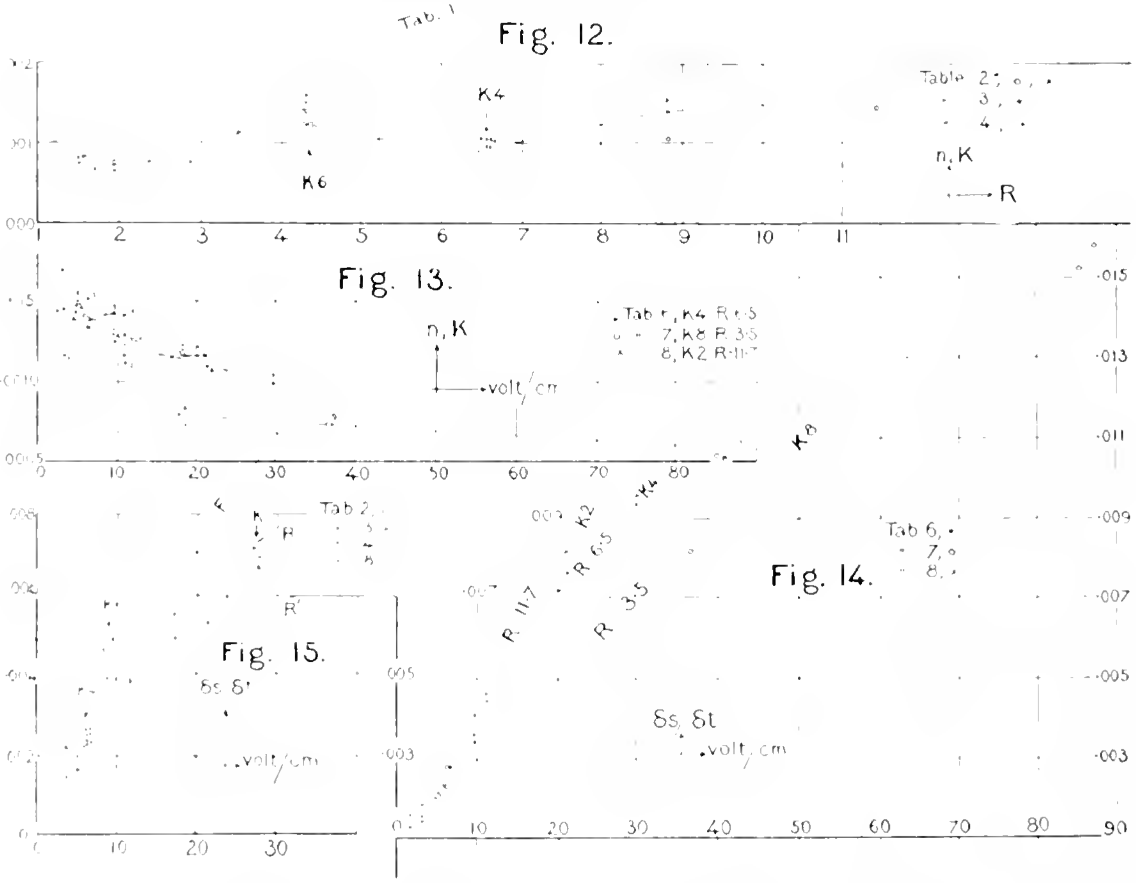
$$n = A'(r-R)/r + k'(r-R)^2/1\times 2Rr + k''(r-R)^3/1\times 2\times 3R^2r + (k'A'^2R^2 + k'')(r-R)^4/3\times 4R^3r + \ldots\ldots$$

supposing that $n = 0$ at $r = R$.

Hence, very near the surface, $n = A(r - R)/r + C(dV/dt)(r - R)^2/8\pi aRr$. As in the preceding simpler instance the discussion of this case would be cumbersome and out of line with the present mode of investigation. As neither case in the light of the observations is suggestive, I shall here abandon both.

CURRENTS IN CONDENSERS FOR SUCCESSIVELY VARYING POTENTIAL DIFFERENCES AND FIXED RADII.

11. *Apparatus and observations.* One important question as to the availability of phosphorus as an ion producer is the intensity of its action, or the number of ions



FIGS. 12 TO 15.—CURVES SHOWING SUCCESSIVE ELECTROMETER DEFLECTIONS (δ), AND THEIR DERIVATIVES, IN THE UNIT OF TIME (t), FOR DIFFERENT RADII (R) OF THE CONDENSERS. $Kn_i = K\partial\delta/\partial \log V\partial t$.

produced per second in limiting cases. To make an estimate of this quality it suffices to pass a current through the spherical condenser for gradually increasing potential differences between the faces, in order to ascertain to what degree the phenomenon fails to obey Ohm's law. In proportion as the number of ions is smaller relatively to the current transferred, the latter will fall short of its normal value. It will reach a constant limit when all ions present are used as carriers of electricity.

TABLE 6.—RESULTS FOR CONDENSER K 4 ($D = 13.0$ cm.) FOR DIFFERENT POTENTIAL DIFFERENCES ($\theta = 25.8$).

V Potential Difference. Do. per cm.	Time. t	Deflection. s	$\delta s/\delta t : n_1 K$	V Potential Difference. Do. per cm.	Time. t	Deflection	$\delta s/\delta t : n_1 K$
	min.				min.		
21 volts 3.2 *v/cm.*	51	3.20	.0019	21 volts (repeated) 3.2 *v/cm.*	91	3.70	.0014
	2	3.05	17		2	3.60	14
	3	2.95	17		3	3.53	14
	4	2.85	.00181		4	3.45	.00109
	5	2.75	162		5	3.35	113
	6	2.65	168		6	3.27	120
21 volts 3.2 *v/cm.*	58	3.10	.0017	130 volts 20.0 *v/cm.*	106	19.20	.0083
	9	3.00	14		7	18.50	69
	60	2.90	14		8	18.05	69
	1	2.80	.00159		9	17.70	.00127
	2	2.75	136		110	17.25	109
	3	2.65	141		111	16.80	112
42 volts 6.5 *v/cm.*	64	6.05	.0031	138 volts 21.2 *v/cm.*	116	20.60	.0083
	5	5.87	29		7	20.00	72
	6	5.70	31		8	19.60	72
	7	5.50	.00149		9	19.10	.00118
	8	5.35	145		120	18.70	105
	9	5.15	159		121	18.30	107
42 volts 6.5 *v/cm.*	70	6.10	.0028	193 volts 29.7 *v/cm.*	122	27.40	.0100
	1	5.90	28		3	26.70	092
	2	5.75	28		4	26.20	094
	3	5.60	.00134		5	25.60	.00107
	4	5.40	139		6	25.05	100
	5	5.25	142		7	24.50	105
63 volts 9.7 *v/cm.*	77	8.80	.0044	193 volts 29.7 *v/cm.*	129	27.70	.0094
	8	8.50	39		130	27.10	92
	9	8.25	39		1	26.55	92
	80	8.00	.00149		2	26.00	.0099
	1	7.80	134		3	25.45	098
	2	7.55	139		4	24.90	100
63 volts 9.7 *v/cm.*	83	9.00	.0039	63 volts (repeated) 9.7 *v/cm.*	136	8.75	.0042
	4	8.70	39		7	8.40	33
	5	8.35	25		8	8.20	33
	6	8.30			9	8.00	.00140
	7	8.00	.00126		140	7.80	116
	8	7.90	131		141	7.60	119

In table 6 results to this end are given, as obtained with the spherical condenser, K 4, diameter 13.0 centims., the internal surface (a copper gauze bag carrying phosphorus) being about 1 centim. in diameter. Potential differences V as high as 200 volts were applied, the external surface being put to earth. The current is, as usual, found from equidistant observations separated by an interval of 3 minutes. A few test experiments were made by repeating the earlier measurements at 21 and 63 volts, but it was thought wisest not to attempt to correct the data for the fluctuating ionizing activity of phosphorus in the lapse of time, nor to assume curvature in the initial ($t = 0$, nearly) contours of the curves. The graphs for s and t (not shown) are in fact of this nature.

TABLE 7.—RESULTS FOR CONDENSER K 8 ($D=6.9$ cm) FOR DIFFERENT POTENTIAL DIFFERENCES V. $\theta=26.8$

V, Potential Diff. Volts per cm.	Time t.	Deflection	$\delta s/\delta t$; $n_1 k$
	min.		
21 volts	39	2.75	.0029
6.1 v/cm	40	2.65	25
	41	2.5	24
	42	2.40	.00142
	43	2.20	154
	44	2.07	156
42 volts	46	5.75	.0044
12.2 v/cm	47	5.43	43
	48	5.15	39
	49	4.93	.00127
	50	4.65	128
	51	4.45	120
63 volts	52	8.80	.0067
18.3 v/cm	53	8.37	59
	54	8.00	58
	55	7.60	.00121
	56	7.3	113
	57	6.95	117
21 volts	59	3.35	.0033
(repeated)	60	3.05	25
6.1 v/cm	61	2.90	25
	62	2.75	.00163
	63	2.60	132
	64	2.45	139
61 volts	5	8.4	.0042
(next day)	6	8.1	39
$\theta=26.5$	7	7.87	37
	min		
17.7 v/cm	8	7.65	.0077
	9	7.40	75
	10	7.20	73
61 volts	11	8.50	.0042
17.7 v/cm	12	8.25	42
	13	8.00	44
	14	7.75	.00076
	15	7.50	79
	16	7.20	87
126 volts	27	17.40	.0083
36.5 v/cm	28	16.90	81
	29	16.42	78
	30	15.95	.00074
	31	15.45	74
	32	15.00	73
300 volts	44	44.55	.0170
87.0 v/cm	45	43.30	153
	46	42.35	150
	47	41.47	.00061
	48	40.55	54
	49	39.65	56
293 volts	50	45.20	.0170
85.0 v/cm	51	43.9	144
	52	43.00	142
	53	42.15	.00058
	54	41.30	50
	55	40.45	50

The chart, figure 14, gives the relation of the current ($\delta s/\delta t$), arbitrarily in scale parts, to the potential difference V in volts per centim., or strength of the field, as contained in table 6. The graph is obviously curved so that Ohm's law is departed from, but the curvature is small, indicating a limit as yet a great way off.

12. *Further data.*—These results are now to be compared with similar data for condensers respectively larger and smaller in diameter. They are given in tables 7 and 8, the diameters chosen being $2R=6.9$ centims. for K 8 and $2R=23.3$ centims. for K 2, respectively. The tables contain, besides the immediate results s and t, the potential difference V and the field, as well as the currents $\delta s/\delta t$, and the quantity n_1K, computed as usual.

TABLE 8.—RESULTS FOR CONDENSER K 2 ($D=23.3$ cm.) FOR DIFFERENT POTENTIAL DIFFERENCES V. $\theta=26.8$.

V, Potential Diff. Volts per cm.	Time, t.	Deflection,	$\delta s/\delta t$; n_1K	V Potential Diff. Volts per cm.	Time, t.	Deflection	$\delta s/\delta t$; n_1K
	MIN.				MIN.		
246 volts	17	36.50	.0081		45	6.80	.00181
21.0 v/cm.	18	36.00	83		46	6.70	123
	19	35.50	78		47	6.60	126
	20	35.05	.00114				
	21	34.50	120				
	22	34.10	113	59 volts.	48	7.50	.0025
				5.1 v/cm.	49	7.27	18
					50	7.17	21
128 volts	27	19.00	.0044		51	7.05	.00175
11.0 v/cm	28	18.65	39		52	6.95	127
	29	18.40	39		53	6.80	149
	30	18.20	.00121				
	31	17.95	106				
	32	17.70	100	19 volts.	55	2.00	.0022
				1.6 v/cm.	56	1.80	17
					57	1.65	11
128 volts	34	17.20	.0056		58	1.60	.0063
11.0 v/cm	35	16.70	39		59	1.50	51
	36	16.45	42		60	1.45	36
	37	16.20	.00169				
	38	16.00	121				
	39	15.70	132	19 volts.	61	1.60	.0017
				1.6 v/cm.	62	1.45	11
					63	1.40	1
56 volts	42	7.25	.0025		64	1.30	.0059
4.8 v/cm	43	7.00	17		65	1.25	42
	44	6.90	17		66	1.20	44

The currents here obtained are also graphically reproduced in the chart, figure 14, where the abscissas are the fields in volt/cm, and ordinates are the currents in the usual arbitrary measure. The relative conductivity of the three condensers is maintained and the saturated state (maxima of the curves) is in all cases enormously distant. The relative curvatures of the three graphs within fields of the same intensity cannot be made out. Table 7 virtually contains two series made on different days, in which the ionizing activity of the phosphorus was very different.

13. *Observations for constant V_0, and for constant R, compared.*—I shall now endeavor to compare the data of the two sections, by referring them either to the same radii or to the same electric fields. The latter method is preferable, not only as yielding a greater range of data but because the values of the currents $\delta s/\delta t$ and of n_1K have not yet been regarded in this light. To begin with the former, figure 15 contains the values of $\delta s/\delta t$ varying with the fields as taken from the tables 2, 3, 4, in which V_0/R varies by reason of varying R. These data, though vague, lie within the limits marked by the curves R and R'. In the same chart, Fig. 15, I have inserted the curve F, taken from figure 14, in which V_0/R varies by reason of varying V_0. It is the curve for K 2 for which $R=11.7$ is largest, and the data surest. The point of importance is clear at once: as the fields grow stronger the curve F lies quite above the curves R. If, therefore, high fields are produced by diminishing the radius of the condenser, the currents may be upwards of 20% or 30% too small, both because of the escape of ions around the stem and of the access of air. Indeed this state of things is not unexpected, inasmuch as the chief object of the investigation with spherical condensers was the avoidance of such losses of ions as occur in plate condensers. Returning for additional consideration to figure 12, it appears that the definitely low data corresponding to the radii 2 and 3 centimeters are erroneously much too low, whence it follows that the probability of a constant n_1K is enhanced.

The quantities next to be considered are the constants n_1K in relation to the strength of field. This is done in figure 13 for the case of the present section in which potential V is varied directly while R is fixed. As the observations must here be considered individually, they are marked for each table by numerals showing the order of sequence, and joined by straight lines. Turning first to the data of table 6 for the intermediate size, $R = 6.5$ cm., it is seen at once that complicated influences are at work, particularly in the case of low fields. The behavior here is not unlike ordinary galvanic polarization. Thus in the zigzag line 1 to 12, there is successive partial exhaustion alternating with partial recuperation of the conductivities. The observations 1 and 7 correspond to nearly the same field, for instance, but with fewer ions available in the latter case. If the fields are increasing, prolonged action decreases n_1K; and vice versa for table 8. On the whole, n_1K, as the fields increase indefinitely, seems to decrease (table 7), remembering always that this decrease is of an order which may be attributed to the ionizer itself.

Finally if the data for n_1K and field strength as given in the tables 2, 3, 4, of the last section, be graphically represented, the results are quite without suggestion as to the character of the variation of n_1K, in different fields. An average value of this constant is only to be deduced.

14. *Conclusion.* Contrary to my expectation and in spite of the labor spent upon them, the results for spherical condensers have not enabled me to give a decisive answer to the question at issue. The difficulty encountered and which occurs here in accentuated form is the same which has hampered me throughout the present research, namely the elusive variability of the ionizer. Moreover, as the conditions determining it exist *immediately at the surface* of the active phosphorus,

I do not see how they are to be put under control[1]; merely keeping the air around the phosphorus at constant temperature, etc., is not a sufficient check on the behavior of the surface itself.

In several respects, nevertheless, definite advances have been made. It has been shown that the best results can be reached with large spherical condensers (say 20 centims., or more, in diameter), in which changes of field are produced by applying larger potential differences while the apparatus itself is left quite without interference.

Finally to ascertain in how far the present experiments agree as a whole with the results for plate condensers, where a theoretically different method is involved, it suffices to compute the value of n_1, the number of particles per cubic centim. at one centim. from the center of the condenser. Since $n_1 K$ in figure 12 is of the order of .0012, or referred to natural logarithms $n_1 K = .0028$, and since $K = 4\pi e U/C$, if we insert J. J. Thomson's value of $e = 2.3/10^{10}$, and put U of the order of one centim. per second, $C = 67/10^{12}$ as above, it follows that $n_1 = 6.5 \times 10^4$. This result agrees very well in order with the datum, $n_0 = 5.5 \times 10^4$, as determined in Chapter IV. from plate condensers by the totally different method there pursued. It also agrees well with the deductions of the last chapter (V) obtained by still a different method. Finally if U be put 1.5 cm/sec, the value for ionized air, $n_1 = 4.3 \times 10^4$, the value deduced by the English philosophers by a totally different process of reasoning.

---

[1] In my recent experiments to be detailed elsewhere (Cf. *American Journal Sci.*, (4), xii, pp. 328–346, 1901) considerable progress beyond the status given in the text is in evidence.

SUMMARY.

With the present chapter I have given a systematic account of the bulk of my work with the phosphorus emanation, the purpose throughout being to map out the phenomena in which I am interested, roughly and preliminarily to the more rigorous study of the subject which I am now beginning. The results as a whole are tributary to an investigation on the colors of cloudy condensation.

In endeavoring to account for the data obtained it was my endeavor to follow the established theory, but I fear that in the explanations given I have little by little made a serious departure. If I had obtained but a single coincidence the result would not have been noteworthy; but after finding data of a correct order of values in all the experiments in spite of the variations of method, I have ventured to think that more than a coincidence is in question. The theory which underlies the series of papers is substantially this:

(1) From experiments made in the absence of an electrical field I inferred that the nucleus has its own specific velocity and that this velocity is identical with the mutual velocity of the corresponding ions[1] in the unit electrical field (volt/centim.).

(2) The nucleus produced by phosphorus is larger than the air molecule and both for this reason and from the fact that it receives promiscuous bombardment of molecules simultaneously, its velocity is of the low order stated, being (say) less than 1/300 that of the air molecule.

(3) It is not necessary to assume that the nucleus decays or vanishes within the ionized medium; the evidence is rather in favor of a number of nuclei somewhat larger as the dilution increases.

(4) Whenever the nucleus comes in contact with a barrier (solid or liquid) it is absorbed or broken up. If the nucleus is ionized as in the case of the phosphorus emanation, the absorption is accompanied with the discharge of an electron, as though the latter held the molecules of the nucleus together in a cluster.

(5) The observations with plate condensers, tubular condensers, and spherical condensers are satisfied by supposing the nuclear velocity k to be independent of the concentration or degree of saturation, n.

(6) The nuclear velocity is independent of the potential gradient. Instead of putting $U.V/R$ for the velocity of the ion along the potential gradient V/R, I have considered the velocity of the nucleus constant, and independent of V/R; while n, the number of nuclei capable of discharging the metallic terminal of a field, varies as V/R.

---

[1] Since the velocity of the positive relative to the negative ions is understood, the nuclear velocity is roughly taken to be three times the absorption velocity, as in this case one third of all the nuclei may approximately be supposed to travel in a given cardinal direction. It should be noticed, however, that if instead of 3, the factor 6, or preferably the probability factor $16/\pi$ be taken, the statements of the text would be accentuated. For since $k = .3$ cm./sec., $k \times 16/\pi = 1.5$ cm./sec., agreeing with the U of the text.

(7) If for *e*, the charge of a nucleus, J. J. Thomson's electron be taken; if the velocity of the nucleus is of the same order as the velocity of the ion in the unit electrical field; then the number of nuclei in the saturated phosphorus emanation agrees with J. J. Thomson's value for the number of ions in ionized air.

INDEX.

SMITHSONIAN CONTRIBUTIONS TO KNOWLEDGE
1373

Hodgkins Fund

THE STRUCTURE OF THE NUCLEUS

A CONTINUATION OF "EXPERIMENTS WITH IONIZED AIR"

BY

CARL BARUS

HAZARD PROFESSOR OF PHYSICS, BROWN UNIVERSITY, PROVIDENCE, R. I.

CITY OF WASHINGTON
PUBLISHED BY THE SMITHSONIAN INSTITUTION
1903

SMITHSONIAN CONTRIBUTIONS TO KNOWLEDGE
— 1373 —

Hodgkins Fund

THE STRUCTURE OF THE NUCLEUS

A CONTINUATION OF "EXPERIMENTS WITH IONIZED AIR"

BY

CARL BARUS

HAZARD PROFESSOR OF PHYSICS IN BROWN UNIVERSITY, PROVIDENCE, R. I.

CITY OF WASHINGTON
PUBLISHED BY THE SMITHSONIAN INSTITUTION
1903

Commission to whom this memoir has been referred

WILDER D. BANCROFT,
EDGAR F. SMITH.

ADVERTISEMENT.

In the present investigation, on the "Structure of the Nucleus," the author answers certain practical questions suggested by the last memoir (Experiments with Ionized Air, in *Smithsonian Contributions to Knowledge*, Vol. XXIX, 1901), in relation to phosphorus when used as a source of nuclei; *i. e.*, of extremely small particles tending to precipitate water from moist air, when this is suddenly cooled. It is, however, the chief aim of the memoir to throw light on the phenomena connected with the presence of nuclei in air, by aid of the coronas or color rings seen in such air when its moisture is condensed and deposited on the nuclei and a distant source of light is looked at through the turbid medium. As these coronas occur in great variety and size, they lend themselves for measurement when other means fail. A systematic study is therefore made at the outset of the number of particles corresponding to all well-defined members of the sequence of coronas obtained under known conditions of supersaturated air. The numbers run from less than 100 to upwards of 50,000 per cubic centimeter.

The results are then applied in an endeavor to find the velocity of the nucleus by non-electrical methods, both of a direct and an indirect kind, utilizing the fact that if nuclei leave the medium, the coronas obtained under like conditions must change correspondingly. Throughout the latter part of the investigation the nuclei are purposely produced in the simplest manner possible, by shaking solutions in air; but in the course of the investigation the author reaches conclusions which seem to show that the solutional nucleus is of much broader meteorological significance in its bearing on atmospheric condensation and electricity, than has heretofore been anticipated. It appears that in an unbounded region of the atmosphere saturated with water, this nucleus must be a persistent structure. This he finds is strikingly apparent even when the air is saturated with very volatile liquids other than water.

In conclusion the author points out that the size of the nucleus must vary with the medium in which it is suspended and that water nuclei, in particular, will depend for their dimensions on the meteorological status of the atmosphere.

Finally the importance of correlating this variation of nuclear diameter with the electrical activity of the water nucleus is insisted on, with a view to its possible application to atmospheric electricity.

In accordance with the rule adopted by the Smithsonian Institution, the work has been submitted for examination to a Committee consisting of Professor Wilder D. Bancroft, of Cornell University, and Professor Edgar F. Smith, of the University of Pennsylvania, and, having been recommended for publication, it is herewith presented in the series of *Contributions to Knowledge*.

S. P. LANGLEY,

SECRETARY.

Smithsonian Institution,
Washington, January, 1903.

PREFACE.

The present memoir is a continuation of my work of 1893 (U. S. Weather Bureau, Bulletin 12), and with less abrupt transition, of the *Experiments with Ionized Air*, published in *Smithsonian Contributions to Knowledge*, Vol. XXIX, in 1901.

Several outstanding questions in the latter volume have been answered. Thus in Chapter I, the nucleation and the ionization emanating from phosphorus are contrasted in their relation to temperature. The results which appear, viz., that the nucleation begins at a definite temperature (about 13°) with a maximum of intensity while the ionization increases more gradually to reach a maximum later at about 20°; moreover that moisture, while unfavorable to nucleation, promotes ionization; these results explain much of the baffling variability of the phosphorus ionizer with which in the volume cited, and particularly in the case of experiments with spherical condensers, I made vain endeavors to contend. The reason why the rate of electrical leakage and the rate at which nucleated air flows through a tubular condenser are linear functions of each other but with a different coefficient in different series of experiments, is also apparent with other results of minor interest.

Having determined to approach the question of nucleation by a new method in this volume, viz., through the measurement of the coronas[1] of cloud particles, it seemed imperative to undertake a detailed investigation of the whole phenomenon of coronas, at the outset, insofar as it would contribute to these experiments. By no other means, to my knowledge, is the magnificence of coronal display so approachable in its entirety, as when evoked by cloud particles of identical diameter, variable at pleasure. The colors of cloudy condensation may be classified into three groups: The first includes the normal coronas (as I shall call them) due to relatively large particles. They are all characterized by a central white disc and there are no axial colors. The second class includes coronas due to relatively small particles; the central disc is colored, and as the particles increase in diameter from a lower limit, the central colors follow the order of Newton's interferences. The third group comprises the axial colors seen in the undeviated ray and due to some kind of harmonic absorption superimposed on the diffractions of the first two groups. These colors are increasingly saturated as the cloud particles decrease in

---

[1] I regret that all my attempts to obtain Kiessling's work on *Dammerungserscheinungen* were unsuccessful.

diameter from a superior limit indefinitely. They may also be arranged in Newton's series at a phase difference from the former. They are particularly vivid for particles so small that the coronas have become vague or a colorless fog. They last until the cloud particles merge into individual molecules, though the last to appear before the air becomes perfectly clear, can only be produced with the steam jet. Indeed this last group of colors, seen without coronas in the color tube, was fully treated in the earlier volume, though their apparently complementary relations to the colors of the discs of the coronas did not then appear.

In determining not only the size but the number of particles producing these splendid phenomena as a whole, I have answered another of the outstanding questions there proposed. It has not been practicable to reach more than a first approximation, and on overhauling the work after about a year's experience with investigations of the same general character, I am left in some doubt whether I have successfully coped with the subsidence error. Nevertheless the results particularly with reference to axial colors are noteworthy. They represent a separate phenomenon superimposed upon and coloring the diffraction phenomenon for reasons which it is difficult to make out. To invoke interferences for these small spherules, one must first explain how the light gets in; being in how it gets out again, and thereafter, why particles are needed which at first blush seem about ten times too large.

The remaining chapters (IV, V, VI) bear directly on the subject of this volume. I have long been in search of a method for producing nuclei which shall have the humblest origin possible; for when one operates with the powerful instruments of modern research and interprets the results by similarly recondite electrical methods one is perhaps less apt to confront the nude facts. This quest culminated naturally in the method of producing nuclei by shaking solutions. Afterwards I found that Lenard[1] in his thorough fashion had incidentally traveled along a similar road before. Lenard's interests, however, were centered in his electrical investigation, and though he discovered the astonishing persistence (27 hours) of nuclei obtained from a jet of river water and their corona-producing quality, he was interested chiefly in the bearing of this result on the electricity of waterfalls and did not contrast the persistence in question with the fleeting nuclei of pure water and weakest solutions, nor enter into the other special lines of investigation in this memoir. The reader will find that I have taken these nuclei as the type of nuclei in general, as there is reason to believe that they may be either electrically charged or not, as the critical density by which the stability of the nuclei is conditioned, varies. To this important question I shall at another opportunity recur.

The final chapter (VI) is an endeavor to prove, again by the simplest possible method of direct observation, that the nuclei diffuse or are endowed with definite velocities. Whoever looks upon nuclei as ions will have no difficulty with this proposition; but for me the nucleus has dimensions which are larger than the molecule, and for such nuclei as are produced by shaking or those sluggish nuclei

[1] Lenard: *Wied. Ann.*, xlvi, 584–636, 1892.

produced by any emanation or by radio-activity in hydrocarbon vapors, for instance, nuclei which stick to the air and differentiate it gravitationally, the question of diffusion is a vital one. The positive answer of the chapter is, I believe, warrantable.

The quaint theory that nuclei which vanish are absorbed on contact with the walls of the vessel and that no other loss of nuclei occurs, has been accepted here as in my earlier volume. I have found none at once so simple and so gracious. Nuclei are always sparsely distributed (10^{2} to 10^{6} per cub. cm.) in comparison with molecules. I have conceived them to be larger than molecules but not so large as to receive symmetrical molecular bombardment when suspended in a gas. In other words, there are not quite molecules enough surrounding the nucleus to insure a virtually persistent uniform pressure upon it in all directions. The motion of the nucleus is the result, and it moves faster in proportion as it is smaller and the asymmetry due to paucity of bombarding molecules below the statistical limit, is accentuated; and vice versa. So conceived, the velocity with which the nucleus diffuses is at once its own and only velocity.

If the nuclei vanished by subsidence, however slowly, this would appear in the coronas. Not only is subsidence of nuclei absent, but they actually diffuse against gravity, while the coronas give evidence (so far as the motion of the unloaded nuclei are concerned) of permanently uniform distribution. This narrows down the question of loss to the possibility of a marked coalescence of nuclei, and to the hypothesis of dynamic diffusion selected, with absorption at the boundaries (if any) of the region. But the amount of loss by diffusion actually found by direct observation in the last chapter is of the same order of values computed by the hypothesis in the two preceding chapters. Thus far then, there seems to be no reason for introducing any source of decay of nuclei other than one involving the motion of the nucleus. Moreover, if there are no boundaries to the region there will be no loss of nuclei.

A final word is due as to the bias of the volume. Recently it has become customary to refer the phenomena of condensation too glibly, I think, to the occurrence of ionization. I am well aware of the precision with which C. T. R. Wilson[1] has stated his results, but others have not been so cautious, and the impression is that negative ions embrace the whole story of condensation. The elasticity and scope of the electronic hypothesis, the ease with which it lends itself to the correlation of hitherto isolated and anomalous facts, may well account for the enthusiasm with which it has been generally applied. Under these circumstances, it has seemed to me fitting that somebody should seriously endeavor to see how much of what is known in relation to condensation, would follow from the older theories of Coulier, Kelvin, and Aitken,[2] and apart from ionization. As this was the position I took in 1893 shortly after an electronic hypothesis had been

[1] C. T. R. Wilson: *Phil. Trans.*, London, vol. 189, pp. 265-307, 1897; *ibid.*, vol. 192, pp. 403-453, 1899; *ibid.*, vol. 193, pp. 289-308, 1899. The last paper is chiefly referred to.

[2] An account of the earlier researches on the subject will be found in my Bulletin of 1893 (l. c.), Chapter II.

definitely proposed by the younger von Helmholtz[1] and long before the era of the X ray, this policy seemed again to devolve upon me. My discussions may therefore appear to proceed from a point of view since superseded, but I believe they are consistent and fair. Hence if the light of this volume is still the antiquated tallow dip, the number of interesting results to which it has guided, encourages me to hope that the quest, apart from any theory, may have been worth the candle.

C. BARUS.

BROWN UNIVERSITY, PROVIDENCE, R. I.,
August, 1902.

---

[1] R. von Helmholtz: *Wied. Ann.*, XXVII, p. 508, 1886; *ibid.*, XXXII, p. 1, 1887. *Cf.* p. 2.

TABLE OF CONTENTS.

CHAPTER I.

CHAPTER II.

CHAPTER III.

CHAPTER IV.

CHAPTER V.

CHAPTER VI.

APPENDIX.

LIST OF FIGURES.

CHAPTER I.

CHAPTER II.

CHAPTER III.

CHAPTER IV.

CHAPTER V.

CHAPTER VI.

APPENDIX.

THE STRUCTURE OF THE NUCLEUS, A CONTINUATION OF EXPERIMENTS WITH IONIZED AIR.

By Carl Barus,

HAZARD PROFESSOR OF PHYSICS AT BROWN UNIVERSITY.

CHAPTER I.

ON THE EFFECT OF TEMPERATURE AND OF MOISTURE ON THE EMANATION OF PHOSPHORUS, AND ON A DISTINCTION IN THE BEHAVIOR OF NUCLEI AND OF IONS.

INTRODUCTION.

1. *Object, etc.*—Endeavoring to differentiate the properties of the nucleus and the ion, it occurred to me that the effects of temperature, when worked out simultaneously by the volumetric and by the electrical methods, would probably present a contrast. If the two functions relating to condensation and to electrical conduction are different, then their thermal variations are not likely to be the same. The temperature which insures the maximum production does not also necessarily insure maximum instability. The results of the following paper bear out this surmise.

Again, if phosphorus is to be used as an ionizer, some definite knowledge as to the cause of its variable intensity is essential from a practical point of view. The substance is so remarkably adapted for the purpose in many ways, that the endeavor to put it in control quantitatively is well worth while. This too, I think, has been accomplished.

Finally, I have shown that the low number of ions ($n = 8 \times 10^4$ per cubic centim.) in the saturated phosphorus emanation, found from the experiments with the tubular condenser, is due to non-saturation. I have been able to nearly double this number, putting these results in accord with the data of plate and spherical condensers. Incidentally, certain curious conditions under which the emanation produces permanent conduction in the condenser are identified with the occurrence of traces of moisture. This behavior so closely resembles the effects of radio-activity that the extreme caution needed before such a property can be predicated becomes apparent.

VOLUMETRIC COMPARISONS.

2. *Apparatus.*—The apparatus to investigate the relation of the emanating activity of phosphorus to temperature is shown in figure 1, the thermal part consisting of a coil of thin lead pipe (1/8 inch bore), L, submerged in a large water bath of copper, AB, 13 centims. high, 15 centims. broad, and 20 centims. long. There were 21 turns of lead pipe, each turn 6 centims. in diameter. The air coming from the gasometer train by way of a desiccator beyond D, and a stop-cock, F (fine screw valve), traversed this considerable length of slender tubing, fully taking the temperature of the water bath, thereafter to be discharged into the central straight pipe of brass, ab, 1.2 centims. in diameter, containing the ionizers (not shown). The charged air is finally conveyed into the influx pipe of the color tube, C, by the removable short neck, G. A thermometer, t, is placed in the water bath; another may be inserted into the end, b, through a perforated cork, so as to be in contact with the ionizers.

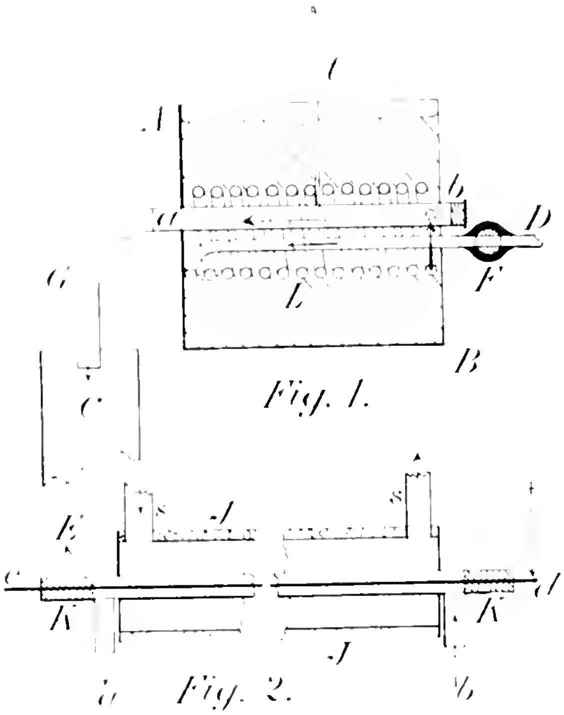


Fig. 1.—Apparatus for Heating Nucleated Air.
Fig. 2.—Section of the Tubular Condenser, Showing the Water Jacket.

Care was taken that all changes of temperature should be slow. Thus it took 3 hours for the temperature to rise from 5° to 13° in the following experiments, for instance.

The ionizers, as usual, were strips of wire gauze, holding thin pellets of phosphorus between them. They were inserted into, or removed from the tube, ab, through b. If saturation is aimed at, an excess of freshly cut phosphorus surface should be used. This was only done when specially called for in the present work, where the form of the temperature function is the chief consideration.

3. *Method and data.*—The method of experiment usual in my work was adopted, the liters per minute (dV/dt) of saturated phosphorous air necessary to produce the fiducial blue of the color tube being observed at different temperatures. The data are given in table 1, in the first part of which observations for falling temperature, and in the second for rising temperature, are recorded. The pressure of the steam jet was about $p = 4$ to 6 centims. The inflowing air showed a temperature of 27° to 28°. The table contains some other colors (including opaque) for orientation.

TABLE 1.—EFFECT OF THE TEMPERATURE OF PHOSPHORUS ON ITS EMANATION. $p = 4\text{–}5$ cm.; AIR TEMPERATURE, 27°–28°. WATER BATH METHOD WITH STEAM JET.

Falling temperature.			Rising temperature					
Color.	$V \times 10^2$	θ	Color	$V \times 10^2$	θ	Color	$V \times 10^2$	θ
	L min	°C	None		5	Bl +	70	12.8
Bl	85	27 (air)	"		6	Bl	65	12.8
Bl +	110		"		7	Opaque margin	80	12.8
Bl	100	30.8	Puffs faint		8.2			
	90	30.7	Puffs evident		8.6	Bl −	55	12.9
Bl	95	28.6	Puffs strong, greenish, need about 5 sec. to form		9.0	Bl	75	13.[illegible]
	100	28.6						
Bl	95	25.2	Puffs bluish		9.3	Bl	85	17.6
	90	25.2	Do.		9.8	Op	105	17.6
Bl	80	22.3	Puffs bluish. No permanent color; 2 sec. suffice for puffs		10.2	Bl	90	31.3
Bl +	90	22.3						
Bl −	61	18.8	Vague green permanent	—	10.7	B +	110	30.8
Bl	90	18.8	Faint yellow-green	380	10.9	Bl	95	30.6
Bl	75	18.8				Bl	90	32.6
Bl +	115	18.8	Bl-Gray	280	11.8	Bl +	105	32.4
Bl +	60	13.2	Bl	350	12.2	Bl	100	32.2
Bl	60	13.2				Bl +	100	35.3
Bl	70	13.3	All colors now show themselves rapidly and intensely			Bl	110	35.2
Opaque margin	100	13.3				Bl	90	34.9
						Colors not clear		

The chief data of the table are reproduced in the chart figure 3, and show the sudden cessation of reaction at 12°–13°.

4. *Discussion.*—For the sake of preliminary comparisons with the corresponding electrical charts given below, it is well to lay off $1/(dV/dt)$ in its variation with temperature: for this reciprocal runs parallel to the concentration of the emanation producing the color. The construction is given in figure 4, in which the sudden rise of activity in producing nuclei is apparent at 13°, and the subsequent gradual decline thereafter as far as examined is again manifest. Anticipating data of subsequent paragraphs I may add that the maximum ionizing activity is at 20°, showing the two thermal relations to be non-coincident.

The charts show in the first place, that as temperature falls from the highest admissible values, say 35°, the emanation of phosphorus actually increases,[1] at a rate

---

[1] This increase may be due to the gradual thorough desiccation of the phosphorus by the dry current of air. The grids were not dried preliminarily over calcium chloride.

of about 2 per cent. per fall of 1° C. The maximum activity occurs at about 13°, and is upwards of 25 per cent. greater than at 30°. Between 12° and 13°, however, the emanation is quenched at an enormously rapid rate, falling just short of suddenness. Practically, therefore, the reaction begins at about 13°, with full if not greatest intensity.

Below 12°, the emanation is insignificant and the maximum permanent colors obtainable are faint blue grays, even when the gasometer flow is forced to, say, 100

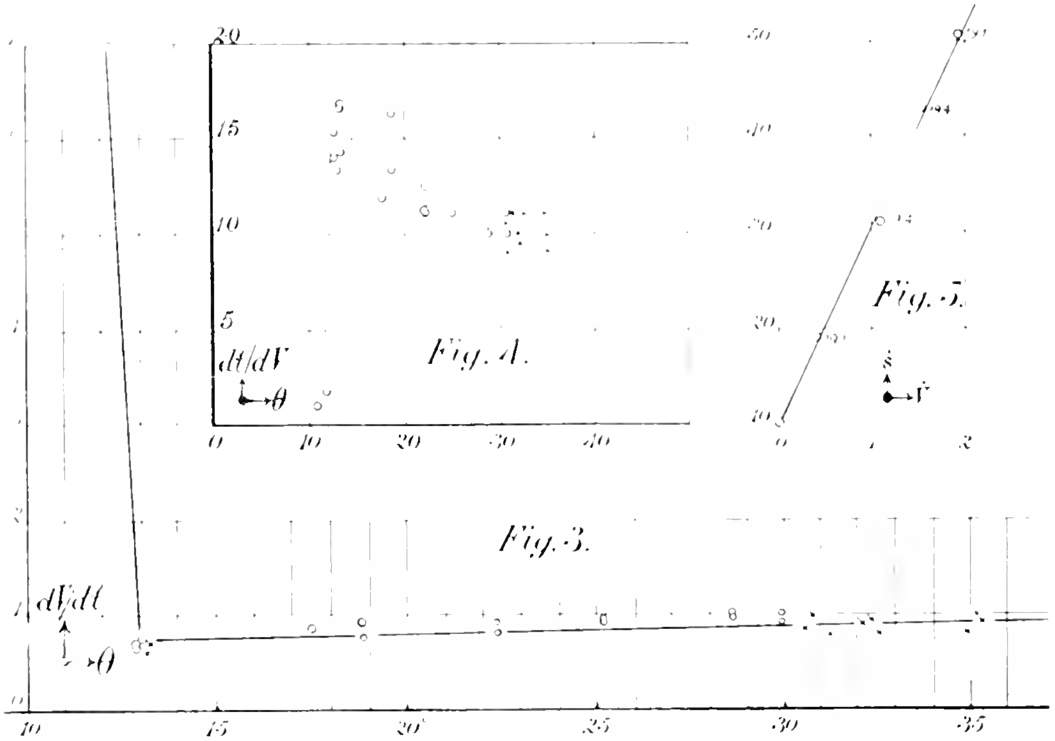


FIG. 3.—DEPENDENCE OF THE RECIPROCAL NUCLEATION RATE (dV/dt) ON TEMPERATURE. FIG. 4.—DEPENDENCE OF THE NUCLEATION RATE (dt/dV) ON TEMPERATURE. FIG. 5.—COMPARISON OF THE RATES OF ELECTRICAL DISCHARGE AND OF VOLUME EFFLUX.

liters minute. There are no opaques. Below 10° there are no permanent colors discernible.

5. Here, however, and slightly above and below this temperature, definite puffs of color or of darkness are obtained immediately after opening the faucet suddenly. The phenomenon may be repeated indefinitely by closing the faucet for a period of 2–5 seconds (longer at the lower temperature), and then suddenly opening it again. The puffs are at first vaguely recognized at about 8°, or even below. They become more marked as temperature rises. They are still marked at even 12°, when the fainter colors are beginning to be permanent. They show a maximum degree of darkness depending on temperature, beyond which they do not increase even if the cock is closed indefinitely.

From a theoretical point of view this result is noteworthy. Below the reaction temperature (say 12.5°), what may be called the vapor pressure of the reaction is a definite quantity, but decreases with temperature at an enormously rapid rate;

above the reaction temperature, the vapor pressure is relatively constant as temperature increases. All this recalls the well-known analogy appropriated by the physical chemist.

Now, if we suppose the nuclear velocity to be a relatively constant quantity, within a short range of temperature, while the emanating activity decreases, the density of the emanation formed within the ionizer will clearly diminish as temperature decreases below the reaction temperature, however long the air is in contact with the ionizer.

Hence the color of the puffs should gradually become fainter with decreasing temperature, as actually observed. If N nuclei are produced per superficial square centim. of phosphorus, if k be the corresponding average nuclear velocity and n the number present per cubic centim., $N = kn$. Thus n depends on the ratio of N and k. The vapor pressure analogy suggested is not wholly tenable, inasmuch as nuclei are actually absorbed at the walls of the vessel (tube ab, figure 1), so that N vanishes with n in the lapse of time. Since k is of the order of one unit, N and n may be regarded as about of the same order, roughly speaking. The number of particles generated per square centimeter of the phosphorus will not greatly differ from the number present per cubic centimeter of the emanation.

6. Above the reaction temperature, if the rate of production, N, were regarded as relatively constant, the means of computing the increase of speed of the nucleus with rising temperature would be at hand. If m be the mass of the nucleus and $mk^2/2$ varies as absolute temperature, $k_2/k_1 = \sqrt{(t_2 + 273)/(t_1 + 273)}$. Turning now to the chart, figure 3, let $t_2 = 30°$ and $t_1 = 20°$. Then $k_2/k_1 = 1.02$, whereas the chart gives $k_2/k_1 = 1.25$. These two results being out of keeping with each

TABLE 2.—SUMMARY OF ADDITIONAL DATA FOR EFFECT OF TEMPERATURE ON THE PHOSPHORUS EMANATION.

Color.	t	$10^2 \times$ dV/dt	Remarks.
Bl	19.9	95	
Bl	19.9	110	
Bl	14.6	90	
Bl +	14.6	100	
Bl	13.1	100	No opaque
Bl	13.1	90	
Bl	13.2	80	Opaque obtainable
Bl +	13.3	95	
Bl −	13.4	70	
Bl	13.4	85	
Bl −	11.9	90	
Bl	12.0	85	
Bl-Gr (faint)	10.0	50	Faster current clears field
Bl opaque	14.0 14.0	80 110	Intense activity

At 12° if a slow current is gradually increased, the field may be darkened to violet, almost to opaque. A faster current then at once clears the field to faint greenish.

other, the thermal variation of k is insignificant compared with the corresponding decrease of N.

7. *Data for low temperatures.* After finishing the electrical investigation presently to be discussed, it seemed desirable to corroborate the above results with new observations made near the temperature at which phosphorus becomes active. These are briefly given in table 2. As a whole, they agree with the above inferences. It was discovered, however, that permanent though faint colors could be obtained even below the limits stated above (13°), by very gradually increasing the speed of the charged air current from zero, until the field showed the limiting coloration for the low temperature selected. When the air current is further increased, however slightly, the field of the color tube at once clears almost with a flash. It is thus possible to "blow out" the emanating activity of the phosphorus with a current only a trifle faster than the one which produces the corresponding color maximum. The puffs of color obtained above are the same phenomenon. Below 13°, opaque did not occur. At 14° the full activity was accentuated.

ELECTRICAL COMPARISONS.

8. *Apparatus.* It is now desirable to compare these data with the results obtainable in measuring the radial currents in the tubular condenser which is made the channel of communication between the pipe, ab, of the water bath, figure 1, and the color tube, C. In other words, the tubulure, G, is now replaced by the condenser, KK, figure 2, for discharging ionized air into C, by fitting the tubulure b to the end a of the ionizer, figure 1. Details of adjustment are given in my earlier volume. The slender condenser, KK, was effectively 50 centims. long, .32 centim. in internal, and .60 centim. in external diameter. The inner face (surface of the rod, cd) is charged to about 40 volts. The tube KK, insulated at the ends from the rod, is put to earth at E. The electrical discharge takes place radially from rod to tube, and should occur only when the emanation passes in the cylindrical shell between the faces (.14 centim. thick and 50 centims. long), entering at b and leaving at a. It is difficult in so slender an apparatus and in view of the use made of it to avoid conduction through the insulators, altogether, particularly in a damp atmosphere. Hence in the following tables the insulation, when the medium is ordinary air, is given; but even if ignored it will not probably affect the relation to temperature. In a warm steam-heated room the insulation is perfect, and advantage was frequently taken of this convenience.

A steam or water jacket, J, surrounds the condenser for special experiments, § 22. Steam enters and leaves by the tubulures, s.

9. *Method.* The method consisted in reading the efflux volumes, V, at the gasometer or aspirator bottle, before and after the series of electrical measurements. As the latter were always duplicated, three volume measurements were made at stated times. From these dV/dt was obtained graphically.

The fall of potential at the electrometer (capacity of the latter 366 centims., in parallel with that of the condenser, 39 centims.) was observed at intervals of 15 seconds apart. Eight readings in two series were made between the volume readings. The initial potential being about 41 volts, and equivalent to 87 or 80 scale parts, respectively, each scale part is equivalent to about half a volt. The absolute values are without interest. As usual, care was taken to await constancy of temperature in the water bath.

10. *Data.*—In the following table 3, the time of observation, in minutes, t, the reading of the gasometer, V, in liters, the reading of the electrometer in scale parts, s, (zero at $s=250$) and the temperature θ, of the water bath are given in successive columns. In the second and third columns, moreover, the rate of efflux of the air, dV/dt, in liters/min., and the initial radial electrical currents ds/dt are tabulated. E_0 is the initial potential difference in volts.

TABLE 3.—RADIAL CURRENTS IN THE CONDENSER AT DIFFERENT TEMPERATURES AND IONIZATION. $E_0 = 40$ VOLTS.

t	$V\times10^2$ $\delta V/\delta t$	$\delta s/\delta t$ s	θ	t	$V\times10^2$ $\delta V/\delta t$	$\delta s/\delta t$	θ
		4 s/m		23^m 30	100	16 s/m	11.9
0^m 0^s	—	163	Insulation	25 30	215		
15	—	164		27 30	310		
30	—	165		0		163	
45	—	166		15	$.58\,\frac{l}{m}$	166	
				30		168	
				45		171	
7 30	70	12 s/m	15.3	28 00	370	12 s/m	12.0
9 30	125			30 00	620		
12 30	205			0		163	
0		163		15	$1.24\,\frac{l}{m}$	166	
15	$.27\,\frac{l}{m}$	166		30		169	
30		169		45		172	
45		172					
13 30	280	27 s/m	15.3	36^m 00	95	5 s/m	9.5
15 30	450			38 00	190		
17 30	610			41 00	335		
0		163		0		164	
15	$.83\,\frac{l}{m}$	170		15	$.47\,\frac{l}{m}$	166	
30		176		30		167	
45		183		45		168	

TABLE 3 (*Continued*).—RADIAL CURRENTS IN THE CONDENSER AT DIFFERENT TEMPERATURES AND IONIZATION. $E_0 = 41$ VOLTS.

t	$V\times10^2$ $\delta V/\delta t$	$\delta s/\delta t$	θ	t	$V\times10^2$ $\delta V/\delta t$	$\delta s/\delta t$	θ
		1 s/m		30^m 0	240	19 s/m	19.1
				32 0	320		
0^m 0^s		170	Insulat.	34 0	400		
60		171		0		170	
120		173		15	$.41\,\frac{l}{m}$	174	
180		174		30		179	
				45		184	

		[illegible]	[illegible]	[illegible]			[illegible]	[illegible]	θ
[illegible]		195	51 s m	19.1	52	0	310	42 s m	24.5
52		407			53	30	47		
50	1	720			55	30	660		
			17			0		17	
	15	1.03	173			15		170	
	3		190			30	1.07	186	
	45		208			45		200	
1		270	37 s m	34.7	9	3	90	18 s m	31.0
14	3	447			11	0	162		
16		615			12	30	235		
	0		170			0		170	
	15	1.16 [illegible]	180			15	.40 [illegible]	174	
	30		190			30		178	
	45		198			45		184	
28	0	65	14 s m	35.0	42	0	80	18 s m	30.5
30	0	145			43	30	160		
32	0	230			45	30	265		
	0		170			0		170	
	15	43 [illegible]	173			15	.52 [illegible]	174	
	30		176			30		179	
	45		180			45		184	
33	0	295	24 s m	34.6	46	0	310	33 s m	30.2
34	30	405			48	0	505		
36	0	52				0		170	
	0		170			15	.97 [illegible]	179	
	15	75 [illegible]	176			30		187	
	30		182			45		195	
	45		188						
2^h	0	350	38 s m	25.0	58^m	0	70	25 s m	25.0
3	3	530			62	[illegible]	195		
4	30	650			64	30	300		
	0		177			0		170	
	15	1.15 [illegible]	182			15	.62 [illegible]	176	
	30		189			30		182	
	45		199			45		189	
20	0	70	31 s m	19.4	34	30	185	13 s m	13.6
21	3	225			36		255		
23	0	390			37	30	330		
	0		170			0		170	
	15	1.10 [illegible]	178			15	.40 [illegible]	173	
	30		186			30		176	
	45		193			45		180	
23	15	43	43 s m	19.4	38	0	370	15 s m	13.6
24	15	585			39		450		
25	3	770			40	30	590		
	0		170		41	30	675		
	15	1.53	181			0		170	
	3		192			15	.87 [illegible]	174	
	45		212			30		177	
						45		182	
17	3	75	21 m	24.7					
19	3	175							
21	3	27							
	0		170						
	15	1.2	175						
	30		181						
	45		186						

As a rule, two values of $d\dot{V}/dt$ are entered for each temperature, one for a moderate current of about .50 liter/min. through the condenser and the other for the stronger current of about 1.0 liter/min.

11. *Discussion.*—The data of these tables might be constructed without further reduction in a graph where the absscissas are temperatures and the ordinates, ds/dt, proportional to the radial currents. Two curves are suggested, one for the high, and another for the low velocity, $d\dot{V}/dt$; but in view of the slightly different values of $d\dot{V}/dt$ implied in each, it is better to reduce to two volume standards. $d\dot{V}/dt=.45$ liter/min. and 1.00 liter/min. were selected as most nearly coincident with the observations as a whole. The reduction was made compatibly with the results of my earlier paper, linearly from two values of $d\dot{V}/dt$ and ds/dt at each temperature. This linear relation is again incidentally shown in figure 5 at about 19°. The slopes of these lines vary with temperature.

Table 4 contains the original data and the values needed in these reductions, as will be seen at once. The 6th and 7th columns show the currents which obtain when the volumes .45 and 1.00 liter pass through the condenser per minute. Color data are omitted as of minor interest. One may note in passing that the coefficients, $d(ds/dt)/d(d\dot{V}/dt)$ or $d\dot{s}/d\dot{V}$, also fall off to zero with the degree of ionization, and that they in general increase with temperature. The last columns of the tables contain results independent of the arbitrary scale of the electrometer.

TABLE 4.—SUMMARY OF ELECTRICAL DATA.

$E_0 = 40$ VOLTS.

θ	$\dot{s}$	$\dot{V} \times 10^2$	$\delta\dot{s}/\delta\dot{V}$	Correction. $\dot{s}_{.45}-\dot{s}$, etc.	$\dot{s}_{.45}$	$\dot{s}_{1.00}$	$-x=\dot{s}_{.45}/\dot{s}_0$	$-x=\dot{s}_{1.00}/\dot{s}_0$
							$s^0=57$	
15.3	12	27	27	5	17		.20	
15.3	27	83	27	5		32		.37
11.9	10	58	3	−0	10		.12	
12.0	12	124	3	−1		13		.15
9.5	5	47	0	0	5		.06	
							$s^0=79$	
19.1	19	41	21	1	20		.25	
19.1	51	193	21	−19		32		.41
24.7	21	48	32	−1	20		.25	
24.5	40	107	32	−2		38		48
31.0	18	46	27	−0	18		.23	
30.7	37	116	23	−4		33		42
35.0	14	43	37	1	15		.19	
34.6	24	75	33	8		33		.42
30.5	18	52	33	−2	16		.20	
30.2	33	97	33	1		34		.43
25.0	25	62	23	−4	21		.27	
25.0	38	118	23	4		34		.43
19.4°	31	110	28	3		29		.37
19.4	43	153	28	−15		28		36
13.6	13	46	5	0	13		17	
13.6	15	87	5	1		16		.20

If Q be the charge, s the deflection, C the effective capacity, E the potential difference, A the factor of the electrometer, $Q = CAs$; $i = dQ/dt = CA\,ds/dt$, where i is the radial current. Thus $i/Q = (ds/dt)/s$.

For the initial currents, as alone measured in this paper, one may always assume the simple exponential relation,

$$Q = Q_0 \varepsilon^{-xt}, \text{ or } s = s_0 \varepsilon^{-xt},$$

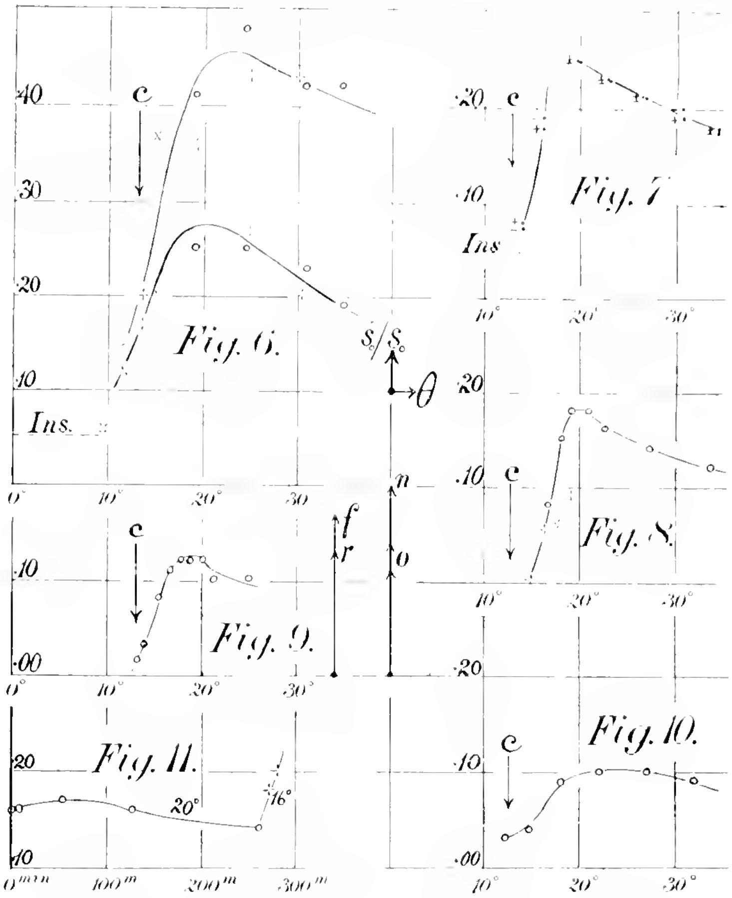
where the subscripts zero refer to the initial charges, deflections, temperatures, etc. Hence, $i_0/Q_0 = (ds/dt)_0/s_0 = -x$ is an appropriate variable for comparing the data. This may also be computed as $-x = d(\log s)/dt$, but the approximate method of computing ds/dt from observations 15 seconds apart is more convenient.

The values of x so found for $dV/dt = .45$ and $= 1.00$ are given in the last columns and make up the curves of the following and subsequent charts.

The corrected values of $x = (ds/dt)_0/s_0$, when dV/dt is .45 and 1.00 liters per minute, respectively, are given in the graph, figure 6. Different dots correspond to different series. The curves are smoother than the uncorrected results would have been, and the values for low efflux are naturally more certain. For apart from instrumental difficulties, there is at high velocities a danger of interfering with the temperature of the ionizing phosphorus. Swift currents are not so easily cooled in the water bath and intense action of the ionizer contributes its own temperature error. In both curves the conduction of the insulators prevents the curves from actually reaching the abscissa.

12. *Contrast with color data.*—The character of these curves may now be examined in comparison with the color data of figures 3 and 4, the latter being specially available. In both there is a rise of activity from about 9° through a maximum, and an eventual less pronounced decline of activity toward 35°; but in their details, the two sets of curves are very different. The nuclei of figure 3 are suddenly produced in maximum concentration at about 13° C., as shown by the arrows c in figure 6 et seq.; they then decline in number regularly and very gradually as far as observed. In figure 6, however, the ions show a gradual increase of number, even as far as 20°, after which their number also falls off to the limits of observation.

One may argue, therefore, that the nuclei as first produced are but weakly ionized in spite of their maximum condensational activity. As temperature rises, the latter property of the nucleus declines, but the ionization increases as far as about 20°. Thereafter both properties decline. As the number of nuclei decreases from the reaction at 13° onward with increasing temperature, one may infer that the ionization increases with temperature; from another point of view, that the ionization increases as the property of the nucleus to induce condensation diminishes. It is then with the nearly non-ionized nucleus that the maximum of condensational activity resides, just as if ionization were the result of a dissociation or a disaggregation of the nucleus. If, however, the nucleus is a concentrated solution as maintained below, then the critical density at which evaporation ceases, *i. e.*, the stable diameter of the nucleus will vary markedly with temperature. *Cf.* Chapter V, § 47. If now the properties of solutions in relation to Volta contacts as conceived by Lenard, also vary with concentration, a second method of explaining the present occurrences is suggested, to which greater prominence will be given at the end of Chapter VI.



FIGS. 6–10.—VARIATION OF THE LOGARITHMIC RATE OF ELECTRICAL DISCHARGE WITH TEMPERATURE. $(ds/dt)_0/s_0$ AND θ.

FIG. 11.—IONIZATION DUE TO DRIED PHOSPHORUS IN THE LAPSE OF TIME

13. *Electrical experiments repeated.*—It is doubtful whether the color experiments can be much improved. These results are bound to lack sharpness; but the electrical experiments are open to further development in the first place by retaining a constant velocity dV/dt throughout. This may be done by inserting a second stop-cock, F' (not shown), to check the air current to a fixed value, even when F, figure 1, is quite open. In the second place the weakly ionized emanation at low temperatures should be tested directly as to its condensational power. One may inquire whether the reduced condensing power of the positive and the negative ionizations differ; whether at a given temperature definite ionization is obtainable quantitatively; etc.

In table 5 results obtained by the same method as above are summarized for brevity. The volumes, dV/dt (liters/min.), of air charged with phosphorus emanation traversing the condenser, are a nearly constant quantity in view of the second stopcock already mentioned. θ is the temperature at which the fall of potential, ds/dt was observed, s being the deflection in scale parts of the electrometer used above. The condenser was given a positive and a negative charge alternately, with the outer face put to earth. Four readings for the negative charge were included between similar sets for the positive charge. The conduction of the insulators is given. The last column contains the datum $x = -(ds/dt)_0/s_0$.

TABLE [illegible].—ELECTRICAL CURRENTS IN THE CONDENSER, WITH THE MEDIUM IONIZED BY PHOSPHORUS, AT DIFFERENT TEMPERATURES.

$E_0 = 41$ VOLTS; $s_0 = 73$.

θ	dE/dt	ds/dt	x	θ	dE/dt	ds/dt	x
Feb. 1903.		+3.6	.05	26.6	.48	+15.5	+.21
14	.48	+5.5	+.07	26.5	.47	−15.0	−.21
14	.49	6.0	.08				
				32.7	.48	+13.8	+.19
16.3	.47	+13.3	+.18	32.7	.47	−14.5	−.20
16.4	.48	−14.2	−.19				
				34.9	.48	+12.8	+.18
19.8	.48	+18.2	+.25	34.8	.48	−13.2	.18
19.8	.48	18.2	−.25				
22.8	.48	+16.5	+.23				
22.8	.48	17.0	−.23				

14. *Discussion.* The initial currents (x) are shown in the graph, figure 7. As a whole the results are much more definite than in figure 6, seeing that no reduction for volume differences is now needed. Though there is a small difference between the currents corresponding to the positive and the negative charges, this difference lies within a scale part and may be taken as an error of observation. The position of the maximum of nuclei is again shown at e. The range of the new data, after deducting the error in insulation, $x = .18$, is smaller than above, $x = 21$, a circumstance presently to be considered and attributable to moisture and leakage errors, or in general to the necessarily unsaturated condition of the ionization within the condenser.

Moreover, the form of figure 7 differs from figure 6 and has approached more nearly to the color results of figure 4. The maximum, however, is still near 20°, so that the inferences above on the earlier appearance of the nuclei and the generation of the ions out of the nuclei, is sustained.

15. *Permanent conduction produced by the emanation.*—At this stage of my work, I encountered a peculiar and puzzling series of phenomena which were not noticed in my earlier work, probably because the room temperature was purposely kept high and the atmosphere dry. After the air was passed over phosphorus freshly put into the tube *ab*, figure 1, the condenser receiving the emanation was thereafter found to remain *permanently conducting* even with the air current shut off, precisely as though it had itself become radio-active. This conduction was

relatively so enormous that the electric currents could not be measured by the same electrometer and the occurrence of an internal metallic contact or break in the insulation was immediately suggested. I therefore overhauled the condenser carefully, inserted an internal bushing, replaced the internal rod by a new one, etc., all without effect. The condenser showed good insulation after putting it together, but became a conductor immediately after the passage of the first phosphorus emanation. Permanent leakage due to dislocation of the solid parts was thus out of the question.

This conduction vanished over night. It was reproduced as soon as fresh phosphorus air passed through the condenser. It then remained permanent, though gradually diminishing for hours, and was nearly gone again next day. Hence two causes are suggested: either a film of residual moisture aspirated off from the phosphorus grid (which, however, was as usual carefully dried by squeezing in a press between folds of blotting paper, and then exposed to the air, so that only traces of moisture can be in question) was precipitated in the condenser to the detriment of the hard rubber insulation; or else some form of emanation given off from the phosphorus made the condenser radio-active. Incidentally, I may advert to the extreme caution needed before such radio-activity can be assumed, the behavior in both cases being essentially alike.

Warming the condenser seemed to be useless. Moderate amounts of dry air (say 7 liters flowing out in about 10 minutes) passing over the phosphorus were nearly ineffective. It was no remedy to remove the phosphorus and pass dry air alone in the forward direction. Separating the condenser from the water bath did not change its conduction. Thus I found, for instance, for the condenser alone and free from air current, $ds/dt = 33$; an hour later, $ds/dt = 25$; next day $ds/dt = 7$; good insulation, $ds/dt = 2$.

At $\theta = 30°$ (water bath temperature), the tendency of the condenser to conduct permanently was at first accentuated but soon completely wiped out. The electric current reached a normal value. This appeared so much like a moisture error that I further tested it by passing the air current backwards, through the condenser first and then over the phosphorus into the atmosphere, in this way drying both parts. Insulation of the condenser was thus at once restored. Again, on passing a considerable volume of dry air (say 15 liters, slowly) over the phosphorus, this too lost its power to make the condenser permanently conducting. Hence in the experiments of the following table the phosphorus was first dried in this way in a current of dry air. The work then progressed smoothly, showing the relation of the emanating activity of phosphorus to temperature in a new light.

I may add again that in none of my earlier experiments were like discrepancies encountered. Possibly a corroded copper grid may be hygroscopic, something like platinum black; or the room may have been exceptionally dry.

16. *Specially dried phosphorus grids.*—In tables 6 and 7, θ is the temperature of the water bath, dV/dt the volume of dry air in liters passed per minute over the phosphorus: ds/dt is the corresponding initial radial electric current in the

condenser in arbitrary units, when the potential difference, E_0, is about 40 volts and the initial deflection, s_0, as stated. In both cases the insulation of the condenser in the absence of the air current is measured for each temperature. This is then deducted and the corrected electrical currents tabulated in the fourth column. In table 6 a channeled hard rubber bushing guards (unnecessarily, as it afterwards proved) against metallic contact of the core and envelope. In table 7 this has been removed. The phosphorus in both tables is dried preliminarily as stated, by a current of dry air from the desiccator, entering the condenser first and passing thence over the phosphorus grid into the atmosphere. The last columns give the currents, $(ds/dt)_0/s_0 = i_0/Q_0$, supposing that initially $Q = Q_0 \varepsilon^{-a(t-t_0)}$, as stated in § 11.

TABLE 6.—IONIZING ACTIVITY OF DRIED PHOSPHORUS. RUBBER BUSHING INSERTED FOR INSULATION. INITIAL POTENTIAL DIFFERENCE, $E_0 = 40$ VOLTS. $s_0 = 74$.

t	$10^6 \times dV/dt$	ds/dt	Corrected. ds/dt	i_0/s_0
19.2	52	11.5	6.5	.09
18	52	9.3	4.3	.06
16.5	52	7.5	4.0	.05
15.0	52	4.0	0.0	.00
16.8	52	9.5	6.0	.08
18.2	52	13.5	11.0	.15
19.2	50	17.3	13.0	.18
20.6	50	19.5	13.5	.18
22.4	50	19.3	12.0	.16
27.2		18.3	10.3	.14
33.0	—	16.3	9.0	.12

TABLE 7.—IONIZING ACTIVITY OF DRIED PHOSPHORUS. RUBBER BUSHING REMOVED. INITIAL POTENTIAL DIFFERENCE $E_0 = 40$ VOLTS. $s_0 = 73$.

t	$10^6 \times dV/dt$	ds/dt	Corrected ds/dt	[illegible]
25.8	50	8.8	7.3	.10
21.2	52	9.0	7.5	.10
20.0	52	10.3	8.8	.12
18.8	50	10.3	8.8	.12
17.8	50	10.0	8.5	.12
16.6	55	9.3	7.8	.11
15.5	52	7.5	6.0	.08
14	50	4.3	2.3	.03
13.3	50	3.0	1	.01
[illegible]	—	2.0		
[illegible] week.				
14.5	81	4.3	—	.06
14.2	125	4.3	—	.06

Color experiments here showed Bl equivalent to .80 lit./min. At the outset, there was a momentary deficiency of nuclei (Bl equivalent to 2.8 lit./min.)

17. *Discussion.*— The results of these tables are shown graphically in figures 8 and 9, where the currents $(ds/dt)_0/s_0$ are, as usual, the ordinates. In a general way, the character of figures 6 and 7 has been preserved, inasmuch as there is maximum ionization at about 20°; but the details of behavior are again different. In the first place the scale of the phenomenon is gradually reduced, as the emanating body is repeatedly subject to desiccation. This merely means deficient phosphorus surface, as I was not at the time aware how soon phosphorus is consumed by slow oxidation in these experiments.

There is no certain tendency of the maximum to move into smaller temperatures in the later experiments. Thus when $dV/dt = .50$, nearly,

figure 6,	maximum $(ds/dt)_0/s_0$	$= .20$	at 20°,
figure 7,		$= .20$	19°,
figure 8,		$= .18$	20°,
figure 9,		$= .12$	19°.

Whether the phosphorus is being actually consumed, or whether merely a superficial change is in question, will be investigated below; but the charged air current is gradually further removed from saturation and will continue on the decline in the following experiments. Moreover, here is an explanation of the differences of slope shown in the volumetric and electrical curves of an earlier paper.[1] For the degree of "dryness" reached wholly determines the electrical curve without in the same degree influencing the volume curves, as will presently be further manifest.

In all cases the dependence of the electrical results on temperature remains quite different from the corresponding dependence of the color data or temperature. Special experiments made at the end of table 6 with identical apparatus showed strong color activity at 13.6°, viz., blue corresponding to .80 lit./min. while the subsequent electrical measurements at 14° (see table 6) reproduced the original exceptionally low conductions.

The position of the phosphorus grid in the tube, *ab*, of the water bath, figure 1, showed an effect insufficient to be of moment in relation to the phenomena under discussion. Thus

Rear position, furthest from end *a* and condenser, $(ds/dt)_0/s_0 = .13$ (see *r*, figure 9).
Front position, nearest to condenser, $= .17$ (see *f*, figure 9).

Nevertheless there is nearly $\frac{1}{3}$ more saturation when the phosphorus grid is nearest the condenser than when remote, a circumstance which, as already intimated, makes it difficult to investigate saturation in this way. Any connecting tube between ionizer and condenser is an absorber, particularly if bent.

18. *Corroborative experiments with the color tube.*— A series of experiments were now begun with the steam jet, to ascertain the difference between the character of the emanation immediately after the phosphorus grid has been prepared (without preliminary desiccation) and after a large volume of dry air (20 to 30 liters) has been passed over it. If the relatively enormous currents obtained in the condenser

---

[1] *Experiments with Ionized Air*, Chap. V, p. 69.

in the first instance are due to nuclei, there must be a corresponding result in the volume per minute of the saturated emanation necessary to produce a fixed color (blue) in the color tube. The reverse is the case, as will be seen in the following table where nuclei and ion production are in a measure reciprocal occurrences. In other words, the initial enormous conductions are accompanied by an abstraction of nuclei.

Three phosphorus strips were as usual dried in press between folds of bibulous paper and then exposed to air for some time. They were then inserted into the tube, *ab*, of the water bath, figure 1. The initial (apparent) ionization as tested by the condenser was invariably too intense to be measurable. The condenser was then removed and a short tube, *C*, added to obviate excessive absorption before discharging into the color tube.

In table 8 the liters of dry air which have passed over the phosphorus strips are given under *L*. The successive liters of emanation per minute to produce the standard blue are given in the third column (dV/dt); the fourth gives the current when the emanation passes through the condenser at the fixed rate of .5 lit./min. selected for convenience.

TABLE 8.—CONDENSATION-PRODUCING ACTIVITY OF THE INITIAL ("WET") AND FINAL ("DRY") PHOSPHORUS EMANATION. TEMPERATURE 18°. CURRENT IN CONDENSER DUE TO .5 LITERS OF EMANATION PER MINUTE. $s_0 = 73$.

Color.	*L*	$10^2 \times$ dV/dt	ds/dt	Remarks.
—	—	—	·	Condenser discharged within 7 sec.
Bl		170		
Bl	6	160	—	Condenser discharged in 10".
	13	—	1[illegible]	Current estimated.
Bl	20	143	15.5	Phosphorus "dry." Insulation 0.5.
Bl	25	140		Ionization constant. s_0/s_0 [illegible] .21.

ANOTHER EXPERIMENT: PHOSPHORUS GRID SCOURED. TEMPERATURE 21°.

Color.	*L*	$10^2 \times$ dV/dt	ds/dt	Remarks.
Bl	3	115	—	Opaque not attainable due to insufficient nuclei; condenser discharged within 7
Bl	8	1[illegible]	2[illegible]	Opaque now attainable; condenser discharged within about 2[illegible]; current estimated.
Bl		90	—	
Bl		103		
Bl	15	92	9.5	Insulation 1.0; nearly perfect
Bl	20	92	—	Ionization constant: $s_0/s_0 = .13$
Bl	27	100		Do.

The first part of table 8 shows definitely that when the currents are too large to be even estimated, the emanation needed to produce the standard blue is larger than at the end of the experiment where the radial currents have fallen off to their small fixed value. Thus the high conduction is without nuclear condensing effect.

In the second part of table 8 the volumes are nearly constant except at the beginning, where it was found impossible to obtain opaque or even full blue, whatever volume is passed through the ionizer. The necessary number of nuclei was not forthcoming. As in the preceding table, however, less than ten liters of air are sufficient to dry the phosphorus into full activity so far as the color is concerned, whereas the conduction still retains abnormally large values.

Another reciprocal relation is shown on the table. dV/dt here happens to be unusually large, so that the phosphorus is for some reason weak as a nuclei producer. I therefore washed and scoured the surface of the grid, obtaining the usual order of values in the second part of the table. On the other hand, the currents in the first part are larger than those of the second part. Here again, therefore, the tendency to produce nuclei reciprocates in intensity with the tendency to produce ions, or better, to produce conduction in the condenser. The latter is facilitated by the presence of traces of moisture, but nuclei are not so produced.

TABLE 9.—BEHAVIOR OF EMANATING PHOSPHORUS COMPARED WITH DAMP PAPER. TEMPERATURE 17.6°. CURRENT IN CONDENSER, .52 LITERS OF AIR PER MINUTE. INITIAL POTENTIAL DIFFERENCE, $E_0 = 40$ VOLTS. $s_0 = 71$.

	I	ds/dt	Time.	$\dot{s}_0/s_0$	
Insulation	—	3	—	.04	Current of dry air. No wet paper.
Wet paper	0	4–18	0'''	.06–.25	Current of dry air passing over wet paper into condenser. Large currents estimated.
"	—	72	1	1.01	
"	—	100	7	1.50	
"	7	100	10	1.50	
Insulation	0	100	—	1.50	Paper removed. Air current gradually dries condenser.
"	—	64	—	.90	
"	—	20	—	.28	
"	7.5	4	—	.06	
Insulation	—	2	—	.03	Phosphorus in place. No air current.
Phosphorus	7.5	—	15''	—	Air current through condenser. Discharged within 7 sec.
Insulation	after 7.5	—	—	—	Discharged in 15 sec. No air current.
Phosphorus	11	80	—	1.13	Current estimated.
"	15	13	30'''	.18	
Insulation	after 15	5	—	.07	No air current.
Phosphorus	21	12.5	45''	.18	
Insulation	—	5.5	—	.08	No air current.
Phosphorus	28	12.0	60'''	.17	
Insulation	—	2.0	—	.03	No air current.
Phosphorus	35	12.5	75'''	.18	
Insulation	—	2.0	—	.03	No air current.

19. *Corroborative experiments with damp paper.* Another method of throwing light on the inquiry would be a comparison of the conduction produced in the condenser by air passing over damp filter paper with the corresponding case of air passing over phosphorus.

Table 9 shows results contrasted in this way. *L* is the number of liters of air aspirated over the body and passed through the condenser, ds/dt the corresponding currents in arbitrary units at the times stated. From these (ds/dt), s_0 is found. The degree of insulation of the condenser is also tested successively, both with dry air currents in the absence of ionizers and with the air currents following in the absence of ionizers. The wet paper behaves in a less intense way something like the phosphorus in the second part of the table. The rise of conduction, however, is gradual, the conduction at best moderate and the return of the condenser to the original degree of insulation relatively rapid. With phosphorus, the conduction after the first minute or so has risen to the immeasurably large values and when the air current ceases the condenser shows similar conduction. Much more dry air is needed to desiccate the condenser and the phosphorus to normal values (fully twice as much as in the preceding case). Eventually the currents also return to the normal, relatively small limit and the insulation of the condenser is nearly perfect again.

Qualitatively, the two phenomena run in parallel; quantitatively, they are enormously different. Inasmuch as the paper is obviously wet, whereas the phosphorus grid has been dried short of the desiccator, inasmuch as any emanation must behave like a water evaporation, I think that the volatile body is probably of the nature of a hydrophosphide. Some electrically active substance is distilled in the presence of moisture and precipitated in the condenser.

20. *Corroborative experiments with desiccators.* The final test made to detect the character of the emanation was one of direct desiccation over chloride of calcium, before insertion. The day happened to be damp and the insulation poor. The experiments, however, are none the less definite.

(1) Phosphorus dried in air and inserted into the dried tube of the water bath, *ab*, figure 1. The condenser was at once discharged on passing the air current through it. On removing the phosphorus the condenser showed too large a leakage to admit of the measurement of current. All appurtenances were now dried in a current of dry air and the final insulation determined.

(2) The phosphorus grid, having been placed for about 15 minutes in the desiccator was again inserted into the tube, *ab*. The current now obtained was $ds/dt = 37$; the insulation proved to be $ds/dt = 30$. Hence the current due to ionized air was but $ds/dt = 7$, and abnormally small value, but indicating the absence of moisture.

The phosphorus grid was once more put in the desiccator for 15 minutes. After replacing it in the water bath the current observed was 40; the insulation 27. Hence the leakage due to ionized air is here $ds/dt = 13$, agreeing with the usual order of ionized values above.

Owing to the unfavorable condition of these experiments, not much definiteness was to be anticipated from them; but they show clearly that the enormous initial emanation from fresh phosphorus is all but wiped out, relatively speaking, after the phosphorus has been dried preliminarily over calcic chloride. Whether in the rigorous absence of all moisture phosphorus would cease to ionize air, remains to be seen. It is also a question whether the desiccation over calcic chloride may not be accompanied by detrimental chemical action, referable to the chloride.

21. *Effect of prolonged drying.*—A final attempt was made to see if, after continued drying over calcic chloride, the ionization would be wiped out altogether. The following table shows this to have been unsuccessful, although the conduction falls to low values. The room was favorably dry and warm and the leakage errors in the condenser not appreciable. The effect of long exposure is shown in the first part of table 10. After nearly 5 hours the potency of the ionizer is not diminished (see figure 11). It has rather increased, due possibly to the attraction of traces of moisture even within the permanently dried tube of the apparatus, figure 1. An extra tube of calcic chloride was attached. In the second part of this table the temperature effect is again tested for this specially dried phosphorus. The corresponding graph is shown in figure 10, and the ionization is weaker than in any earlier experiment. Nevertheless the results show maximum activity in the neighborhood of 20°, though even at 12° the ionization is not quite extinguished.

TABLE 10.—PROMISCUOUS EXPERIMENTS WITH VERY DRY PHOSPHORUS. $E_0 = 40$ VOLTS. ROOM HOT. INSULATION PERFECT. EFFECT OF TIME. $s_0 = 70$.

θ	$10^2 \times dV/dt$	ds/dt	Time	s_n/s_0
19.5°	45	11	0^h 0^m morning	.16
19.5	45	11	8^m	.16
20.2	45	12	55^m 7 h. dry air over	.17
20.8	43	11	2^h 07^m	.16
21.2	43	10	4^h 21^m afternoon	.14
16.0	47	13	33^m	.19
16.2	45	14	44^m	.20
EFFECT OF TEMPERATURE.				
21.9°	45	7		.10
14.7	44	3		.04
12.1	44	2		.03
18.1	40	6		.09
27.0	43	7		.10
32.0	43	6		.09

The exceptionally low ionization is not accounted for except as due to deficient phosphorus, the natural result of long continued consumption.

22. *Promiscuous experiments.*—Having investigated the effect of the temperature of the body of phosphorus on its emanation, I next purposed to ascertain the

d[illegible] of the emanation itself on temperature. This could be done by s[illegible] the condenser with a steam jacket (shown in figure 2, *jj*, *s*, *s*, being the [illegible] efflux pipes) and noting the effect of the rise of temperature of nearly 100°. After repeated trials, however, I found that the high temperature so far diminished the insulation of the hard rubber bushings of the condenser, that no measurements would be trustworthy. On cooling the condenser, the insulation again became perfect. Quartz insulators suggest themselves as probably alone available.

23. *Comparison of old and new grids.*—Trial was made with freshly cut phosphorus, the grids used in the above work being as much as a year old. The results show a like order of values for both, in spite of the intense fuming of the new grids. Nevertheless, the latter is apt to be from 2 to 3 times stronger than the old grid. Thus after thoroughly drying the new grid over calcic chloride and testing it at 21.5° the data were:

$\delta/t = .42$, $(\delta s/n)_0 s_0 = .26$,
$.43$. $= .2$[illegible]

Exposure to the air of the room for about half an hour after desiccation was without effect.

The question as to the maximum number of nuclei producible by phosphorus, thoroughly dried over calcic chloride, under favorable conditions, was deemed sufficiently important to justify the additional experiments detailed in table 11. The data are obtained from an entirely new adjustment of apparatus, including the electrometer; but they are nevertheless a corroboration of what has just been stated. The attempt to prolong these experiments indefinitely was cut short by spontaneous ignition.

This experiment proves that the air in all the earlier experiments was undersaturated, agreeing with an earlier paper from which values are quoted in the next paragraph.

TABLE 11. BEHAVIOR OF FRESH DRY PHOSPHORUS IN EXCESS. $E_0 = 41$ VOLTS. θ [illegible] 2 [illegible] INSULATION PERFECT. DESICCATED 20° OVER $CaCl_2$.

[illegible]	[illegible]	[illegible]	[illegible]
34	13	192	26
	14	175	19
	14	18[illegible]	19
	14	170	19
	14	174	19
[illegible]		6	
	5 [illegible] later. P in place.		
	14	150	20
	14	148	20

[illegible] removing from water bath.

24. *Older data compared with the present data.* It is finally worth while to adduce the corresponding data of an earlier paper. The equivalent colors of the steam tube are the yellows and crimsons of the second order. The temperatures are 20°–30°.

TABLE 12.—RELEVANT DATA FROM EARLIER PAPERS. $E_0 = 40$ VOLTS.

Color.	Temperature, θ	$10^2 \times dV/dt$	$10^2 \times (di/dt)_{u=0}$
Yellow	30	50	16
Yellow	30	65	17
Crimson	30	43	11
Yellow-Green	21	50	13
Yellow	24	58	22
Crimson	24	42	14

Clearly then, for $dV/dt = .43$, nearly, the order of values for the currents is the same here (the experiments made over a year ago, but with the same grids) as in the above experiments. The room being very hot insured dryness in that work without preliminary desiccation. Large volumes of dry air had been passed over the grids, moreover; for colors of the first order were principally observed, requiring even as much as 3 liters/min. per observation.

The arrows (n, new and o, old) in figure 9 show the relation of the results in the last table to the values for freshly cut phosphorus in excess given at the beginning of paragraph 23. Since from the old values the number of nuclei was computed as $n = 8 \times 10^4$, the new values would make them approach $n = 16 \times 10^4$, about half the datum found with plate and with spherical condensers by entirely different methods, remembering that from the occurrence of an absorbing influx pipe, the air within the tubular condenser can nowhere be quite saturated.

25. *Conclusion and summary.*—The experiments with phosphorus show that nuclei adapted to condense atmospheric moisture are produced most abundantly at about 13° C. Below this, the rate of production decreases with enormous rapidity (just short of suddenness), probably ceasing at about 8°. This holds true for very different velocities of the dry air passing over the phosphorus. Above the reaction temperature, the activity decreases slowly as temperature rises, having not decreased more than 25 per cent at 35°. Since the phosphorus is superficially heated by the reaction, sharp statements are out of the question.

Below 13°, the opaques of the color series are absent and the maximum tints are fainter and of increasingly higher orders. The strongest permanent color may be reached by very gradually increasing the charged air current. A limiting velocity decreasing with temperature may thus be reached, beyond which all colors vanish and the reaction is quite "blown out," as it were. It is probable that in these experiments the chemical reaction supplies the deficiency of temperature. Suddenly opening the stop-cock after a period of quiescence shows puffs of color under these conditions, which also vanish as temperature decreases below 13°. Putting $N = kn$, where N is the number of particles generated per second per superficial square centim. of phosphorus, n the number per cubic centim. of the ionized medium, k their velocity in any cardinal direction, the variation of N is to be ascribed to n, k being relatively constant.

In contrast with the color data (nuclei), the ionization of air passing over phosphorus increases with temperature to a maximum at about 20°, after which there is a less pronounced decline. This ionization is not an arrival comparable in suddenness with the appearance of nuclei, nor are the maxima identical as to temperature. One may infer that the nuclei as first produced are weak in ionization but of normal strength in condensational activity, that thereafter the latter property declines because (probably) the ionization increases as far as 20°. Finally both properties decline. This reciprocity is accounted for if the ionization is a result of the dissociation of nuclei; but another explanation will follow in Chapter VI, § 17 et seq. The degree of ionization found is here independent of the sign of the charge used in testing.

If the phosphorus grid is not preliminarily quite dry, traces of moisture are apt to escape with the emanation and produce permanent conduction in the condenser. Considerable variation of the electrical coefficients may thus ensue, though the color results are, relatively speaking, but slightly affected. As the electrical discrepancy seems to be out of proportion with the quantity of moisture present, it is probable that the emanation escapes in some combination with it. The whole phenomenon vanishes on thorough desiccation both of the phosphorus and the apparatus. Grids frequently treated in this way show a gradually decreasing ionizing intensity, probably due to the continued consumption of phosphorus or to a removal of effective surface. Throughout the experiments the relation of the color curves to the electrical curves remains practically unchanged, in spite of the different degrees of saturation (ionization).

The relatively enormous conductions associated with non-desiccated phosphorus are without a color effect when tried in the steam tube. They rather give evidence of an abstraction of nuclei. Moreover, such reciprocal properties are manifest in other instances, § 18. Air passed over damp paper behaves similarly to the emanation from non-desiccated phosphorus, with a difference of intensity in favor of the latter. Desiccation over calcic chloride removes the incidental conduction entirely. The emanation may thus be dried to a limiting degree of ionization which is not then further reduced on drying. In practice all operations should be made with desiccated phosphorus; otherwise the baffling discrepancies encountered in the case of plate and spherical condensers[1] may be anticipated.

By using freshly cut fuming phosphorus in excess in the ionizer, it was possible to increase the radial currents in the condenser to nearly twice their usual value, remembering that the emanation within the condenser is in all parts essentially unsaturated. Hence the low concentrations formerly[2] found for tubular condensers (8×10^4 nuclei per cubic centim.), is made to approach the value found from plate and spherical condensers more nearly.

---

[1] *Experiments with Ionized Air*, l. c., Chap. VI.

[2] *Ibid.*, Chap. V.

CHAPTER II.

GENERAL OBSERVATIONS RELATING TO CORONAS AND AXIAL COLORS.

INTRODUCTORY.

1. *Purposes of the present chapter.*—I have stated above that it is the chief purpose of the present volume to throw light on the structure of the nucleus from measurements made of the apertures of the coronas of cloudy condensation, variously produced. As these coronas are not merely expansions of the well-known form, but present complications which make the direct measurement of aperture beyond a certain order of magnitude of but little value for classification, it was thought necessary to enter somewhat at length into the investigation of these phenomena. Incidentally, an outstanding inquiry of my first volume, as to the relation of steam jet or (axial) color tube colors and coronal colors is thereby definitely answered.

2. *Classification of the experiments.*—The object of the present chapter is, in the first place, to map out the sequence of coronas in case of water vapor, in terms of the numbers of particles producing them, relatively. The extreme diversity of coronal display seen in moist nucleated air lends itself well to a geometric method of classification when the colors are produced by successive exhaustions. The classification is thus primarily suggested by experiment.

In the second place, I shall make certain theoretic deductions from the time losses of nuclei observed, which clear up some moot points left in abeyance in my earlier experiments on the same subject.

I purpose in the third place to contrast the color of the central patch of the coronas with the axial colors seen in the steam jet, or under like circumstances with even greater saturation, in the adiabatically exhausted drum. The coronas must in large measure be diffraction phenomena; the axial colors cannot be so explained, but are evoked by some unknown kind of harmonic absorption. The contrast is sharply brought out by the experiments.

Finally, I shall make an estimate of the absolute dimensions of the water particles in action and of their number, and indicate a method which will be pursued in the next chapter (III), in a quest for definite absolute results.

APPARATUS.

3. *Tubes.*—In my first experiments, tubular apparatus were used, after the manner of Kiessling and Aitken. But in these instances the colors are too fleeting and, if obtained artificially with nuclei, are apt to be too dull for good dis-

crimination. The charge of nuclei is removed too rapidly by the condensation, the being too small to admit of much evaporation. If the tube is horizontal, two longitudinal vortices, as shown in figure 1*a*, are seen immediately after exhaustion, as the air heated by the sides of the tube rises on the outside and descends into the axis. Fog is soon dissipated in this way (a condition of things which may be traced even in very wide vessels), or else its homogeneity is impaired. When the tube is held vertical, there is a corresponding difficulty. Under no circumstances is there a guaranty that the charge of nuclei added is ever uniformly distributed. It will be of unequal density along the length.

Tubes have an advantage inasmuch as they insure the occurrence of truly axial colors, and for this reason I spent some time with them. The general form of tube is given in figure 1, *AA* being the tube, *d* the tubulure for exhaustion, *e* the tubulure for influx of pure air through the filter, *f*, containing compressed cotton. When the cotton is removed, nuclei may be admitted here. White light, *L*, enters by the window, *b*, and is observed through *a*.

Even with tubes but 3 cm. in diameter and less than a meter long, the axial colors are strong, but the dull colors soon vanish. Immediately after charging with nuclei, dense opaques are the result of the smallest exhaustions. No special advantage was gained favorable to purity of color when the diameters of the metal tubes were increased to 5 cm., the tubes being 2 meters long. In case of glass tubes of these dimensions illuminated by sunlight, the gradual extinction of the light along the axis is well observed. The diffraction colors are also seen on oblique vision from the outside of the tube. The end colors are of no value and the light scarcely penetrates beyond one meter.

4. *Disc.*—Incidentally I also tried a disc-shaped apparatus, figure 2, consisting of two glass plates, *g* and *g*, secured by a metallic ring, *r*. Without removing the above difficulties, the colors even of the coronas were here very weak and the apparatus too fragile. The disc is a close approach to a surface apparatus, however, and from this point of view, often useful.

5. *Globes.*—For studying coronal colors, spherical receivers, *A*, figure 3, as used by Coulier and by Kiessling, are preferable. Their diameter should exceed 25 cm. With divergent sunlight the display is gorgeous, the colors glowing metallically. The mantel of a Welsbach burner *W*, seen through a round hole, *a*, in the screen, *s*, is better for the usual observational purposes. To an eye at *E*, the axial colors (colors seen in the color tube[1] in case of the steam jet) are not very vivid, for the absorption along the column *ab* is not sufficient to subdue the intensity of white light from *W*. The diffraction colors, as *acb*, are splendid, particularly on blotting out the axial beam, *ab*, by a small black circular screen, pasted to the sphere in front of the eye. The vortices suggested in figure 1*a*, are now no longer violent. They serve rather a useful purpose in keeping the contents of the receiver homogeneous as to dust contents. It is with this apparatus that the colored central patches of the coronas, carefully to be distinguished from the axial colors, are best observed. The lid of the globe secures the gauge *G*, the exhaust pipe *d* and the filter *f*, all with appropriate stop-cocks.

[1] *Experiments with Ionized Air*, l. c., Chap. I.

The description of other apparatus (drums) specially adapted for axial colors will be given in § 19.

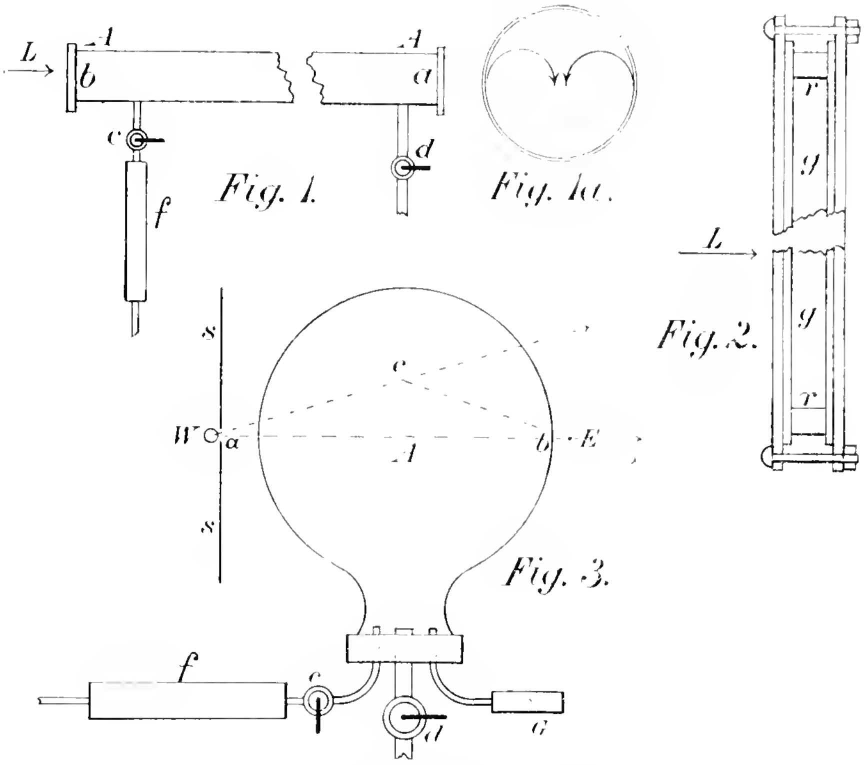


Fig. 1.—Condensation Tube. Fig. 2.—Condensation Disc.
Fig. 3.—Condensation Globe.

RESULTS FOR CORONAS.

6. *General character of the phenomena.*—As a whole, the diffraction pattern in homogeneous light is a contraction inward of dark rings, in proportion as the particles during the course of exhaustion of the nucleated moist air grow larger. This motion is almost instantaneous on sudden exhaustion, but may be made visible on gradual exhaustion. The rings, moreover, which are at first very diffuse, contract as the exhaustion proceeds to small, sharper diameters. Ordinary coronas may be seen even when the precipitate is rainlike.

The occurrences, however, are by no means a succession of ordinary coronas (*normal coronas*, I shall call them), like those produced by lycopodium. The initial and particularly brilliant coronas corresponding to finer particles have colored central fields, and it is only after many exhaustions that the normal white centered corona is reached. If the nucleation is very intense the coronas are apt to be distorted with certain vapors and to tend to become stratified. Frequently (and here even with water vapor) the colors mount from the pool of liquid below. These irregularities occur more easily with hydrocarbons like benzine, etc., which loads the nuclei more heavily and maintains larger nuclei than water. It is occasioned by the subsidence of loaded particles, rapid as compared with their rate of diffusion when unloaded. On shaking the receiver violently and comminuting [illegible] the charged air again becomes homogeneous as to nuclei and [illegible] uniform, though this shaking introduces a new phenomenon. With [illegible] gradual distortion of the coronas will repeatedly occur, and for this reason the following results refer to water vapor exclusively. Distorted coronal [illegible] will be taken up later.

The time during which a given charge remains active if not interfered with is indefinitely long, but with a continually progressing evanescence of nuclei. Coronas are well produced three hours after charging. They occur faintly and contracted in form even after more than twenty-four hours. In such cases there are many mysterious qualitative changes, which will be treated in turn below. On standing over night, rainlike precipitation is apt to occur. Fogs may be spontaneously produced in a highly nucleated receiver without any supersaturation whatever. On the other hand, coal gas carries nuclei indefinitely, as if they were part of itself.

7. *Observations with small globes.*—The information first to be sought is some practical classification of the sequence of coronal colors, and of the axial colors seen in these experiments. The latter have already been referred to as the flame colors seen along *ab*, figure 3; the others are largely diffraction colors seen along *ab*. It will be found that these colors are very different. If the corona has a central field other than white, the axial color is always nearly complementary to the central patch of the corona. As the cloud particles grow in size, both central color phenomena pass through Newton's series, at a definite phase difference apart.

I give in the following table certain preliminary results obtained with a small globe, but 23 cm. in diameter. The numerals in the first column relate to table 4, as a standard case, and show the number of exhaustions there needed to reach a similar corona. The remaining columns show the number of exhaustions made with the present apparatus, to obtain the adjoining color sequence, the colors being reckoned from within outward. An attempt has been made to arrange both

TABLE [illegible].—PRELIMINARY DATA FOR CORONAL COLORS. SMALL GLOBE, DIAMETER 23 cm. EXHAUSTION 76–63 cm. DISTANCE OF SOURCE, D = [illegible] cm.

[illegible]	[illegible]	[illegible]	From Table 4.	Exhaustion No.	Corona.
[illegible]	1	Wh-yl, reddish		1–2	Fog, dull rd, dull gr
[illegible]	2	Gr, rd		3–4	Fog, rd
	3–5	Yl, rd, slate		5–7	Yl, cr, slate
	6	Yl-gr, gr, viol, gr		8	Yl-gr, bl-gr, rd
	7	Yl-gr, rd, gr, rd		9–11	Yl-gr, cr, bl-gr
[illegible]	8–9	Yl-gr, rd, gr, rd, slate		12	Yl-gr, rd-br, bl, gr
	10–11	Yl-gr, rd, bl, gr, rd		13–14	Wh, dk bl, rd, gr
[illegible]	12–14	Wh, rd, bl, gr		15–20	Wh, cr, bl, gr
[illegible]	15–16	Wh, bl, rd			
	17	Wh, cr, bl, gr			
	[illegible]	Normal coronas			

[illegible]

observations in such a way that corresponding coronas fall on the same line. This is here but partially successful, probably because the importance of the time losses is underestimated. The feature of the table is the prevalence of blues, and the results differ in this respect from those for the larger globes below.

The color abbreviations used easily suggest themselves, except in the cases of gr green, bl blue, ol olive, cr crimson, op opaque or black, dk dark. Gray and black will be written in full. I have thought it expedient to give a very complete series of color observation, both because it is not clear that the sequences for large and small globes are the same, and because of the difficulty of identifying different series.

8. *Observations with a larger globe.*—The following table contains examples of results chosen at random, for the larger globe 30 cm. in diameter, for different distances of the light, different exhaustions, and nucleations. These coronas are easily recognized by aid of table 4, but their full classification is again difficult because the time losses are not adequately allowed for. The coronal colors are given from within outward, and the number of exhaustions made is attached. In the first part of the table the exhaustion is smaller than in the second. When compared

TABLE 2.—PRELIMINARY DATA FOR CORONAL COLORS. LARGER GLOBE, DIAMETER 30 cm. EXHAUSTION, 76–58 cm. DISTANCE OF SOURCE, 100 cm. OR LESS.

From Table 4.	Exhaustion No.	Corona.	Exhaus. No.	Corona.[1]	Exhaus. No.	Corona.	Exhaus. No.	Corona.
1–2	1–2	Fog, rd rim	1–9	Sulphur nuclei			1	Wh, reddish
3–4	3–4	Gray gr, gr		Dense fogs	1	Wh, reddish	2	do.
5–8	5–8	Gr, rd, gr		rising from	2	Wh, cr, yl-gr	3	Wh, cr, olive
9–10	9	Wh, ol, bl, gr		bottom	3	Wh, olive, rd	4	Gr, rd
11	10	Wh, gr, bl	10–12	Wh-gr, rd	4	Gr, rd, gr	5	do.
12–13	11–12	Gr, bl, rd			5	Yl-gr, rd, ol, rd	6	Yl-gr, rd, olive
14–16	13–15	Wh, yl, rd, gr	13–19	Yl-gr, rd, bl-gr	6	Wh, rd, gr, rd		
17	16	Wh, gr, bl, rd						
18	17	Wh-yl, br						
21	18–20	Normal coronas	20	Gr, bl, rd				
			21	Wh, gr, bl, rd				
			22	Wh-yl, rd, gr				
			23–26	Normal coronas				

[1] A second experiment required 13 exhaustions before coronas appeared. Sequences of color, similar.

EXHAUSTIONS 76–53 cm.

3	1	Fog reddish	1–2	Wh, tawny	1–2	Gray, tawny[3]		
5	2	Wh, bl-gr, rd	3	Wh, olive, br-rd	3	Wh,olive,rd,br		
7	3	Yl-gr, rd, slate	4	Yl-gr, viol	4	Yl-gr, slate		
9	4	Yl, rd, gr	5	Wh, or-br, gr	5	Wh, or-rd, gr		
10	5	Wh-yl, cr, gr,[2] pk	6	Wh, cr, ol, rd, bl				
11–12	6	Wh-gr, gr-bl, rd	7	Wh, gr, cr				
13	7	Yl, br, gr, pk	8	Wh,or-rd,gr,viol				
14	8	Wh, br, bl, rd, gr						
15	9	Wh, cr, bl, gr, rd						
—	10	Wh,rd,br,bl,gr,rd						

[2] Blue later. Retrograde passage after exhaustion very marked.

Flame colors respectively, bl, bl, yl-br, pk.

with table 4, the latter therefore advance faster than those in the first part. After exhaustion (reheating) the coronas follow each other in reversed order, but they soon vanish. When the nuclei are very dense (as when obtained from burning sulphur) it may take ten or more exhaustions to clear the fogs before the colors appear probably as a result in part of unevenness of nucleation. It is then difficult to place the coronas in the second and third columns. The nuclei are not removed in thirty exhaustions, though to determine the limit greater care must be given to the filtration than was here thought necessary. The occurrence of new coronal sequences (change of the gr, rd, etc., into the rd, gr. series), after so many exhaustions is none the less striking.

9. *Axial colors.*—The final exhibit to be preliminarily made is the contrast between the color of the central field of the corona and the axial or flame color. It has been stated that the interior circular field of the coronas is at first colored and that this color is more and more invaded by diffuse white light growing from the center outward. Only after many exhaustions does the normal corona with a permanently white central field and the regular distribution of colored annuli, appear. The color of the central field always differs strongly from the axial color, and this is one of the important observations of this chapter. Indeed, the following tables show that the axial color is nearly complementary to the color of the inner field of the corona. The two are thus distinct as to the nature of their origin, and one is tempted to conclude that the colors absorbed in the axial beam are the ones which illuminate the central coronal patch.

Observation is naturally very difficult. Both colors are fleeting. The axial color is always strongly admixed with white light, which soon overpowers the effect of absorption altogether. A long column is thus needed for strong axial colors, even under favorable conditions (colors of the first order). The globe, therefore, which shows the coronas very well (admirably when projected against a black background), will not show the axial color favorably as they are necessarily projected against the flame. I endeavored to overcome this difficulty by a variety of devices, using polarized light, but without substantial results.

TABLE 3.—PRELIMINARY COMPARISON OF CORONAL CENTER AND AXIAL COLOR. EXHAUSTION, 76–58 cm.

From Table 4	Exhaust No.	Axial Color.	Coronal Center	Exhaust No.	Axial Color	Coronal Center	Exhaust No.	Axial Color	Coronal Center.	Exhaust No.[1]	Axial Color.	Coronal Center.
1	1	Bl	Fog	1	Bl	Wh-bl	1	Bl		1	Bl	Fog
2	2	Bl	"	2	Bl	"	2	Bl		2	Bl	Fog
3	3	Bl	Wh-cr	3	Bl	"	3	Bl				
4	4	?	—	4	Bl-gr	Wh-cr	4 5	Yl	Viol Bl-gr	3	Yl-br	Olive
5–6	5	Rd	Gr	5–6	Yl	Olive Gr'n	6	Or	Gr			
6–7	6	Prp	Yl-gr	7	Viol	Gr	7		Gr-yl	4	Pink	Yl-gr
7–8	7	Viol	Yl	8	Viol	Yl-gr	8	Viol	Yl			
9	8	Bl	Or	9	Bl	Yl-or						
9–10	9	Bl	Or-br									
10	10	?	Cr									

[1] Exhaustion, 76–53 cm.

Though it has not been possible to catch these colors with sufficient sharpness to pronounce them complementary, their strong and persistent contrast will at once be admitted.

10. *Polarized light.*—All the colors are produced equally well by polarized light. They are wiped out entirely between crossed nicols. The flame color is sometimes seen under these conditions, probably due to diffuse light which escapes through the polarizer or is depolarized at the windows of the apparatus. It is not possible to keep these clear during a long series of experiments, and they must be assumed to produce a ground-glass effect. Strengthened axial color may moreover be a subjective illusion.

11. *Geometric sequences of coronas.*—I shall first consider the distribution of coronas as related to the loss of nuclei by exhaustion.[1] After the preliminary results of tables 1–3, I will proceed to investigate data of a quantitative character, serving to distribute the coronas in a scale of decreasing numbers of nuclei. It will not be feasible to arrive at the complete factor at once; for the number of nuclei must at the outset be supposed to vary both with the loss or drain due to the successive equal exhaustions, and with causes independent of manual interference, such as are involved in the motion of the nucleus and its possible decay. The absorption of the nucleus by the walls of the vessel, its subsidence by gravity when loaded, etc., are here included. The experiments are necessarily complicated and according as one places more stress on the incidental or the normal causes, different conclusions are to be drawn. It is the purpose first to determine the most potent and obvious cause of dissipation.

Accordingly in table 4 the effect of exhaustion alone is first fully treated. The large globe was exhausted and refilled with filtered air about 20 times in succession, the pressures falling off suddenly from normal to about 18 cm. less. To secure efficient filtering of the air which supplied the place of that removed, very slow influx through the compressed cotton and the check valve was maintained. It is assumed that with each exhaustion a definitely decreasing number of nuclei are removed with the air. Thus after z isothermal exhaustions from the pressure p_0 to the pressure p, the residue of nuclei should be $(p/p_0)^z$; after z adiabatic exhaustions between the same limits $(p/p_0)^{z/\gamma}$, where γ is the ratio of specific heats, admitting (which is by no means the case as is afterwards shown), that the whole experiment is made expeditiously enough to neglect the time losses of nuclei due to the normal causes mentioned. In order to give greater probability to this assumption I selected large exhaustions, from $p_0 = 76$ cm. to $p = 58$ cm., or a mean pressure decrement of 18 cm.

In two successive experiments which showed a reasonable order of agreement, the color sequences of the coronas were observed from the center outwards, while the corresponding flame or axial colors were simultaneously noted; but here there is uncertainty from the small relative thickness (30.5 cm.) of the axial layer of water

---

[1] Loss due to subsidence of fog is not considered here but will be treated in Chap. III, §§ 5, 7, 11. The time during which fog is in evidence must be made as short as the observations will permit. As a rule the corona is lost by evaporation, at once.

Table 4 contains the results, the exhaustion being from 76–58 cm. Where different colors were seen, which may be either errors of judgment or real differences of contiguous coronas, this is usually noted by inserting both colors on the same line. The colors being very fleeting it is out of the question to await rigorous isothermal conditions; neither is it certain that the colors were caught for the adiabatic state of compression. A small allowance of time after exhaustion must be granted for judgment. Hence the computations will be made both for isothermal and for adiabatic conditions, leaving the true result to be derived below. The general agreement of coronas seemed to vouch for this method of combating, partially at least, an inherent difficulty. The third column of the table shows n [illegible] (P/P_0).

TABLE 4.—COLOR SEQUENCES OF SUCCESSIVE CORONAS. EXHAUSTION 76–58 cm.

Exp. No.	Colors.	[illegible]	[illegible]	[illegible]
1	[illegible]	764	[illegible]	793
	[illegible]	553	[illegible]	629
3	[illegible]	446	[illegible]	499
4	Y, rd, bl-gr	342		396
	B, gr, rd	266	Yl	313
6	Gr, or	199	Or	249
	Gr-bl, bl, rd, gr, rd	152		197
	Y, br, or, gr, rd	116	[illegible]	156
9	Y, [illegible], gr, [illegible] rd	79		124
10	W, or, y, gr, rd, gr	65		98
11	Wh, [illegible] bl, rd, gr, rd	52		75
	[illegible], green, rd, bl-gr, rd	39		62
13	Y, gr, or-rd, gr, rd	37		49
14	W, br, gr, rd	23		39
15	W, or, gr, rd, gr	18		31
16	W, br, bl-gr, rd gr	13		24
17	W, bl, gr, rd, br, gr	10		19
18	Y, [illegible], bl-gr, [illegible]	9		15
19	W, br, gr, rd	6		12
	[illegible]	5		10

Ignoring decay and similarly spontaneous time losses due to the motion of the nucleus, there is here given a scale of optical effects related to the nuclei in a given volume of air saturated with aqueous vapor and to the given exhaustions. As more nuclei are present the condensed water globules are finer, remembering that the medium is always identically super-saturated. For this and other reasons (re-heating of the adiabatically cooled air), only the momentarily fixed corona follow ing a given exhaustion has a real meaning, and the cloud particles are as a rule so fine that their subsidence during the observation periods may be neglected except when the final and normal coronas are approached. The interpretation of these coronal sequences is now possible with a degree of probability, by using the scale of colors of Newton's interferences, with which they are liable to agree in succession. An excellent scale of this kind is given by Quincke and quoted in Kohlrausch's *Leitfaden der praktischen Physik.* The correspondence of the colors of coronal annuli, if worked out in this way, will not be very perfect; but there is an obvious general agreement of sequences, if the central field only of the corona is taken.

The axial color or color of the full flame stated in table 4 is seen to make up a similar sequence ahead in phase and nearly complementary to the central patch of the corona. This will be separately investigated below, § 19 et seq.

If the normal loss of nuclei in table 4 could be excluded, the succession of coronas would represent a geometric progression as to the number of nuclei, each term corresponding to a number $y = p/p_0$ or else $(p/p_0)^{1/\gamma}$ times less than the preceding. The advantage of this system will presently be shown, together with an attempt to remove the time loss, which is also probably geometric. Meanwhile, the corona of the x^{th} order is due to $N = y$ particles, relatively speaking.

12. *Loss of nuclei in the lapse of time* (without exhaustion). To ascertain in how far such an interpretation as is given in the last paragraph is admissible and to correct it for other simultaneous losses, it is necessary to determine the decrease of nuclei when the receiver is left for long intervals, as far as possible without exhaustion or other manual interference. In the following experiments the time between the inevitable exhaustions (usually about 96 sec., above) is prolonged to thirty minutes or even an hour. The first column of table 5 denotes the number of the exhaustion (with refilling of filtered air), the second the time at which it was made, the third the minutes elapsed since nucleation. The fourth column gives the color sequences of the coronas obtained, and these as a rule are easily recognized in order, by comparison with table 4. The coronal number in the series or order is put in the last column. Knowing the number of the corona, the approximate or uncorrected residual number of nuclei (p/p_0) may be taken from table 4. The remarks show that fogs are often spontaneously produced without change of pressure (open stop-cock communicating with the atmosphere through the cotton filter). The bearing of this on the present results is chiefly in the form of an error induced by the subsidence of the loaded nuclei. Its theoretical bearing beyond this is also to be kept in mind. Table 5 contains three independent experiments, in which the times between exhaustions are varied.

The next step to be taken is in reference to the losses of nuclei inherent in the method by which the data were obtained. For orientation the data of table 5 containing the residual nuclei, may be constructed in their dependence on the lapse of time. The graph, figure 4, is of the exponential character expected, with this difference, however, that the number of nuclei in the three cases does not diminish with the frequency of the exhaustion. Thus in case (1) the number is even less than in case

(2) and not much greater than in case (3). In spite of the fact that the experiments can not be said to begin with the same initial saturation of nuclei, the effect

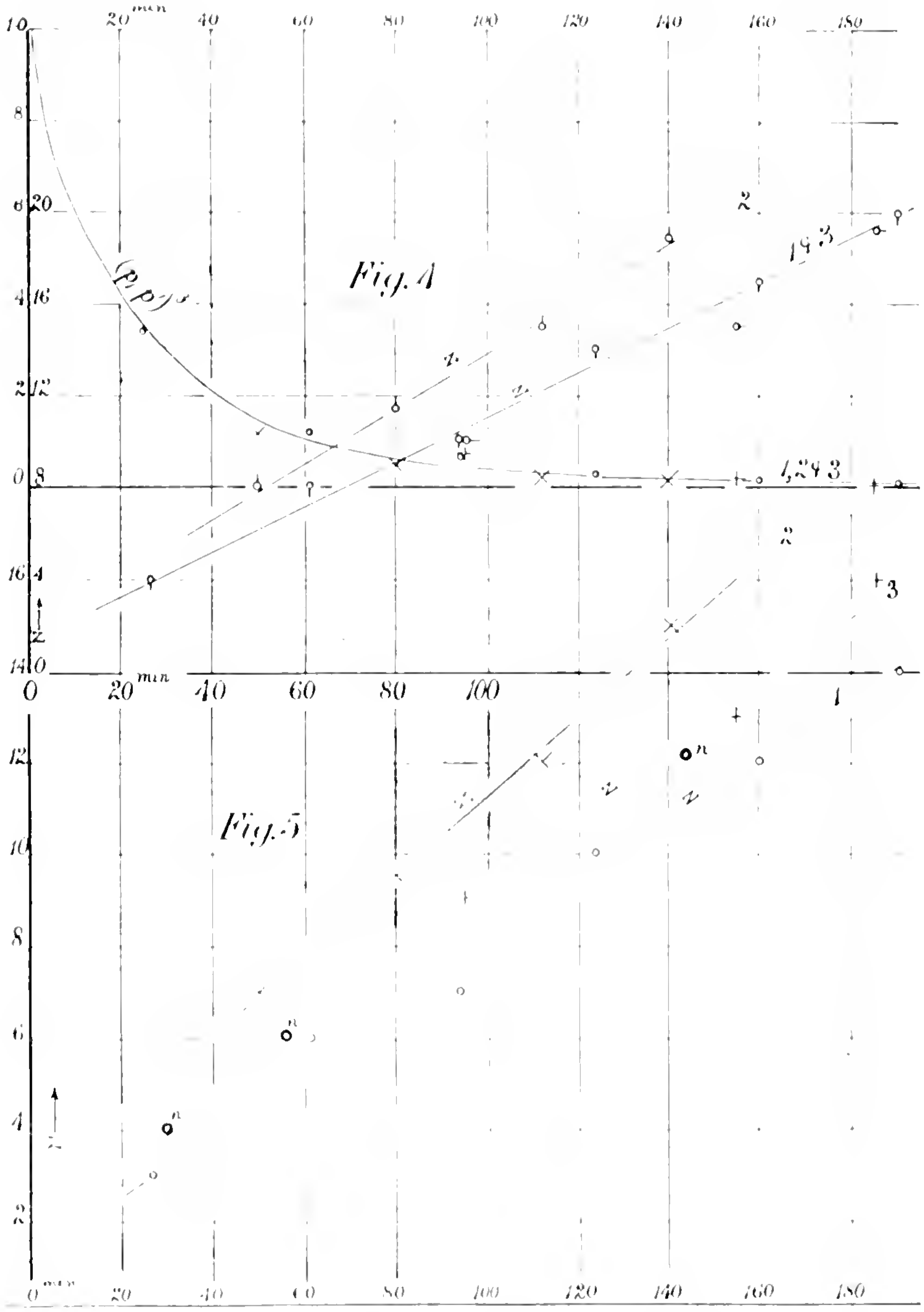


Fig. 4. Chart illustrating the Nature of the Time Losses.
Fig. 5. Chart for Computing the Time Coefficient.

of exhaustion should be more apparent inasmuch as nearly 1/4 of the nuclei are removed. One infers that either the number of nuclei is not changed by exhaustion, correspondingly greater numbers being produced at low pressure to make up for the loss, or more probably, that the time losses obey similar exponential laws to the exhaustion losses. In the former case if n is the nucleation and p the pressure, np = const. is apparently suggested; but this startling proposition is at variance with the results as a whole. The following theory is therefore a more rational systematization of the data and follows the alternative view, for which other cogent evidence might be adduced. Thus in table 4, the losses which occur in the 1–2 minutes between the exhaustion, in table 5 take place in a much longer time, say 7 minutes between the exhaustions; corona 4 is reached in table 5 in about 30 minutes, but in table 4 it appears in about 4–8 minutes, etc.

TABLE 5.—LOSS OF NUCLEI FROM NORMAL CAUSES IN THE LAPSE OF TIME. EXHAUSTION, 76–58 cm.

Exhaust. No.	Time.		Time elapsed, t.	Corona.	Remarks.	From Table 4	
						Coronal order, z.	(f/f_0)
	h.	m.	min.				
0	9	53	0	Nucleation	Spontaneous fog before exhaustion	0	1.000
1	10	20	27	wh, viol, yl		4	.340
2		54	61	wh, yl, br, gr, rd		8	.116
3	11	27	94	wh, cr, yl-gr, rd, gr		10	.068
4		57	124	wh, br, gr, rd		14	.023
5	12	33	160	wh, gr, cr, yl-gr, gr		17	.010
6	1	3	190	wh, br, gr, rd	Small coronas	20 ?	.005
7	2	45	292	no color		——	.000
0	2	50	0	Nucleation	Twice nucleated Spontan. fog	0	1.000
1	3	40	50	yl, cr, gr, rd		8	.116
2	4	10	80	gr, rd, gr, rd		11–12	.040
3	4	42	112	cr, br, gr, viol, rd		15	.018
4	5	10	140	wh, br, gr, rd, gr	Small coronas	20 ?	.005
0	9	30	0	Nucleation		0	1.000
1	11	5	95	wh,viol,cr,yl-gr,rd,gr		10	.068
2	12	5	155	wh-cr, br, gr, rd		15	.018
3	12	35	185	wh-cr, br, gr, rd		19	.005

For the sake of completeness figure 4 also contains the succession of orders z observed in the lapse of time in the three series.

13. *Working hypothesis.*— Let z be the order of the corona (exhaustion number), N the number of nuclei producing it for the fixed supersaturation. Without correction for time losses, $N = y^z$, where $y = p/p_0$ under isothermal and $y = (p/p_0)^{1/\gamma}$ under adiabatic conditions, p_0 and p begin the pressures before and after exhaustion.

The data of the preceding section show that N apart from exhaustions suffers a time loss varying as $(a + bt)$ in the time t, where a and b are constants. Hence the above equation must be corrected to read,

$$N = y^{z(1+bt)},$$

to admit of both losses of similar geometrical character. Finally the initial nucleation is not identical in the different experiments, whence if $N_0 = y^{z_0}$,

$$N = 10^{(z_0 + z(1+bt))\log y}$$

is the final form of the equation.

If in two experiments beginning with two different nucleations, N_0 and N'_0, the same corona or N is reached for different times, t and t', and different numbers of exhaustions, z and z', of the same ratio, y, then $N = N'$, and therefore

$$10^{(z'+bt')\log y} = 10^{(z'_0 + z(1+bt))\log y}$$

where for brevity $z_0 = 0$ and $N_0 = 1$. Thus

$$b = \frac{z' - z - z'_0}{t' - zt}.$$

If two identical coronas are reached, the z'_0 may be eliminated or

$$b = \frac{z_1 - z_2}{(t' - zt)_1 - (t' - zt)_2},$$

where the first identical coronas are seen for N_1, z_1, t_1; N'_1, z'_1, t'_1;
and the next for N_2, z_2, t_2; N'_2, z'_2, t'_2.

The plan is, therefore, to obtain an even number of identical coronas in case of tables 4 and 5, and then to compute b from equidistant groups of two in the way suggested.

TABLE 6.—TIME RATES, $b =$ [illegible]

[illegible]	n	n'	[illegible]	mean b
27	1	4	86	.081
61	2	8		
94	3	1	71	
124	4	14	87	
16[illegible]	5	17		
19[illegible]	6	2		
202	7			
5	1	8	140	.140
[illegible]	2	11.5	140	
11[illegible]	3	15		
14[illegible]	4	19		
			96	.107
95	1	1	119	
1[illegible]5	2	15		
1[illegible]5	3	19		

14. *Application.* The results of tables 4 and 5, if treated in this way, give rise to table 6. The time interval between the successive coronas in table 4 was about $t = 1.6$ min. The other quantities are fully given in the table. It will be seen that for each of the series (1), (2), (3), the value of b is as nearly constant as is possible under the method of observation. The lines of figure 5 are constructed to

show this, and to show also that the slopes, b, are different, being .08, .14, and .10, respectively. The mean of these values, if a double weight be given to the first, is $b = .1$, and as this agrees with the independent experiments made with the drum below, § 24, and marked n in figure 5, it will be taken. In fact, a correction of table 4 is here chiefly aimed at, and it is thus not necessary to insist on accurate values of b. In succeeding chapters, however, b will be used to estimate the velocity of the nucleus, and it must then be called to mind that an order of values is alone foreshadowed.

If now the value of N in table 4 be corrected in accordance with

$$N = 10^{z(1+bt)\log y}$$

where in case of isothermal exhaustion $y = .764$, $t = 1.6$ minutes, $b = .1$, the data of table 7 result, giving the number of particles N_i corresponding to the successive coronas.

TABLE 7.—VALUES OF $N_i = 10^{z(1+bt)\log y}$
$y = p/p_0 = .764$
$b = .10$
$t = 1.6$ min.

z	$N_i \times 10^3$	z	$N_i \times 10^3$	z	$N_i \times 10^3$	z	$N_i \times 10^3$
0	1000	6	153	12	23	18	4
1	731	7	112	13	17	19	3
2	535	8	82	14	12.5	20	2
3	391	9	60	15	9		
4	286	10	44	16	7		
5	209	11	32	17	5		

For adiabatic conditions, since $y = (p/p_0)^{1/\gamma}$, if $\gamma = 1.4$, $y = .825$. Hence for identical t and b the values, N_a, of table 8 result.

TABLE 8.—VALUES OF $N_a = 10^{z(1+bt)\log y}$
$y = (p/p_0)^{1/\gamma} = .825$
$b = .10$
$t = 1.6$ min.

z	$N_a \times 10^3$	z	$N_a \times 10^3$	z	$N_a \times 10^3$	z	$N_a \times 10^3$
0	1000	6	262	12	69	18	18
1	800	7	210	13	55	19	14.4
2	640	8	168	14	44	20	11.5
3	512	9	134	15	35		
4	409	10	107	16	28		
5	327	11	86	17	22.5		

15. *Globe experiments repeated.*—In the above experiments, § 14, the time between exhaustions was only approximately determined and its importance was not at that time apprehended. Hence in the following cases, tables 9–12, the time record is continuous. A variation is also made in the nucleation. The first two tables hold for punk nuclei, the third for sulphur nuclei emanating from the flame, the last for phosphorus nuclei supplied by a small pellet and therefore weak. In general all the series terminate when the coronas are normal and about double

the size of lycopodium coronas under like conditions. The method of finding N will be presently further explained. It has been corrected for precipitation of moisture.

TABLE 9.—CORONAS IN LARGE GLOBE, DIAMETER 30 cm. PUNK NUCLEI. EXHAUSTION, 76–58 cm. $b = 10$. $t = 1.65°$ $y = 819$. LIGHT DISTANCE, 50 cm. $\log N = z\,(1+bt)\log y$.

Exhaustion No., z.	Time.	Corona.	N	$\sqrt[3]{1/N}$
0	0^m 0	Double nucleation	1.000	1.000
1	1 15	Tawny uniform	.793	1.08
2	3 0	Tawny	.629	
3	4 45	Tawny, reddish	.499	
4	6 30	Gray, reddish	.396	
5	8 0	Wh, viol, gr-yl	.313	1.47
6	9 45	Wh, bl-gr, yl, rd	.249	
7	11 20	Wh, ap-gr, rd	.197	
8	13 0	Wh, yl-gr, prp	.156	
9	14 45	Wh, yl, rd, gr	.124	
10	16 15	Wh, or, rd, gr	.098	2.17
11	18 0	Wh, cr, gr, rd	.078	
12	19 45	Wh, viol, gr-yl, rd	.062	
13	21 15	Wh, ap-gr, rd, gr	.049	
14	23 0	Wh, gr-yl (?), rd	.039	
15	24 30	Wh, cr, gr, rd	.031	3.19
16	26 15	Wh, cr, gr, rd, gr	.024	
17	27 45	Wh, ol-gr, rd, gr	.019	
18	29 30	Wh, br, bl, gr, rd	.015	
19	31 0	Wh, cr, gr, prp	.012	
20	32 30	Wh, br, bl, rd, gr	.010	4.69
21	34 15	Wh, br, gr, rd	.008	

TABLE 10.—CORONAS IN LARGE GLOBE. CONSTANTS AS IN TABLE 9. PUNK NUCLEI. $\text{Log}\,N = z\,(1+bt)\log y$.

Exhaustion No., z.	Time.	Corona.	N	$\sqrt[3]{1/N}$
0	0^m 0	Single nucleation	1.000	1.00
1	1 0	Tawny fog	.793	1.08
2	2 45	Tawny	.629	
3	4 15	Wh, cr, gr	.499	
4	5 45	Wh, viol-rd, gr-yl	.396	
5	7 30	Viol, ol-gr, or-br	.313	1.47
6	9 0	Wh, ap-gr, or-rd	.249	
7	10 30	Wh, yl-gr, prp	.197	
8	12 15	Wh, yl, rd, gr	.156	
9	14 0	Wh, yl-or, rd, gr	.124	
10	15 30	Wh, cr, gr, rd	.098	2.17
11	17 15	Wh, viol-rd, gr-yl, rd, gr	.078	
12	18 45	Wh, gr, rd, gr	.062	
13	20 30	Ap-gr, rd-v, gr-yl	.049	
14	22 0	Wh, yl-gr, br, gr, rd	.039	
15	23 30	Wh, cr, gr, rd	.031	3.19
16	25 15	Wh, br, rd, gr, rd	.024	
17	27 0	Wh, gr, rd, gr	.019	
18	28 30	Wh, br, gr, rd	.015	
19	30 0	Wh, cr, gr, rd	.012	
20	31 45	Wh, bl, rd, gr	.010	4.69
21	33 15	Wh, br, gr, rd	.008	

TABLE 11.—CORONAS IN LARGE GLOBE. SULPHUR NUCLEI (FLAME). $t = 1.71$ min. OTHER CONSTANTS AS IN TABLE 9. $\text{Log}\, N = z\,(1 + bt) \log y$.

Exhaustion No., z.	Time.		Corona.	N	$\sqrt[3]{1/N}$
0	$0^{m.}$	$0^{s.}$	Double nucleation	1.000	1.000
1	1	30	Densely tawny	.791	1.08
2	3	15	Densely tawny	.626	
3	5	0	Tawny. Red edged	.495	
4	6	45	Tawny. Red edged	.392	
5	8	30	Fog. Red edged	.310	1.48
6	10	0	Fog. Red edged	.245	
7	12	0	Fog. Red edged	.194	
8	13	45	Fog. Red edged	.154	
9	15	30	Wh, bl-gr, rd	.122	
10	17	0	Wh, gr, rd	.096	2.18
11	18	45	Wh, yl-gr, rd	.076	
12	20	30	Wh, yl-br, gr	.060	
13	22	15	Wh, or, rd, gr	.048	
14	24	0	Wh, rd, gr, prp	.038	
15	25	45	Wh, viol-rd, gr-yl	.030	3.19
16	27	30	Wh, ap-gr, rd, gr-yl	.024	
17	29	15	Wh, yl-gr, prp, gr-yl	.019	
18	31	0	Wh, br, gr, prp	.015	
19	32	45	Wh, cr, gr, prp	.012	
20	34	30	Wh, br, bl, br, gr	.009	4.76
21	36	15	Wh, gr, bl, prp, gr	.007	
22	37	45	Wh, cr, gr, prp	.006	
23	39	45	Wh, br, gr	.005	
24	41	30	Wh, gr, bl, rd, gr	.004	
25	43	15	Wh, br, gr, rd	.003	7.04
26	45	0	Wh, br, bl, gr, rd	.002	

TABLE 12.—CORONAS IN LARGE GLOBE. PHOSPHORUS NUCLEI. $t = 1.75$ min. OTHER CONSTANTS AS IN TABLE 9. $\text{Log}\, N = z\,(1 + bt) \log y$.

Exhaustion No., z.	Time.		Corona.	N	$\sqrt[3]{1/N}$
0	$0^{m.}$	$0^{s.}$	Nucleation	1.000	
1	1	0	Wh, reddish	.791	
2	2	45	Wh, reddish	.626	
3	4	30	Wh, cr, gr-*rl*	.495	
4	6	10	Wh, viol-rd, gr-yl	.392	
5	8	0	Wh, gr, or-br	.310	
6	9	45	Wh, gr, rd	.245	
7	11	30	Wh, yl-g*r*, prp	.194	
8	13	15	Wh, gr-*rl*, prp, gr	.154	
9	15	0	Wh, rd, gr, prp	.122	
10	16	45	Wh, cr, gr, prp	.096	
11	18	30	Wh, bl, rd	.076	
12	20	15	Wh-gr, rd, gr-yl	.060	
13	22	0	Wh, yl-br, gr, rd	.048	
14	23	45	Wh, rd, gr, prp	.038	
15	25	45	Wh, rd, bl, gr, rd	.030	
16	27	30	Wh, gr, bl, rd, gr	.024	
17	29	0	Wh, br, gr, rd	.019	
18	31	0	Wh, cr, gr, prp	.015	
19	22	30	Wh, br, bl, rd, gr	.012	
20	34	15	Wh, br, bl, gr, rd, gr	.009	

The coronas of tables 9 and 10 correspond very nearly, except that the former is one exhaustion ahead of the other. This clearly corresponds to the double nucleation (nuclei added in each of the first two successive exhaustions) in the first case. Table 11 shows the apparently intense nucleating efficiency of the sulphur flame, and nearly 8 exhaustions are needed to bring out the first corona. This series is thus five exhaustions ahead of table 10 and four exhaustions ahead of table 9. Apart from this the coronas, if minor differences of tint be neglected, may readily be placed. In table 12, the colors agree with table 9 up to the tenth, after which the former skips one corona and is in advance of the latter.

VALUES OF THE NUCLEATION CORRECTED.

16. *Amount of precipitation.* In the preceding tables the limits of the nucleation N are defined between isothermal and adiabatic conditions. The actual case (apart from experimental difficulties) is neither the one nor the other, because of the accession of heat received from the precipitated water. The rigorous equation for this is, I believe, known, but the computation may be made sufficiently close and perspicuously by the following method of successive approximation.

Let ϑ and ϑ' be the original and final absolute temperatures, corresponding to the pressures p and p' and the densities ρ and ρ'. Then approximately

$$\frac{\vartheta'}{\vartheta} = \left(\frac{p'}{p}\right)^{(\gamma-1)/\gamma} = \left(\frac{\rho'}{\rho}\right)^{\gamma-1}. \tag{1}$$

Let S be the entropy (per gram) of a mixture of vapor and liquid in the ratio of $x/(1-x)$. Then

$$S = C\lg\vartheta + rx/\vartheta,$$

if ϑ is the temperature of the mixture, r the latent heat of evaporation, C the specific heat of the liquid, and natural logarithms are used. Since $C = 1$, and the mixture is initially all vapor expanding adiabatically, $\lg\vartheta + r/\vartheta = \lg\vartheta' + r'x'/\vartheta'$, which with the approximate equation (1) becomes

$$x' = \frac{\vartheta}{r'}\left(\frac{r}{\vartheta} - \lg\frac{\vartheta'}{\vartheta}\right)\frac{\vartheta'}{\vartheta}, \tag{2}$$

where $1 - x'$ is the quantity of water precipitated per gram of mixture, if the heat thus evolved is neglected. Since at 20°, $\vartheta = 293°$, $r = 589$, $r' = 582$, $\gamma = 1.1$, $p'/p = 58/76$, therefore $x' = .949$ and $1 - x' = .050$, where r' is introduced under the assumption that the cooling reaches 0° C., in equation (1).

The next approximation is an allowance for the heat evolved. The saturated air at 20° contains 17.2×10^{-6} grams of moisture per cub. cm. or .0142 grams of moisture per gram of air. The amount of water condensed is thus $.050 \times .0142 = 710 \times 10^{-6}$ grams, and the heat evolved $710 \times 10^{-6} \times 590 = .419$ calories per gram of saturated air.

But from equation (1) $\vartheta' = 271.2$ and since the specific heat of air is .237, about $.237 \times 21.8 = 5.17$ calories are absorbed in the adiabatic expansion of one gram of air. The available .419 calories due to condensation will heat this, $.419/.237 = 1.77°$ C., which is the correction to be added to ϑ'.

The data for computing x' are now $\vartheta = 293°$, $\vartheta' = 271.2 + 1.8 = 273°$, $r' = 582$, $r = 589$, whence

$$x' = \frac{\vartheta'}{\vartheta}\left(\frac{c}{r} + \frac{\vartheta}{r}\lg\frac{\vartheta}{\vartheta'}\right) \qquad .954$$

and $1 - x = .046$ grams of water obtained from each gram of vapor. Thus $17.2 \times 10^{-6} \times .046 = 790 \times 10^{-9}$ grams of water separate out per cub. cm. of moist air.

17. *Numerical values.*—One observes in passing that if 5×10^4 nuclei are present per cub. cm., of the saturated emanation, the number inferred in the first volume of these researches, then $(790 \times 10^{-9}) / (5 \times 10^4) = 16 \times 10^{-12}$ cub. cm. is the volume of each water particle or about .00025 cm. its diameter at the outset. This agrees very well in order with the results obtained directly for coronas below.

To find N in the tables, the equation

$$N = 10^{s(1 + bt)\log y}$$

is given by experiment, where y is the ratio of densities after and before any exhaustion. Hence since initially $\vartheta = 293$, $p = 76$ cm., and finally $\vartheta' = 273$ and $p = 58$ cm.,

$$y = \frac{\rho'}{\rho} = \frac{p'/\vartheta'}{p/\vartheta} = \frac{58 \times 293}{76 \times 273} = .819.$$

Again the interval of time, t, between the exhaustions, is on the average 1.65 minutes in table 9, 1.61 minutes in table 10, 1.74 minutes in table 11, 1.75 minutes in table 12. Consequently, for tables 9 and 10

$$N = 10^{-s\,(1.163) \times .0866} = 10^{-.1007\,s}$$

may be assumed, and in tables 11 and 12

$$N = 10^{-s\,(1.175) \times .0866} = 10^{-.1017\,s}$$

is the corresponding equation. With these constants the values, N, of the tables were computed.

18. *Relative size of cloud particles.*—Assuming that the same amount of vapor is condensed per cub. cm. in each expansion between fixed pressures of the moist air in the receiver, the relative size of particles may be computed for the given orders of coronas. If the size of the particles of any one order is known, all would be found absolutely. It is only after about 20 exhaustions that the ordinary normal coronas are encountered. The next table (13) contains an example of typical cases. It shows that there is not a striking variation of diameters to correspond with the startling variation of coronas. These are therefore a rather sensitive criterion of the changes of diameter of the cloud particles.

TABLE 13.—RELATIVE SIZE OF CLOUD PARTICLES.

Order of corona, s.	$N \times 10^3$.	Bulk of particle.	Diameter of particle.
0	1000	1.0	1.0
1	793	1.3	1.1
5	313	3.2	1.5
10	98	10.2	2.2
15	31	32.1	3.2
20	10	103	4.7
25	3	329	6.9
30	1	1075	10.2

RESULTS FOR AXIAL COLORS.

19. *Apparatus, conical drums.* It will next be necessary to devise apparatus to show greater intensity of axial color (the colors of the steam jet or color tube of my first volume), with the necessary relation to the coronas. This was originally attempted with tubular apparatus; but, in the interest of homogeneity, wide conical apparatus was finally constructed, either a single or a double conical drum subserving the purpose. Effective convection is then continually in action within, and the density of distribution of cloud particles is uniform, slow work presupposed. With the double drum (apices outward), not only can greater length of column be secured, but small end windows of glass suffice. The instrument is thus less troublesome than the single drum, the broad glass base of which is liable to break explosively, after many exhaustions, from fatigued elasticity.

The single drum is shown in figure 6, being made of sheet copper, about 77 cm. long, 5 cm. in diameter at the smaller glass window, *a*, 30 cm. in diameter at the large glass window, *bb*. *W* is the Welsbach burner behind a small circular screen, *d*, is the exhaustion and *c* the influx tubulure holding a cotton filter, *f*. The supply of water, *w*, keeps the air within saturated. The interior walls must be dull black to obviate reflection from the sides of the drum as much as possible; for all coronas are advantageously projected against a dark ground. Ribs *r*, *r*, *r*, *r*, prevent collapse under external pressure when the interior is exhausted.

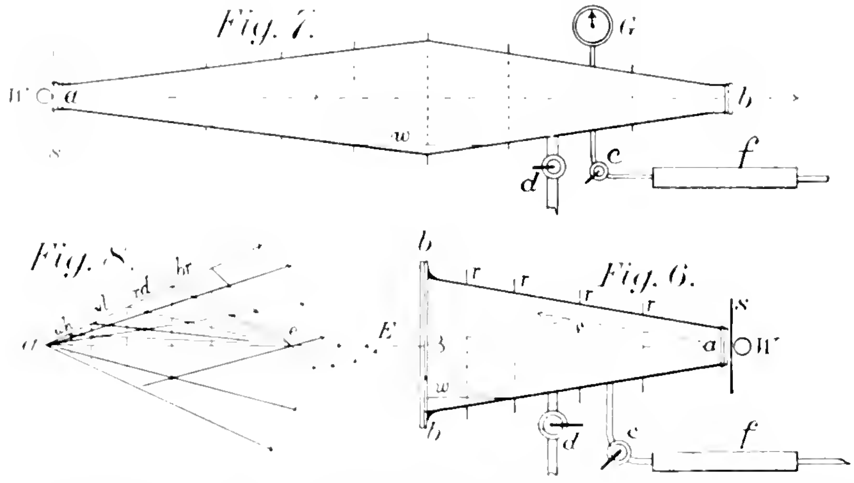


FIG. 6.—CONICAL DRUM FOR [illegible] CONDENSATION. FIG. 7.—DOUBLE CONICAL DRUM FOR [illegible] CONDENSATION. FIG. 8.—DIAGRAM RELATING TO DIFFRACTION AND TO AXIAL COLORS.

When flame or axial colors are to be specially studied, it is best to remove the screen from the burner and look at the full extent of the flame. Ground glass as large as the window, *a*, and illuminated by sunlight, is also very good. With the eye at *E*, *aE* marks the path of an axial color, *aeE* the path of a diffraction color.

The double drum, figure 7, differs from the single drum merely by offering a greater length of column for observation. It is 180 cm. long, 30 cm. in its largest diameter, and is carefully blackened within. The small windows, *a*, *b*, insure greater safety of observation. Each window may be replaced by an aluminum window for X-rays, etc. *G* is the gauge, *d* the exhaustion, *ef* the influx tubulure. When nuclei are to be introduced, the filter, *f*, is removed.

20. *Preliminary observations. Single drum.*—The following are a few results with the single drum, the window being screened off to a small circle:

TABLE 14.—AXIAL COLORS SEEN IN THE SINGLE DRUM, 77 cm. LONG, 30 cm. DIAMETER AT BASE. EXHAUSTION 76-50 cm. PUNK NUCLEI.

Exhaustion No.	Order from table 19.	Corona.	Axial color.	Remarks.
1	1	Yl, rd	Stone blue	
2		Yl, rd	Stone blue	
3	9	Ol-gr	Or-br	Preceding colors flashed through
4	12	Yl, cr	Pink	
5	15	Cr, gr, rd	Gr	
6	18	Ap-gr, rd	Yl	
7		Wh, cr, gr	Wh-gr	
8		Wh, br, gr	Wh-gr	
9		Wh, br, dk-bl, rd	Wh-gr	
10–12		None	Wh	Rain

The following results were obtained with a ground glass screen, affording a large patch of flame color. The contrasts of color between the flame and the coronal center are again the marked feature:

TABLE 15.—AXIAL COLORS SEEN IN THE SINGLE DRUM. CONSTANTS AS IN TABLE 14. GROUND GLASS SCREEN.

Exhaustion No.	Coronal center.	Axial color.	Coronal center.	Axial color.
1	Colorless	Sky bl	Colorless	Bl
2	"	Bl-gr	"	Bl-gr
3	Ol-gr	Yl-br	Viol	Yl-gr
4	Gr	Pink	Gr-bl	Yl-br
5	Yl	Viol	Gr	Yl-br
6	Rd	Gr ?	Yl	Prp-viol
7	Cr	Yl	Or-rd	Viol
8	Gr	Viol	Violet ?	Yl

The exhaustion proceeds too rapidly here to bring out all the coronal sequences. Intermediate cases are skipped, which is confusing. All color display begins with a rush from the first flame and first corona to the last, as the particles increase in size to a limit. Thereafter the phenomenon shows a tendency to reverse, but it is much slower, soon obscured, and then vanishes. Owing to the difficulty of deciding between these fleeting color contrasts, I have in the following table included a group of incidental results for different exhaustions made at different times.

TABLE 6. PROMISCUOUS COMPARISONS OF AXIAL AND FIELD COLOR (CORONAL CENTER) MADE IN THE SINGLE DRUM.

No.	(1)		(2)		(3)		(4)		(5)		(6)		(7)		(8)	
	Axis.	Field.	Axis.	Field.	Axis.	Field.	Axis.	Field.	Axis.	Field.	Axis.	Field.	Axis.	Field.	Axis.	Field.
1	Bl		Bl	Colorless	Bl	Colorless	Bl	Colorless	Bl	Colorless	Bl	Colorless	Bl	Colorless	Bl	Colorless
2	Bl-gr		Bl-gr	"	Bl-gr	"	"	"	Bl-gr	"	"	"	"	"	Bl	"
3	Green		Yl-gr	Slat	Yl-gr	Prp	"	"	Gr-yl	"	Bl-gr	"	"	"	Yl	"
4	Or	Gr	Green	Bl-gr	"	"	"	"	Br	Bl-gr	Bl	"	Or	Bl-gr	Or	Bl-gr
5	Prp	Yl	Viol	Yl	Or-br	Bl-gr	Bl-gr	"	Or	"	Gr-yl	Purplish	Prp	Yl-gr	Prp	Yl-gr
6			Bl	Rd	Yl	Gr	——	"	Prp	Yl	Yl	Bluish	Bl	Or	Viol	Yl
7			Gr	Gr	Prp	Yl-gr	Yl-gr	-	Bl	Or, gr	Straw-yl	Bl-gr	Gr	Rd	Bl-gr	Or-rd
8					Viol	"	Yl		Gr	Cr, yl	Br	"	Yl?	Gr		
9					Bl	Or	Or-br	Bl-gr	Wh	Cr, gr	Prp	Yl-gr				
10							"	"			Viol-bl	Wh, yl				
11							Or-yl	Gr			Wh-gr	Prp				
12							Prp	Yl-gr			Wh-yl-gr	"				
13							"	"			Wh	Wh				
14							Viol	"								
15							Bl	"								

(1), (2), exhaustion 76–50 cm.
(3), (5), (6) " 76–57 cm.
(4) " 76–66 cm.

(6), sunlight and ground-glass screen.
(5), (6), punk nuclei.

The coronal center which corresponds to the initial blues and blue greens of the table, is not determinable as to color, when seen in the drum; in the globe, it appeared to be a diffuse red-rimmed fog. The first pronounced color contrast which appears is the orange-red axial color and the blue-green or green-blue field. This is usually easily obtained, and is complementary in character. The axial colors then move toward violet and the field colors toward yellow. After this, the axial colors are already nearly white, or the tinge of color is so faint that it would be hard to recognize it, if the color sequences were not known from the steam jet. Nevertheless the march of axial colors into bluish, greenish, and yellowish tints, corresponds to a march of the field from yellows into reds and purples. The colors thus follow each other around the circle, apparently, diametrically opposed in position. If the exhaustions are either too large (1 3) or too small (1 6), the colors are less easily recorded than for intermediate cases.

In none of my experiments were the yellows of the first order, which appear so splendidly in the steam tube, obtained, blue being the first axial color. The endeavor was made to reach these results by placing the phosphorus ionizer within the drum. The result was unfavorable; ordinary smoke filaments tracing the path of the convection currents appeared. The first exhaustions produced irregular fogs only. Colors did not appear clearly until the 9th exhaustion, and they had then already run into higher orders.

As the colors of the annuli are projected on the walls of the drum, as in figure 8, their angular value for a fixed position of the eye at *e* might be read off on an annular scale within the drum. Diffraction of the particles within the axial beam, *ae*, would remove white light. Hence absorption (which may be interference) of some kind must be looked to, to explain these colors and it is not unreasonable to suppose that the central field is illuminated by the color axially absorbed.

21. *Polarized light.*—On looking through the single drum with an analyzer, it appears that neither the axial colors (as a rule) nor the coronas are polarized. Both are produced with the same vividness, *cæt. par.*, when the source of light is polarized as when it is not so. No coronal light passes between crossed nicols. With the axial colors a peculiar result was obtained for the particular length of column here used (77 cm.). The colors of higher orders, if produced by polarized light, seemed to pass with increased saturation through the crossed polarizer, while the lower orders of colors were quite damped out. This was particularly the case with the violet purple of the second and even of the third order, the latter of which I had not seen before. The observation is brought out in the following table, the results of which were obtained independently, twice.

TABLE 17.—AXIAL COLORS, ETC., IN POLARIZED LIGHT.

Exhaustion No.	Polarized light. Polarizer and analyzer crossed. Axial colors.	Common light.	
		Axial colors.	Field colors.
1	Dk	Bl	Fog
2	"	"	"
3	"	"	" red rimmed
4	" to purple	Yl to cr	Ol
5	Deep violet [1]	——	Gr, yl-gr
6	Violet	Wh, violet ?	Gr-bl
7	Bl	White	Yl
8	Bl	"	Wh, prp
9	Yl	"	Wh, bl-gr
10	Violet	"	Yl gr
11	Gr	"	Wh-cr
12	Blue ?	"	

[1] Colors 5–12 seen through crossed nicols.

Having obtained these suggestive results, I anticipated a similar intensification of the axial colors, when produced by columns either longer or shorter. Accordingly, the globe, giving a column 30 cm. in length, and the double drum, with a column 180 cm. in length, were similarly adjusted between crossed nicols. In neither case was any noteworthy result obtained. The dark polarized field remained dark throughout. This throws some doubt on the preceding investigations. The importance of a possible depolarization produced by the particles themselves, is, however, too great to justify a hasty dismissal of the subject and I have therefore recorded it. Axial colors reflected from water are usually more saturated, but table 17 does not admit of references to merely subjective phenomena.

22. *Preliminary observations with the double drum.*—The following table, 18,

containing results with the double drum of figure 7, justifies the conclusion that more saturated colors and finely graded effects are obtainable with the longer columns of nuclei (180 cm.). Still, the colors of the second order beyond the violet (8th exhaustion), are very faint. The tendency to complementary contrasts between axial color and coronal field is again in evidence, but has not been ultimately determined.

TABLE 18.—PRELIMINARY EXPERIMENTS WITH THE DOUBLE DRUM. EXHAUSTION, 76–66 cm. Time, 11^h to 1^h 30'

Exhaustion No.	Axial.	Field.[1]	Axial.	Field.	Axial.	Field.	Exhaustion No.
0	Nucleation		Nucleation		Nucleation		0
1	Bl	Colorless	Bl	Colorless	Bl	Colorless	1
2	"	"	"	"	"	"	2
3	"	"	"	"	Bl-gr	"	3
4	Gr	"	Gr	"	Yl	Ol	4
5	Yl-gr	"	Or	"	Br	"	5
6	Or-br	Olive	"	Ol	Rd	———	6
7	Prp	Bl-gr	"	"	Prp	Yl ?	7
8	Viol	Yl-gr	Prp	———	Viol	Bl-gr	8
9	Wh-bl ?	Or	Bl-gr	Prp	Bl	Wh-cr	9
10	Wh-gr ?	Cr	Gr	"	Gr	"	10
11	Wh-yl ?	"					11
12	Yl	Bl-gr					12
13	Viol	Gr					13
14	———	———					14
15	———	Br					15

[1] Color of the central field of the corona.

23. *Definite observations for axial color.*— A final series of investigations was now made to find the distributions of axial color in its dependence on the number of nuclei. The double drum, with its vapor column of 180 cm. in length, was used, the white mantel of the Welsbach burner just beyond the further window being the source of light. The exhaustions were necessarily kept low to avoid a collapse of the drum; but the low supersaturation is rather an advantage since a more finely graded sequence of color is obtained. The usual limits of exhaustion were from 76 to 67.5 cm. of mercury. The question whether an isothermal or an adiabatic change of state is to be assumed must again be answered and it seems best to compute both.

Two series of virtually coincident experiments were made. In the second, the nucleation was repeated or doubled at the outset, but without appreciable difference. The colors are, as usual, very fleeting; and though they tend to pass through the preceding colors, as the cloud particles evaporate, they soon become too faint for recognition. The first blues apparently fade through the yellows of the first order, which I have not in these exhaustion experiments been able to produce with certainty in any case whatever. They are characteristic of the steam-jet.

In table 18, the two series are given in parallel columns and the second series being more complete will be made the basis of computation. It remains extremely difficult to observe the faint axial colors of higher orders, z, for which reason differences of color for large z are inevitable. Moreover, as all errors on exhaustion are cumulative, the general coincidence of the two series is rather surprising.

As in § 13, let N be the number of nuclei after the zth exhaustion. Assuming that both the normal time losses and those removed by exhaustion follow the same exponential law, put

$$N = 10^{z(1+bt)\log y},$$

where b is the coefficient of the time loss and y the ratio of the geometric progression of exhaustions, computed either isothermally N_i or adiabatically N_a. In the first case, $y = p/p_0 = .888$; in the second, $y = (p/p_0)^{1/\gamma} = .919$.

TABLE 19.—AXIAL AND CORONAL COLORS (Central Field) SEEN IN THE DOUBLE DRUM. PUNK NUCLEI. EXHAUSTION, 76–67.5 cm.

$t = 3.5$ min., $b = .10$. $y = (p/p_0) = .888$.
$\log N = z(1 + bt) \log y$. $y^{1/\gamma} = .919$.

Exhaust. No., z	First series.			Second series.			$N \times 10^3$
	Axial color.	Field.	Time.	Axial color.	Field.	Time.	
0	Nucleation			Nucleation			1000
1	———	———	— —	Viol-bl	Gray fog	41	889
2	Bl	———	27 m	Bl	Tawny	44.5	790
3	Bl	———	31	Bl	Tawny	48	702
4	Bl-gr	———	35	Bl-gray	Colorless	51.5	624
5	Bl-gr	———	38	Yl-gr	"	55	555
6	Gr-yl	———	41	Gr-yl	"	58.5	493
7	Yl	———	45	Yl	Olive-gr	62	438
8	Yl-or	———	48	Or	"	65.5	389
9	Or	Olive-gr	52	Or	"	69	346
10	Or-rd	———	56	Or-rd	"	72.5	308
11	Rr	Gr-yl	59	Prp	Gr-yl	79	273
12	Viol-rd	———	63	Prp	Gr-yl	79.5	243
13	Viol	Or-yl	66	Violet	Yl	83	216
14	Viol-bl	Rd	70	Viol-bl	Or-rd	86.5	192
15	Bl-gr	Prp	73	Viol-bl	Rd	90	171
16	Bl-gr	Prp	77	Gr	Prp	93.5	152
17	Gr-yl	Prp	80	Yl	Prp	97	135
18	Yl ?	Apple-gr	84	———	Wh-viol	100.5	120
19	Prp-viol	Yl-gr	87	Viol ?	Apple-gr	104	106
20	———	Or-rd	91	Viol	Yl-gr	107.5	95
21	———	Gr	94	———	Or-rd	111	84
22				———	Viol-prp	114.5	75

24. *Loss of nuclei in the lapse of time.*—To complete the computation, it is, as above, necessary to make special experiments on the time losses. These are given in tables 20 and 21, for exhaustions between 76 and 68 cm.

Thus, after long standing, the effect of identical successive exhaustions is more rapid than in the preceding table. Moreover, after two hours certain qualitative variations, apart from mere loss of number, seem to occur. There is again a suggestion of the spontaneous and proportionate increase of nuclei at low pressure which has already been adduced above. As a whole, the table shows that after 144 minutes about the 12th order of corona has appeared, admitting some uncertainty due to the anomaly specified.

TABLE 20.—LOSS OF NUCLEI DUE TO NORMAL CAUSES IN THE LAPSE OF TIME. EXHAUSTION, 76–68 cm.

Time elapsed since nucleation.		t	Axial colors.	Field.	Order from table 19, z	Probable, z
2	24	144^m	Prp	Gr yl	12	12
		147	Viol bl	Or-prp	14	
		151	Gr	Prp	16	
		154	Gr-yl	Viol	18	
		158	Yl?	Gr	19	

The following experiments were made in like manner for shorter lapses of time:

TABLE 21.—LOSS OF NUCLEI DURING SHORTER LAPSES.

Time elapsed since nucleation.	t	Axial colors.	Field.	Order from table 19, z	Probable, z
	56^m	Yl	Ol	7	6
	60	Or	"	8	
	63	Or	"	9	
	67	Rd	Yl-gr	10	
	30	Gr	Fog	5	4
	34	Yl-gr	Ol	6	
	42	Yl	"	7	
	46	Or-yl	"	8	

Thus the data

$t = 30$, $z = 4$,
$t = 56$, $z = 6$,
$t = 144$, $z = 12$,

if compared with the earlier data, figure 5, lie nearly on the intermediate line (marked n) and linear variation may therefore be admitted here as above. The value of the constant b computed from tables 20 and 21, where $t = 3.5$ min., is $b = .092$, and this is in sufficient agreement with the earlier data ($b = .1$) to admit of the same value in the corrections. The corrected number of nuclei is finally computed under both isothermal and adiabatic conditions in tables 22 and 23.

TABLE 22.—VALUES OF $N_z = 10^{z(1+bt)\log y}$

$y = p/p_0 = .888$
$b = .10$
$t = 3.5$ min.

Exhaustion No., z	$N_z \times 10^3$	Exhaustion No., z	$N_z \times 10^3$	Exhaustion No., z	$N_z \times 10^3$	Exhaustion No., z	$N_z \times 10^3$
0	1000	6	383	12	147	18	56
1	851	7	326	13	125	19	48
2	726	8	278	14	106	20	41
3	615	9	237	15	91	21	35
4	527	10	202	16	77	22	30
5	449	11	172	17	66		

TABLE 23.—VALUES OF $N_a = 10^{z\,(1+bt)\log y}$

$y = (p/p_0)^{1/\gamma} = .92$
$b = .10$
$t = 3.5$

Exhaustion No., z	$N_a \times 10^3$	Exhaustion No., z	$N_a \times 10^3$	Exhaustion No., z	$N_a \times 10^3$	Exhaustion No., z	$N_a \times 10^3$
0	1000	6	503	12	253	18	127
1	892	7	449	13	226	19	114
2	795	8	400	14	201	20	101
3	709	9	357	15	180	21	90
4	633	10	318	16	160	22	81
5	564	11	283	17	143		

25. *Correction for precipitated moisture.*—The method of paragraph 17, for computing the actual number of nuclei between isothermal and adiabatic numbers, when extended to the double drum, gives $p = 76$, $p' = 68$, $\vartheta = 293°$, and therefore $\vartheta' = 283.3°$ as a first approximation. Inserting these data with $r = 582$ and $r' = 586$ in the equation for entropy, the approximate value, $1 - x = .0243$ grams of water precipitated per gram of mixture, results. This is equivalent to .204 calories evolved per gram of air by the precipitation of the available $17 \times 10^{-6}/12 \times 10^{-4} = .0143$ grams of water. The rise of air temperature is thus .86°.

Hence the new data are $\vartheta = 293°$, $\vartheta' = 283.3° + .9°$, and these with the above values of r and r' give $1 - x = .021$ grams of water. Thus, $17.2 \times 10^{-6} \times 21 \times 10^{-3} = 361 \times 10^{-9}$ grams are precipitated per cub. cm. of moist air. If, as before, 5×10^4 nuclei are present at the outset, the volume of each precipitated cloud particle is 7.2×10^{-12} cub. cm., and its linear dimensions therefore about 1.9×10^{-4} cm.

To compute y in the equation for table 19, where

$$N = 10^{z\,(1+bt)\log y},$$

the equation

$$y = \frac{\rho'}{\rho} = \frac{p'/\vartheta'}{p/\vartheta}$$

may be assumed; whence $\log y = -.0379$; and since $1 + bt = 1.35$

$$N = 10^{-.0512\,z}.$$

In this way the values marked N in table 19 were computed.

DISCUSSION.

26. *Data for coronal and axial color compared.*—If the data for the drum, table 23, and those for the globe, tables 4, 9–12, be compared for the same axial or flame color, the latter will be seen to be about three orders in advance of the others. This is equivalent to a greater initial nucleation in case of the globe where the exhaustion was greater, so that in like apparatus more exhaustion would subsequently also be needed for the globe, if the same color is to be reached in both

cases. The exhaustions for the globe and the corresponding supply of nuclei are greater in the ratio of $1 - y = .18$ to $1 - y = .08$, and there is probably greater homogeneity in case of the globe. This implies that the initial nucleation is usually undersaturated, if indeed saturation is the term to be used when the source of nuclei is not active within the medium, as it would in any case depend on the intensity of this source. To begin with saturation, therefore, one should devise other means of nucleation than the phosphorus methods used above, which have been shown to be inefficient within a damp medium.

In general, the nuclear ratio corresponding to two different colors in the drum and the globe is about the same for the two cases, so far as it can be made out.

The results of tables 19, 22 and 23 may be constructed in a chart, the order of the coronas being horizontal and the nucleation vertical. Instead of this, log N is often a preferable ordinate, as the curves are then linear and need only be shifted laterally for different initial nucleations, since,

$$\log N = z\,(1 + bt)\,\log y + z_0.$$

The fundamental difference between axial and coronal color as to origin, etc., has already been insisted on above.

27. *Time losses interpreted.* — Some conclusion must be derived as to the nature of the time loss, which, in the above equation, has been very fully reproduced (apart from the inevitable errors) by $N = N_0 y^{bt}$, where N is the number of particles per cub. cm., surviving in the receiver after the lapse of time, t; $y = .825$, $b = .1$ by experiment. Thus, on reduction, if $\beta = .0083$, $N = N_0 10^{-\beta t}$. (1)

As in my preceding papers, I will suppose that the absorption velocity of the nucleus is k cm./sec., independent of the density of distribution. Moreover, that in a spherical receiver, nucleated at the time $t = 0$, N nuclei are found per cub. cm. at a distance r from the center. The distribution is in any case concentric, but otherwise disposable at pleasure. Since the absorption of nuclei is supposed to take place at the inner surface of the receiver only, there is a continued flux outward. The solution of the problem requires some understanding as to the manner in which this flux takes place.

(1) If there is a mere motion outward for all particles, the partial differential equation is found to be $d(r^2N)/dt + k\,d(r^2N)/dr = 0$, of which the integral determined by Lagrange's method is $N = N_0 f(r - kt)/r^2$, where f is an arbitrary function. This is found for an initial distribution independent of r. The result is clearly not in keeping with the actual case of experiment, as is to be inferred if the nucleus moves in all directions.

(2) The next case would be that of diffusion. The partial differential equation is $d(rN)/dt = k\,d^2(rN)/dr^2$, where rN is zero at the surface and the center, and the initial condition is $rN = rN_0$. This equation is integrable in the well-known way, but the result again fails to meet the actual condition of the experiment as set forth in the next paragraph.

(3) Remembering that the investigations above were purposely conducted in wide receivers, with the object among others of keeping the contents in a homo-

geneous state of nucleation through the agency of convection currents, it may be safely assumed that N is not a function of r but of time only. If this were not so the coronas would show color distortion (as they do in marked degree in benzine vapor) as well as the time changes observed. In case of water vapor, the ever-present convection will not allow either the distribution (1) or (2) to persist. Hence, whatever removal of nuclei takes place at the inner wall of the large receivers is a deduction or drain of nuclei from the *whole* volume of vapor, uniformly. This experimental condition simplifies the computation and offers an easy interpretation of the results obtained. In case of absorption with the adequate convection, therefore (if R be the radius of the receiver), $-(4\pi R^3/3)\, dN/dt = Ak\, 4\pi R^2\, N$, where k is the absorption velocity of the nucleus and A a co-efficient, stating what part of k as found in my last volume for nuclei moving in air ($k = 18$ cm./min., about), is effective in view of the fact that the nuclei are now suspended in water vapor. Hence,

$$N = N_0 10^{-3Akt \log \varepsilon / R}, \qquad (2)$$

an equation identical in form with that actually found in the experiments.

From equations (1) and (2), $\beta = 3Ak(\log \varepsilon)/R$; and if $k = 18$ cm./min., $R = 15$ cm., then $A = .0053$. Thus the absorption velocity found from these experiments is but 5/1000 of the value found when the saturated emanation is forcibly passed through fine bore tubes less than .5 cm. in diameter, or that found from electrical experiments for nuclei in air. This observed velocity of the nucleus in water vapor would therefore be but .095 cm./min., a result which will be further discussed below (Chap. VI, § 19).

28. *Estimated size of cloud particles.*—The rate of subsidence of the fog is not a good criterion[1] of diameter, because this datum is complicated by the evaporation of water particles (apparent subsidence at the top), and by their inevitable growth, remembering that the coronas are all fleeting phenomena. Some notion of their size, and this an upper limit, may be obtained. If the fog subsides at the rate of 1 cm./sec., the radius of the particle will be $r = .0009$ cm. For any other velocity expressed in terms of this normal rate, $r = 9 \times 10^{-4} \times \sqrt{v}$. Now the rates are never a small fraction of cm./sec., so that the radii are not liable to be much below say 10^{-4} cm., a datum which at first sight is surprisingly large, but is corroborated by the following independent estimates. *Cf.* Chap. III, § 11.

It has been shown above that in the case of spheres the moisture precipitated per cub. cm. of air partially exhausted, as stated, is 79×10^{-8} grams, and that with 5×10^4 nuclei per cub. cm. in the saturated emanation, this is equivalent to an initial diameter of the water particles of about $2.5/10^4$ cm. This datum is an order of values like the preceding, whereby two results are to this degree confirmed, viz: the order of size of particles producing axial color and the number of particles estimated for the saturated emanation.

The same method applied to the results obtained from the double drum showed

---

[1] Air, cleared of fog by the warmer walls of the receiver after exhaustion, also rises to the top.

$2/10^4$ cm. as the diameter of the particles in the first exhaustions. The smaller size here corresponds to less exhaustion.

A final estimate is obtainable from the size of the normal coronas after, say, twenty or thirty exhaustions. Estimating this as about twice as large in diameter as the ordinary lycopodium corona, if the particles of the latter measure .0032 cm., one may rate the residual water globule at .001 cm. Indeed, Fraunhofer and Kaemtz's measurements showed particles in lunar coronas as large as .0017 to .0053 cm., depending on the season. Thus, if the final size is .001 cm., the initial size must have been .0003 to .0002 cm., corresponding to twenty or thirty exhaustions. Similar results are deducible from the drum and they are thus again in agreement with the preceding estimates. Finally, the normal coronas may be measured absolutely and the dimensions computed from the deviation on diffraction. This is the practical plan, which I will waive for further discussion in the next chapter.

If the independent estimates just stated be summarized, the data are clearly of an order ten times greater than would follow if the axial colors of the drum or the steam jet were produced by interference of thin plates, granting that the old vesicular theory of atmospheric condensation is disproved. I admit that data as large as those found for the water particles are contrary to my expectations.

29. *Estimated size of nuclei.*—This has been variously estimated by the aid of Kelvin's vapor pressure equation, successively modified by the younger Helmholtz,[1] and by C. T. R. Wilson.[2] Naturally, the nuclei are supposed to be of the same size and the supersaturation carried far enough to condense water on each. Helmholtz found $15/10^6$ to $26/10^6$ cm. as the size of his nuclei. Wilson finds $8.7/10^8$ for the case of rain-like condensation, and $6.4/10^8$ and $5.9/10^8$ cm. for cloudy condensation, foggy and colored. The above data for the globe, similarly interpreted, give $8/10^8$ and $18/10^8$ as the smallest radii of the nuclei on which condensation would just take place if the supersaturations used were essential to condensation, which they are not. The actual dimensions must lie somewhere between Wilson's estimate, which holds for water vapor free from artificial nuclei, and that of Helmholtz for nucleated vapor. *Cf.* Chapter V, § 2.

The small size of the nucleus obtained in this way is startling, but as the method involves a huge extrapolation from the radius of capillary action (say 5×10^{-6} cm.) almost as far as the molecular diameter, it cannot be received with much confidence, and the size of the nucleus must be left in abeyance.

On the other hand, the size of the water particle is sufficiently large to admit of the application of Kelvin's equation. Moreover, there is here a mere accretion of water upon water. If the change of pressure to pass from a given to a succeeding corona, or to any recognizable change of corona, be determined by two successive exhaustions, the particles of the first corona are the nuclei of the second, and consequently the radius of the former should be determinable absolutely. With this datum for the particles of one corona, tables 9–12 and 19 would furnish the diameters of all.

---

[1] R. v. Helmholtz, *Wied. Ann.*, vol. xxvii, p. 526, 1886.

[2] C. T. R. Wilson, *Phil. Trans.*, London, vol. clxxxix, p. 306–307, 1897.

Unfortunately, this theoretically very promising method breaks down on experiment. For, let a small exhaustion be made adiabatically at the mean pressure p, and the mean absolute temperature, θ. Then in the modified form of Kelvin's equation for water (density = 1), let the logarithm be expanded. If T is the surface tension of water, p' its vapor pressure, the radius of water nucleus will be, approximately,

$$r = \frac{2T}{R\theta(\delta p'/p' - \delta p/p)}, \qquad (1)$$

where R is the gas constant of water vapor and δ denotes increments. If the condensation takes place near the freezing point, as in the above experiments, we may write $\delta p'/p' = .076\delta\theta$. Again, for the occurrence of adiabatic expansion $\delta\theta/\theta = ((\gamma-1)/\gamma)\delta p/p$. After substituting both results in equation (1)

$$r\,\delta p = \frac{2\,Tp}{R\theta(.0217\theta - 1)},$$

where δp is an adiabatic increment of pressure, applied to the moist air at θ and p. Using this equation for water particle of the order of dimensions estimated above at $\theta = 273°$ and $p = 76$ cm., an exhaustion of but 1/10 millimeter is in question. Now I satisfied myself in special experiments that exhaustion as small as 1 cm. would be perceptible in color changes of the coronas, particularly in the case of certain higher orders; but the small change corresponding to .01 cm. is out of the question. I do not see, therefore, that methods other than those based on measurements of coronas will be applicable for the determination of the absolute dimensions.

Pursuing this subject, I found that the coronas of benzol following the initial fogs are all normal, relatively large particles being precipitated at once. Hence, if m be the mass of benzol condensing, computed for given exhaustions as in § 16, and if d be the diameter of the benzol particles found by measuring the coronas, then $n = 6m/\pi d^3$. The number of nuclei active in different methods of nucleation may thus be found by a few exhaustions, compared with the more prolonged observation necessary for water vapor. Unexpected difficulties were encountered in the use of benzol, however, whereas the method led to a satisfactory issue for water vapor, as will be detailed in the next chapter.

CHAPTER III.

DIMENSIONS AND NUMBERS OF THE CLOUD PARTICLES PRODUCING CORONAS AND AXIAL COLORS.

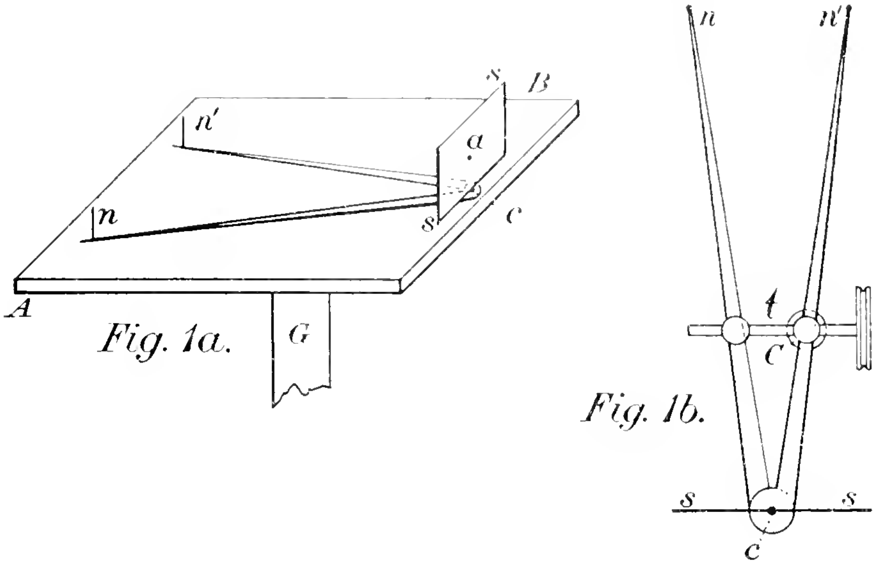
INTRODUCTORY EXPERIMENTS WITH BENZOL.

1. *Purposes.*—The remarks made above, that the coronas in benzol vapor are all normal, and that fewer exhaustions would therefore be needed to make definite measurements of the size and distribution of cloud particles, induced me to attempt the following introductory experiments. These, however, were destined to fail of a decisive issue, because such thermodynamic constants as I was able to find in the standard tables are insufficiently correlated to admit of the severe test which the computations, here in question, imply. In the second place, even if the constants were forthcoming, the impossibility of maintaining regular coronas in benzol, without shaking or some equivalent method of keeping the vapor uniformly nucleated, is an almost insuperable difficulty; while shaking, as seen in Chapter IV et seq., introduces a new supply of nuclei and removes others, for which no adequate allowance can be made. The data for benzol have certain peculiar features of interest, and I shall therefore record them because of their bearing on the method subsequently carried through for water vapor.

The method has been suggested: the thermodynamic conditions of expansion suffice for computing m, the liquid precipitated per cub. cm. The apertures of the coronas afford a means of measuring d, the diameter of the particles. Hence their number per cub. cm. is $n = 6m/\pi d^3$.

2. *Apparatus. Goniometer.*—The fleeting character of the coronas, their small aperture, their faint and vague definition, made all attempts at using telescopic instruments, or even the sextant, futile. I therefore constructed the following simple goniometer which, in one form or another, proved very efficient. On a smooth board, AB, a fixed arm, nc, carries at n a vertical needle about 3 cm. long. Similarly, a movable arm, swivelled at c, carries a like vertical needle n', so adjusted that the points of the needles may be moved into contiguity by rotation. Finally, a screen, s, with a small peep-hole at a in the axis of rotation and also about 3 cm. above the table, completes the instrument. On use, the needles n, n', are adjusted so as to be tangent to a selected annulus of the corona when viewed by an eye looking through a. These measurements are made very quickly, and under the conditions given below the needles are rarely more than 2 cm. apart, usually less. Let R be the length of the arms of the goniometer, α the angle between them. Hence the distance nn' is pricked into a small piece of paper, which on measurement gives at once $nn' = s = 2R \sin \alpha$. (1)

In measuring the angular aperture a of the central white patch of the coronas, the circular source of light was placed at the same distance (250 cm.) on one side of the receiver as the eye on the other side. In this case the angles of incidence



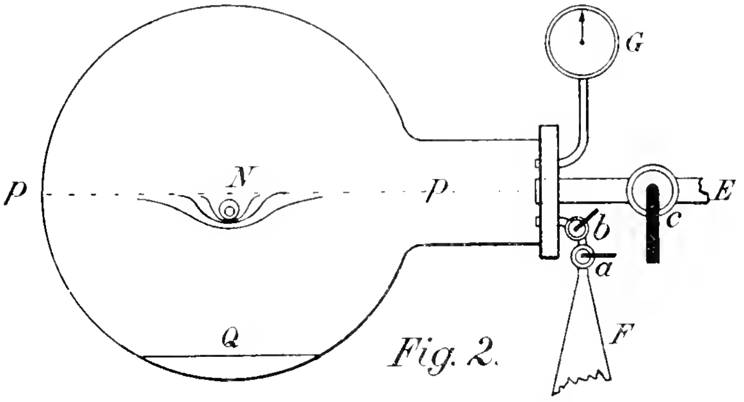


FIG. 1.—GONIOMETERS AND APPURTENANCES. *1a*, HORIZONTAL FORM. *1b*, VERTICAL FORM.
FIG. 2.—CONDENSATION CHAMBER, N; FILTER, F; GAUGE, G; EXHAUST PIPE, E.

and of aperture are equal, being $\frac{1}{2}$ the angle of diffraction. and the equation becomes,

$$d = \frac{n\lambda}{2\sin\alpha}, \qquad (2)$$

where λ is the wave length of the dark ring in question, $n = 1$ usually, a the common angle of incidence and of aperture, and d the diameter of the diffracting particle. If $n = 1$, equation (2) becomes in view of (1),

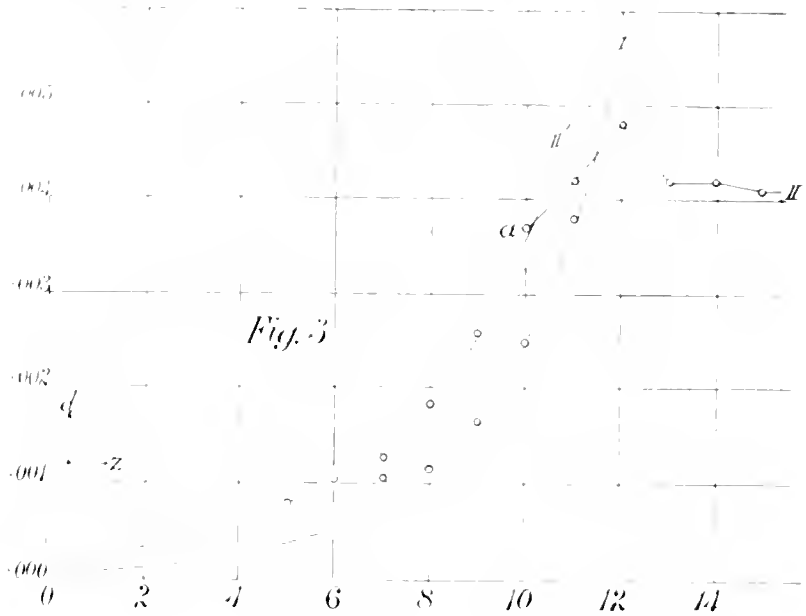
$$d = \frac{\lambda R}{s}. \qquad (3)$$

In the instruments used in this chapter $R = 19.5$ cm., and 20.1 cm., though larger values are preferable.

Instead of using equation (3), it is for many purposes advantageous to compare the coronas of water particles with the coronas produced under like circumstances by lycopodium particles (diameter D_0), for which $d = D_0 = \lambda R/s_0$. Hence

$$d = D_0 s_0/s = .00144/s, \text{ if } D_0 = .0032 \text{ cm.}$$

This makes it needless to select any particular wave length provided the same annulus is used throughout.



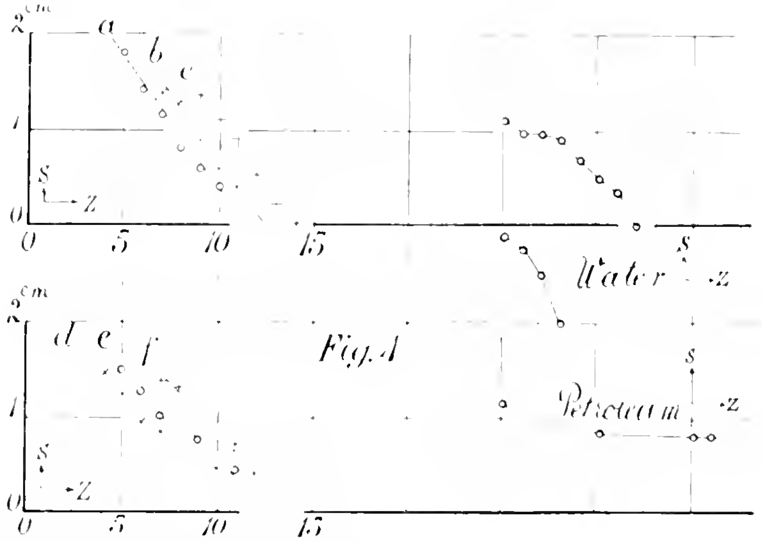


Fig. 3.—Chart showing the Diameters (cm) of Cloud Particles of Benzol [illegible] the Successive Exhaustions.

Fig. 4.—Chart showing the Decrease in Aperture (s) of the Coronas of Benzol Vapor, during the Successive Exhaustions; also the Final Apertures of Water and Petroleum Vapor in the same Scale.

In the present chapter the goniometer, fig. 1*a*, opened horizontally, being carried in a light tripod, *G*, which could be moved at pleasure on a smooth table. In the following chapters the goniometer, fig. 1*b*, was used vertically, the jaws being longer (30 cm.) and adjusted by an appropriate tangent screw, *t*. In such a case, the instrument as a whole must be swivelled around a horizontal axis, *C*, so that both tangencies may be quickly caught. *s* is the screen, *n*, *n'*, the needles, *c* the axis. In practice, the jaws *cn*, *cn'*, are turned around *C* until they are nearly horizontal, and the screen *s* vertical.

The remainder of the apparatus—receiver, in which the coronas are produced, exhausting train, etc., Figure 2—did not differ materially from the forms given above and need not, therefore, be specially described. *E* is the exhaust-pipe with its cock, *c*; *F*, the cotton filter with two stop-cocks, *a* and *b* (the latter being a check-valve insuring slow influx); *G*, the vacuum gauge. *Q* is the water level, *pp* a fog line showing compamulate coronas at *N*.

3. *Results.*—The first question to be answered relates to the sizes of the cloud particles suspended in benzol. These are found from measurements of the apertures of the respective coronas. The results are given in table 1, on the general plan already detailed in the preceding chapter. The first three columns have an obvious meaning. It is necessary, as stated, to shake the receiver to obtain annular coronas without color distortion, and the apertures will not therefore sink below a small value corresponding to the special nucleation so introduced.

The fourth column of table 1 gives the chord, *s*, on the goniometer, subtending the aperture of the coronas, whence the fifth column containing the diameters of the water particles, *d*, in cm., is computed for the coronas examined, as explained in the preceding paragraph. These results are plotted in the curve, figure 3, corresponding to the two parts of the table. The curves do not coincide, since the initial nucleation is necessarily different, but they are of the same nature. Curve II, which is the more complete, shows a sudden breakdown beyond *a*, after 10 or 12 exhaustions, and it is here that the raining subsidence of cloud particles is marked, and the nucleation thereafter, shaking presupposed, is appreciably constant. The table shows that it would be possible to make an approximate allowance for these extra particles.

Why this rainy subsidence and purification begins in the sudden fashion evidenced is an interesting question for further investigation. Something similar will be noticed in the case of water below. *Cf.* § 5, 7, 11.

TABLE 1.—CORONAS IN BENZOL VAPOR, KEPT REGULAR BY SHAKING. SULPHUR NUCLEI. EXHAUSTION, 76–58 cm $d_0 = .000,044$ cm ; computed $d = d_0 10^{\beta z}$; $\beta = .176$.

Exhaustion No., z	Time.	Corona, etc.	Aperture, s	Observed, $d \times 10^3$	Computed, $d \times 10^3$	Computed, $d \times 10$
	min.		cm.	cm.	cm.	
0	0	Nucleation	—	—	.044	
7	14	Corona forming	1.38	1.04	.74	
8	16	Corona clear	1.27	1.13	1.11	
9	18	"	.88	1.64	1.67	
10	20	"	.58	2.48	2.50	
11	22	"	.38 ?	3.80	3.75	
12[1]	24	"	—	—	5.61	

[1] Coronas before $z = 7$ lost in fog ; after $z = 12$ too small for measurement.

TABLE 1.—SECOND SERIES.

No.	t	[illegible]	Aperture,	Observed, $d \times 10^4$	Computed, $d \times 10^4$	Computed, $d \times 10^4$
	min.		cm.	cm.	cm.	
0	[illegible]	Nucleation	-		.21	
1	2	Fog	-		.27	
2	4	"			.36	
3	6	"			.47	
4	8	Fog clearing			.62	
5	10	"	1.8	.8	.82	.74
6	12	Corona forming	1.4	1.[illegible]	1.07	1.01
7	14	Clear corona	1.15	1.25	1.41	1.38
8	16		.70	1.82	1.85	1.89
9	18		.56	2.57	2.44	2.58
10	20		.39	3.70	3.21	3.53
11	22		.34	4.20	4.22	4.82
12	24		.30	4.80	5.55	6.60
13	26		.34	4.20	7.29	9.02
14	28		.34	4.20	9.59	12.55
15	30		.35	4.12	12.62	16.04

Persistent small coronas due to shaking. How fast they would otherwise vanish is shown by the computed d.

$d_0 = 207 \times 10^{-6}$; $\beta = .119$.

$d_0 = 154 \times 10^{-6}$; $\beta = .136$.

4. *Results interpreted.*—As the coronas do not begin to be clear until after the 6th or 7th exhaustion, the size of the initial particles must be computed. Using the equation for the number of particles after z exhaustions, N, deduced in the preceding chapter, $N = 10^{[illegible]}$, $y = .825$ if the computation is made adiabatically, while the corrected value for water was $y = .819$. Neither of these values is applicable without investigation; and b, the coefficient of the time losses, cannot be the same here as above, in view of the shaking needed to keep the coronas annular. It may be worth while, however, to compare the values, $N = 10^{[illegible]}$ (corrected for precipitation), applicable in the case of water, with the results of the table, using the exhaustions from $z = 5$ to $z = 10$ of the second part for the purpose.

Since $d = d_0 \sqrt[3]{1/N} = d_0 \sqrt[3]{10^{[illegible]}} = d_0 10^{[illegible]}$ for water, put $d = d_0 10^{\beta}$, whence $\beta = \delta(\log d)/\delta z$. Utilizing the first four observations of the first part of the table, the mean values found are

$$\beta = .176 \text{ and } d_0 = .0000135 \text{ cm.}$$

The figure shows good agreement between the observed and the computed results, but the large value of β as compared with water ($\beta = .0083$), and the small value of d_0 are noteworthy.

In the second part of the table, 6 observations are available ($z = 5$ to $z = 10$), after which the distortion at a, already indicated, begins. A variety of pairs of values of β and d_0 were tested: $\beta = .119$ and $d_0 = 207/10^6$ show too little curvature, the direct means, $\beta = .136$ and $d_0 = .000154$, are still deficient but may be taken. The curve and table then show the marked spontaneous evolution of particles by the breakdown of the locus after about 10 exhaustions.

Again, since $-3\beta = (1+bt)\log y$, where y will not differ materially from the value for water under the same exhaustions, put $-\log y = .087$. Hence, since $t=2$ min., $b = 2.6$ in the first part of table 1, and $b = 2.0$ in the second part. These values are enormously large as compared with those found for water ($b = .1$); and since the diffusion velocity of nuclei in benzol is actually smaller than in water vapor, these large coefficients are either an indication of the efficiency of removal by shaking (for which there is no collateral evidence), or more probably of removal by subsidence.

In fact, the equation temporarily accepted is incomplete since it does not include the production of nuclei by shaking, *i.e.*, the horizontal streamer, a, in figure 3. Put therefore $N = N_0\,(10^{-z(1+bt)\log y} + c)$, where N_0c is the constant number of nuclei contributed by each shaking and again removed by the subsequent exhaustion, after $z = \infty$ or is very large. Since $Nd^3 = d_0^3$, if $N_0 = 1$, the resulting equation is

$$d_0^3 = d^3\,(10^{z(1+bt)\log y} + c) \qquad (1)$$

where d_0 is the initial and d the final diameter of the cloud particle of the order, z. When $z = \infty$, $d^3 = D^3 = d_0^3/c$, and is therefore given in figure 3, curve II, by the results following a, as $D = .0042$. With this substitution, equation (1) becomes, on differentiation and reduction,

$$-\frac{\delta\,(\log d)}{\delta z} = \frac{\log y}{3}\,(1 - d^3/D^3)\,(1+bt), \qquad (2)$$

where b is the only unknown quantity. When $D = 0$, the above value of β is reproduced. The first member of (2) may somewhat crudely be taken as the change of $\log d$, for a unit or single change of the order, z. The correction, $1 - d^3/(.0042)^3$, is constructed graphically and the mean value for the interval between two successive observations is found from the curve, which naturally shows rapidly varying rates. The corrected value for water, $\log y = .00866$, must be accepted in the absence of a better factor. The results of the computation for b then appear as follows:

TABLE 1 (1).

$z =$ 7–8	$b =$ .15 cm./min.,
8–9	2.4
9–10	3.0
10–11	5.0

TABLE 1 (2).

$z =$ 5–6	$b =$ 1.4 cm./min.
6–7	1.0
7–8	2.5
8–9	2.5
9–10	4.1

so that removal is faster as the particles are larger. This is a natural consequence of the *subsidence* of cloud particles, whereas the removal of nuclei by diffusion would show the contrary effect. To bring out the latter, therefore, very long time-intervals between the observations are, as a rule, the indispensable requisite, particularly when the cloud particles are so large as here in the case of benzol and in the final observations with water vapor. The same result reappears from a new point of view in § 7.

5. *Number of particles.*—It is next in order to indicate the difficulty encountered in endeavoring to find the number of nuclei initially present from the data found for the initial diameters $d_0 = 44 \times 10^{6}$ and $d_0 = 154 \times 10^{6}$. The data available for benzol in Landolt and Boernstein's tables (pp. 336 and 348), are not sufficiently harmonious to lead to a solution. If, as above, $1 - x$ is the mass of precipitate from 1 gram of saturated vapor, after adiabatic cooling from the absolute temperature ϑ to ϑ',

$$x = \frac{\vartheta'}{r}\left(C \lg \frac{\vartheta}{\vartheta'} + \frac{r}{\vartheta}\right).$$

It is therefore necessary to know both the variation of specific heat C, and of latent heat, r, with temperature, and the whole question depends on the character of this variation. Since r from Regnault's data is very nearly constant within the 20° in question ($r = 109$ to 107), it will facilitate computation to regard it so and to compute $dx/d\vartheta$ from $x = (\vartheta/r)(S - C \lg \vartheta)$ for the adiabatic process in question, S being the entropy of the mixture. Hence, with ϑ and C as variables,

$$\frac{dx}{d\vartheta} = \frac{S - C(\lg \vartheta + 1)}{r} - \frac{\vartheta}{r}\,\frac{dC}{d\vartheta}\lg \vartheta.$$

From the observations of de Heen and Deruyts, between 10° and 60°, $dC/d\vartheta$ may be estimated as .028, nearly at 0° centigrade. Furthermore, for $\vartheta = 293°$, $x = 1$, $r = 109$, $C = .31$; $\vartheta' = 271$, $C = .37$, $S = 2.46$ (computed). Hence at $\vartheta' = 271°$, $dx/d\vartheta = -.0341$ and at $\vartheta = 293°$, $dx/d\vartheta = -.0437$, or the amount of vapor within the mixture should increase markedly with fall of temperature in both cases, which is directly contrary to the experiments. If C is considered constant, $dx/d\vartheta$ will be positive for the given interval, and precipitation must therefore occur on cooling, as observed; but it is obvious that results so obtained are quite arbitrary.

In the absence of compatible data, an estimate might be made by assuming the masses precipitated to be inversely as the latent heats of the vapors. The results are equally meaningless.

TABLE 2.—CORONAS IN BENZOL VAPOR. PERFECTED FILTER. EXHAUSTIONS, 76–58 cm.

Phosph. nuclei.			Punk nuclei.			Punk nuclei.			Sulphur nuclei.		
	Time.	Corona, etc.		Time.	Corona, etc.		Time.	Corona, etc.		Time.	Corona, etc.
	0	Nucleation		13	Nucl. shaken	0	20'	Nucl. sh.	0	3'	Nucleation
1	1.5	Fog band	1	14.5	Wh, rd	1	21.5	Gray, rd	1	4.5	Fog on bottom
2	3	Shaken	2	16	Gray, rd, gr, vl, diffuse	2	23	" "	2	6	Shaken
3	4.5	Gray, rd	3	17.5	Distorted	3	24.5	s = 1.45	3	7.5	Fog gradually, finally quite, banded again
4	6	" "	4	19	s = 1.50 sh.*	4	26	1.24	4	9	
5	7.5	" " s = 1.37	5	20.5	1.28	5	27.5	.94	5	10.5	
6	9	Coronas, s = 1.30	6	22	1.00	6	29	.85	6	12	
7	10.5	Diffuse, s = 1.40	7	23.5		7	32.5	.85 diffuse	7	13.5	
8	12	Shaken	8	25	.75	8	33	.73	8	15	Shak., s = 1.35
9	13.5	Coronas, s = .70	9	26.5	.75	9	34.5	Shaken, .45	9	16.5	1.10
10	15	s = .40	10	28	Shaken, .43				10	18	.80
11	16.5	Absent	11	29.5	Absent				11	19.5	.50
12	18	"	12	31	"				12	21	Faint corona
									13	22.5	Absent

* Narrow fog stratum between hemispheres of clear air.

6. *Repetitions.*—Owing to the tendency of benzol to secrete residual nuclei in strata near the surface of the liquid, a peculiarity of which I was not at first aware, it seemed advisable to repeat some of the results for the successive coronas. Examples of the data are given in table 2. The persistent coronas are all normal. Punk nuclei were used for comparison with the sulphur nuclei of the preceding table, but the conditions of experiment were not materially altered. The results are of the same nature.

7. *Differences between nuclei.*—The different rates at which s diminishes in case of punk nuclei and of sulphur nuclei, is noteworthy. To bring this out, both series of results (new and old) are constructed in the chart, figure 4, the abscissa being the number of the exhaustion (all identically $y = 58/76$); the ordinate, the aperture of the corona. Of these curves, a, b, c were obtained with sulphur nuclei; a, b being the results of table 1, where the liquid was shaken between each exhaustion, c being the new series made without continued shaking. The curves d, e, f refer to punk nuclei. Shaking was irregularly resorted to, and the effect has impressed itself on the curves. The new and the old curves for sulphur nuclei show about the same steepness, no matter whether the liquid was shaken between the successive exhaustions or not. To some degree this is also true for the punk nuclei, all the curves showing strikingly less steepness than the sulphur curves. In fact, the decrement of aperture δs is per exhaustion:

For sulphur nuclei, $\delta s = .14$ cm.
For punk nuclei, $\delta s = .09$ cm.

Since $\delta d = .00144\ \delta s/s^2 = \delta s \times (d^2/.00144)$, the result in terms of d is less simply stated.

Hence the coronas vanish more rapidly for sulphur nuclei than for punk nuclei, and since by § 5 this removal is due to subsidence of cloud particles it, follows that the benzol-sulphur particles are larger than the benzol-punk particles. A corresponding result is found below § 8 for sulphur-water particles.

The accompanying results drawn to the same scale and obtained in the final exhaustions ($z = 20$–30) with water vapor are of the same order of steepness and have been similarly explained. Petroleum cloud particles, in view of the small vaper tension, are much smaller and nearly free from subsidence, as figure 4 shows. This case corresponds to coronas of abnormal type; it has, therefore, seemed reasonable, in the definite computations below, to ignore the effect of subsidence altogether when the order of the exhaustion was sufficiently far removed from the end of the series. *Cf.* § 11.

Since $d^3 N = d_0^3$ and $\delta d = (d^2/.00144)\ \delta s$, if the first equation is differentiated logarithmically and δd replaced by the second,

$$\frac{\delta N}{N} = 3\, d\, \frac{\delta s}{.00144}.$$

Hence for sulphur nuclei, $\delta N/N = 290\, d$, and for punk nuclei, $\delta N/N = 190\, d$, equations which show the part of all the residual nuclei precipitated per exhaustion at any mean diameter d, and under the time interval and the supersaturations stated. Thus, at the mean diameter (in centim.) $d = 0.01$, $\delta N/N = .29$ and $.49$, respectively. If $d = .0034$ and $.0052$ respectively, all the nuclei will be precipitated in a single exhaustion of the value specified (76–58 cm.).

EXPERIMENTS WITH WATER VAPOR.

8. *Constants and apertures of coronas.*—Following the unsuccessful investigation with benzol, I will now determine as nearly as I can the diameters of the cloud particles of water and their numbers. It was necessary for this purpose to make a special series of measurements in which the diameters of the normal coronas were measured, as far as practicable. These results are given in tables 3 and 4, in which the first four columns have the usual signification. The time interval between exhaustions was uniformly 1 min. 45 sec. The circular source of light was placed 2.5 meters from the spherical receiver (diameter, 30 cm.). With the light so far distant, the central patches of the coronas following the 7th, 8th, etc., were not white centered, but nearly uniformly colored, showing that the close light in the above experiments gave a diffuse effect not belonging to the coronas proper. Coronas 11, 12, and those following 16 are truly white centered, the latter being of the normal type, for which alone the measurements of aperture are directly applicable. One may note in passing that sulphur nuclei are sooner emptied out by precipitation than punk nuclei. Although the former give denser initial fogs, the latter give the greater number of coronas. § 7 shows that sulphur-water particles are the larger, *cat. par.*

The column marked s shows the aperture of the corona, being the chord of the radius 20.1 cm. for the goniometer described in § 2. In the next column $\sqrt[3]{1/N}$ is given, a quantity proportional to the diameter, d, of the particles, so that $d = d_0\sqrt[3]{1/N}$. N, the relative number of cloud particles, is found as above, since shaking is never necessary, from $N = N_0 10^{-.14\,bt\log y}$, where $N_0 = 1$, $b = .1$, $t = 1.75$ min., $\log y = -.0866$, for exhaustions from 76 to 58 cm., nearly.

As the coronas were advantageously compared with those of lycopodium spores for which $s = .45$ cm. and $d = .0032$ cm., for the same goniometer, the equations used above will again be applicable here. Consequently, since $d = 1.44/s \times 10^{-3} = d_0\sqrt[3]{1/N}$,

$$d_0 = \frac{1.44 \times 10^{-3}}{s \times \sqrt[3]{1/N}}.$$

The values of $s \times \sqrt[3]{1/N}$ are given in the tables. They are nearly enough constant for measurements of this kind, where the thing to be observed is always a more or less hazy and fleeting outline. *Cf.* § 11. Their mean value in table 3 is 4.16, and in table 4 is 5.47. The corresponding values of d_0, or the initial diameters of the cloud particles, are $d_0 = .35 \times 10^{-3}$ cm. in table 3 and $d_0 = .26 \times 10^{-3}$ cm. in table 4. All other diameters are then found from $d = d_0 \times \sqrt[3]{1/N}$.

The final datum of the tables, n, is the *absolute* number of nuclei per cub. cm., briefly called the *nucleation*, as found from the value of d and the grams of moisture precipitated per cub. cm. In the globe of 79×10^{-8} grams were precipitated within the given exhaustion; whence, since the density $\rho = 1$,

$$79 \times 10^{-8} = n \tfrac{1}{6} \pi d^3 ;$$

or, since $d^3 = d_0{}^3/N = (2.63 \times 10^{-4})^3/N$, the equation for punk nuclei finally becomes

$$n = N \times 8.3 \times 10^{4}.$$

For sulphur nuclei, similarly, $d^3 = (3.5 \times 10^{-4})^3/N$; whence

$$n = N \times 3.6 \times 10^{4},$$

n being the absolute, N the relative number of nuclei per cub. cm.

9. *Tabulated results.*—The new results are fully given in tables 3 and 4, in the manner just explained. The two tables are independent series of measurements differing even as to nuclei.

TABLE 3.—DIMENSIONS OF SUCCESSIVE CORONAS, SIZE AND NUMBERS OF CLOUD PARTICLES IN WATER VAPOR. SULPHUR NUCLEI. EXHAUSTION, 76 to 58 cm. $t = 1.75$ minutes. $b = .1$. $N_0 = 36{,}000$. Mean $s N^{-\frac{1}{3}} = 4.16$.

Exhaustion No., z	Time.		Coronas.	s; $s N^{-\frac{1}{3}}$		$N^{\frac{1}{3}}$	$d \times 10^4$	$n \times 10^{-4}$
	m	s		cm.			cm.	
0	0	0	Nucleation	——		1.00	3.50	3.60
1	2	30	Fog	——		1.08	3.78	2.85
2	4	30	"	——		1.17	4.10	2.25
3	7	15	"	——		1.26	4.41	1.78
4	8	00	"	——		1.37	4.80	1.41
5	9	45	"	——		1.48	5.18	1.12
6	11	30	"	1.66		1.60	5.60	.882
7	13	15	"	1.65		1.73	6.05	.70
8	15	00	"	1.70		1.86	6.51	.55
9	16	45	"			2.01	7.03	.44
10	18	30	"			2.18	7.63	.346
11	20	15	Wh, or	1.30		2.36	8.26	.274
12	22	00	Wh, cr	1.40		2.55	8.93	.216
13	23	45	Wh ?	1.40		2.76	9.66	.171
14	25	30	Gr, viol-prp	1.40		2.98	10.43	.136
15	27	15	Yl-gr, or		4.52	3.23	11.30	.107
16	29	00	Wh, rd, gr	1.25	4.36	3.49	12.21	.085
17	30	45	Yl-gr ?, rd, bl	1.20	4.52	3.77	13.20	.067
18	32	30	Wh, or, rd, gr	1.05	4.27	4.07	14.24	.053
19	34	15	Wh, or, bl-gr, rd	.92	4.05	4.41	15.43	.042
20	36	00	Wh, or-rd, gr	.73	3.47	4.76	16.66	.033
21	37	45	Wh, br, gr	.79	4.07	5.15	18.02	.026
22	39	30	"	.72	4.01	5.57	19.50	.021
23	41	15	" (faint)	.54		6.02	21.07	.016
24	43	00	None	——		6.51	——	——
25	44	45	None	——		7.04	——	——
26	——		None. Clear	——		7.61	——	——

TABLE 4.—DIMENSIONS OF SUCCESSIVE CORONAS, CLOUD PARTICLES, ETC. PUNK NUCLEI. $N_0 = 83,000$ PARTICLES. OTHER CONSTANTS AS IN TABLE 3. Mean $sy = 5.47$.

No.	[illegible]	Time		Corona	s		y	$d \times 10^4$	$n \times 10^{-3}$	$10^3 \div n^{1/3}$
		m.	s.		cm.			cm.		
		0	00	Nucleation			1.00	2.63	83	22.0
1	—	1	45	Fog	2.7		1.08	2.84	65	24.8
2		3	30	"	—		1.17	3.08	5.2	
3		5	15	"	—		1.26	3.31	4.11	
4		7	00	"	—		1.37	3.60	3.25	
5	—	8	45	"	1.3		1.48	3.89	2.57	33.0
6		10	30	"	—		1.60	4.21	2.03	
7	9	12	15	Olive green (no white)	1.5		1.73	4.55	1.61	
8	10	14	00	Green (no white)			1.86	4.89	1.28	
9	11	15	45	Yl-gr (no white)	2.70		2.01	5.29	1.01	
10	} 11, 12	17	30	Yl-gr, rd	2.50		2.18	5.73	.80	50.0
11	13	19	15	Wh, or rd	2.00		2.36	6.21	.63	
12	14	21	00	Wh, cr, gr	1.50		2.55	6.71	.50	
13	15	22	45	"	1.50		2.76	7.26	.394	
14	16	24	30	Apple gr	1.52		2.93	7.84	.313	
15	17	26	15	Gr	1.58	5.10	3.23	8.49	.247	74.0
16	18	28	00	Wh, br, gr	1.45	5.06	3.49	9.18	.196	
17	19	29	45	Wh, cr, gr	1.36	5.13	3.77	9.91	.155	
18	20	31	30	Wh, br, *bl-gr*	1.35	5.49	4.07	10.70	.123	
19		33	15	Wh, br	1.34	5.91	4.41	11.60	.097	
20	22	35	00	Wh, cr, gr	1.25	5.95	4.76	12.49	.077	111
21	23	36	45	Wh, br	1.05	5.91	5.15	13.54	.060	
22	-	38	30	Wh, br	.96	5.35	5.57	14.65	.048	
23	25	40	15	Wh, br	1.03	6.20	6.02	15.83	.038	
24		42	00	Wh, br	.75	4.88	6.51	17.12	.030	
25	—	43	45	Wh, br	.75	5.28	7.04	18.52	.024	161
26	—	45	30	Wh, br (faint)	.69	5.25	7.61	20.01	.019	
27	—	47	15	Wh, br	.66	5.43	8.23	21.64	.015	
28		49	00	"	.63	5.61	8.90	23.41	.012	
29	—	50	45	Vanishing	.46		9.63	25.33	.009	
30	—	52	30	Absent ?	.35		10.04	——		

DISCUSSION.

10. *Number and distributions of cloud particles.*—In the case of the sulphur nuclei there are originally 36,000 particles present per cubic centimeter and finally but 160 particles per cubic centimeter; this makes 33.0 particles per linear centimeter initially, and 5.5 particles finally.

For the case of punk nuclei there are 83,000 particles in each cubic centimeter at first, and 90 particles per cubic centimeter at the end of the experiment. This is equivalent to 43.6 particles per linear centimeter initially and but 4.5 particles finally. In both instances they are thus about 2 millimeters apart when the coronal display virtually ceases.

The reason for the different numbers at the outset can hardly be succinctly stated. It seems reasonable that differences in the initial numbers of nuclei should correspond to the general difference of behavior, and this is qualitatively the case. Of the determinative loci, $s/N^{\frac{1}{3}}$ in terms of z, in tables 3 and 4, the former (sulphur) shows a tendency to decrease, the other (punk) a tendency to increase with increasing z. As s is observed, it follows that N is respectively too slow and too fast in its variation, instead of being constant with z. Consequently, I suspect that the mean of tables 3 and 4 is a more correct sequence for n than either table separately. The same conclusion is reached on comparing a given corona (for instance, the green centered type for $z = 14$) in the two tables. Obviously, this definite diffraction pattern must, *cat. par.*, correspond to the same number of nuclei in the two cases. Finally, in the experiments of the foregoing chapter, doubling or quadrupling the initial nucleation by correspondingly repeating the charges, was found to shift the coronas but a few orders ahead, while the effect should be 3 or 6 orders of displacement.

11. *Removal by subsidence.*—The rapid removal of cloud particles toward the end of the tables shown in figure 5, and due to the subsidence of large drops, is noteworthy, and the difficulty of coping with the subsidence error has induced me to insert a few special subsidence data here. The products, $s \times \sqrt[3]{1/N}$, were discarded in the last case of table 3 and the two last observations of table 4, because of the magnitude of this error. Since $r = 9 \times 10^{-4} \times \sqrt[2]{v}$, the reciprocal variable $v = r^2 \times 10^8/81$ may be computed, as is done for the vanishing coronas in the following table.

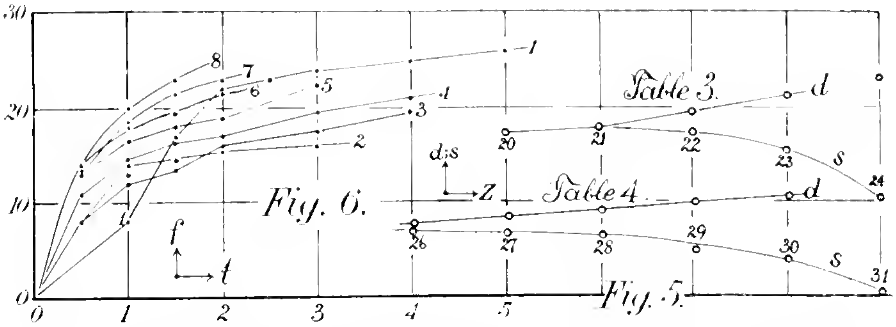


FIG. 5.—CHART SHOWING THE ACCELERATED REMOVAL OF CLOUD PARTICLES IN THE FINAL EXHAUSTIONS (NUMBERS z, ON CURVES).

FIG. 6.—CHART SHOWING THE SUBSIDENCE OF FOGS OF DIFFERENT ORDERS (NUMBERS z, ON CURVES) IN THE LAPSE OF TIME. FALL (f) IN CM, TIME (t) IN MINUTES.

TABLE 5.—SUBSIDENCE OF CLOUD PARTICLES COMPUTED.

Exhaustion, No., z.	Radius, $r \times 10^4$.	Velocity, $v \times 10^3$.
	cm.	cm. sec.
0	1.31	21
1	1.41	25
26	3.8	180
27	4.1	210
28	4.4	240
29	4.8	280
30	5.0	310

For the sake of comparison with these computed results, the experiments described in table 6 and figure 6 were specially investigated. Observations of the fall, f, of the plane of demarcation in the lapse of time were made in full daylight. The first 8 exhaustions were successively examined in the large globe, and the rates of descent of the 2d and 8th computed graphically.

TABLE 6.—SUBSIDENCE OF FOG STRATA OF SUCCESSIVE ORDERS. OBSERVATIONS. *Cf.* Fig. 6.

Ex. No.	Time (min.)	Fall of surface, f (cm.)	Rates, v.	Ex. No., n.	Time, t (min.)	Fall of surface f (cm.)	Rates, v.	Ex. No., n.	Time, t (min.)	Fall of surface, f (cm.).	Rates, v
1	0	0		4	0	0		7	0	0	
	1	8			.5	11			0.5	13.5	
	1.5	17			1.	14.5			1.	18.5	
	2	22			1.5	16.5			1.5	21.5	
	2.5	23			2	17			2	23	
	3	24			3	19.5					
	4	25			4	21					
	5	26						8	0	0	.05 $\frac{\text{cm}}{\text{sec}}$ finally.
									.5	14	
									1.	20	.47 $\frac{\text{cm}}{\text{sec}}$
				5	0	0			1.5	23	initially.
2		0	.017 $\frac{\text{cm}}{\text{sec}}$	color	.5	13					
	.5	8	finally.		1	16.5					
	1.	14	.27 $\frac{\text{cm}}{\text{sec}}$		1.5	18		Coronas.			
	1.5	14.5	initially		2	19					
	2	15.5			3	22.5					
	3	16						9	$s=1.0$		
								10	.90		
								11	.78		
				6	0	0		12	.73		
3	0	0			.5	14		13	.59		
Erect globe	.5	8			1.	18		Long standing shak'g	.45		
	1.	12			1.5	19.5			.40		
	1.5	13.5			2	21.5					
	2	16									
	3	17.5									
	4	19.5									

The observed rate of subsidence is seen to be a remarkedly decreasing quantity, from which one at once suspects that it is largely apparent. Naturally, the observations are vague from the difficulty of seeing a sharply defined upper fog limit; but the curves as a whole nevertheless unmistakably indicate much more rapid descent at the beginning than at the end of the curves, and a rate of descent increasing with the number of exhaustions, *i.e.*, with the mean size of the cloud particles. The decreased rate of subsidence must be referred to evaporation at the top, where the smallest particles congregate, and the following chapters will show how important this source of loss of cloud particles really is. To this must further be added the tendency of cleared warmer air to rise on the outside of the bulk contained, producing false subsidence or an apparent descent of the fog limit to replace the removal by convection. The table shows how little confidence may be placed in these rates of subsidence, complicated as they are with so many vague secondary phenomena.

A comparison of tables 5 and 6 shows that the *final* velocities in the experimental curves (.017–.050 cm./sec.) correspond very closely to the velocities computed in table 5 (.021 cm./sec., etc.) for the particles produced in the earlier orders of exhaustion ($z = 0$, etc.). The two tables, therefore, mutually corroborate each other, proving that the order of values investigated for the size of the cloud particles is reasonably correct; proving also that the initial *apparent* subsidence is spurious, as anticipated. In fact, if water is precipitated by sudden cooling from atmospheric air in an otherwise dry vessel (*Cf.* Chapter VI, § 10), the apparent subsidence is astonishingly rapid, being of the order of more than meter/second. Clearly, from the excessively small particles precipitated, this can be nothing but quick evaporation under conditions of minimum moisture. As the temperature rises after the exhaustion, the air at once ceases to be saturated.

A few rough estimates may be made for the globe, 30 cm. in diameter. The descent of the body of fog per minute will be about 1.5 cm. during the first exhaustions ($z = 1$), and about 11 cm. during the final exhaustions ($z = 26$). The loss of particles may be taken as the ratio of the volume submerged to the total volume of fog, and the results show that during the first exhaustions a loss somewhat exceeding 5 %, during the last exhaustions a loss approaching 50 %, is to be apprehended. Hence, the time during which subsidence occurs (presence of fog within the receiver) must be reduced to a minimum, only maintained just long enough to make the observation. But even in this case the subsidence error toward the end of the series becomes increasingly menacing, and to it are to be ascribed the jagged outlines of the data for $s/\sqrt[3]{N}$ in tables 3 and 4. Very fortunately, the subsidence error is in large measure counterbalanced by the evaporation of particles, and for this reason the removal of particles by subsidence has been ignored in this chapter. Any correction applied would be arbitrary; but there is no question that the results could be materially improved if a new form of apparatus were contrived adapted to insure the utmost dispatch between the exhaustions and observations.

12. *Normal and other coronas.*—With particles as near together as they are originally (.02 to .03 cm.), it is not remarkable that other optical phenomena may make their appearance due to the mutual action of the edges of the particles, and it is not improbable that this mutual effect contributes to the colored central patch of the coronas, occurring as a superposition of a new phenomenon on the old. The normal coronas do not begin until the number of particles is 530 or 600 per cub. cm., or about 8 per linear cm., putting them somewhat more than 1 millimeter apart. Normal coronas are seen until the particles are about 2 millimeters apart, after which they shrink beyond observation. The particles themselves are but .0014 to .0025 cm. in diameter, at the beginning and the end of the series of normal coronas respectively, and are thus very small as compared with their distance apart. Again, initially—*i. e.*, immediately after nucleation, where the particles are but .02 cm. apart—their dimensions are .0003. In all cases, therefore, the interstices are large.

The ratio may be found generally. Since the nucleation $n = 6 \times 790 \times 10^{-9}/\pi d^3$ denotes the number per cubic centim., $\sqrt[3]{n}$ is the number per linear cm., and $\sqrt[3]{1/n}$, their distance apart. Otherwise $1/n$ is the volume of each and $\sqrt[3]{1/n}$ the edge of a cube occupied by a single particle. Hence,

$$\frac{\sqrt[3]{1/n}}{d} = \sqrt[3]{\frac{\pi}{6 \times 790 \times 10^{-9}}} = 87.$$

The edge of a cube containing one cloud particle and the diameter of that particle are proportional quantities in the ratio of 87 : 1. The density of the suspended water is thus on the average $.8 \times 10^{-6}$, throughout.

13. *Size of the particle producing axial color.* It is finally necessary to make a similar computation for the number of particles active in the drum when axial colors are seen. The correlation will be made by means of identical coronas. Writing as usual, $d = 1.44\, s \times 10^{-4} = d_0 \sqrt[3]{1/N}$, the initial diameter is $d_0 = 1.44\, (s \times \sqrt[3]{1/N} \times 10^{-4})$. Using the second series of axial colors, Chapter II, table 19, as these are more complete, two distant coronas are eminently available for comparison. These are the early member with the olive-green center and the subsequent member with an apple-green center.

Table 10 shows, (olive-green) $N = .368$ $y = 5.5$ $\sqrt[3]{1/N} = 1.4$
(apple-green) $N = .113$ $y = 18.5$ $\sqrt[3]{1/N} = 2.7$
Table 4 shows similarly (olive-green) $d = 4.6 \times 10^{-4}$ cm. $d_0 = 3.3 \times 10^{-4}$
(apple-green) $d = 8.1 \times 10^{-4}$ cm. $d_0 = 3.0 \times 10^{-4}$

It is hardly reasonable to look for better agreement in two observations so remote, and hence the mean value, $d_0 = 3.6 \times 10^{-4}$ will be taken for the reductions in case of the axial colors observed in the drum. Hence,

$$d = 3.6 \times 10^{-4} \times \sqrt[3]{1/N}.$$

The precipitation per cubic centimeter in the drum was found to be 361×10^{-9} grams of water per cubic centimeter of moist air, the pressure ratio being smaller. Hence, finally,

$$n = \frac{361 \times 10^{-9}}{\pi d^3/6} = 1.52 \times 10^4 \times N.$$

The data of table 7 were derived in this way.

This is an average exhibit of the dimensions and numbers of particles active in producing axial color. The final column shows their average distance apart. That the absorption phenomenon occurs for particles as large as d is in many ways surprising, for it does not suggest optical interference. The particles are, as before, thinly disseminated. The ratio of their distance apart and their diameters being

$$\frac{\sqrt[3]{1/n}}{d} = 113.$$

The density of distribution is somewhat smaller than before, but the length of column more than makes up for the difference.

If, therefore, a cube .01 cm. along each edge be imagined, this cube at the outset contains one particle of the diameter of 360×10^{-6} cm. Thus 113 cubes on end would make a row of particles normal to, and 113×113 cubes on end could be made to virtually fill up, the square content across the line of vision. Hence, .04 × 113² = 512 cm., or about 5 meters of column would be needed to virtually blot out the unaffected white light (excepting that which filters between rectangularly contiguous, co-planar spheres). At the end of the experiment a column .096 × 113² = 1280 cm. or about 13 meters long would be needed if axial color is to be seen. In the above experiments the column or drum was nearly 2 meters long and this proved to be insufficient.

TABLE 7.—DIMENSIONS AND NUMBERS OF CLOUD PARTICLES PRODUCING AXIAL COLOR. CONTENTS AS IN TABLE 19, CHAP. II. N_0 = 15,000 particles.

z	Corona.	Axial color.	$N \times 10^3$	$d \times 10^6$	n	$n^{-1/3}$
				cm.		cm.
0	Nucleation	——	1000	360	15000	.0405
1	Fog, colorless	Viol-bl	869	374	13300	.0420
2	" "	Bl	700	389	11800	
3	" "	"	702	407	10500	
4	Fog	Bl-gray	624	421	9360	
5	"	Yl-gr	555	439	8320	.0493
6	Fog, colorless	Gr-yl	493	457	7400	
7	Olive gr	Yl	438	475	6570	
8	"	Or	389	493	5830	
9	"	"	346	511	5190	
10	"	Or-rd	308	533	4620	.060
11	Gr-yl	Prp	273	554	4100	
12	"	"	243	576	3640	
13	Yl	Viol	216	601	3240	
14	Or-rd	Viol-bl	192	619	2880	
15	Rd	"	171	648	2560	.073
16	Prp	Gr	152	673	2280	
17	"	Yl	135	702	2020	
18	Wh-viol	——	120	731	1800	
19	Apple-green	Viol ?	106	760	1590	
20	Yl-gr	Viol	95	788	1420	.089
21	Or-rd	——	84	821	1260	.093
22	Viol-prp	——	75	853	1120	.096

14. *Summary.*—In conclusion, I give a tabulated summary of the chief constants relating to the coronas and axial colors, produced by water particles. In this table the colors of the coronas have been again overhauled, and the data refer to punk nuclei. N is the relative number of particles, n the absolute number per cub. cm.; d denotes the diameter of the particle in cm., $1/\sqrt[3]{n}$ the edge of a cube containing on the average just one particle. It may be useful to recall that

$$N = N_0 10^{z(1+bt)\log y},$$

where z denotes the number of the exhaustion or order of the corona in the series, b is the coefficient of the time losses apart from exhaustion, y the ratio of densities before and after exhaustion regarded as an adiabatic process, but corrected for the heat evolved by the precipitated water. In measuring the diameter, d, of the particles, the normal coronas succeeding the 20th exhaustion were used directly by comparing their angular aperture, s, with the coronas due to lycopodium spores, assuming for the latter, diameter d'_0 = .0032 cm., while s'_0 = .15 cm., by observation.

The source of light and the goniometer were each distant 2 1/2 meters from the receiver of cloud particles. The diameter of the earlier cloud particles was computed from N, and found to be

$$d_0 = 263 \times 10^{-6} \text{ for punk nuclei, in the globe,}$$
$$d_0 = 350 \times 10^{-6} \text{ for sulphur nuclei, in the globe.}$$
$$d_0 = 360 \times 10^{-6} \text{ for punk nuclei, in the drum.}$$

These values depend merely on the number of nuclei originally put in, but they were purposely made as large as practicable.

The precipitation for adiabatic expansion was computed from $rx = S\vartheta - C\vartheta \lg\vartheta$, where ϑ is the absolute temperature, r the latent and C the specific heat of the liquid, S the constant entropy and $x/(1-x)$ the ratio of vapor and liquid in the chilled mixture. For coronas in the globe, $m = 79 \times 10^{-8}$ grams of water were precipitated per cub. cm., and for axial colors in the drum, $m = 36 \times 10^{-8}$ grams of water were precipitated.

Finally, the absolute number was found from $m = n \times \frac{\pi}{6} \times d^3 = n \times \frac{\pi}{6}$ whence

for coronas in the globe, $n = 8.3 \times 10^4 \times N$, in case of punk nuclei,
$n = 3.6 \times 10^4 \times N$, in case of sulphur nuclei;
for axial colors in the drum, $n = 1.5 \times 10^4 \times N$,

with a weaker nucleation of punk nuclei. If $N = N_0 = 1$ or at the beginning of the experimental series,

$$n = 83{,}000, \qquad = 36{,}000, \qquad = 15{,}000, \text{ respectively,}$$

depending on the number of nuclei arbitrarily introduced.

The axial colors completely vanish before one half of the coronas have been passed. Experiment shows, therefore, conformably with the interpretation just adduced and apart from discrepancies due to insufficiently uniform distributions, that columns 5 to 13 meters long are necessary if saturated axial colors are to be observed.

Axial colors may, therefore, be produced by light which has passed through the particles and to the same agency the colored fields may be referred. It is easy to obtain color in the undeviated ray[1] (here the coronal center or axial color) when plates or films are dealt with, by superimposing an interference phenomenon on the diffraction phenomenon. For the sake of having a convenient scale of distribution, I mapped out the axial colors in this way in my earlier volumes. The case seems, however, to be very different when droplets as small as $2/10^4$ to $4/10^4$ cm. are in question. Here it is on the one hand difficult, in view of these small globules, to interpret the entrance of light in such a way as to produce interferences. On the other hand, the particles are too large to correspond to thicknesses which produce the vividly colored Newtonian interferences of the first and second order, for in such a case the plate must be of small thickness as compared with the wave length of light. In the absence of an adequate theory or even an adequate suggestion, it seems best, therefore, to leave the subject in abeyance, seeing that the light reflected from the outside of the particles must at the same time be accounted for, as well as the effect of the approach of the particles themselves.

---

[1] References to the well-known experiments of Quincke and others, and an analysis of Rowland's theory, will be found in Kayser's *Handbuch der Spectroscopie*, Leipzig, 1900, p. 428, et seq.

TABLE 8.—SUMMARY OF DATA FOR CORONAL AND AXIAL COLORS. MEAN VALUES.

$$N = N_0\ 10^{-(1+50 \log y)}.$$

$b = .1$. For coronas (globe, 30 diam.), y (corrected density ratio) $= .82$; $t = 1.75''$.
For axial colors (drum, 187 cm. long), $y = .92$; $t = 3.5^{\text{min}}$ nuclei from glowing charcoal.

Exhaustion No.	Corona.	$s \times 10^3$	$d \times 10^6$	$n \times 10^{-3}$	$n^{-\frac{1}{3}} \times 10^3$	Exhaustion No.	Axial color.	Corresponding corona	$s' \times 10^3$	$d \times 10^6$	$n \times 10^{-2}$	$n^{\frac{1}{3}} \times 10^3$
			cm	$1/\text{cm}^3$	cm					m	$1/\text{cm}^3$	m
0	Nucleation	1000	260	830	23	0	Nucleation.		1000	360	150	40
1	Fog	791	280	660	25	1	Viol-bl	Fog	880	370	130	42
2	Fog	626	310	520		2	Bl	"	790	390	120	
3	Fog	495	330	410		3	Bl	"	702	410	105	
4	Yellowish, Reddish	392	360	320		4	Bl-gray	"	624	420	94	
5	" " smaller	310	390	260	34	5	Yl-gr	"	555	440	83	49
6	Wh-yl, prp, gr-yl	245	420	200		6	Gr-yl	"	493	460	74	
7	Bluish, dk gr-bl, or, rd	194	450	160		7	Yl	Bl-Gr	438	470	66	
8	Greenish, dk-gr, prp, gr	154	490	130		8	Or	"	389	490	58	
9	Gr-yl, prp, gr, rd	122	530	100		9	Or	"	346	510	52	
10	Yl, or-rd, gr, prp	96	570	80	50	10	Or-rd	"	308	530	46	60
11	Yl, or, rd, gr, viol, gr	76.0	620	63		11	Prp	Gr-yl	273	550	41	
12	Wh-viol, prp, bl, gr, rd	60.2	670	50		12	Prp	Gr-yl	243	580	36	
13	Wh, prp, gr, rd, gr	47.6	730	39		13	Viol	Yl	216	600	32	
14	Gr, dk bl-gr, rd gr	37.7	780	31		14	Viol-bl	Or-rd	192	620	29	
15	Gr-yl, br, gr, rd	29.8	850	25	74	15	"	Rd	171	650	26	73
16	Yl-wh, or-rd, gr, viol	23.6	920	20		16	Gr	Prp	152	670	23	
17	Wh, prp, gr	18.7	990	15		17	Yl	Prp	135	700	20	
18	Wh-gr-yl, dk bl-gr, rd, gr,	14.8	1070	12		18	—	Viol	120	730	18	
19	Wh, rd-br, gr, bl, rd	11.7	1160	10		19	Viol ?	App-gr	106	760	16	
20	Wh, rd, gr	9.2	1250	7.7	111	20	Viol	Yl-gr	95	790	14	89
21	Wh, br, bl, gr, rd, gr	7.3	1350	6.0		21	—	Or-rd	84	820	13	93
22	"	5.8	1460	4.8		22	—	Viol-prp	75	850	11	96
23	"	4.6	1580	3.8								
24	"	3.6	1710	3.0								
25	"	2.9	1850	2.4	161							
26	" (faint)	2.3	2000	2.9								
27	"	1.8	2160	1.5								
28	" (very faint)	1.4	2340	1.2								
29	Vanishing	1.1	2530	.9								
30	"	.9	—	—								

CHAPTER IV.

GENERAL SURVEY OF CONDENSATION IN THE VAPORS OF IONIZING AND NON-IONIZING LIQUIDS.

The subjects to be treated promiscuously in the present chapter, are the behavior of nuclei in vapors of non-ionizing liquids, the form of coronas observed, the intensity of axial color effects, the production of nuclei spontaneously, by shaking liquids, etc., and the distribution of the initial nucleation as evidenced on exhaustion by the initial fogs. The methods used, though efficient for exploration, are not adapted to secure results of precision. The next chapter will show that the merest traces of solute will materially modify the behavior of a nominally pure solvent; and hence the liquids of the following paragraphs should in critical instances be regarded as dilute solutions.

GRADED CONDENSATION.

1. It would be difficult to read the admirable work on the relation of rain and atmospheric electricity which has issued from the Cavendish Laboratory, without being convinced of the strength of the arguments put forth. That in a repetition of these researches, in particular of the experiments of C. T. R. Wilson[1] on the comparative efficiency as condensation nuclei of positively and negatively charged ions, one would but reproduce his results, admits of no doubt.

In so important a question, however, it is none the less desirable to reach identical conclusions from entirely different methods of approach. It has been part of my purpose to be driven to like inferences; in other words to reach a point in my work where I should have to abandon the nucleus as an agency which for purely mechanical or thermodynamic reasons facilitates condensation, and be compelled to recognize the special activity due to its charge.

I had hoped to accomplish this in the following experiments[2] with benzine when contrasted with the corresponding behavior of water; but the results, contrary to my expectation, are so curious and pronounced an accentuation of the nuclear theory that it seems worth while to specially describe them.

2. The work originated in the following point of view: If the action promoting condensation is in any degree of a chemical nature (such suppositions have been made; the production of hydrogen superoxide, for instance, has been suggested), then there should be a marked difference in the efficacy of the same nucleus

---

[1] C. T. R. Wilson, *Phil. Trans.*, London, vol. CXCIII, pp. 289–308, 1899.

[2] Cf. *Science*, XV, pp. 175–178, 1902.

when the saturated water vapor is replaced by the vapor of some electrolytically neutral liquid, like a hydrocarbon. I accordingly made a series of experiments with benzine, endeavoring at first to utilize benzine jet and color tube in the usual way. In this I failed, for reasons without much relevant interest here. I then adopted the method of adiabatic cooling, partially exhausting a spherical receiver (Coulier, Kiessling[1]) about 23 cm. in diameter, illuminated by white light diverging from an external point. In this way not only were copious fogs obtained, but the coronas produced were additionally available as evidence.

In the benzine jet, particles are probably cooled too suddenly, and at once attain a size incompatible with axial color effects. Using the exhaustion method, however, these axial colors appearing in benzine are not only of pronounced depth, but they run into higher orders than in the case of moist air subjected to like exhaustions. Sequences passing through blue, green, yellow, brown, purple, etc., green, brown, etc., may be seen in the axis of a column only 23 cm. long. The reason, no doubt, is associated with the lower latent heat of benzine,[2] insuring the formation of drops not less uniform, but of a size, caet. par., regularly larger than for water vapor. The fact that axial colors are producible both with water and with a pronounced insulator like benzine, is a result of fundamental importance in its bearing on any theory adduced to account for the axial absorption in question.

3. The exhaustion experiments[3] were thus at once successful. Cloudy condensation was as densely produced in benzine vapor as in water vapor, with phosphorus, flame, and other nuclei. Care was taken to insure dryness of vessel by test experiments both before the benzine was introduced and after it had been quite removed by evaporation. The exhaustion of about one sixth, say 13 cm., seemed best adapted to bring out the following phenomena. When the receiver was left standing overnight no marked condensation occurred in the absence of nucleation, or else the condensation was rain-like, a fine mist falling about 2 or 3 cm. per second.

The introductory experiments were made with light nearly in parallel, the sun's image being used as a coronal center. The even dense tawny benzine fog after the first nucleation was expected to develop on subsequent exhaustions (each followed by an influx of filtered air) into the magnificent coronas which characterize this experiment in the case of water vapor. On the contrary, however, the fogs were more fleeting, showing a more rapid descent than aqueous fogs, and the color fields obtained were not ring-shaped as expected, but *sharply stratified horizontally*, roughly speaking, in alternations of green and red.

Moreover, if the exhaustions were made successive without influx of air between each, the colors rose in strata from below, as they fell in strata when left to themselves. On mounting, the strata grew successively wider and thinner till

---

[1] For a digest of earlier observations, see my *Report on Cloudy Condensation*, Bull. 12, U. S. Weather Bureau, 1893.

[2] Latent heat is not the only determinative factor, nor even the most important, as has been seen above.

[3] Coronas afterwards produced by *paraffine* nuclei in benzol vapor (Chap. V, § 37) might have been effectively inserted here.

they vanished from sight, brown, yellow white being the last colors observed. Uniform color fields (strata of limiting width) were eventually producible in this way. Yellow, brown, crimson, arose from a whitish blue base, then descended again on completed exhaustion, reminding one of the extension of an accordion. The speed of apparent viscous subsidence of the top bands has no direct meaning, since fall (or rise) is here complicated by evaporation.

On entrance of air, vortices were evidenced by ring-shaped threads of color so that mixture was at first inevitable. One must wait till this ceases before again exhausting. Convection currents due to local reheating of the adiabatically cooled gas by the walls of the receiver, were equally apparent, stringy colors rising on the outside and descending into the middle of the receiver. It is the same phenomenon which interferes with the usefulness of narrow tubular apparatus.

4. As this subsidence of color bands in benzine vapor is an observation of importance, I resolved to repeat the work under more normal conditions. Accordingly, I used as my source of light the bright area of the mantle of a Welsbach burner, seen through a small hole in the metallic screen by an eye, looking centrally through the receiver containing saturated benzine vapor and nucleated air. Punk nuclei replaced the phosphorus nuclei. On exhaustion (without nucleation) after standing overnight, the coronas were white centered, fringed with brown, about as large as ordinary lycopodium coronas seen under like conditions. These large drops are a proof of the relative absence of nuclei initially.

After nucleation, the first dense fogs were vaguely annular during the first five successive exhaustions, filtered air being supplied between each. The next five exhaustions produced more nearly, finally very fully, stratified colors, in spite of the point source of light. Shaking the receiver violently at any time, so as to scatter the liquid benzine within, always reproduced a nearly perfect corona, which, on standing, became distorted again, in color at least. I now made special experiments, shaking the receiver before each observation, bringing out successive coronal effects[1] never as perfect as with water, however, always showing the tendency to stratification. The characteristic coronas succeeded each other so rapidly that it would be difficult to make them out. Nuclei, however, were still present after over two hours, the eventually white centered coronas showing a continued shrinkage to smaller diameters in accordance with the diminishing number of nuclei present. Twenty exhaustions did not remove them.

Here, as above, therefore, the fleeting character of the coronas, their tendency to depart from the normal annular character into stratification, the speed of descent of the color bands,[2] their rise upward on exhaustion like a fog from a lake, are the special characteristics of the colored cloudy condensation occurring in benzine. To these are to be added the striking axial colors mentioned above.

5. To explain the above phenomena in their variation from the normal aqueous corona, it is first necessary to account for the more rapid subsidence of

[1] These will be described in a subsequent paragraph.

[2] Due both to evaporation at the fog surface as well as to subsidence, very volatile and relatively heavy drops promoting both occurrences.

nuclei. I am not aware of appreciable differences of viscosity in the two vapors; but benzine has the smaller latent heat of evaporation by over seven times. To the extent in which the relevant constants of benzol are known, the phenomena may be provisionally explained with this ratio (*Cf.* Chap. III, §§ 4 and 5). Hence, under identical conditions of nucleation and for like exhaustions or like adiabatic cooling of a given mass of saturated air, the drops would be larger, the colors more advanced in benzine than in water; and since the square of radius is in question, this would point to subsidence of the loaded nuclei in benzine nearly four times more rapid. It would also account for more rapid evaporation or more fleeting colors, which is the case.

Again, if the loaded nuclei be regarded as mechanical particles, the largest will eventually be found in the lower strata, the smallest in the upper strata, as in a case of ordinary subsidence of suspended matter in water. It is well known, moreover, that smaller droplets wane, larger droplets grow. Hence, on increasing exhaustion condensation takes place first at the bottom and last at the top, since the smallest nuclei correspond to greatest vapor pressure or difficulty in condensation, and since the largest nuclei have been loaded with condensed liquid first, have parted with it last, have had greater time in falling, and have therefore sunk deepest before losing their liquid load. The strata must mount upward as fresh exhaustion proceeds. The last colors to appear are the browns and yellows of the first order, like those seen in the steam tube for vanishing condensations. The whole phenomenon is thus the result of strata of invisible nuclei, *graded in virtue of the loading mechanism*, and partakes throughout of a mechanical character to the extent that the nuclei are not even a uniform product. The forced distribution is sufficiently powerful to entirely mask the elementary optical phenomenon.

On shaking the liquid benzine in the receiver, uniform distribution is again promoted, with the result that annular coronas reappear. It is particularly to be noticed that subsidence is due to loaded nuclei. The free nucleus does not appreciably descend. Even with water vapor, loading does not produce stratification. Water fogs when exceptionally dense may sometimes be seen to rise, but the diffraction pattern is always annular and usually without color distortion.

6. After completing the above work, I made similar experiments with benzol, reaching the additional result that the nuclei here behave as if they were produced by the liquid itself in the dark. The sequel will show that they are not really so produced, but have a habit of brooding over the surface and thus escaping detection until revealed by diffusion. They then ascend against gravity in horizontal strata. They may be precipitated by partial exhaustion, leaving the air nearly free from nuclei, but the above flask was refilled with nuclei in 10 or 20 minutes. The experiment may be repeated any number of times. The sharp demarcation between the pure air above and the rising surface of nuclei below, is beautifully evidenced by the coronas, which are annularly perfect for axial beams below the surface, asymptotically bowl-shaped near the surface, and absent for axial beams above the surface. *Cf.* figure 2, Chapter III.

Truly spontaneous nucleation in the dark was only discovered in a few cases, notably that of carbon disulphide and certain solutions. In these the number of nuclei ultimately reaches a fixed maximum or saturation at an excessively small vapor pressure, and the final coronas have fixed diameters for fixed supersaturations.

THE FLOWER-LIKE DISTORTION OF CORONAS DUE TO GRADED DISTRIBUTIONS OF NUCLEI.[1]

7. The foregoing general descriptions have brought out a series of coronas obtained very easily with volatile hydrocarbon solvents, benzol, etc., in which the coronas met with are not closed and annular, but of a variety of patterns from oval, with the long axis vertical, to the symmetrically open doubly inflected types (lyre-shaped, basin-shaped), running continuously into horizontal strata in the limiting case. It will be expedient to examine more closely into these conditions before proceeding to a detailed study of the phenomena in hydrocarbon liquids generally.

These distortions are due to the non-uniform distribution of nuclei as to size, the largest having sunk deepest and the finer nuclei floating uppermost, in virtue of the precipitation mechanism. When supersaturation is produced by adiabatically cooling the benzol vapor, the condensation begins at the lower strata and then passes upward as exhaustion proceeds and higher degrees of supersaturation are reached. The evolution of coronas is peculiar in this case, and reminds one of a person throwing out his arms laterally and upwards until his hands strike above his head. The sweep of coronal streamers is outward and upward symmetrically with respect to the vertical plane through the source of light. If the gradation is not too rapid, they eventually coalesce above it.

The droplets produced are finer above than below; but it does not follow that there are more particles in the upper layers. The reverse will naturally be assumed. The lower particles being larger, have first received the condensation as already suggested, and have thus grown biggest, as the opportunities for growth came earliest and lasted longest.

8. It is my purpose in this section to work out the shape of the *loci of like color* when the nucleation is not uniform as to size or number. The distributions arise from the subsidence of loaded nuclei; they are, therefore, horizontally stratified.

In figure 1, let o be the distant point source of light into which the coronas would shrink annularly and symmetrically from without inward, to a limit in a normal case. Let φ be the angle between the horizontal through o and the radius vector, r, to a line of uniform color, ab, in the distorted corona, and let h be the height of the extremity, c, of the radius vector above the datum line through o. If R be the distance of r from the eye of the observer, $2r/R = s/R$ is the angular aperture of the corona.

Let δ be the diameter of the particles at the level passing through c. Then if δ_0 and s_0/R be the corresponding quantities (diameter and aperture) of particles in the datum level,

$$\delta s = \delta_0 s_0 = .00144, \qquad (1)$$

---

[1] Cf. *Am. Journ. of Sci.*, (4), pp. 309–312, vol. xiii., 1902.

the number being found by experiment for normal coronas. Hence, $r d\delta + \delta dr = 0$ (2) where $r = s/2$. Again, if the angle φ increases counter-clockwise by $d\varphi$,

$$r d\varphi \cos\varphi + dr \sin\varphi = dh. \qquad (3)$$

Let $d\delta = a dh$ (4) so that the diameter of the water particles is supposed to decrease (a being negative) uniformly upward. Other laws of distribution would merely complicate the problem without conducing to the present purposes, seeing that the observed facts will be sufficiently interpreted by equation (4). Combining (4), (3), (2),

$$r.\cos\varphi d\varphi + \sin\varphi dr = -(\delta/a)(dr/r) = -.00072\, dr/ar^2, \text{ by equation (1).} \qquad (5)$$

Put $A = .00072/a$ and integrate (5) whence $\sin\varphi = C/r + A/r^2$. To determine C, equation (1) is available, since for $\varphi = 0$, $r = r_0$. Therefore

$$\sin\varphi = -(4A/s)(1/s_0 - 1/s).$$

To construct these coronas, distorted in consequence of the linear distribution of size of particles, it will generally be more convenient to express s in terms of φ, so that finally,

$$s = -(2A/s_0 \sin\varphi)\left(1 - \sqrt{1 + s^2_0 \sin\varphi/A}\right) = -(\delta_0/a \sin\varphi)\left(1 - \sqrt{1 + 2A/s_0 \sin\varphi/\delta_0}\right). \qquad (6)$$

Fig. 2.

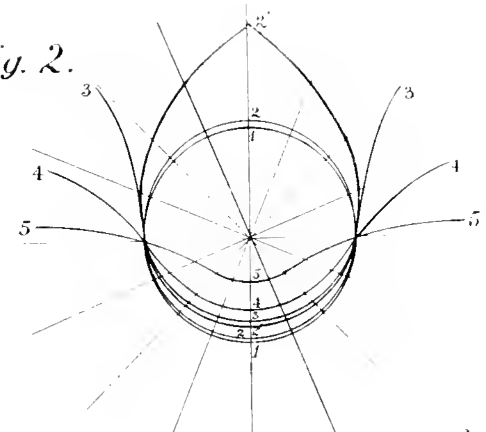


Fig. 1.

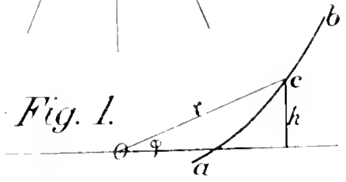


FIG. 1.—DIAGRAM.

FIG. 2.—CAMPANULATE CORONAS DUE TO DISTRIBUTIONS OF NUCLEI, GRADED IN THE RATIO OF $a = d\delta/dh = .0005$, .00010, .00035, .00050, AND .00100. CORRESPONDING CURVES HAVE THE SAME NUMBER ABOVE AND BELOW THE HORIZON.

9. With this equation the following table has been computed (a is for convenience entered positively). To have an average case at the datum level, put $\delta_0 = .001^{\text{cm}}$, as the diameter of particles. The values of s are given for 9 values of φ and for 6 values of a; viz., $a = .00005$, .0001, .00035, .0005, .001, or for $a/\delta_0 =$ .05, .1, .35, .5, 1.0, as decrements of diameter per linear centimeter of level above h_0.

TABLE [illegible].—[illegible] CORONAS DUE TO GRADED CONDENSATION.

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	1	1.10	1.12	.97	.58	−90
[illegible]	[illegible]	1.2[illegible]	1.2[illegible]	1.14	.99	.6	−67.5
[illegible]	[illegible]	1.3[illegible]	1.24	1.19	1.[illegible]5	.66	45
[illegible]	1.43	1.4	1.32	1.28	1.18	.8	−22.5
	1.44	1.44	1.44	1.44	1.44	1.44	–
[illegible]	1.46	1.4	1.61	1.72			+22.5
[illegible]	1.47	1.52	1.76	—			45
[illegible]	1.49	1.55	2.25	—			67.5
	1.5	1.56	[illegible]				90

[illegible]	.5	1	.35	[illegible]5	1	.5
[illegible]	[illegible]4	[illegible]	2.[illegible]7	−1.44	.72	.144
[illegible]	[illegible]	1	2.[illegible]7	2	1	.2
[illegible]	1.44	2.88	1	1.44	[illegible]8	14.4
φ		[illegible]	[illegible]	13.9	2[illegible]3	3.9

The curves showing the loci of uniform color for these different conditions are constructed in the chart and numbered 1–5 in succession. No. 1 is still very nearly circular, while No. 2 is more oval, the members having risen above No. 1. Both curves are closed. No. 2′ is the interesting transitional case between closed and open curves, concerning which presently. No. 3 is already quite open and bell-shaped; No. 4 more so; No. 5 is basin-shaped, and succeeding curves would more and more nearly approach the horizontal line through the source. Naturally, all curves pass through the same two points in this line.

Moreover, equation (6) shows that s becomes imaginary when $1 \; (s^2_0/A)\sin\varphi$ since A is negative. The final values of s and φ are thus given by $\sin\varphi_m = -A/s^2_0$, so that on reduction $s = 2s_0 = 2.88$. These data are also given in the table. It is further apparent that the corona will just begin to open on top when $1 = -s^2_0/A$, or $\sin\varphi = 1$. Since $A = .00072\,a$ and $s_0 = 1.44$ the gradient $a = .0035$. This is the curve No. 2′ between the conditions of Nos. 2 and 3. In all these cases the equation given strikingly interprets the opening of a harebell or what would be called campanulate efflorescence in botany.

I may add, in conclusion, that all the types of curves given are continually and repeatedly met with in working with volatile liquids, among which I have now examined gasoline, benzine, benzol, and carbon disulphide, at length. The law of distribution reproduces the cases as nearly as they can be tested in the fleeting coronas, though the real law is not liable to be linear and will have to be specially worked out.

Finally, if all gradation of particles is absent, or if the air passes abruptly from uniformly nucleated to non-nucleated air passing through a horizontal plane of discontinuity, the coronas seen in the horizon are semicircular, and not distorted as above. This is often the case with carbon disulphide.

PRELIMINARY EXPERIMENTS WITH NUCLEI IN HYDROCARBON AND OTHER VAPORS.

The following experiments contain a cursory view of a number of occurrences which may be observed in working with vapors of the kind specified. Attention will be directed to the coronal colors and shapes, to the axial colors, to the spontaneous generation of nuclei in the dark, to the nuclei producible by shaking liquids and solutions, to the velocity of these and other nuclei, etc. The more interesting features will be reserved for quantitative determination in the subsequent chapters. The apparatus is shown in Chapter III, figure 2, and will need no special description. During nucleation the filter, *f*, is replaced by an ionizer.

10. *Gasolene. Coronas and axial colors.*—To test the sequence to axial colors for this vapor, the drum was carefully dried and the successive exhaustions made in the usual way. The results, though showing great intensity and abundance of axial color, were so irregular as to the coronas that no systematic conclusions could be drawn. Horizontal bands, dense or in colored strata, appeared in place of the coronas. A copious gasolene rain was observed on the day following the nucleation, together with small coronas. The difficulty, therefore, is absence of homogeneity, and the endeavor to improve the conditions by rocking the drum violently between the exhaustions proved of no avail. Energetic shaking of the liquid within the drum alone evokes annular coronas, but this is a serious interference with the experiment. The following table is an example of the results reached:

TABLE 2.—BEHAVIOR OF SULPHUR NUCLEI IN GASOLENE VAPOR. DRUM. EXHAUSTION, 76–68 cm.

Exhaustion No.	Time.	Corona.	Axial color.[1]
0	$10^h\ 18^m$	Nucleation	——
1	21	Opaque	——
2	25	"	Bl-op
3	28	Fog	Bl, rd, op
4	31	"	"
5	35	"	Or, op
6	40	"	Or, gr, op
7	43	"	Op, bl, gr
8	48	"	Rd, bl-gr
9	51	"	Or, gr
10	55	Colored fog	Or, gr
11	59	" "	Viol, gr
12	$11^h\ 3^m$	" "	"
13	11	Strata	Or, yl
14	15	"	Prp, viol
15	20	"	——
16	$12^h\ 0^m$	——	Axial color still present

[1] Bl, blue; op, opaque; rd, red; gr, green; or, orange; prp, purple; viol, violet.

Thus the axial colors flash through a variety of tones, terminating in opaque, which is here a mere evidence of irregular size. Very little reliance can therefore be placed on the color sequences, but the marked occurrence of axial color is well brought out.

The following table is a full series of experiments made to determine the coronas in gasolene vapor. They were obtained in a glass globe, 23 cm. in diameter, with careful filtration. Some of the coronas are measured.

TABLE 3. BEHAVIOR OF PUNK NUCLEI IN GASOLENE VAPOR. GLOBE, 23 cm. IN DIAMETER. EXHAUSTION, 70–50 cm. DIAMETER OF DROPLETS *d*, IN cm.

Exh. No.	Time	Corona	*d* (cm.)
	52	Nucleation	
1	54	Fog in *upper* hemisphere only	
2	56	Shaken, wh, rd, dk-gr, diffuse	
3–5	58–62	" " " "	
6	64	" " " "	.00139
7	66	" " " "	.00136
8	68	" " " "	.00144
9	70	Vague	
10	72	Absent	

Here the initial fog floats gravitationally on the clear air below, as the punk nuclei were introduced from glowing charcoal.

11. *Spontaneous nucleation.*—If the nuclei are left standing, they are liable to persist for many hours, and good coronas (nucleation now homogeneous) may be obtained on the succeeding day. A clean vessel, however, remains clean. There is no spontaneous nucleation.

Thus, I found in a vessel freed from nuclei by exhaustion at 9^h 50^m, no coronas or rain at 1^h 10^m, nor at 2^h 45^m. Similarly, when left over night, the clean vessel remained free from nuclei.

12. *Shaken nuclei.*—On shaking the gasolene violently, coronas were produced as follows:

Exhaustion,	1	2	3	4
Corona,	Strong $s = .50$ $d = .0029$	Faint, $s = .50$ $d = .0029$	Absent.	Absent.

It is noteworthy that the nuclei of these coronas are themselves very persistent. Examined 7 minutes after shaking, the corona was of undiminished strength; after 30 minutes it was scarcely weaker. It will be seen below that nuclei so obtained are as persistent as any other kind, and may be traced 15 or 25 hours after shaking. They cannot, therefore, be gasolene globules, which would vanish instantly, but rather (at first sight) the residual solute of a dilute solution. The examination of water, however, in which both solid and gaseous solutes were tested, showed that they are concentrated solutions and that they persist in view of the occurrence of peculiar conditions of equilibrium. (*Cf.* Chapter V, §§ 44, 47, 48, or, below, § 30.)

13. *Benzine. Spontaneous nucleation.*—The main occurrences have already been given. With air nuclei ($s = .50$, $d = .0029$ cm., and larger), the coronas may be removed in two exhaustions. Spontaneous nucleation does not occur. A clean vessel examined an hour later was still clean; examined next day, it remained so.

14. *Coronas and axial color.*—The following table is an example of the occurrence of strong axial color, all the more noteworthy as the diameter of the vessel was only 23 cm. The occurrence of the initial fog in the upper half of the vessel is rare, but the nuclei came from a sulphur flame.

TABLE 4.—BEHAVIOR OF SULPHUR NUCLEI IN BENZINE VAPOR. GLOBE, 23 cm. IN DIAMETER. EXHAUSTION, 76–50 cm

Exhaustion No.	Time.	Coronas.	Axial colors.[1]
0	43^m	Nucleation	——
1	44	Fog in *upper* hemisphere only	——
2	45	Fog	Bl-gr
3	46	"	Gr-yl
4	47	"	Prp
5	48	Olive-gr	Viol
6	49	White, red	Gr-yl
7	50	?	"
8	51	?	Prp
9	52	?	Gr-yl
10	53	Normal coronas	Yl ?
11	54	" "	——
12	55	" "	——
		Etc.	

[1] Abbreviations as in table 2.

15. *Petroleum. Coronas and axial colors.*—The behavior of petroleum presents a wide divergence from the preceding instances of very volatile hydrocarbons. A full series of coronas is producible, in every respect like those for water as to color sequences, though nothing can be stated as to the relative size of the nuclei in action. The axial colors show a like succession, though naturally they are weaker, from the small quantity of vapor available. For the same reason the coronas are, as a rule, larger than those of water obtained under like conditions.

Petroleum is not free from a tendency to produce stratified coronas; the tables show that annuli, differently colored above and below their centers, soon occur, and that the interferences met with on shaking the liquid cannot be avoided if annular coronas are wanted.

TABLE 5. CORONAS IN PETROLEUM VAPOR. EXHAUSTION, 76.59 cm. PUNK NUCLEI. GLOBE, 23 cm. IN DIAMETER. FIRST SERIES. DIAMETER OF DROPLETS, d IN cm.

No.		Coronas	No. Exh.		Coronas	d	
	35	[illegible]	18	54	Wh, rd, gr		*Next day.* Coronas absent in each of five exhaustions
1	37	Gr-y, tawny, [illegible] flame	19	55	Wh, br, bl, gr		
2	38	Or, " flame	20	56	Regular coronas, d	[illegible]	
3	39	Br, " "	22		" "	[illegible]	Shaken: Five exhaustions do not remove corona
4	40	Shaken. Bl gr	23		" "	.0009	
5	41	Yl gr	24		" "	.0010	
6	42	Gr-yl	25		" "	.0011	After 2: Vessel again free from coronas
7	43	Shaken. Gr-yl	26		" "	= .0012	
8	44	Wh, or-rd, gr	27		" "	.0014	
9	45	Wh, purp, gr	28		" "	=.0014	Ten exhaustions breed a faint corona, showing filter not quite perfect
10	46	Wh $\begin{cases} cr \\ gr \end{cases}$ (distorted)	29		" "	=.0014	
11	47	Shaken. Apple-gr	30	69	" "	=.0014	
12	48	Yl gr	31		" "	=.0015	
13	49	Wh, or-rd, gr	32		Faint	.0019	
14	50	Wh, cr, gr	33		"	[illegible]	
15	51	Yl, gr, br	34		"	.0019	
16	52	Gr-yl, bl, rd	[illegible]		"	= .0019	
17	53	Wh, rd, gr			Sealed up for next day		

Abbreviations as in table 2.

TABLE 6. CORONAS IN PETROLEUM VAPOR. AIR NUCLEI. EXHAUSTION, 76.59 cm. DIAMETER OF DROPLETS, d IN cm.

Exh. No.	Series II New Filter.	Series I	Exhaustion No.	Series I	Exhaustion No.	Series I.
1	Yl, or, rd	Gr-yl	20	——	39	——
2	" " faint	"	21	—	40	d = .0144
3	Wh, rd "	Normal	22	——	41	——
4	"	" distorted	23	Shaken d = .0011	42	——
5	" d = .0013	Greenish	24		43[1]	d = .0018
6	"	"	25	" d = .0011	44	d = .0019
7	"	Shaken	26	" .0011	45[4]	d = .0022
8	"	"	27	" =.0011		
9	"		28			
10	" d = .0017		29	" [illegible]		
11	"		30			
12	"		31	" .0010		
13	"		32	" [illegible]		
14	Very faint		33	d =.0012		
15	" d = [illegible]		34	d =.0012		
16	" d = [illegible]		35	—		
17	Lt		36	—		
18			37[2]	d = .0144		
19			38	d = .0144		

[1] W[illegible] [2] Waited [illegible] [3] Waited 4[illegible] [4] Waited 3[illegible]

TABLE 7.—CORONAS IN PETROLEUM VAPOR. PUNK NUCLEI. EXHAUSTIONS, 76–59 cm. DIAMETER OF DROPLETS, d IN cm. NEW FILTER.

Exhaustion No.	Time.	Corona.	Exhaustion No.	Time.	Corona.
1	35^{m}	Nucleation	14	54.5^{m}	Wh, prp
2	36.5	Gray, reddish	15	56	Wh, prp Wh, gr
3	38	" "	16	57.5	Wh, gr
4	39.5	Bl-gr	17	59	Normal coronas
5	41	Yl-gr[1]	18	60.5	$d = .0013$
6	42.5	Gr-yl	19	62	$d = .0012$
7	44	Yl, rd	20	63.5	
8	45.5	Wh, or-rd	21	65	
9	47	Wh, prp	22	66.5	—
10	48.5	Wh-gr[2]	23	68	
11	50	Gr	24	69.5	$d = .0018$
12	51.5	Gr-yl	25	71	$d = .0014$[1]
13	53	Wh, rd			

[1] Shaken. [2] Irregular.

TABLE 8.—CORONAS IN PETROLEUM VAPOR. SULPHUR NUCLEI. EXHAUSTIONS, 76–59 cm. DIAMETER OF DROPLETS, d IN cm. NEW FILTER.

Exhaustion No.	Time.	Corona.	Exhaustion No.	Time.	Corona.
1	38^{m}	Nucleation	13	54.5	Wh, prp
2	39	Fog, uniform	14	56	Gr
3	40.5	"	15	57.5	Gr
4	41	" reddish	16	59	Gr-yl
5	42.5	" "	17	60.5	Wh, rd, irregular
6	44	" "	18	62	Yl, rd
7	45.5	Bl-gr	19	63.5	Wh, prp
8	47	Gr (shaken)	20	65	Gr
9	48.5	Gr-yl	21	66.5	Gr, rd
10	50	Yl, rd	22	68	Coronas
11	51.5	Yl, rd	23	69.5	$d = .0012$
12	53	Wh, prp	24	71[1]	$d = .0013$

[1] Successive coronas too faint and fleeting for measurement.

A feature of these experiments is the result that mere exhaustion is almost powerless to clear the vessel of nuclei. Thus, in table 6, 40 exhaustions do not suffice (though the effect is doubtless counteracted by the shaking applied), so that any imperfection in the filter is at once fatal. Even air nuclei, in table 6, are apt to persist indefinitely, unless long lapses of time intervene between the exhaustions. Consequently, in tables 6, 7, and 8, the observations were repeated with a new conical filter 40 cm. long and of compressed cotton. The coronas in this case are somewhat smaller in diameter, showing fewer nuclei and larger particles, but their persistence nevertheless remains a striking feature.

16. *Spontaneous nuclei, etc.*—The nuclei vanish completely on the lapse of

time, as shown in table 5. Hence, anything in the nature of spontaneous nucleation does not occur.

Nuclei produced by shaking, though removable with difficulty on exhaustion, come out after the lapse of one or two hours. Probably the accession of liquid due to each exhaustion is too small to materially affect the rate of subsidence, a circumstance suggested by the large coronas. The early decay of nuclei produced by shaking is an indication of the absence of foreign material in solution.

Benzol. In case of this reagent it will be expedient to describe the phenomena more at length than was done for the preceding liquids.

17. *Coronas.*—When sulphur or other nuclei are put into the globe containing benzol vapor, the result is peculiar. Instead of distributing themselves homogeneously throughout the receiver, they usually collect in a heavy band near the bottom. This is invisible until revealed by the first exhaustion, when a heavy sluggish fog-bank is seen, only a few centimeters high. After violently shaking the benzol in the receiver, strong coronas gradually show themselves in the successive exhaustions. They are always of the normal type, however, being white centered and gradually narrowing to a vanishing diameter, as the nuclei are more and more precipitated. Without shaking, the coronas are soon distorted again, evidencing as in the case of gasolene, etc., a marked tendency to stratification. Out of this confusion, normal coronas may be regained at any time while the nucleation lasts, and the droplets produced by shaking can have but a secondary influence on the main phenomenon. Careful inspection of the experiment during exhaustion shows that the earlier coronas are flashed through; but the normal type alone persists, the whole indicating drops of large size. A vanishing corona after exhaustion expands and clears.

18. *Banked fogs.* The most curious feature in connection with benzol, as well as the preceding liquids, is the subsidence of the invisible nucleated air immediately after influx and without exhaustion. It is not necessary to load the nucleus by special exhaustion. This experiment recalls in some respects the very slow subsidence of clay particles in pure water, and its almost tempestuous descent in ether and similar liquids; but it is more probable that the nucleus loads itself with a definite amount of liquid invisibly and without supersaturation, and that the succeeding arrangement of strata is gravitational, the nucleated air being heaviest. The subject will be fully treated in the next chapter.

19. *Diffusion of nuclei.*—Another feature easily observed with benzol, is the apparent issue of nuclei from the liquid, already referred to. Supposing the air in the receiver to have been practically freed from nuclei, good coronas will appear in 5 minutes within the lower third of the globe, while the upper two-thirds is still quite clear. A single exhaustion will usually throw them out again. After 20 minutes waiting the vessel is quite full of nuclei, and the coronas found are perfect throughout. Several exhaustions are needed to clear the vessel. At the surface of demarcation the coronas are campanulate, showing that the particles are graded, with the smallest uppermost, either from evaporation or from belated precipitation. Eventually the coronas return to the annular form, compatible with the uniform dis-

tribution of nuclei, and reach a maximum diameter, from which they slowly decrease indefinitely. Violent agitation (shaking) of the vessel and contents diminishes the number of nuclei to a fixed minimum. The vessel is thus partially cleansed by mere shaking. The following are a few data:

TABLE 9.—SIZES OF CORONAS IN BENZOL VAPOR. EXHAUSTION, 76 − 52 cm. VESSEL, 23 cm. IN DIAMETER. GONIOMETER RADIUS, 20.1 cm. DIAMETER OF DROPLETS, d IN cm. $d = .0144/s$.

Experiment.	s	Coronal aperture	d	
	cm.		cm.	
First	.62	1° 48′	.0023	Apparently spontaneous (residual) nuclei
Later	.72	2 6	20	
After 45m	.71	2 6	20	
	.60	1° 42′	.0024	Shaken once
	.40	1 9	36	" twice
	.40	1 9	36	" 3 times
	.45	1 18′	32	" 4 "
	.40	1 9′	36	" 5 "
	.45	1 18′	32	" 6 "

Thus, the white center of the corona originally exceeds 2° in diameter, while the coronas left after shaking is somewhat over 1° in diameter. If s is the chord subtended by the aperture on the goniometer, the diameter of the particles are found from $d = 1.44 \times 10^{-3}/s$, and the large size indicates that relatively few were present. For reasons given above (Chapter III, §§ 4, 5), the absolute number of particles cannot be found.

The semi-annular coronas with sharp horizontal demarcation make it possible to measure the speed of diffusion of the nuclei upward. As shown in the figure, the source of the nuclei is a couche very near the surface of the lake, a, (Chapter III, Fig. 2), and the vessel is left without interference for different lengths of time. Using the globe 23 cm. in diameter, with a lake of benzol about 10 cm. in diameter, the rise (roughly estimated) was about 1/3 of the height in 5m, 1/2 in 10m, and 3/4, the full height, in 18m. The rates would therefore be .03, .02, .02 centims. per second, respectively. The experiment repeated with fresh benzol showed similar results. After purifying the vessel and waiting 2 hours, a magnificent multiannular corona (an evidence of exceptional homogeneity) showed itself, but vanished too soon for measurement. Cleaning and waiting for an additional half hour, $s = .52$, $d = .0028$ cm. was found. The following data were now investigated for the rate at which these apparently spontaneous nuclei diffuse upward:

Time elapsed,	Rise,
5m	7 cm.
10m	9 cm.
15m	13 cm.
20m	17 cm.

The last three data show a uniform rate of about .014 cm./sec. The first datum corresponds to a larger rate (.023 cm./sec.), meaning, probably, that the initial couche was not sufficiently lowered. The results are furthermore in accord with a rate of diffusion independent of the shape of the vessel. (*Cf.* Chapter VI.)

20. *Repetition.*—The occurrence of apparently spontaneous nucleation in benzol and not in the other liquids, induced me to investigate the origin of these particles again, using the more perfect filter already described. Beginning with air nuclei, the results were:

Exhaustion No.,	1	2	3	4	5	6
Corona,	Strong.	Weaker.	Vanishing.	Absent.	Absent.	Absent.

After 36 minutes this cleaned charge was again tested, but no coronas were in evidence. Hence, nuclei were not spontaneously produced. The experiment was carefully repeated later in the day, with the same results. The vessel, examined next day, showed, nevertheless, that nuclei had arisen from somewhere during the night. They were removed in two exhaustions. It was thus necessary to add new tests, with a specially cleaned vessel and long waiting (15–20 hours) between the experiments. These finally placed the absence of spontaneous nucleation in benzol beyond a doubt. What does occur is the diffusion of the residual band overlooked on exhaustion, and brooding immediately over the liquid surface. Thus a fine sheet of fog, due to air nuclei near the surface of the liquid, will diffuse sufficiently in 30 minutes to produce a full corona on exhaustion, and 5–10 exhaustions may be required to remove the nuclei.

21. *Shaken nuclei.* The following incidental example of the persistence of the nuclei produced by shaking benzol may be inserted here for comparison. The subject will be examined at length below with other apparatus:

Lapse of time after shaking,		Corona,
	5^m	strong
	44	strong
	30^m	strong
	60^m	distinct
	180^m	distinct
	15	absent

These nuclei are not as remarkably persistent as the cases examined below, but they cannot be particles of pure liquid, as this would instantly evaporate.

22. *Toluol.* This liquid behaves similarly to benzol. The following table contains results showing the coronas produced by air nuclei on exhaustions from 76 to 60 cms.:

Exhaustion,	
1	Campanulate semi-coronas
2	Faint oval coronas
3	" annular coronas
4	" " "
5	Coronas vanishing
6	" absent
7	" "

Even with air nuclei, therefore, the first corona is a campanulate form, indicating strongly graded nucleation. After continued precipitation the grading is wiped out, and the coronas become nearly regular until they vanish.

The nuclei produced by shaking toluol were found to persist in experiments lasting 10 minutes, 150 minutes, and 240 minutes, respectively, with but negligible diminution of brilliancy in the coronas.

23. *Carbon disulphide.*—In the given apparatus, in which rubber stoppers and tubes made an essential part, it was impossible to preserve this regent free from impurities in solution, even when the liquid is apparently kept in contact with glass only. To do this it would have been necessary to construct all parts of the apparatus of glass, which did not seem to be warranted, and which would have made it much less suitable for the general purposes of the present paragraph. Apart from this, the decomposition which the liquid itself undergoes in the light or on continued evaporation, seems to be concerned, and any rubber tube through which the vapor has passed becomes nuclei-producing. With this reservation, carbon disulphide produces nuclei spontaneously and in abundance, a property which makes an interesting special contribution to the subject.

24. *Coronas.*—The removal of air nuclei is already peculiar, and is practically complete in a few exhaustions. Thus I found successively,

Exhaustion No.,	1	2	3	4	5
Corona,	Full, $s = .58$	Semi-corona.	Coronas nearly absent.		

The first corona is of the ordinary type and quite possibly due to spontaneous nuclei. The second is semi-circular, and the remaining coronas mere colored veils at the bottom of the vessel. On adding an excess of sulphur nuclei from the flame the display is again insignificant and curtailed to mere fogs, as the following table shows.

TABLE 10.—PROPERTIES OF SULPHUR NUCLEI IN VAPOR OF CARBON DISULPHIDE. EXHAUSTION, 76–58 cm.

Exhaustion No.	Time.	Corona.	
0	10^{m}	Nucleation	
1	11.5	Sedimentary fog.	Flask nearly clear
2	13	" "	Rising
3	14.5	Fog near bottom.	Vessel now shaken
4	16	$\frac{3}{4}$ of vessel fogged	
5	17.5	$\frac{1}{2}$ " " "	
6	19	Sedimentary fog	
7	20.5	" "	
—	45	" "	

Hence, sulphur nuclei are ineffective, or have the usual property of brooding over the surface particularly pronounced. Thence they very slowly diffuse upward.

The following table evidences an entirely similar behavior in relation to punk nuclei.

TABLE 11.—PROPLETHS OF NUCLEI IN VAPOR OF CARBON DISULPHIDE. EXHAUSTION, 76.57 cm. AIR NUCLEI.

Ex. No.	Corona.
1	Strong irregular campanulate corona
2	Quarter corona
3	Eighth corona
4	Nearly absent
	Funk Nuclei.
1	Fog stratum at bottom, about 3 cm. high
2	" " " " " "
3	After shaking. Heavy coronal fog, 20 cm. high
4	" " Fog homogeneous. $d = .0011$ cm.
5	Full corona, thin above
6	Half corona
7	Third corona
	Etc.

Here, as above, all nuclei in vapor of carbon disulphide form a heavy stratum. Condensation seems to occur spontaneously without supersaturation, and the invisible stratum of loaded nuclei at once seeks its density level, where it is found on exhaustion.

25. *Shaken nuclei.* In contrast with this erratic behavior, the effects of shaking and the spontaneous generation of nuclei is particularly regular. Shaking heats the liquid, and a corona is liable to occur on the resulting efflux of vapor. This disturbance must be guarded against. The following table is a summary of observations with coronas due to nuclei obtained by vigorously shaking the liquid. Intense fogs are usually apparent on exhaustion.

TABLE 12.—NUCLEI IN VAPOR OF CARBON DISULPHIDE DUE TO SHAKING THE LIQUID. EXHAUSTION, 76.58 cm. DIAMETER OF VESSEL, 23 cm.

Exhaustion No.	Coronas. First series.	Coronas. Second series.	Coronas. Third series.	Coronas. Fourth series.
1	Strong, persistent, full	Strong, full	Strong, full, $d = .0018$	Strong, full
2	Absent	Weaker, $d = .0014$	Half corona	Corona lyrate
3	Absent	Vanishing	Quarter corona	Half corona
4		Absent	Eighth corona	Quarter corona
5			" "	Etc.

In the first series the nuclei were easily removed; but this was not the case later, probably because the reagent, after continued distillation, had concentrated the impurities. The semi-annular, quarter, and other coronas are indicative of an almost sudden passage from nucleated to pure air at the surface of demarcation.

The veil at the bottom of the flask effectually resists removal, as may be inferred from what has been stated. The first coronas are invariably full, strong, and coarse.

The nuclei shaken out of the liquid are remarkably persistent; as, for example:

Time elapsed after shaking.	Exhaustion 1.	2
20$^{\mathrm{m}}$	Intense fog and corona.	—
3$^{\mathrm{h}}$ 20$^{\mathrm{m}}$	Corona, $s = .76$, $d = .0019$	1, 2 corona, etc.

In the last instance, the corona has coalesced with the coronas of spontaneous nucleation, presently to be mentioned. In fact, the rise of coronas and their diffusion may be tested by exhaustion in the way stated above. Thus, a quarter corona will rise to a half corona in about 10 minutes.

26. *Spontaneous nuclei.* The distinctive feature of these experiments is thus the spontaneous production of nuclei in carbon disulphide vapor, and a number of examples of these occurrences are summarized in the following table:

TABLE 13.—SPONTANEOUS NUCLEI FROM CARBON DISULPHIDE. PERFECT FILTER, CLEAR VESSEL.

Lapse of time.	Coronas observed during the exhaustion Nos.					
	1	$d \times 10^3$	2	3	4	5-10
35$^{\mathrm{m}}$	Large, coarse	—	Half	Quarter	Eighth	Film at bottom not quite removable
15	Veil of fog 5 cm. high	—	—	—	—	—
5$^{\mathrm{h}}$ 30	Intense	1.20	Half	Quarter	Eighth	Film
30	Fog 5 cm. high	—	Film	Film	Film	Film
1 0	Full, diffuse	—				
15 0	Intense	1.31	Half, $d = .0014$	Quarter	—	—
2 40	Fine	2.30	$\frac{3}{4}$ Corona	$\frac{1}{4}$ Corona	Film	—
15 0	Intense	1.44	Half	$\frac{1}{4}$ Corona	—	—
3 0	Intense	1.85	$\frac{3}{4}$ Corona	Abs.?	Abs.	—
2 0[1]	Intense	1.28	Half	Third	Quarter	Film.

[1] Vessel in bright, warm, sunlit room; not in darkness, as usual.

Though the large filter and clean vessels were used, it was not feasible to quite remove the sedimentary fogs by exhaustion. The rise of fog is at first filmy, and never strong as a rule. After one or more hours, however, the corona stands out full and coarse, and the graph shows that the diameter, *s*, of the corona, and with it the number of particles per cubic centim., increases in the lapse of time to a limit. Their diameter, *d*, decreases.

When the vessel is left in a warm, sunlit room, *i. e.*, when the evaporation is accelerated in full daylight, the maximum spontaneous nucleation is reached in a correspondingly shorter time, as the observation, *a*, of the coronal aperture shows. These incidental difficulties are further indicated in the general irregularity of the graphs. If a smoother curve were obtainable, it would be useful for computation. When the stationary condition is reached, nuclei are lost at the boundary of the vessel at the same rate at which they are produced by the liquid. This process is exhaustive and may account for the maximum indicated by the curve. Experiments showed, however, that the curvature of Fig. 3 is exaggerated.

Fig. 3.

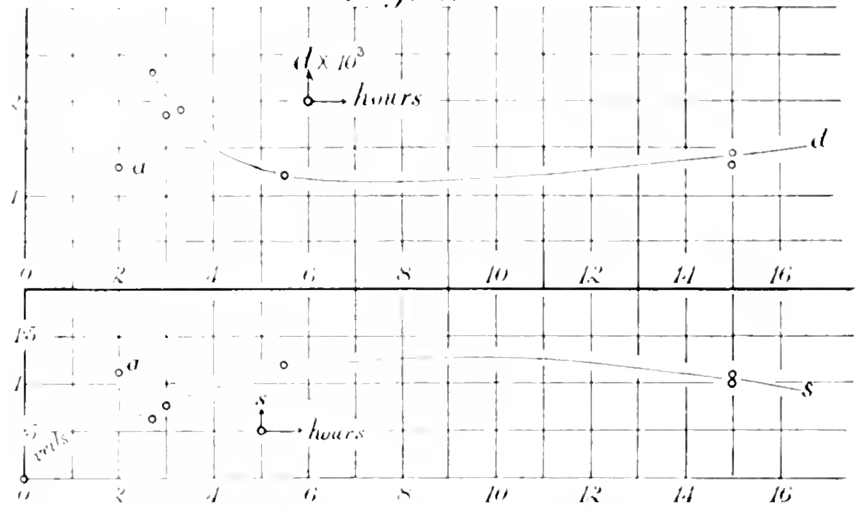


FIG. 3.—GRAPHS SHOWING THE INCREASE OF NUCLEATION OCCURRING SPONTANEOUSLY IN CS_2 VAPOR; *s*, CORONAL APERTURES IN THE LAPSE OF HOURS; *d*, DIAMETERS OF PARTICLES (IN CENTIMETERS FOR IDENTICAL SUPERSATURATIONS) AFTER THE LAPSE OF HOURS.

27. *Ethyl alcohol.*—The liquids treated throughout the above paragraphs were non-ionizing solvents; it is important to add, by way of contrast, the corresponding behavior of certain ionizing solvents, like the alcohols, acetone, and water. I was long under the impression that a sharp distinction could be drawn between the two classes of solvents, but the behavior of acetone does not bear out this surmise. Table 14 is an example of the coronal display in alcohol vapor. It is particularly to be noticed that, whereas color distortion does occur in the annuli of the coronas, there is no appreciable distortion of form. In this respect alcohol resembles water more than any re-agent examined.

At high exhaustions and a small residue of nuclei, the occurrence of two kinds of condensation may be shown. The coronas due to the nuclei are the first to appear at relatively low exhaustions. At the high exhaustion (pressure-difference, 24 cm.) very large faint coronas are apt to be seen, and to appear suddenly, as if by collapse. The nuclei here are probably molecular, and it is not impossible that traces of water vapor, if present, may suffer condensation; but it is the succession of independent condensation to which I wish to advert.

In both the present and the following experiments the final coronas are regular. This is also true of the coronas obtained from air nuclei in case of alcohol vapor.

TABLE 14.—BEHAVIOR OF PHOSPHORUS NUCLEI IN VAPOR OF ETHYL ALCOHOL. EXHAUSTION, 76–59 cm.

Exhaustion No.	Coronas.	Axial color.
1	Fog colorless	viol
2	" rd edged	---
3	Wh, cr	Gr
4	"	Yl
5	" color distortion	—
6	Gr, bl-gr	
7	"	
8	Yl-gr ; fog rises from bottom ; much color distortion	
9	Wh, rd and wh, gr ; annuli of different color above and below	
10	Wh, prp	
11	Wh, prp and wh, br	
12	Wh, prp and wh, gr	
13	Wh, gr and wh, rd	
14	" " "	
15	Wh, br and wh, rd	
16	Wh, rd and wh, br	
17	" " "	
18	Corona nearly normal and perfect	
19	" " " " "	
20 [2]	" " " " "	

[1] Axial colors very marked.

[2] Two hours later, small, perfect multiannular coronas are seen.

28. *Methyl alcohol.*—The coronas of methyl alcohol vapor resemble those of common absolute alcohol, but there is greater tendency to distortion of color and even of form.

TABLE 15.—BEHAVIOR OF PHOSPHORUS NUCLEI IN VAPOR OF METHYL ALCOHOL. EXHAUSTION, 76–59 cm.

Exhaustion No.	Coronas.[1]
1	Colorless fog ; blue base
2	" " rises from base
3	Olive-green fog ; rises from base
4	" " " rises from red base
5	Gr, red base
6	Yl-gr, red base
7	Yl, red base
8	Yl, rd, gr
9	Wh, cr
10	Wh, rd and wh, gr
11	Gr. Slight distortion
12	Gr, rd and gr, bl
13	Yl-gr, rd. Distortion
14	Wh, rd
15	Wh, rd and wh, br
16	Distortion
17	Gr
18	Wh, prp
19	Wh, prp and wh, br
20	Coronas becoming regular [2]

[1] Axial colors not seen ; coronas very fleeting and not measurable.

[2] Examined next day, the residual nuclei produced small but fine multiannular coronas.

The table shows that the remarks already made for alcohol may be repeated here.

The nuclei produced by shaking methyl alcohol were incidentally examined and found to persist over 30 minutes after shaking. The occurrence of traces of impurity is again to be inferred, for the results below will show that only in cases of absolute purity can the immediate decay of these nuclei be expected.

29. *Acetone.* This re-agent must be classed with the ionizing solvents, and yet the coronas obtained are identical in character with those peculiar to the non-ionizing solvents above. There is strong distortion of both form and color, as the following table of coronas shows:

TABLE 16. BEHAVIOR OF PHOSPHORUS NUCLEI IN ACETONE VAPOR. EXHAUSTION, 76–50 cm. PERIODS BETWEEN EXHAUSTIONS USUALLY 3^{m}.

Exhaustion No.	Coronas.
1	Wh, rd; subsides rapidly
2	Wh, rd and wh, prp. Distortion
3	Red below, blue bands above
4	" " " " "
5	Nuclei near bottom
6	Corona below, rises as exhaustion proceeds, then at top
7	Strata below
8	Strata rise from bottom
9	Strata only 5 cm. high
	Longer periods between exhaustions
10	At 50^{m}, strata 7 cm. high
11	65^{m}, fog 15–20 cm. high, corona nearly full
12	73^{m}, fog 5–10 cm. high, faint
13	Etc.

One may note that when time is allowed for diffusion, the coronal pattern eventually becomes regular again.

The coronas due to shaking persist as usual. Observations made 44^{m} and 45^{m} after shaking, brought out strong, multi-annular forms.

30. *Water.* In the light of the above observations the corresponding behavior of water is brought forward with renewed interest. Water has the additional advantage of being less liable to contamination in apparatus of which rubber tubing is an essential part, than the hydrocarbon solvents. Aqueous solutions will therefore be treated at length in the next chapter. Here I will merely add certain results, not found in the same connection there, for completeness.

If all precautions be taken to insure clean and new apparatus and appurtenances and perfect filtration, the air above the water, if free from nuclei, remains so indefinitely. Spontaneous nucleation does not occur. One is liable to be led astray, however; thus a connection of rubber tubing through which vapor of carbon disulphide has passed, is an abundant source of nuclei for days after.

If a clean vessel, free from nuclei and charged with pure water, is vigorously shaken so as to comminute the water, nuclei are produced in considerable quantity. But the nuclei are short lived, as seen from the following table:

TABLE 17.—NUCLEI DUE TO SHAKING PURE WATER.

Time elapsed after shaking.	Corona.
7^m	All but absent
6	" " "
5	" " "
3	" " "
2	" " "
1	Faint corona and rain. Not measurable.
.5	Corona. $d = .0028$
.1	Strong corona lasting 15 sec.

The nuclei are nearly pure water globules, which speedily evaporate.

Let a small quantity of sodic carbonate be added to the water. The result is a phenomenal increase in the persistence of the nuclei. Table 18 containing data obtained by shaking the solution shows this.

TABLE 18.—NUCLEI DUE TO SHAKING A DILUTE SOLUTION OF SODIC CARBONATE.

Time elapsed after shaking.	Corona.
1^h	Strong. $d = .0029$ cm.
2	" .0025
3	" .0045
15	Just visible
15	Absent
15[1]	Distinct and clear

[1] Violent shaking. Initial apertures vary from 1.4–2.0°, depending on the violence of shaking.

The size and persistence depend on the violence of shaking, but coronas may still be obtained even after 15 hours.

The body in solution in this case is a solid. One is liable to conclude that the persistent nucleus is the solid residue left after evaporation. This is not true. The nucleus, both here and in the above experiments with hydrocarbons, etc., is a concentrated solution.

To decide the question as to the cause of the indefinite persistence of the nuclei produced by shaking, it is necessary to test a chemically dissolved gas, like HCl or H_3N. Pure water was first taken and the evanescence of nuclei confirmed. Pure HCl was now added in small quantity, and the following marked degree of persistence established:

TABLE 19.—NUCLEI DUE TO SHAKING DILUTE HYDROCHLORIC ACID.

Time elapsed after shaking.	Corona.
5''	Strong. $d = .0025$ cm.
10'	"
30'	"
15'	Distinct but weak

Tested with pure water again, the fleeting coronas persisted somewhat longer (10 minutes), showing that traces of H Cl still lingered in the clean apparatus. On again adding H Cl, the above results were confirmed.

Dilute ammonia was next tested in the same way. Great care had to be taken, even after the vessel was thoroughly cleaned, to remove the last traces of H Cl. When this was done, air free from nuclei remained so above dilute ammonia indefinitely. Spontaneous nucleation does not occur. On shaking, however, the ammonia nucleus behaved like the HCl or the $NaCO_3$ nucleus, showing long persistence.

TABLE 20.—NUCLEI DUE TO SHAKING DILUTE AMMONIA.

Time elapsed after shaking.	Corona.
31^m	Strong. $d = .0030$ cm.
96	" $d = .0032$

With these experiments, the indefinite persistence of the nuclei produced by shaking solutions, apart from the loss by diffusion, may be considered established, no matter what may be the original state of aggregation of the solute. It is next necessary to inquire into reasons.

CHAPTER V.

PROPERTIES OF THE NUCLEI PRODUCED BY SHAKING LIQUIDS.

INTRODUCTION.

1. *Thermodynamic and electronic hypotheses.* When I first encountered the present kind of nucleation, the observation did not seem to me to be of much interest or the occurrences unexpected. It was not until I had satisfied myself of the extreme minuteness of the particles that I became convinced of their value as a means of elucidating the phenomenon of condensation. Clearly the importance of these nuclei is enhanced in proportion as the means by which they are produced are similar. Lenard,[1] as I afterwards found, had met them incidentally in connection with his electrical investigations before, and treated them chiefly with reference to their bearing on those phenomena.

I first endeavored to explain the persistence of the nuclei produced by shaking solutions, by pointing out that whereas the vapor pressure increases as the droplet grows smaller by evaporation, this pressure decreases again as the result of the continued concentration of the evaporating droplet, until a state of equilibrium is reached. Afterwards, however, I was unable to look at this straightforward explanation without considerable misgiving, as it is not easy to agree that nuclei at the same time so small and so nearly of a size as to produce sharp coronas on precipitation could be produced by a random process of the kind in question. Not enough is known, moreover, of the vapor pressure of such concentrated solutions as those with which the evaporation of the droplet terminates.

From another point of view, it is not impossible that these nuclei may owe their persistence to the occurrence, for instance, of an ion within them. In other words, one may suppose that ions have been separated by the comminution due to violent shaking, or have been separately entrapped in the water nuclei observed. Again, the results of the investigations on the electricity produced by the attrition (if I may call it so) of water in falling (Lenard, *l. c.*), may have immediate relations to the present phenomenon of persistence. In short, the theoretical bearing of the experiments is not quite so simple as a first inspection had led me to infer.

Considerations like these suggest an extended inquiry into the properties of nuclei produced by shaking very different solutions, and the present chapter is an endeavor to bring together a number of relevant data. The results show, I think, that the concentration hypothesis first mentioned has very powerful evidence in its favor.

---

[1] Lenard, *Wied. Ann.* xlvi, pp. 595–596, 1892, "Elektricität der Wasserfälle."

2. *Order of size of the nuclei.* It will conduce to clearness if a preliminary estimate of the order of size of the nuclei produced by the present method is inserted at the outset. They may be considered first with reference to the minimum time of subsidence, which would be admissible, if gravitational subsidence of nuclei occurred at all. If the viscosity of the air through which the nuclei are supposed to fall be taken as .00019 (it will be seen below, that in relation to the actual size of the nucleus, the term viscosity no longer has any definite meaning), the subsidence equation reduces to $r = 9.3 \times 10^{-4} \sqrt{v}$, centim. To fall about 15 centim. per hour, where 15 cm. is about half the diameter of the spherical receiver, the size of the particle would have to be about $r = 58 \times 10^{-6}$ cm. Thus the following estimates may be assumed for reference:

Time of falling out,	1	Radius of particle, $r =$	.000058 cm.
	4		29
	16		14
	25		7

Inasmuch as the nuclei obtained by shaking solutions may in some instances be found to persist over a day, they must be small as compared with the last datum. Apart from this, the coronas *remain annular*, until, with the total removal of nuclei, they fade from sight as a whole and regular figure. Hence there is here no evidence of subsidence whatever. Not only is this true, but the nuclei obtained by shaking solutions actually diffuse against gravity with a velocity which, in spite of the difficulties of measurement, is none the less characteristic and definite. *A fortiori*, therefore, the particles here in question are very small as compared with 10^{-6} centim., and it is from this point of view that the following results are to be understood. A corresponding estimate is given in paragraph 17.

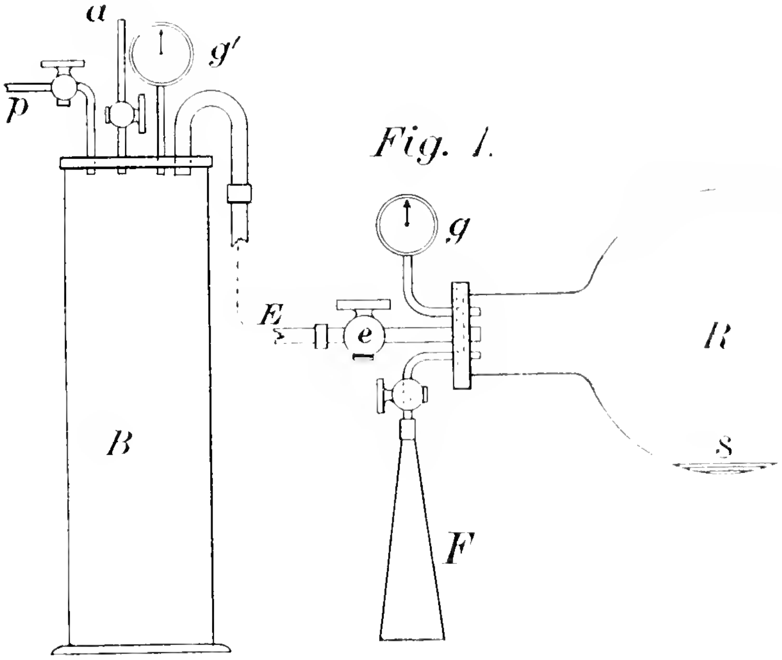
It is curious to note in passing that a rough estimate of the size of these nuclei made on the electronic hypothesis brings out a plausible result. Thus, if in case of the nuclei produced by shaking solutions, the excess of vapor pressure at a surface of radius, r, be regarded as eventually equal to the electrical surface pressure; if moreover, the nucleus is considered to be so constituted that a central electron forms a closed field with a charge (possibly due to friction) uniformly distributed over the surface of the nucleus, the equation may be written,

$$\frac{2T\rho}{r} = \frac{2\pi e^2}{16\pi^2 r^4 K},$$

whence $r^3 = e^2/(16\pi T\rho K)$, where e is an electron or 7×10^{-10} electrostatic units, T the surface tension of water (81), ρ the density of its vapor (.000017), K its specific inductive capacity (80). From this follows the radius of the nucleus, $r = 1.5 \times 10^{-7}$, which, in the light of other values to be derived inferentially below, seems not to be an unreasonable estimate; but one must note that if in solutions T, ρ, K are all increased, r^3 is correspondingly decreased.

3. *Apparatus. Methods.*—The experiments themselves are sufficiently simple and roughly satisfactory with the exception of one element, the method of shaking, which has not yet been brought under control. In figure 1, R is the spherical receiver, about 33 cm. in diameter, at the bottom of which is placed the solution,

S, to be examined. A *definite* volume, say 500 cub. cm., is necessary. The receiver has two outlets provided with stop-cocks, and a third, g, leading to the vacuum gauge. The outlet leading to F is the filtering arrangement; the outlet, E, e, is the avenue of sudden exhaustion, and therefore made of wide tubing, say 1 cm. in diameter.



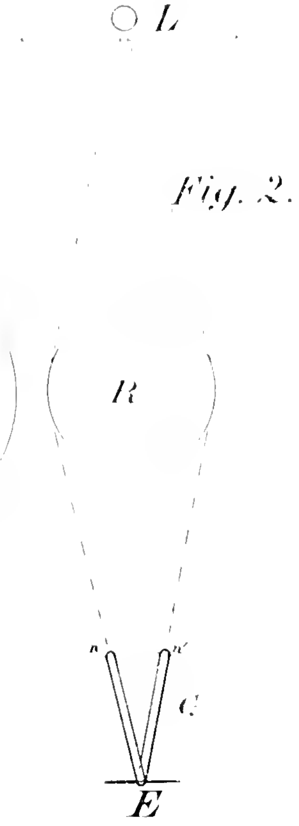


FIG. 1.—CONDENSATION CHAMBER, R; EXHAUSTION RESERVOIR, B, AND APPURTENANCES. SCALE $\frac{1}{5}$

FIG. 2.—LAMP, RECEIVER, AND GONIOMETER. DIAGRAM.

The auxiliary flask, B, of about 1/3 the capacity of RA, is a reservoir for air at low pressure. It communicates with the jet pump (through a desiccator, if necessary) by the pipe p, with R through E, and with the external atmosphere for the adjustment of pressure, by the pipe a. The attached vacuum gauge is shown at g'.

Figure 2 is a plan in diagram of the apparatus for viewing and measuring the coronas, R being the receiver, G the goniometer, and L the source of light, at distances, respectively, 1 and 3 meters (not shown in figure) from the center of the receiver. The eye is at E. Under these conditions the coronas may be measured in a darkened room with facility, though, of course, from the absence of sharp lines, not with great accuracy. The goniometer is of the kind described in § 2, Chapter III, needle points at n n' being adjusted and their distance apart pricked in paper.

The method of work requires that R should be first freed from nuclei, by precipitation or aspiration, combined with filtration in the usual way, until the degree of exhaustion selected for the experiments is no longer accompanied by even a trace of condensation. There must be neither coronas, no matter how faint, nor rain. All exhaustions are to be identical as to the pressure differences applied, unless special purposes are aimed at.

The receiver is now vigorously shaken, by jerking it sharply up and down a definite number of times. A rotational swirl of the liquid contents is to be avoided, as the friction of the liquid upon itself and not the rush of liquor over the spherical sides of the receiver is efficient in producing the nuclei. It will be shown that the quantity of liquid contained, the violence of the agitation, the number of times shaking is repeated, *i. e.*, the number of jerks, etc., all materially influence the result. There are, therefore, elements of vagueness inherent in the method, and at first sight they might be supposed to be fatal. The results show that this is not so, and that the utilization of the simple means for investigation has certain peculiar advantages which make it desirable to carry the method through before investigating more determinate methods of agitation. It is presumable, however, that a scattering spray may be so installed as to yield a definite maximum of nucleation; but thus far this has not been attempted.

At specified times after shaking, the coronas are produced and measured. Expeditious manipulation of the goniometer is here frequently necessary, and it is for this reason that the form of goniometer already described has been used throughout.

Filtered air is then introduced through F into R. Usually an intermediate exhaustion is necessary to clear the air of nuclei, and must always be applied as a test. When the coronas are large, a certain number of the nuclei escape precipitation. After shaking again, the experiment is repeated under the same or modified conditions.

4. *Tabulated results.*—The results are given in the following series of tables, in which the first columns contain the percentage of dry salt or acid in solution. The second columns show the amount of partial exhaustion, by giving the pressure decrement below atmospheric pressure at which the corona is observed. The third columns contain the time elapsed in minutes, after shaking; the fourth, the number of times the receiver was jerked up and down to generate the nuclei.

The columns under s are the diameters of the coronas subtended at the end of the arm of the goniometer, here 30 cm. long, so that $s/30$ is chord of the aperture of the corona in any given case, for distances one and three meters, respectively, of the goniometer and light from the center of the receiver. The most satisfactory method of standardization is a direct comparison with lycopodium spores, of diameter .0032 cm. These showed at different distances from the goniometer, if the positions of the latter and the light are fixed at 4 meters apart, and if s_0 is the chord in question,

.95 meters	s_0 = 1.00 cm.
1.00	1.00
1.05	.95
1.10	.95
1.60	.95

whence $s_0 = .97$ cm. may be taken as the mean result, at the anterior and posterior tangent planes of the receiver, 1.05 and .95 meters, respectively. Hence, since $s_0 \times .0032 = sd$, $d = .0031/s$ cm., from which the columns under d, showing the diameters of the coronal particles, are computed. As a rule the diffracting water globules of the coronas are about as large as lycopodium spores, the supersaturation being high and the number of nuclei relatively few.

The columns marked n contain the nucleation, *i. e.*, the number of particles generated by shaking, per cub. cm. These are computed from d and the total amount of precipitation per unit of volume, as set forth in § 6.

A number of miscellaneous data contained in the tables will explain themselves. Thus dn/dt are the time rates at which the nuclei vanish, or the decrement of the number per minute; dn/dS shows the average number generated in one shake or jerk up and down; etc.

A series of values of k, the absorption velocity, are finally added from computations given below. The meaning of k is as follows: It is supposed that the loss of nuclei in the lapse of time is due to their absorption at the walls of the spherical receiver (radius, $R = 15$ cm.). If this loss is a decrement from the contents of the receiver *as a whole* $-(4\pi R^3/3)(dn/dt) = k\,4\pi R^2\,n$, whence

$$n = n_0 10^{-3kt(\log \varepsilon)/R},$$

and it is therefore sufficiently approximate to write, $k = 11.5\,(\delta \log n/\delta t)$. As the results are inevitably crude, very little confidence can be felt in the minor variations of k, these being introduced by differences in shaking. The order of values obtained, however, presents a wide sweep and is of great interest.

TABLE 1.—PROPERTIES OF NUCLEI DUE TO SHAKING DILUTE SOLUTIONS OF HCl; RECEIVER 3 METERS FROM LIGHT AND 1 METER FROM GONIOMETER; ARM OF SAME 30 cm $d = .0031/s$.

% HCl	Pressure diff.	Lapse of time.	No. of times shaken.	s	Observed, $d \times 10^4$.	n	$d \times 10^4$ computed.	k
	Cm. of Hg	min.		cm.				
2.9 %	8	0–1	10	1.10	28	31	23	
	12			1.05	30	41	27	
500^{cc}	16			1.05	30	55	29	
$n = 56$	20			1.00	31	59	31	
	10			1.07	29	58	29	
	12			1.07	29	43	27	
	8			1.10	28	31	23	
	4			1.20[1]	26	19	18	
	16	0–1	10	.95	33	40	31	
6	12			1.10	28	45	28	
	8			1.00	31	23	25	
$n = 45$	8			1.10	28	31	25	
	4			1.30[1]	24	24	20	
	8			1.40[2]	22	63	25	
	12			1.30	24	77	28	
	16			1.00	31	47	31	

[1] Faint corona, forms gradually. [2] Violent shaking.

TABLE 1.—*Continued.*

Remark	Pressure diff.	Lapse of time.	No. of times shaken.		Observed $d \times 10^4$	n	$d \times 10^4$ computed	
	Cm. of Hg	min.		cm.				
	2			[illegible]	39	3[illegible]	34	
[illegible]	16	0–1	12	1.10	28	62		
	12	0–1	1	1.10	28	46		
$n = 45$	8	0–1	1	1.15	27	27		
	4	0–1	12	1.50	21	37		
	4	0–1	50	2.00	15	88		
[illegible]	16	16	12	1.15	27	71	$\frac{dn}{dt} = -.16$	
	16	39	12	1.12	28	66	$= -.22$	.0122
$n = 56$	16	72	12	1.10	28	62		.0210
	16	162	12	.95	33	37		
[illegible]	16	0–1	1	.50	62	5.9	$\frac{dn}{ds} = -2.6$	
	16	0–1	3	.70	44	16.1		
$n = 56$	16	0–1	5	1.00	31	47.0		
	16	0–1	12	1.00	31	47		
	16	0–1	12	1.08	29	57.4		
	16	0–1	36	1.35	23	116		
	16	0–1	50	1.50	31	158		

[1] Faint but marked coronas.

TABLE 2.—NUCLEI DUE TO SHAKING PURE WATER (FOLLOWING WORK WITH HCl). $d = .0031\, s$

Remark.	Pressure diff.	Lapse of time.	No. of times shaken.		Observed, $d \times 10^4$.	n	$d \times 10^4$ computed	k
Pure but	Cm. of Hg	min.		cm.				
following	16	0–1	12	.90[1]	35	34	31	
dilute	20	0–1	—	1.00	31	59	33	
HCl in	16		—	1.00	31	47	31	
apparatus	12			1.13	28	50	28	
$n = 47$	8			1.17	27	37	24	
	4			1.30[2]	24	26	19	
Same	8	0–1	12	1.20	26	40	24	
[illegible] → 50	12			1.03[2]	30	38	28	
	16		—	1.00[2]	31	47	31	
	20		—	.90[3]	34	53	33	
Same	16	1	12	.50	39	24	$\frac{dn}{dt} = -1.6$	.216
$n = 3$[illegible]	16	15		.60	52	10		.437
	16	12		.55	56	(1.6)		.062

[1] Tested for absence of nuclei before shaking. [2] Corona faint but marked. [3] Faint and fleeting.

TABLE 2.—*Continued.*

Remarks.	Pressure diff.	Lapse of time.	No. of times shaken.		Observed $d \times 10^4$	n	[illegible] $\times 10^3$ computed	
	Cm of Hg	min.		cm				
	16	0–1		.90	34	34		
	16	0–1		.95	33	40		
Pure water	16	0–1	10	.87	36	31		
following	16	0–1	10	.85	36	29		
preceding								
pure water	16	5	10	.50[1]	62	6	$\frac{dn}{dt}$ 6	1.68
	16	3	10	.68[1]	46	15		1.28
$n = 32$	16	17	10	Absent	—	—		
	16	0–1	10	—.90	34	34		
	16	0–1	10	—.90	34	34		
Following the work with Na_2SO_4								
Pure water;	16	0–1	— 10	1.25	25	92		
thrice	16	0–1	—	1.25	25	92		
rinsed	16	0–1	—	1.15	27	71		
	16	15	10	Absent	—	—	$\frac{dn}{dt} = -40$	
$n = 85$		5		Absent	—	—		
		2		.50	62	6		6.7
Fresh	16	0	— 10	.78	40	22		
water	16		—	.84	37	28		
$n = 26$	16		—	.83	37	27		
Same	16	1	10	.40[2]	77	3	$\frac{dn}{dt} = -23$	1.08
$n = 26$	16	1		.40	78	3		1.08
	16	2		.35	89	2		.64
Same next	16	0	— 10	1.00	31	47		
day		0	—	1.00	31	47		
$n = 47$		0	—	1.00	31	47		
Fresh	16	0	— 10	1.10[3]	28	62		
water	16		—	1.10	28	62		
$n = 57$	16		—	1.00	31	47		

---

[1] Very faint and fleeting.

[2] Nearly absent.

[3] Cause of these relatively large results not discerned, but from the effect of traces of impurity the smallest results must be rare.

TABLE 3. PROPERTIES OF NUCLEI DUE TO SHAKING SODIC CHLORIDE.

NaCl	Pressure diff.	Lapse of time	No. of times shaken		$10^4 \times a$	n	Computed data	c
	Cm. of Hg	min		cm				
2	16	1	1	1.65	18	211		
	16	0.1	10	1.55	20	175		
	16	20	10	1.60	19	193	$\frac{dn}{dt} = -3$	
$n = 175$	16	68	10	1.75	18	252		.014
	16	163	10	1.40		120		
2	8	1	1	2.30	13	281	$10^4 \times a =$ 15.8	
	4			2.60	12	104	12.4	
$n = 175$	6			2.20	14	240	15.8	
	12			2.00	15	286	18.2	
	16			1.55	2	175	20.0	
2	16	1	1	Clear			$\frac{dn}{dS} = 10.30$	
			5	1.35	23	116		
			10	1.40	22	120		
			20	2.25	14	530		
			40	2.00	15.5	376		
			60	2.40	13	640		

TABLE 4. PROPERTIES OF NUCLEI DUE TO SHAKING CALCIC CHLORIDE.

$CaCl_2$	Pressure diff.	Lapse of time	No. of times shaken.		$10^4 \times a$	n		
	Cm. of Hg	min		cm				
2	16	0.1	10	1.70	18	231		
$n = 240$	16			1.75	18	252		
	16			1.75	18	252		
2	12	1	10	2.10	15	325	$10^4 \times a =$ 16.4	
	6			2.55	12	382	14.2	
	4			2.05	11	268	11.2	
$n = 24$	8			2.40	13	317	14.2	
	12			2.20	14	371	16.4	
	16			1.7	18	231	18.0	
	20			1.50	20	232	19.4	
2	16	75		1.50	21	158	$\frac{dn}{dt} = -1.3$	.038
24	16	1		1.70	18	231		—

TABLE 4. *Continued.*

Successive precipitation (complete subsidence each time)

% $CaCl_2$	Pressure diff.	Lapse of time	No. of times shaken		$10^3 \times a$	n		
	Cm. of Hg	min.		cm.				
2	4	0–1	10	2.90	11	268		
	8			2.10	15	213		
	12			.70	44	12		
	16			Absent		0		
	20			Absent		0		
2	8	0–1	10	1.84	17	143		
	8			*faint* .7	44	8		
	16			Absent		0		
2	4	0–1	10	2.90	11	268		
	4			1.20	26	100		
	8			Absent		0		
	16			Absent		0		
2	4	0–1	10	2.85	11	254		
	4			1.80	17	64		
	4			.8 ?	39	6		
	16			Absent		0		
2	2	0–1	10	3.10	10	149		
	2			2.60	12	88		
	2			2.10	15	56		
	2			1.10	29	7		
	2			Absent	—	0		
	16			Absent	—	0		
$\frac{1}{1000}$	16	0–1	10	1.80	17	274		
	16			2.25	14	536		
	16			2.28	14	557		
$n = 456$	8	0–1	10	2.70	11	453		
	8			2.70	11	453		
$\frac{1}{1000}$	16	100	10	1.60	19	103	$\frac{dn}{dt} = 2.6$	.0430
$\frac{1}{500}$	16	0–1	10	1.60	19	103		
	16			1.50	21	158		
$n = 242$	16			2.00	15	370		

TABLE 5.—PROPERTIES OF NUCLEI DUE TO SHAKING FERRIC CHLORIDE.

[illegible]	Pressure diff.	Lapse of time.	No. of times shaken.		$10^4 \times d$	n
	cm. of Hg	min.		cm.		
2	16	0–1	1	1.8	17	274
234	16			1.5	21	158
	16			1.8	17	274
	8	1	10	2.05	15	198
	16			1.70	18	231
5	16	1	10	2.1	15	435
2	16			2.1	15	435
n = 435						
5	16	1	1	1.55	20	175
5	16			1.60	19	193
174						

TABLE 6.—PROPERTIES OF NUCLEI DUE TO SHAKING FERRIC NITRATE.

c Fe 3 NO$_3$	Pressure diff.	Lapse of time.	No. of times shaken.		$10^4 \times d$	n	$-\frac{dn}{dt}$	k
	cm. of Hg	min.		cm.				
1.2	16	0–1	10	1.55	20	175		
5	16	0–1		1.60	19	193		
n = 175								
1.2	16	79	10	1.30	24	173	.9	.034
	16	21		1.60	19	193		
1.2	16	5–1	1	1.50	21	158		
	8	1		2.00	15	184		
	4	1		2.50	12	172		
	16	1		0	35	34		
1	16	1	1	1.50	20	158		
	16			1.45	21	143		
161	16			1.42	22	134		
	16			1.4	22	129		
1.2	16	1[illegible]		1.20	26	81	.8	.034

After subsiding at 4 p.m. without shaking.

TABLE 7.—PROPERTIES OF NUCLEI OF ALUMINUM NITRATE (TURBID)

% Al 3 NO_3	Pressure diff.	Lapse of time	No. of times shaken	s	10^3	n		
	Cm. of Hg	min.		cm.				
1.2	16	0–1	10	1.65	19	211		
500^{cc}	16			1.50	21	158		
$n = 197$	16			1.68	18	223		
	16	54		1.20	26	81	1.6	.08
	16	151		.95	33	42		.053
0.12	16	0–1	10	1.20	26	81		
$n = 81$								
500^{cc}		22		1.15	27	71	.5	.39

TABLE 8.—PROPERTIES OF NUCLEI OF CALCIC NITRATE.

% Ca 2 NO_3	Pressure diff.	Lapse of time.	No. of times shaken.	s	n	$-\frac{dn}{dt}$	k
	Cm. of Hg	min.		cm.			
1.4	16	0–1	10	1.75	252		
500^{cc}	16			1.78	265		
$n = 256$	16			1.75	252		
.014	16	0–1	10	1.15	71		
500^{cc}	16			1.25	92		
$n = 87$	16			1.25	92		
.014	16	1	10	1.25	92	.39	.0216
	16	75		1.10	63		
.0014	16	0–1	10	1.05	55		
500^{cc}	16			1.10	63		
$n = 61$	16			1.12	66		
.0014	16	76	10	.65	13	.63	.101
.00014	16	0–1	10	1.05	55		
500^{cc}	16	0–1		1.15	71		
$n = 63$							
.00014	16	5		.70	16	9.4	1.38
		17		Absent	–0		
		32		Nearly absent	–0		
Repetition							
1.4	16	0–1	10	1.87	307		
$n = 250$				1.70	231		
				1.65	211		
1.4	16	126	10	1.28	99	1.20	.037

TABLE [illegible]. PROPERTIES OF NUCLEI DUE TO SHAKING DILUTE ALUM SOLUTIONS.

[illegible]	Pressure diff.	Time elapsed.	No. of times shaken.		n		
	Cm. of Hg.	min.		cm.			
1 [illegible]	16	[illegible] 1	10	1.7	230		
[illegible]	16			1.67	221		
2 [illegible]	16			1.50	167		
1 [illegible]	16	91	10	1.18	77	1.4	[illegible]54
15	16	[illegible] 1	10	1.3	102		
5				1.2	81		
91							
15	16	37	10	.95	47	1.4	.111

TABLE [illegible]. PROPERTIES OF NUCLEI DUE TO SHAKING DILUTE SOLUTIONS OF AMMONIC NITRATE.

H_4NNO_3	Pressure diff.	Time elapsed.	No. of times shaken.		n	$\frac{m}{n}$	
	Cm. of Hg.	min.		cm.			
2	16	0–1	10	1.45	143		
500	16			1.75	251		
$n = 192$	16			1.62	200		
	16			1.55	174		
2	16	151	10	1.20	81	.74	.0288
2	16	0–1	10	.65	13		
5							
2	16	[illegible] 1	1	1.45	143		
5[illegible]				1.35	115		
$n = 129$							
2	16	41	10	1.05	54	1.85	.0[illegible]6

TABLE 11.—PROPERTIES OF NUCLEI DUE TO SHAKING DILUTE SODIC SULPHATE SOLUTION.

g Na_2SO_4	Pressure diff.	Time elapsed.	No. of times shaken.		n	$\frac{dn}{n}$	k
	Cm. of Hg	min.		cm			
.9	16	0–1	10	2.08	423		
500^{cc}	16			2.20	512		
$n = 453$	16			2.08	423		
.9	4	0–1	10	2.80	242		
	4			[1] 1.60	45.		
	4			absent	0		
	16			absent	0		
.9	16	110		1.24	90	3.3	.74
.009	16	0–1	10	1.40	129		
500^{cc}	16			1.15	71		
$n = 100$	16			1.40	129		
.009	16	29	10	1.05	54	1.9	122
.00 00 9	16	0–1	10	1.00	47		
500^{cc}	16			.97	43		
$n = 48$	16			1.04	53		
.00 009	16	5	10	.50	5.9	10	2.08
	16	5	10	.50	5.9		2.08
Repeated some days later.							
.8	16	0	10	1.75	252		
$n = 214$				1.70	231		
				1.50	159		
2.6	16	0	10	2.00	376		
$n = 442$				2.22	516		
				2.10	435		
2.6	16	40	10	1.60	193	6.2	0.103
Two days later.							
2.6	16	0	10	1.55	175		
		0		1.75	251		
		0		1.95	348		
		0		1.95	348		

---

[1] Successive exhaustion without refilling.

TABLE 12.—PROPERTIES OF NUCLEI DUE TO SHAKING DILUTE POTASSIC SULPHATE SOLUTIONS.

K_2SO_4	Pressure diff.	Time elapsed.	No. of times shaken.		n	$\frac{m}{n}$	k
	Cm. of Hg.	min.		cm.			
2	16	0.1	1	1.85	298		
				1.62	[illegible]		
$n = 272$				1.5[illegible]	274		
				1.5[illegible]	274		
2	16	10	10	1.3	113	1.70	57
		98		1.2	81	2.05	
.2	16	0.1	10	1.45	143		
$n = 143$				1.45	143		
				1.45	143		
2	16	23	10	1.20	81	2.7	.121
		88		1.28	99	.50	.018

TABLE 13.—PROPERTIES OF NUCLEI FROM DILUTE SOLUTIONS OF SODIC PHOSPHATE.

Na_2HPO_4	Pressure diff.	Time elapsed.	No. of times shaken.		n	$\frac{m}{n}$	k
	Cm. of Hg.	min.		cm.			
86	16	0.1	10	1.55	175		
				1.75	252		
$n = 195$				1.50	150		
86	16	69	1	1.20	81	1.05	64

TABLE 14.—PROPERTIES OF NUCLEI FROM DILUTE SOLUTIONS OF HYDROCHLORIC ACID (FRESH SAMPLES[1]).

HCl	Pressure diff.	Time elapsed.	No. of times shaken.		n	$\frac{m}{n}$	k
	Cm. of Hg.	min.		cm.			
5	16	0	1	1.22	87		
				1.42	134		
				1.50	158		
$n = 134$				1.50	158		
5	16	15	1	1.30	103	2.07	.085
[illegible]	16	[illegible]	1	1.50	158		
5		63	10	1.17	75	1.32	.060

---

[1] [illegible] from spontaneous nucleation due to traces of impurities in the pipes.

TABLE 14.—*Continued*

% HCl	Pressure diff.	Time elapsed.	No. of times shaken.	s	n	$-\frac{dn}{dt}$	k
	Cm. of Hg	min.		cm.			
.005 $n = 140$	16	0	10	1.47 1.37 1.47	149 121 149		
.005	16	48	10	1.37	121	40	.0152
000,05	16	0	10	1.28	99		
				1.22	86		
$n = 84.$				1.20	81		
				1.15	71		
.000,05	16	2	10	.70	16	34	2.3
		5		.55	8	15.	
		21		? .60	10	3.5	51
Properties of nuclei from solutions, HCl.							
3.2	16	0	10	1.45	143		
				1.40	129		
$n = 140$				1.27	96		
				1.60	193		
3.2	16	6		1.20	81		.450
		20		1.25	92	2.4	.104
		64		.95	40	1.6	.098

TABLE 15.—PROPERTIES OF NUCLEI DUE TO SHAKING DILUTE SULPHURIC ACID.

% H_2SO_4	Pressure diff.	Time elapsed.	No. of times shaken.	s	n	$-\frac{dn}{dt}$	k
	Cm. of Hg	min.		cm.			
65	16	0–1	10	1.82	284		
500^{cc}	16			1.50	157		
$215 = n$	16			1.63	204		
Same	16	54	10	1.50	158	1.05	.028
	16	0–1	10	1.50	157		
.0026				1.35	115		
$n = 127$				1.33	110		
.0026	16	42	10	1.14	69	1.4	.072
Pure water	16	0–1	10	1.00	47		

TABLE [illegible]. PROPERTIES OF NUCLEI DUE TO SHAKING DILUTE CANE SUGAR SOLUTIONS.

[illegible]	Pressure diff.	Time elapsed.	No. of times shaken.	[illegible]	n	[illegible]	[illegible]
	Cm. of Hg	m.		cm.			
[illegible]	16	1	10	1.55	174		
	16			1.30	153		
1.5	16			1.62	193		
	16	45	10	1.02	47	2.8	.133
2	16	0–1	10	1.08	59		
	16			1.02	47		
51	16			1.02	47		
2	16	40	10	.60*	10		.177
	16	18	15	.60	24	9 to 1.5	.200

* Nearly absent, vague.

TABLE 17. PROPERTIES OF NUCLEI FROM DILUTE GLUCOSE SOLUTIONS.

Glucose.	Pressure diff.	Time elapsed.	No. of times shaken.	[illegible]	n	$\frac{dn}{dt}$	[illegible]
	Cm. of Hg	min.		cm.			
1:6	16	0	10	1.50	158		
n = 15				1.45	143		
				1.47	149		
1:6	16	38	10	.88	32	3.1	.275
		62		1.05	54	1.6	.083
		51		.95	40	2.2	.126
1:5	16		1	1.02	50		
n = 5				1.05	54		
				1.00	47		
1:6	16	5		.85	29	4.2	.54
		6		.55	8	7.0	1.53

TABLE 18.—PROPERTIES OF NUCLEI DUE TO SHAKING DILUTE GLYCERINE SOLUTIONS.

% Glycerine.	Pressure diff.	Time elapsed.	No. of times shaken.	s	n	$-\frac{dn}{dt}$	k
	Cm. of Hg	min.		cm.			
2.6 500′ n — 95	16 16 16 16	0–1	10	1.12 1.35 1.20 1.35	66 116 81 116		
2.6	16	13 8	10	Absent .70	0 16	 9.9	1.10
.026 500″ n — 49	16	0	10	1.00 1.15 .85	47 71 29		
.026	16	4	10	.55	8	10.3	2.3

TABLE 19.—PROPERTIES OF NUCLEI FROM DILUTE SOLUTIONS OF UREA.

% Urea.	Pressure diff.	Time elapsed.	No. of times shaken.	s	n	$-\frac{dn}{dt}$	k
	Cm. of Hg	min.		cm.			
2 $n = 107$	16	0	10	1.35 1.27 1.25	116 96 92		
2	16	14 23 79	10	.75 .95 .55	20 40 8	6.2 2.9 1.3	.60 .21 .16
2	16	0	10	1.30 1.40	103 129		

TABLE 20.—PROPERTIES OF NUCLEI FROM DILUTE SOLUTIONS OF TARTARIC ACID.

% Tartaric acid.	Pressure diff.	Time elapsed.	No. of times shaken.	s	n	$-\frac{dn}{dt}$	k
	Cm. of Hg	min.		cm.			
2 $n = 126$	16	0	10	1.30 1.40 1.45 1.40	103 129 143 129		

TABLE 2[illegible].—Continued.

[illegible]	[illegible]	[illegible]	No. of times shaken	s		n	
[illegible]	1	2[illegible]	1	1.45	143		
		11		1.27	99	.61	.25
		62		1.2[illegible]	81	.69	.034
		17[illegible]		1.2[illegible]	99	.22	.0097
[illegible]	16		10	1.35	116		
				1.3[illegible]	1[illegible]3		
				1.2[illegible]	81		
				1.2[illegible]	84		
				1.35	116		
2	16	3	1	1.28	99		
		157		1.10	47	.33	.024
[illegible]	16		10	1.22	86		
				1.30	103		
[illegible]	16	5	1	.55	8	1.1	.154
		4[illegible]		.05	13	2.1	.248

N[illegible] [illegible] the persistence of nuclei. They all vanish in a single exhaustion, showing [illegible]

TABLE 21.—PROPERTIES OF NUCLEI OF WATER, FOLLOWED BY A DILUTE SOLUTION OF ALCOHOL IN THE GIVEN WATER.

[illegible]	Pressure [illegible]	Time of [illegible]	No. of times shaken	s	n	m/[illegible]	
	Cm. of Hg.	min.		cm.	cm.		cm mm.
[illegible]	16	[illegible]	10	1.05	55		
		[illegible]		1.15	55		
	16	2	10	.55	8		4.8
1.6	16		1	.92	.37		
				.95	.4		
43				.99	.46		
				1.	.47		
1.6	16	2	1	.8	.24	9.5	1.45
		4		.55	.8	9	2.09

TABLE 22.—PROPERTIES OF NUCLEI DUE TO SHAKING DILUTE SOLUTIONS OF NAPHTHALENE IN BENZOL

% Naphthalene.	Pressure diff	Time elapsed.	No. of times shaken.	s	n*	$\frac{\delta n}{t}$	
	Cm. of Hg	min		cm			
2 500 $n = 71$	16	0	10	1.15[1] 1.15 1.15	71 71 71		
2	16	10 23 30	10	1.10 1.13 1.08	62 68 59	1.6 .44 .63	.172 .058 .041
2 $n = 85$	16	0 0 0	10	1.08 1.30 1.25	59 103 92		
2	16	169	10	1.10	62	0.18	.0099
$n = 100$		0 0 0	10	1.35 1.25 1.25	116 92 92		
2	16	300 880	10	.95 1.00	40 47	.18 .052	.0131 .0035
2 $n = 87$	16	0 0 0		1.15 1.35 1.20	71 116 81		
$n = 81$ .02	16	0	10	1.20	81		
.02	16	67	10	1.00	47	.61	.046
.02 $n = 96$	16	0 0	10	1.33 1.20	110 81		
.02	16	186	10	1.02	50	.20	.0150
.02 $n = 78$	16	0 0	10	1.22 1.15	85 71		

[1] Very sharp and decided. Multiannular; s very constant as compared with water.

* n is computed as if the solvent were water.

TABLE 22.—*Continued.*

[illegible]	[illegible]	[illegible]	No. of times shaken.		*n**	$\frac{dn}{dt}$	*k*
	[illegible]			cm.			
N 7	16	1	1	1.15 1.17 1.20	71 77 81		
N	16	59 155	1	1.[illegible]5 1.[illegible]	54 47	.27 .17	[illegible]207 [illegible]136
Distilled [illegible] = 62	16	0 0	1	1.37 1.10 1.10	121 62 62		
[illegible]	16	240	10	.60	17	.20	.042

* *n* is computed as if the solvent were water.

TABLE 23.—PROPERTIES OF NUCLEI PRODUCED BY SHAKING DILUTE SOLUTIONS OF PARAFFINE IN BENZOL. ALSO OF BENZINE.

	Pressure diff.	Time elapsed	No. of times shaken		[illegible]	$\frac{dn}{dt}$	
	[illegible] H.	min.		cm.			
1 12	16	0	10	1.45 1.37 1.45	143 121 143		
1	16	93 124	1	.70 1.15	16 71	.12 .46	[illegible]111 .0241
1	16	[illegible]	1	1.35 1.35	116 116		

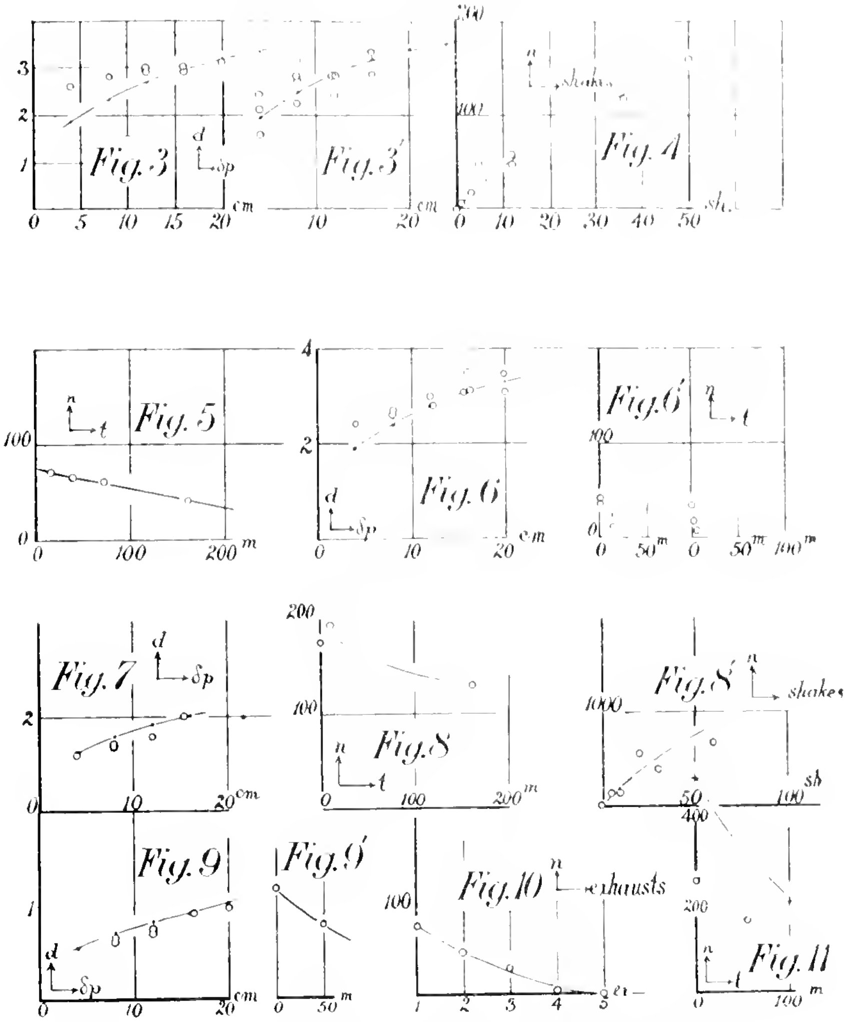
Pure benzine.

No. [illegible] *n* = 7[illegible]	16		10	1.1 1.2[illegible]	62 81		
No. [illegible]	16	3	1[illegible]	.65	13	1.1	.161

Str[illegible] as in case of naphthalene, paraffine, etc., in benzol.

REMARKS ON THE RESULTS.

For convenience in discussion the methods of computation to be employed will be fully indicated in case of the first of the solvents, which happens to be



Figs. 3, 3′.—Diameter of Cloud Particles (cm 10⁵) and Supersaturation for HCl.
Fig. 4.—Number of Particles Generated with Increased Shaking of HCl.
Fig. 5.—Number of Particles Lost in the Lapse of Minutes for HCl.
Fig. 6.—Diameter of Cloud Particles (cm 10⁵) and Supersaturation for Water.
Fig. 6′.—Number of Particles Lost in the Lapse of Minutes for Water.
Fig. 7.—Diameter of Cloud Particles (cm 10⁵) and Supersaturation for NaCl.
Fig. 8.—Number of Particles Lost in the Lapse of Minutes for NaCl.
Fig. 8′.—Number of Particles Generated with Increased Shaking for NaCl.
Fig. 9.—Diameter of Cloud Particles (cm 10⁵) and Supersaturation for CaCl.
Fig. 9′.—Number of Particles Lost in the Lapse of Minutes for CaCl.
Fig. 10.—Number of Particles Precipitated with each Exhaustion of Pressure Decrement δp = 20 cm., for CaCl.
Fig. 11.—Number of Particles Lost in the Lapse of Minutes for CaCl. Bulbs 500 and 1000 cub. cm., respectively.

hydrochloric acid. They will then be briefly referred to in case of the remaining solvents.

5. *Hydrochloric acid. Concentration. Supersaturation.*—The two concentrations of 3 % and 6 % used show results which, as seen in figures 3 and 3, need a detailed investigation to interpret them. The effect of pressure difference is much more marked and irregular in case of the 6 % than in case of the 3 % solutions. Since the operation of shaking can be only roughly controlled, the endeavor must be made to smooth the data by theory.

The pressure effect can easily be explained, as the particles will be larger and the coronas smaller for the greater pressure differences, in view of greater supersaturation. Since the number, n, of nuclei is fixed for a given intensity of shaking, if m be the mass of water precipitated per cub. cm., the equation is $\pi d^3 n/6 = m$, or $d = \sqrt[3]{6m/\pi n}$, where m vanishes with the pressure difference.

6. *Number of particles.* To determine m, the equation for the constant entropy, S, of the mixture in the ratio of $x/(1-x)$ of vapor and liquid,

$$S = C \ln \theta + xr/\theta,$$

where C is the specific heat of the liquid, θ its absolute temperature, r its latent heat of evaporation, may be used. Initially (before exhaustion), $x = 1$ and since $C = 1$ nearly, the conditions before and after exhaustion may be determined. The equation if solved for the ensuing x', becomes

$$x' = \frac{\theta'}{r}\left(\frac{r}{\theta} + \ln\frac{\theta'}{\theta}\right),$$

θ and θ' being the initial and final temperatures, etc. If p and p' be the corresponding pressures, the adiabatic equation

$$\frac{\theta'}{\theta} = \left(\frac{p'}{p}\right)^{(\gamma-1)/\gamma} = \left(\frac{\rho'}{\rho}\right)^{\gamma-1}$$

may be assumed as a first approximation. Furthermore, if $\theta = 273° + 20°$ and $p = 76$ be generally taken as the point of departure, $\gamma = 1.41$ and $(\gamma - 1)/\gamma = .29$,

$$\theta' = 293(p'/76)^{.29}$$

After allowing for the heat due to condensation as shown above (Chapter II, §§ 16 et seq.), the following data approximately express the grams of water condensed per cub. cm. of saturated air at 20°, for the different sudden falls of pressure from 76 cm.:

Pressure difference, δp	4	8	12	16	20	24 cms.,
Precipitation, $m \times 10^7 =$	17	36	55	73	92	111 grams.

Consequently as d varies as $\sqrt[3]{m}$, the character of the variation sought may be predicted. The computation may be completed by finding n from the observations made at the pressure difference $\delta p = 16$ or $\delta p = 20$ cm., as these are obtained under the best conditions of measurement, the coronas being sharpest and least diffuse. With this determination the theoretical curve for d results. The reductions show that

$$n = 64\, s^3 m \times 10^6$$

and the mean results for the two series in question are $n = 56$ and $n = 45$, for the concentrations of 3 % and 6 %. The individual data indicate that no stress can be placed on the differences between mean values of n thus obtained.

It is now possible to compute the curves for d from $d = .324 \sqrt[3]{m}$ and

$d = .348 \sqrt[3]{m}$, and the results are inscribed in table 1. So far as conclusions are concerned, it is quite as satisfactory to use the theoretical data $n = 64\ s^3 m \times 10^6$, and these results are also found in the table.

Curiously enough, the irregular results of the 6 % solution agree better with this curve than the smoother results of the 3 % solution; but the reason, I think, is the quicker evaporation of the smaller particles (smaller pressure differences) into the larger particles in the case of the latter. The observed coronal apertures appear too small and the diameters of the particles (since $sd =$ const.) are thus too large. Possibly the smaller nuclei may not be large enough to induce condensation at the lower pressure differences, but there is evidence below, § 17, against this supposition.

The same result may be reached by consulting the column for n. This number is least for the smallest pressure differences, proving that here many of the particles have evaporated because of their small size.

7. *Effect of intensity of shaking.*—The exhaustion being equivalent to a pressure decrement of 16 cm. throughout, $m = 73 \times 10^{-8}$, whence $n = 47\ s^3$, nearly. If the graph of n varying with the number of shakes be constructed (figure 4), a curve of surprising smoothness is obtained, which is ultimately nearly linear. In other words, about 2.6 nuclei are produced each time the 500 cub. cm. of HCl solution are vigorously jerked once up and down. This would make 130 nuclei for 50 jerks. The actual number is about 160, owing to the accelerated action at the beginning of the experiment.

If each nucleus represents an electron, or a charge of $2.3/10^{19}$ coulombs, 1.7×10^{18} shakes would be needed to produce a coulomb per cub. cm. of air, or 5.6×10^8 shakes to produce an electrostatic unit in each cub. cm. of the particular quantity of air contained in the receiver. As this amounted to about 14,000 cub. cm., 4×10^4 shakes would be needed to set free an electrostatic unit within it. It will be shown presently, however, that the productivity in nuclei depends directly on the bulk of liquid subjected to shaking, and that the number of nuclei obtained in the example computed is abnormally small. Still the result that a very small quantity of electricity would be in question, in any case, is already apparent.

8. *Time losses.*—These nuclei gradually vanish in the lapse of time for reasons which can not be easily discerned, since they diffuse against gravity and subsidence is out of the question. There may be some species of decay or evaporation, or the nuclei may be absorbed on contact with the walls of the vessel in which they are contained. That nuclei are removable in the latter way is clear from the efficiency of precipitation when used for this purpose. The removal by evaporation should be an exceedingly rapid process, and, in fact, in the case of water, which is the liquid most easily kept pure, the nuclei are phenomenally fleeting. The nuclei from even very dilute and volatile solutions, however, often persist for over a day. They vanish not adventitiously, but in accordance with a definitely prescribed law, however difficult it may be to follow it. They vanish, moreover, most rapidly when the number of nuclei produced is least, and therefore the evanescence can not

be caused by any species of decay due to the interaction of the nuclei. In the light of all that follows it has seemed to me that the hypothesis of diffusion and loss at the walls of the vessel is in best agreement with the data as a whole, and the results are therefore interpreted from this point of view. (*Cf.* § 2.)

As the pressure decrement is 16 cm., the nucleation, n, may be computed, as already specified, from $n = 47\,s^3$. The results are given in table 1 and the chart, figure 5. The time losses per minute are on the average about .19, so that over 5 minutes would be needed to remove a single nucleus or over 6 hours to remove the initial number of 71 particles at the same rate. But as this rate is not generally even approximately constant, it is expedient to compute k as in the next paragraph.

9. *Absorption velocity.* If the loss of nuclei be due to their absorption at the boundary of the vessel with a velocity, k, so that kn nuclei are absorbed there per minute per square centim., supposing that a mere radial march of nuclei outward occurs, or that the drain of nuclei is from the content of the receiver as a whole, the nucleation will decrease exponentially. Briefly,

$$n = n'\varepsilon^{-3k(t-t')/R},$$

where n and n' are the nucleations at the times t and t', and where R is the radius (15 cm.) of the spherical receiver. Combining the above results in pairs, the mean value $k = .016$ cm/min. follows from the four available observations, with some discrepancy as the observations happen to conform closely to a straight line. The number thus obtained is from 600–1000 times smaller than the numbers found from similar hypotheses for the velocity of fresh phosphorus nuclei *in air*. From this one may infer in a general way that the nucleus in water vapor is a relatively large body as compared with the nucleus of the same origin in case of air. The phosphorus nucleus in the same receiver but under conditions of much denser nucleation showed $k = .096$ cm/min., and thus the following data for the absorption velocity have appeared:

Fresh phosphorus nuclei, in air,	$k = .3$	cm/sec.
Dense phosphorus nuclei in water vapor,	.0016	
Sparse nuclei due to shaking dilute HCl,	.00026	

results apparently due to successively larger diameters. But the last value of k is unusually low and rather in the nature of an inferior limit. Values five times larger (*Cf.* table 14) are not unusual with HCl, and in proportion as water is approached in very dilute solutions, the value of k may actually be as high as over one half the air value cited.

10. *Repetition.* In a repetition of the experiments with HCl, the above exceptionally low values of n and k were not again obtained. As seen in table 14, for a series of diluted solutions of .5%, .005% and .00005%, the constants approach very closely to the usual order of values for salt solutions. It is difficult in a vessel containing metallic parts, rubber tubing, etc., to escape the introduction of impurities from so corrosive a body, notwithstanding the caution naturally taken with the work. But the difference remains unexplained.

Another peculiar feature met with in case of this volatile acid is the difficulty of cleaning the apparatus free from nucleation, after the charge of strong HCl has been removed. Nuclei are thereafter spontaneously produced in the apparatus itself. Neither precipitation nor aspiration will remove them. They survive with undiminished intensity even after twenty-four hours. If all parts of the apparatus are washed out with flowing water, however, this nucleation usually disappears. It is probably due to traces of HCl, reacting on the sulphides produced from the rubber tubing through the intervention of metals. Curiously enough, these nuclei only diffuse into the neutral atmosphere above solutions; they do not appear in the acid atmosphere above the 3 % HCl solution, for example.

The marked difference between the early and the later data for HCl leads one to expect that some occult or undiscovered influence is in action. The same unaccountable displacement of data is met with again in the case of the dilute solutions of sodic sulphate, §§ 26, 27, below. In both cases, the data at a given time of observation are determinate.

11. *Pure water. Supersaturation.*— Table 2 contains data for five samples of water, all of nominally the same degree of purity. The first experiments follow the work with HCl, and in spite of the rinsing and precipitations which the vessel had experienced, show the effect of lingering traces of HCl in the relatively persistent coronas. The second filling of water is strikingly pure by contrast. The third and fourth charges show similarly lingering traces of the sodic sulphate from the work which had preceded the experiments. The fifth charge is promiscuous. Other examples for water will be found below, § 35. The influence of traces found in this way is remarkable, and suggests the sensitiveness met with in electrolytic phenomena. It recalls the impossibility of dealing with absolutely pure water in glass vessels.

To determine the number of nuclei per cub. cm. in an average case, $n = 64\ ms^3 \times 10^6$, and the data for pressure differences 16 and 20 cm. are preferable. From these one may deduce, successively (since $m = 73/10^8$ and $92/10^8$), $n = 47\ s^3$ and $n = 59\ s^3$, respectively. With these constants the pressure effects are easily computed, since d is now $.34\sqrt[3]{m}$. The results for d and n are summarized in the table, and the graph figure 6 smooths the observed data except, as usual, at low pressure differences, where, from the evaporation of water globules, the corona seen is too small.

Similarly, the data for n at different pressure differences show too few particles at the lower exhaustions.

12. *Time losses.*—Computed as above from $n = 47 \times s^3$, the results are given in table 2 and the graphs, figure 6′. The feature of these results is the excessively small number of particles in action, often falling below 5 per cub. cm., and the corresponding faintness of the coronal display. Measurements are mere estimates.

Several interesting results need mention. The fleetness of the first series which followed the work with HCl is 1.6 particles per minute. In case of the purer water following, 6 particles vanish per minute. In series 3 (after sodic sulphate), 40 particles vanish per minute; in series 4, 23 particles vanish per minute. There is no immediate correspondence here between the size of the corona and its fleetness in vanishing; and this will be seen to be frequently the case in the experiments with salt solutions. Usually, however, small coronas vanish more rapidly, under otherwise like conditions.

The enormous rapidity with which the nuclei vanish in case of pure water needs no further comment. Mere standing of the water in the receiver may at times increase the persistence of coronas.

13. *Sodic chloride. Supersaturation.* Four measurements (table 3) made at $\delta p = 16$ cm., are available for standardization; viz., $s = 1.65, 1.55, 1.55, 1.40$, from which $n = 47 s^3 = 211, 175, 175, 129$. Here as elsewhere a gradual diminution of the number of nuclei is apparent, and it is possible that at the outset some unknown source of nuclei is still active.

To compute the sizes of the particles, the equation now becomes $d = .222\sqrt[3]{m}$, and the corresponding graph is seen in figure 7.

14. *Time losses.* Though the results are not smooth, the loss will not exceed .3 particle per minute. *Cf.* figure 8.

15. *Effect of shaking.* The results here are again pronounced and indicate the most fertile cause of difficulties in the present investigation. The productivity is much in excess of the early datum for HCl, being as high as 10–30 particles per jerk, corresponding to the larger coronas resulting. *Cf.* figure 8.

16. *Calcic chloride. Supersaturation. Time losses.*—The coronal diameters accompanying the normal pressure decrements of 16 cm. were, successively, 1.70, 1.75, 1.75, 1.70, 1.70. The average number of particles is thus, $n = 47s^3$ or about 240. From this the range of diameters for the other pressure differences is computed and the results given in table 4 and the graph, figure 9.

The coefficient in case of the time losses is 1.3 particles per minute.

17. *Minimum pressure decrement (supersaturation) for complete precipitation.*—The second part of the table contains results with a new bearing, showing that if particles are completely precipitated at a low pressure decrement, by repeated exhaustion, they will also be absent at the higher pressure decrements. In other words, the nuclei may be completely precipitated out at pressures falling suddenly to less than 2 cm. below the atmospheric pressure. This affords a means of estimating a superior limit for the size of the nuclei. Table 4 shows the number of nuclei surviving from the same initial shaking, after each of the successive exhaustions specified, pure filtered air being supplied between the operations. As a rule, two exhaustions are needed to completely remove the nuclei, even if care be taken to wait for the subsidence of each fog. It follows, therefore, that evaporation occurs abundantly, and at the moderately low pressure decrements, about one half the nuclei escape by shifting their load. At the lowest pressure decrements (2 cm.) four exhaustions were required and the mean rate here is about 13 particles dropped per exhaustion, or less than one third the total number. If persistence were due to a retardation of exhaustion, this would not be the character of the phenomenon. The present result, moreover, agrees with the data computed for the size of particles, d, at the lower pressure decrements, the coronas observed being too small.

For slight partial exhaustions, therefore, an increasingly greater number of particles escape precipitation by evaporating their loads as far as the persistent nuclear stage. The repeated precipitation at these low pressure decrements (allowing each fog to subside) nevertheless quite removes the nuclei, as is shown by the tests subsequently made by applying large pressure decrements.

Assuming that $\delta p = 2$ cm. are needed for condensation, the size of the nucleus may be estimated by the approximate method of computation, explained elsewhere, the equation being

$$r.\delta p = \frac{2\rho T}{R\theta(.0217\theta - 1)},$$

where condensation takes place for the small pressure decrement δp at the pressure p and the absolute temperature θ. If in this equation $\theta = 293$, $p = 76$ cm., $T = 80$, $R = 4.6 \times 10^6$ for water vapor,

$$r = 1 \times 10^{-6} \text{ cm.},$$

which should be an inferior limit. This result agrees with the order of quantities estimated in § 2; but as the value of the surface tension, T, accepted is certainly too large for such excessively small particles as the nuclei, r must lie indefinitely below 10^{-6} cm.

18. *Effect of concentration and of bulk. Time losses.*—The third part of the table 4 contains data for solutions of half the preceding strength. Furthermore solutions of double the preceding bulk as well as the usual bulk (500 cub. cm.) were shaken in like manner for comparison.

The first important result is the effect of quantity. When 1000 cub. cm. are shaken under otherwise like conditions, fully twice as many nuclei are produced as for the case of 500 cub. cm. It would appear from this that the nuclei arise in the water itself. Practically as well as theoretically this observation deserves attention. *Cf.* figure 11.

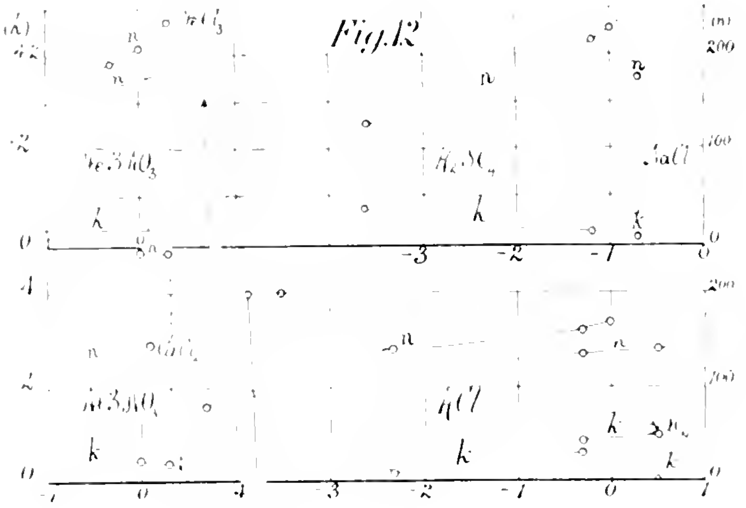
As usual, the number of nuclei produced at half the usual pressure decrement ($\delta p = 8$ cm. instead of 16 cm.), is somewhat smaller on the average.

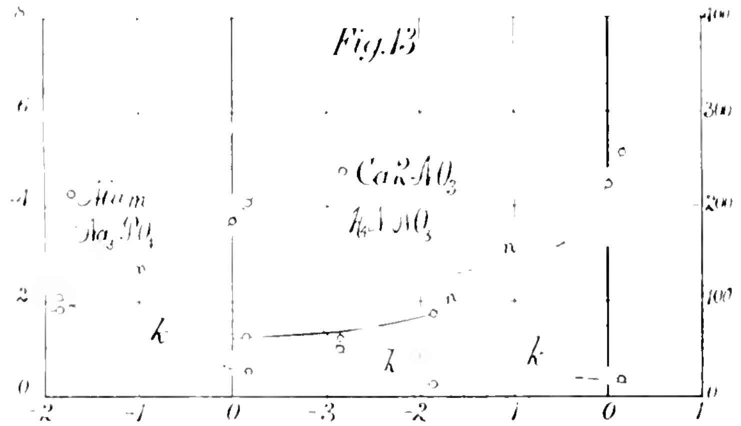
The time coefficient for this doubled bulk of liquid is $\delta n / \delta t = -2.6$, or about twice as large as for the other solution. But as the effect of the difference of concentration involved is insignificant (this is shown by all the cases below), and as the number of nuclei has been about doubled for the greater bulk, it follows that the time coefficients increase proportionally to the number of nuclei produced. This therefore is direct evidence in favor of the constancy of the absorption velocity, k.

19. *Ferric chloride. Effect of concentration, bulk, etc.*—The average number of nuclei produced in the normal case is 234, or about as many as in the preceding solutions (*Cf.* table 5). Valency, therefore, can have no appreciable effect on the generation of nuclei. The effect of pressure decrement is also like the above: fewer nuclei are entrapped by precipitation at the lower pressure decrements than at the higher.

When the concentration is reduced one fourth the nucleation falls from 234 to 184 so long as the same bulk (500 cub. cm.) is in question. It is probable that the true decrease of nucleation is less than this.

When a volume of 2000 cub. cm. is shaken (4 times the usual bulk), the number of nuclei is increased about 2.1 times. The nucleation here does not keep pace with the bulk—a circumstance which is in a measure explained because the large volume fills too much of the receiver and interferes with efficient shaking. It is well to note, however, that it is from experiments of this kind that the true relation of the absorption velocity, k, to the nucleation, n, is to be learned.





FIGS. 12, 13. NUMBER OF PARTICLES, n, AND THEIR ABSORPTION VELOCITY, k, GENERATED BY SHAKING SOLUTIONS OF DIFFERENT SOLUTES AND OF DIFFERENT LOGARITHMIC CONCENTRATIONS (log. c).

20. *Ferric nitrate. Concentration, supersaturation.* The normal number of nuclei produced is 175 for the larger and 161 for the smaller concentration, the dilution being 1 : 10. *Cf.* table 6. The difference lies below the limits of error. *Cf.* figure 12.

The effect of pressure decrement is also indecisive, and all nuclei are precipitated for pressure decrements of less than 1 cm.

21. *Time losses.* The time coefficients for the two concentrations are not appreciably different. Dilutions of the order stated are thus negligible so far as the present method goes.

22. *Turbid aluminum nitrate. Concentration. Time losses.* According to table 7, the nucleation is $n = 197$ for the larger concentration and $n = 81$ for the smaller, the dilution being again 1/10. This result is exceptionally large, recalling ferric chloride, which was also turbid. *Cf.* figure 12

The time coefficients show an equally pronounced difference in the two cases which, together with the preceding result, point out a change in passing from one solution to the other. In the light of the other tables, the discrepancy is probably not due to the concentrations, and one may suspect that some subtle effect of surface tension is involved.

23. *Calcic nitrate. Concentration. Time losses.*—The chief results (*cf.* figure 13) aimed at in table 8, are the effects of dilution. The original nucleation is $n = 256$; for the dilution 1/100, $n = 87$; for the dilution 1/1000, $n = 61$; for the dilution 1/10,000, $n = 63$. It is to be suspected that in the last instance the impurities of the water itself mask further decrement, and yet such an inference is not warrantably safe. These experiments indicate the enormous dilution needed to bring out the true nature of the concentration effect. In most of the above instances the dilutions used are insufficient.

The time coefficients are an equally interesting feature. They show further progressive change as dilution increases, even after the number of particles produced has reached an inferior limit. Thus, whatever causes the solution, on indefinite dilution, to reach fixed conditions of nucleation is not able in the same degree to influence the persistence of the nuclei. This persistence is therefore to be associated with the residue of calcic nitrate left in the successive cases.

24. *Alum. Concentration. Time losses.*—The effect of the dilution of 1/100 is to decrease the nucleation over 50 %. The time coefficients do not show this effect because the interval for which the second applies is too small as compared with the first. In such cases reference must be made to the rates, k. *Cf.* figure 13.

25. *Ammonic nitrate. oncentration. Time Closses.*—The effect of the dilution 1/100 is here about 33 %. The time coefficients show corresponding variations. *Cf.* figure 13.

26. *Sodic sulphate. Concentration. Time losses.* Three concentrations are given, the strengths being in the ratios of 1, .01, .0001. *Cf.* figure 14. The number of nuclei are respectively $n = 453$, 110, 18. These large numbers, appearing in spite of the small initial concentrations, are a feature of this body. The work was sufficiently often repeated to vouch for an unmistakable result; and yet the nucleation is not stable in the lapse of time, as the repetitions at the end of table 11 attest.

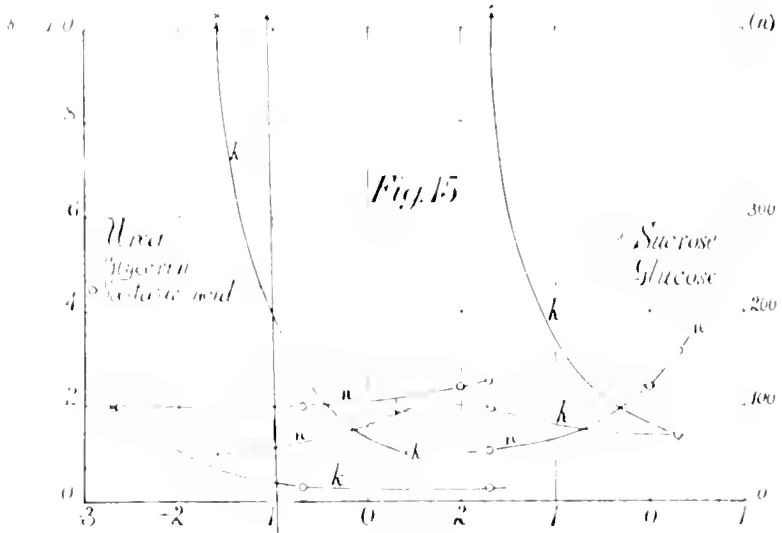
Time coefficients show the usual marked variations.

Data in the first part of table 11 give evidence that the precipitation may be made complete for a pressure decrement of less than 4 cm.

27. *Repetitions.*—Later experiments with the same solutions (marked "Repeated" in table 11) did not reproduce the excessively high values of n, though they reappeared at the higher concentrations tested. The new n in the lapse of time showed a tendency to diminish in its turn. As was the case with HCl above, so here some occult influence must be invoked to account for the undeniable differ-

ence of behavior of the same solution at different times. The present solution seems to have properties just after it is made up which eventually vanish.

28. *Potassic sulphate. Concentration. Time losses.* The results in the main resemble the final experiments with sodic sulphate. *Cf.* figure 14.



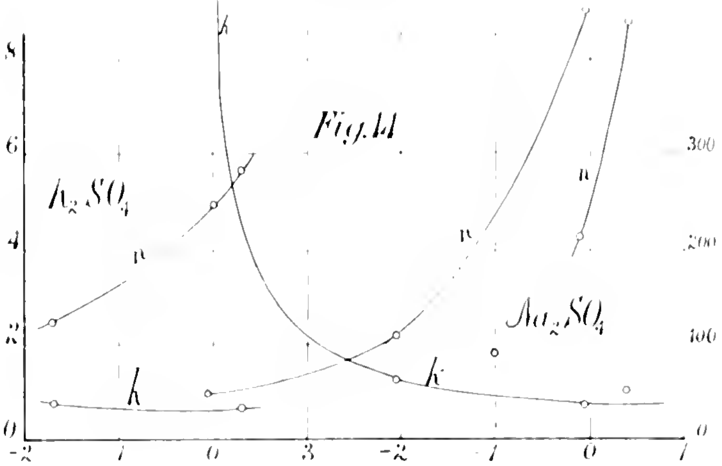
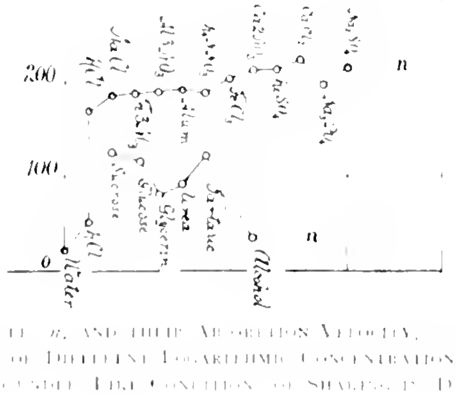


Fig. 16



FIGS. 14, 15.—NUMBER OF PARTICLES, *n*, AND THEIR ABSORPTION VELOCITY, *k*, GENERATED BY SHAKING SOLUTIONS OF DIFFERENT SOLUTES AND OF DIFFERENT LOGARITHMIC CONCENTRATIONS (log *c*).

FIG. 16.—NUCLEATION PRODUCED UNDER LIKE CONDITIONS OF SHAKING IN DIFFERENT SOLUTIONS OF THE SAME CONCENTRATION.

29. *Sulphuric acid. Concentration. Time losses.* The results of table 15 show no marked peculiarity. Acid and saline solutes, therefore, conform to the same general behavior. *Cf.* figure 12.

30. *Sugars. Sucrose. Concentration. Time losses.* The following bodies, with the exception of tartaric acid, are neutral organic solutes dissolved in water. They are characterized by the common behavior (*cf.* figure 15) of producing fewer nuclei on the average than the saline and other solutes discussed above. The time coefficients are correspondingly large, and the nuclei, therefore, under the usual conditions very fleeting, in spite of the crystalline body in solution. Thus, the cane-sugar solutions of 2 % and .02 % produce but 157 and 51 nuclei, respectively. The time coefficients are 2.5 and 1.2, showing that solutions of 1 % are already very fleeting as to nuclei. Thus, the presence of a solid solute is not a condition essential to the phenomena of the present chapter; in other words, if the nuclei were mere solid residues all solutions of the same strength should behave alike.

31. *Glucose. Concentration. Time losses.*—Glucose in table 17 (figure 15) behaves much like sucrose with the nuclei relatively even more fleeting.

32. *Glycerine. Condensation. Time losses.*—This stable liquid is (figure 15) even weaker as source of nuclei than the sugars. The absorption velocities of glycerine and glucose compare with those of pure water.

33. *Urea. Concentration. Time losses.*—Table 19 shows that urea as a source of nuclei is weaker than sugar, with which it in other respects compares. *Cf.* figure 15.

Results such as these prove, I think, that the hypothesis of the removal of the nuclei by diffusion and absorption is sound. Otherwise it would be difficult to state why the residue after the evaporation of the solvent becomes ineffective as a nucleus for condensation.

34. *Tartaric acid. Concentration. Time losses.*—This solid organic body follows the usual rule of producing few nuclei; but, curiously enough, this number varies but little even when the solution has been diluted 10,000 times. *Cf.* figure 15.

The time coefficients give evidence of a similarly unexpected behavior, being actually smaller for the .02 % solution than for the 2 % solution. They moreover show a low order of absorption velocities for organic bodies, indicating the occurrence of nuclei, which are very remarkably persistent.

35. *Alcohol and pure water. Concentration. Time losses.*—The addition of 1.6 % of absolute alcohol to water reduces the number of nuclei generated by shaking. The effect is small; but one may suspect from this that the variations of surface tension have some bearing on the value of n. Thus the surface tension of the above saline solutions is larger than that of water and so is the nucleation observed. On the other hand, dilute alcoholic solutions, according to table 21, generate fewer nuclei on shaking to correspond with their reduced surface tension as compared with water.

At the same time the alcoholized nuclei are clearly more persistent, for the value of k is definitely smaller for the solution even if the nuclei are all very fleeting. *Cf.* figure 17.

36. *Naphthalene in benzol. Concentration. Time losses.*—These experiments introduce a new factor, as the solvent is not electrolyzing. From the absence of adequate data, n will have to be computed as if the solvent were water. Mere inspection of the very strong and sharp coronas obtained, however, indicates the occurrence of a proportionately much larger number of particles than are met with in the experiments with aqueous solutions, and it is the precipitation of a greater mass of liquid (m in the deductions of § 6) that accounts for the fact that only small and normal coronas are obtained. *Cf.* figure 17.

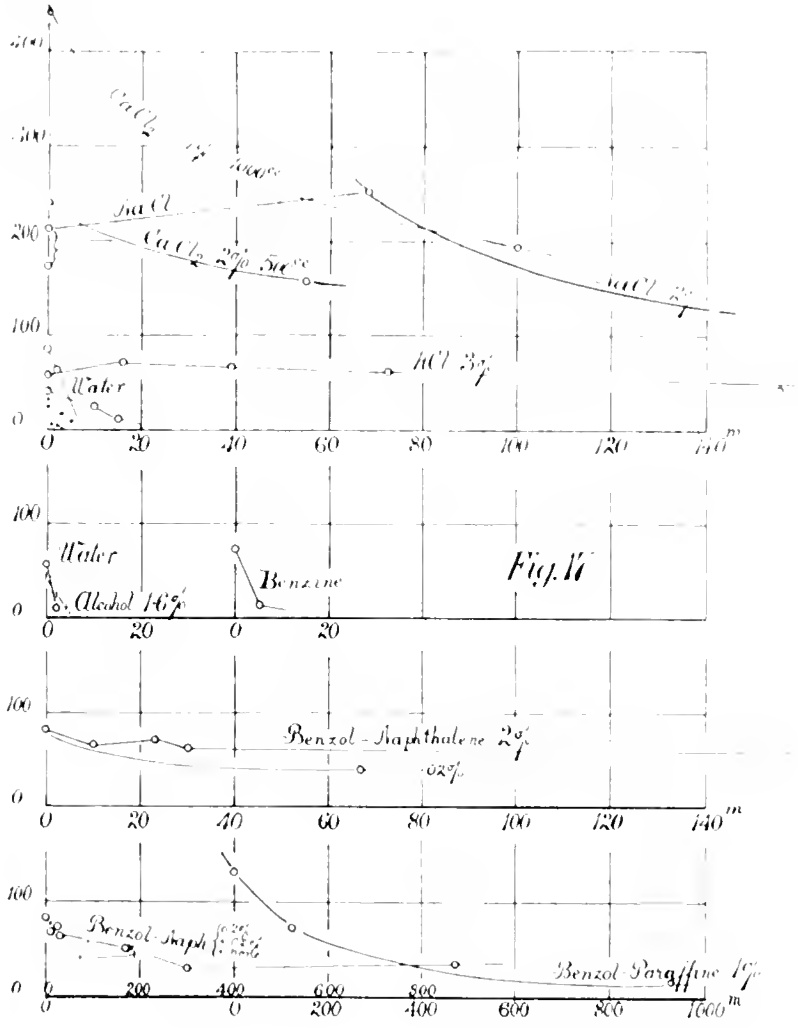
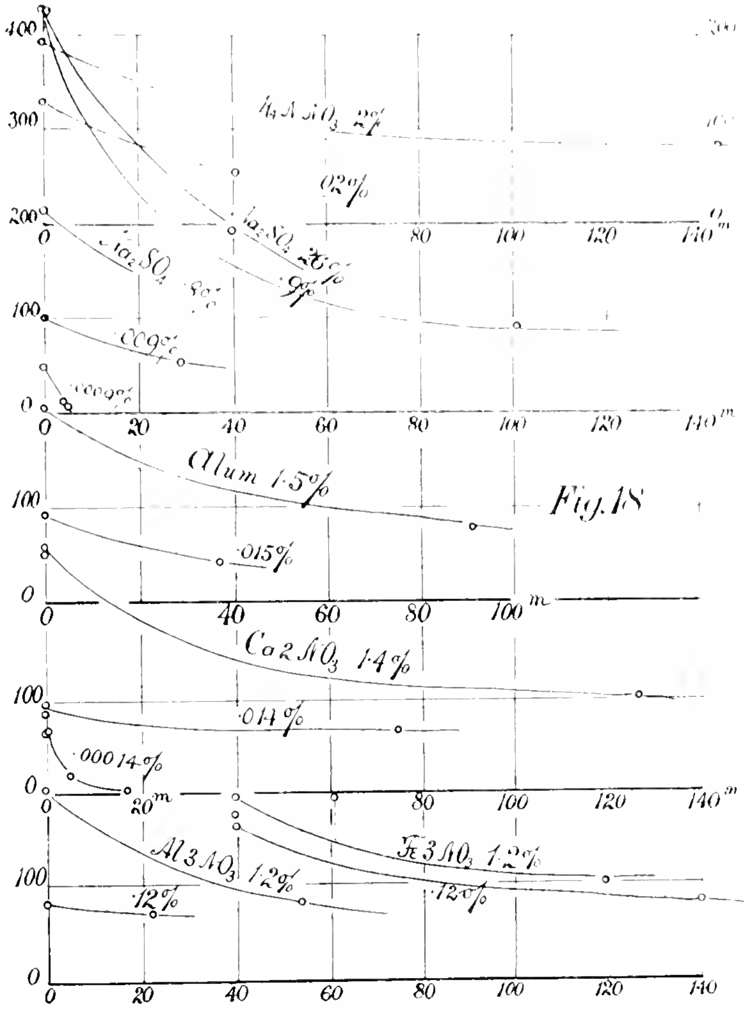


FIG. 17 (1).—LOSS OF NUCLEI IN THE LAPSE OF MINUTES FOR DIFFERENT SOLUTIONS.

Dilution with benzol in the ratio of 1 : 100 is not apparently effective, though it must be remembered that great difficulty is experienced in keeping hydrocarbon solvents pure. Even the influence of a complete absence of naphthalene is uncertain. The benzol itself furnishes about as many nuclei.

The value of the absorption velocity, k, is characteristic. In spite of the volatility of the solvent, the nuclei seem to be quite indefinitely persistent. The stronger solution corresponds to a somewhat smaller value of k than the diluted solutions, but the difference is not far from the limits of observation. The graph shows the same result for pure benzol. The intensity of the coronas even after 15 hours, and their tendency to reach a fixed diameter, in the lapse of time, make it probable that the vapor pressure of naphthalene, however small, is the cause of this long maintenance of the supply of nuclei, and one may suspect that other bodies with strong odors and which show a tendency to slow sublimation, will be found



FIGS. 17-19.—LOSS OF NUCLEI IN THE LAPSE OF MINUTES FOR DIFFERENT SOLUTIONS.

in like degree nuclei-producing. As a means of throwing further light on the nature of the nucleus, the present simple method of evolving nuclei spontaneously is worth attention. It is in this particular, chiefly, that an effect of naphthalene has been discerned, the original benzol otherwise showing, both in relation to n and to k, data of a common order of values.

In the case of these intense coronas in volatile solvents, at least three exhaustions are needed to free the air in the receiver of nuclei. The circumstances are particularly favorable to escape by evaporation.

37. *Paraffine in benzol. Concentration. Time losses.*—The case of paraffine

in benzol (table 25) is on the other hand very definite as regards the increment of , due to concentration. *Cf.* figure 17.

A curious result was incidentally obtained on admitting the air too rapidly through the filter by accident. Air nuclei were thus introduced simultaneously with the nuclei due to shaking. The exhaustion showed two groups of coronal particles interpenetrating and subsiding through each other, one group subsiding relatively fast and showing intense coronas, the other, much more slowly with weaker coronas. In order that the two phenomena may preserve their identity throughout, it is necessary that one group of nuclei should regularly exceed the other in size, thus insuring earlier condensation on the larger particles. This occurrence of interpenetrating subsidences was still observed in the next exhaustion, though more faintly. As precipitation proceeded three strata were visible, the upper corresponding to clear air, the lower two showing coronas of different size and intensity and different rates of subsidence. Both fog banks were capped by descending planes. This observation recalls the behavior of sulphur and punk nuclei in Chapter III, § 7.

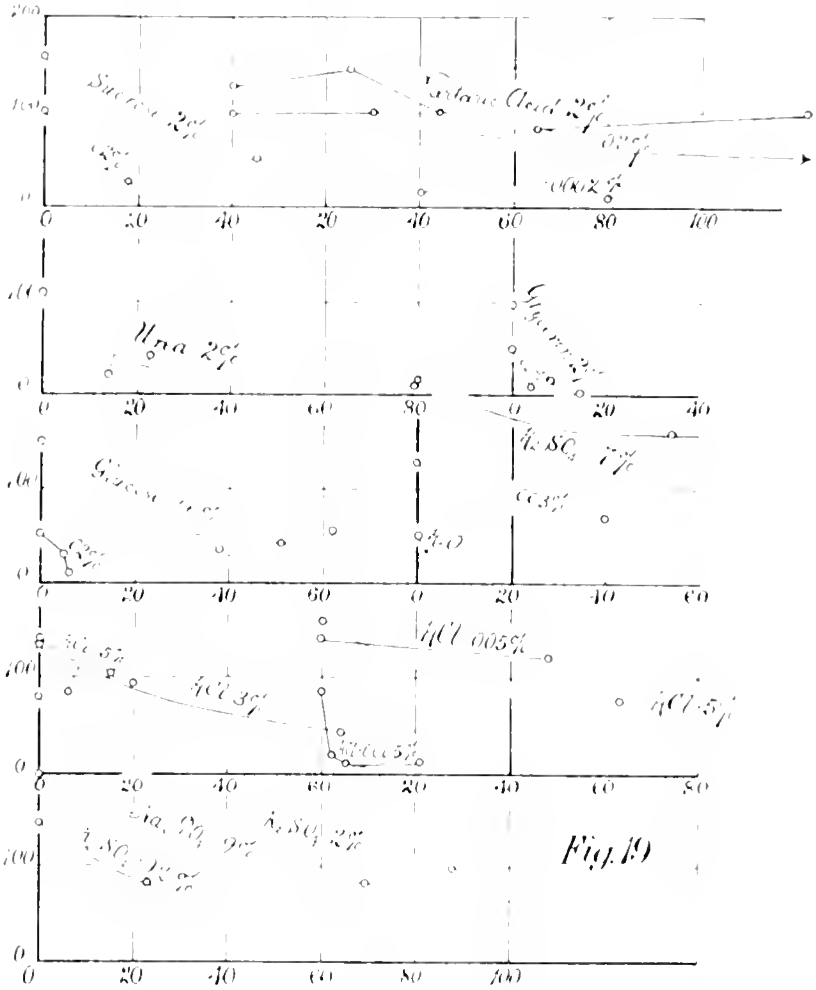


FIG. 17-19. LOSS OF NUCLEI IN THE LAPSE OF MINUTES FOR DIFFERENT SOLUTIONS.

The values of k for paraffine are also in sharp contrast to those for naphthalene. After 15 hours, for instance, nearly all nuclei have vanished, a result which indicates that the phenomenal persistence of nuclei in the preceding experiment, after 15 hours of waiting, must be regarded as referable to a sublimate from the naphthalene. Experiments with pure benzol were not made for this length of time.

38. *Benzine. Concentration. Time losses.*—Pure benzine (table 23) was tested to show the larger absorption velocities, k, in the absence of a solute. The rates do not, however, compare with those of water, from the difficulty (frequently stated) of keeping hydrocarbon solvents pure in an apparatus containing rubber tubing in any of its parts, even if not in contact with the solvent. *Cf.* figure 17.

These relatively small values of k lead to an important ulterior deduction, viz., that an electrical influence on persistence due to the frictional effect of shaking need not be apprehended. There is quite as much reason why benzine as paraffine-benzol should evolve electrically persistent nuclei; for whatever charges are evolved are in like manner capable of being stored and distributed. And yet benzine fails while the other liquid is intensely active.

SYSTEMATIC COMPARISON OF THE DATA.

39. *Dependence of the number of particles on the concentration of the solution.*—It is next desirable to select mean values from the above data for comparison. The character of the variations of n with the concentration, c, of different solutes has not been identified. It does not depend on valency or molecular weight as is frequently the case with other constants holding under the same general relations. The powerful hygroscopic solutes show no exceptional behavior. The tendency of some of the solutes to crystallize with water of crystallization has left no mark in the results. Nor can any of the better-known electrical or similar constants of the solutions be associated with the variations of n or k observed. Until some thread of this kind has been found it will therefore be necessary to proceed empirically.

In tabulating the data for n it is advisable to refer them to a common concentration, and the 1 % solution is a useful standard. The equation to be selected for this purpose is not easily found from the large discrepancies inevitably present in the data. Thus an equation like $n = n_0 10^{bc}$ where c is the concentration and b a constant would be roughly available, but probably too simple. By properly manipulating the graphs, the equation $c = B\,10^{-A(n-n_0)c}$ is found to be in reasonable accord with the properties of most of the curves and deserves trial. This may be further simplified by putting $n_0 = 0$, assuming that from absolutely pure water no nuclei of appreciable persistence could be produced by shaking. A trial case for calcic nitrate may be shown, in which the first two observations are used to compute the constants because of their relatively much greater accuracy.

		(1)	(2)
$c = .014$	n (observed) $= 256$	n (computed) $= 256$	n (computed) $= 256$
.00014	87	87	87
.000014	61	71	65
.0000014	63	62	52

The first values of n are computed from $n = 30$, $A = 152.3$, $B = .0661$; the second from the values, $n = 0$, $A = 263.6$, $B = .150$. The latter equation, though simpler, is decidedly better, for the dilution of $1/10^6$ can not be vouched for even in case of the best of pure water.

The data for c (grams of dry salt in 100 cub. cm. of solution), n observed, B, A, as well as n_1 (computed number of nuclei obtained by shaking a 1% solution) are all inserted in table 24. The table also contains the time rates or ratios of promiscuously distributed increments $\delta n/\delta t$, the absorption velocities k in centims. per minute, at which the nuclei vanish, and other relevant matter. A number of graphs in n and k are shown in their relations to the logarithmic concentration, $\log c$, are given in figures 12–15. The need of a logarithmic abscissa should be noted.

10. *Mass action.* An inspection of the data for n for the 1% solutions seems to reveal no relation to their molecular or equivalent weight, nor to any of their better-known electrical constants, as has already been intimated. If we except pure water and certain exceptional cases needing further interpretation, like the early data for HCl on the one hand and those of Na_2SO_4 on the other, the mean number of nuclei produced from the saline series in 10 shakes is about 200 per cub. cm., and this holds for a variety of salts of which the valencies of the metal involved vary largely. In general, therefore, the number of nuclei produced under like conditions is dependent on the mass of saline solute in solution. These facts are also illustrated by the graph figure 16, in which the abscissas are merely distributive and the ordinates show the values of n.

The organic solutes and in particular the neutral bodies may be easily distinguished from the salts as a separate class, the latter showing about one half the nuclei producing power of the former.

The constants A and B have no obvious relation. In other words, the effect of dilution on n is sometimes marked, at other times negligible.

11. *Dependence of the absorption velocity on the concentration of the solution.* It will next be necessary to proceed with a somewhat similar deduction for the absorption velocity, $k = -(R/3)(dn/n\,dt)$, so that kn nuclei are absorbed per minute per square centim. at the boundary. Figures 17, 18, and 19 will be of assistance to this end. A relation between k and n, apart from the solute, has not been made out. The relation of k to n is characterized by specific constants for each body, which in every case are of such a nature that k markedly increases while n decreases, and particularly on approaching the very dilute solutions. *Cf.* figures 12–15. Hence k begins to increase at enormously accelerated rates when the variations of n have subsided. This region is very near pure water, or occurs when the logarithmic concentration falls below $\log c = -3$, or -4. The reciprocal relations of n and k are noteworthy.

Low values of n and high values of k seem to be associated with the neutral organic solutes. In case of tartaric acid, however, though n is small, the value of k is exceptionally high. If we take this as a type of acid organic solutes, the nuclei produced are remarkably persistent apart from cases of the very lowest dilution.

A few exceptional observations in the tables point out that some occult effect has escaped detection. Thus the earlier values of n for HCl are inexplicably low ($n = 50$) as compared with the later values (n [illegible] 150). The earlier values of Na_2SO_4 are on the other hand exceptionally high. As all observations were made in triplicate or even oftener, they are trustworthy. In both cases the later observations are normal values.

TABLE 24.—SUMMARY—AQUEOUS SOLUTIONS SHAKEN (JERKED) TEN TIMES. CONCENTRATION, $c = B$ 10 [illegible] NUCLEATION, $n = n_0$ [illegible] $R = 15$ cm. BULK OF SOLUTION USUALLY 500 .

(1) Inorganic Solutes

Solute dry.	Concentration, c	Nucleation, n	B/A	[illegible]	[illegible]	
	%					cm/min.
Water	—	37	—	(30)	1.6	32
	—	32	—		6	1.47
	—	85[1]			40.	6.7
	—	26			23.	9.4
HCl	3	56	—		.19	.016
	6	45	—			
HCl Another sample	3	140	—		2.	.10
	.5	134	—		2.1	.085
HCl Another sample	.5	158	174	169	1.3	.06
	.005	140	717		.4	.016
	000.05	84			25.	2.3
H_2SO_4	.65	215	19	227	1.05	.028
	.0026	127	745		1.4	.072
NaCl	2	175	—	—	30	.014
$CaCl_2$	2	240	—	242	1.3	.038
	1	242	—			
Bulk 1000	1	456			2.6	.042
$FeCl_3$	2	234	3.3	206		
	.5	184	518			
Bulk 2000	5	435				
$Fe(NO_3)_3$	1.2	175	3.8 × 10^{6}	173	.9	.034
	.12	161	2010		.8	.034
$Al(NO_3)_3$ (Turbid)	1.2	197	.060	177	1.6	.067
	.12	81	138		.5	.030

[1] Note the large k in spite of the exceptionally large n.

TABLE 24.—*Continued.*

[illegible]	Concentration	Nucleation	R		s/s	
						mm
[illegible] NO	[illegible]	256	15	224	1.2	.037
	14	87	264		.39	.021
	14	61			.63	.100
	214	63			9.4	1.4
Alum	1.5	254	61	184	1.4	.053
	15	91	329		1.4	.110
Na_2SO_4	9	450	.040	487	3.3	.074
	9	110	291		1.9	.122
	[illegible] 9	48			10.	2.1
Na_2SO_4	8	214				
Another sample	2.0	442			0.2	.104
H_4N NO_3	2	192	25	179	.72	.020
	.02	120	786		1.85	.126
K_2SO_4	2	252	2.26	240	1.9	.057
	.02	143	580		1.6	.071
[illegible] PO_4	.9	195		(195)	1.6	.064

(2) Organic solutes.

Cane sugar	2	157	182	120	1.0	.133
	.02	51	151		1.4	.103
Grape sugar	1.6	152	200	115	2.3	.138
	.016	50	150		5.6	1.03
Glycerine	2.6	95	3.5	79	9.9	1.12
	.026	49	202		10.3	2.3
Urea	2	157	—	—	3.5	.189
Alcohol		55		(55)	23	4.8
	1.6	43			9	1.5
Tartaric acid	2	126	$4.3 \times 10^{[illegible]}$	121	.51	.024
	.02	99	924		.33	.024
	.002	95			1.6	.200

TABLE 24—*Continued.*

(3) Other solvents than water

Solute dry.	Concentration, c	Nucleation, n	B/A	n_{01}	$\delta n/\delta$	
	%					m.m.
Naphthalene in benzol	2	90	—	—	[illegible]	37
	.02	87			19	30
None		78			20	217
Distilled benzol	[illegible]	82			.29	941
Paraffine in benzol	1	128	—	—	29	117
Pure benzine	—	72	—	—	1.1	160

SUMMARY AND INFERENCES.

42. *Values of the nucleation, n.*—The number of nuclei generated under identical conditions of agitation varies with the violence of the agitation and the bulk of solution used, and, from a theoretical point of view, particularly with the concentration of the solution and its chemical nature to the extent of a discrimination between saline and neutral organic solutes. The first two factors indicate an origin of the nuclei within the liquid. So far as concentration alone goes, one may write, $n = n_0 + A/(\log B/c)$, where n is the number of nuclei produced per cub. cm., under otherwise like conditions, n_0 the number in case of infinite dilution (water), c the concentration, and A and B constants. If absolutely pure water were available, it is probable that n_0 would vanish. The degrees of dilution effective recall the sensitiveness of electrolytic phenomena. For organic neutral solutes, the number of nuclei is not only smaller as a rule, but they are characteristically fleeting.

So far as examined, solutions of the same class (saline or neutral), with the same mass of solute per cub. cm. of solvent, generate about the same number of nuclei if identically agitated.

43. *Values of the absorption velocity, k.*—All nuclei gradually vanish in the lapse of time, except in those cases where the solute produces nuclei spontaneously, as in the emanations from CS_2, naphthalene, etc. But the rates of evanescence are very different. This evanescence of nuclei is not due to evaporation except in case of pure water. When the nuclei are fleeting, this quality must be otherwise explained. From the marked diffusion of nuclei (Chapter VI), their dimensions must be comparable with molecular dimensions. Subsidence is out of the question. The nucleus is not large enough to admit of symmetrical molecular bombardment, and it is to the unilateral character of this bombardment that the nucleus owes its velocity.

If, as I interpret it, the loss of nuclei in the lapse of time is due to absorption at the solid walls of the spherical receiver, one may write for the absorption velocity, k, the equation $k = (R/3n)(dn/dt)$, meaning that kn molecules are absorbed per square centim. per second. Computing k in this way (essentially as a logarithmic rate), one finds from all the saline solutions an important general result; for the case of solutions of a few per cent (1 to 3), k is of the order of .03 to .07 cm/min., though varying from solute to solute; for the .01 per cent solutions, k is of the mean order of .08 cm/min.; for the .0001 per cent solutions, k is of the order of about 1 to 2 cm/min. For ordinary distilled water in glass vessels, k may reach over 5 cm/min., etc. Specific data are given in table 24. Similar deductions may be made for the organic solvents (*Cf.* Chapter VI, § 19).

It follows, therefore, in general, that not only does the number of nuclei produced by shaking (*cat. par.*), increase with the concentration of the dilute solution, but the apparent rate of decay diminishes, *i. e.*, their absorption velocity decreases with the strength of the solution. For ordinary distilled water, these velocities, *if referred to three dimensions*, are already beginning to approach the ionic velocities. Again, as the number of nuclei, n, is greater, they vanish more slowly, so that an apparent decay decreasing with the density of the nucleation is out of the question. The whole, therefore, constitutes an entirely new and striking confirmation of the isolated point of view taken throughout my work.[1]

11. *The thermodynamic hypothesis.* The inference is therefore tenable that the nuclei shaken out of stronger solutions are larger. These nuclei are produced by evaporation from a larger diameter, for the very dilute solutions must become more concentrated, and it follows that the dimensions at which evaporation ceases at the surface of a particle are larger for stronger than for weaker dilute solutions. Naturally, a given degree of concentration is reached in a larger globule in the former case as compared with the latter. The theory for the production of nuclei here in question is thus at hand. A particle of absolutely pure water, produced by shaking, will either vanish by complete evaporation, or it will grow and eventually vanish by subsidence. If, however, the evaporating globule is a solution, the increment of vapor pressure at a surface of increasing convexity will gradually be compensated by the decrement of vapor pressure due to the increasing concentration of the solution. Hence, there must be a critical diameter at which the increased vapor pressure due to surface tension just counterbalances the decreased vapor pressure due to concentration. This is the stable diameter of the nucleus. A smaller particle will grow because the concentration effect supervenes; a larger particle will evaporate because the effect of surface tension supervenes.

In connection with the critical diameter, a critical density is also implied, which varies naturally with the diameter. Thus, in the more concentrated solutions, a lower density and larger diameter must occur than in the corresponding case of stability in the weaker solutions. If the particle is so small before evaporation that, compatibly with the given supersaturation (pressure decrement), the

---

[1] Cf. *Experiments with Ionized Air*, these contributions, p. 92, 1901.

critical density is not reached, it will escape precipitation on exhaustion. There is no direct evidence of such particles in the above research.

The loaded nucleus during precipitation will also tend to re-evaporate to its original nuclear size and density, and thus escape removal. For the stable diameter is conditioned solely by the amount of solute *initially* entrapped. It is from this point of view that the partial precipitations at the lower pressure decrements are to be explained. The above case of calcic chloride for pressure decrements of 2 cm. may be cited. If it be supposed that all particles in evidence are precipitated, the succession is as follows, for a total of 300 particles:

Exhaustion,	1	2	3	4	5
Precipitation,	149	88	56	7	none
Escape,	151	63	7	none	

The very slow subsidence of the small particles in these diffuse coronas gives exceptional opportunity for evaporation; but all strong coronas, in spite of the more rapid precipitation which accompanies them, require more than one exhaustion to free the air of nuclei.

In spite of this repeated partial precipitation, there is never any irregularity in the coronas, showing the characteristic rapid diffusion of the aqueous nucleus. It is common experience that the diffuse coronas for small pressure decrements form gradually. Probably, as a result of the evaporation in question, the shrinking coronal figure becomes more luminous. The strong, sharp coronas at high pressure decrements are formed at once. For some occult reason, early coronas are liable to be larger than later coronas, *cæt. par.*, a result appearing in many of the triplets above.

45. *Equations for dilute solutions.*—The endeavor may be made to give these results a more definite form. Not much will be gained by this, for the chief desideratum is an experimental investigation of the vapor pressure of the more nearly concentrated solutions. The following group of equations will, therefore, fall short of meeting the actual conditions, though the estimates in § 18 leave much of the question open.

If p_r and p_∞ be the vapor pressures corresponding to radii r and ∞, T the surface tension, ρ and σ the density of the liquid solution and its vapor, Kelvin's equation asserts,

$$p_r - p_\infty = \frac{2T\sigma}{(\rho - \sigma)r} = \frac{2T\sigma}{\rho r}, \text{ nearly.} \qquad (1)$$

The present liquid is a solution and its vapor pressure, p_∞, is thus below the normal value for the pure liquid.

For the reasons stated in the last paragraph, it is conceivable that a state of equilibrium will be eventually reached in which drops large or small may all have the same vapor pressure, namely that of the free surface of the liquid, and that evaporation must therefore cease and the droplets persist, however small. In fact, after the lapse of time, equation (1) for a given droplet will be replaced by

$$p'_r - p'_\infty = \frac{2T'\sigma}{\rho r} \qquad (2)$$

since the pressure, tension, size, and density of the droplet of solution have all changed by the partial evaporation of the drop. But as the more concentrated drop of radius r' now persists, $p'_{r'} = p_x$, the vapor pressure at the flat surface of the original solution. Hence

$$p'_x = p_x - 2\sigma\frac{T'}{\rho' r'}. \quad (3)$$

For the case in which a solid is dissolved, its mass remains fixed within each suspended drop of water. The case of a gas may be supposed to approximate to these conditions. Hence ρ' may be expressed in terms of ρ, or

$$\rho' = 1 + (\rho - 1)(r^3/r'^3),$$

whence finally,

$$p'_x = p_x - 2\sigma\frac{T' r'^2}{r'^3 + (\rho - 1)r^3}. \quad (4)$$

For dilute solutions, $\rho = 1$, nearly, or $p'_x = p_x - 2\sigma T'/r'$. If $r' = \infty$, $p'_x = p_x$, the vapor pressure at the flat surface.

It will be seen that in ρ' and T' the original radius of the droplet is implicitly involved. If $\delta p = p_x - p'_x$, and $c = r^3/r'^3$, equation (4) may be written: $r' = 2\sigma T'/((1 + (\rho - 1)c)\delta p)$. If δp be expressed in terms of Raoult's law, n/N and n_1/N' being the original and final ratios of the number of molecules in solute and solvent and $p_x = p$,

$$\delta p = p(n_1/N' - n/N)/(1 + n/N).$$

Finally, in a law $(T = 83 + 187n_1/N')$ discovered empirically by Quincke[1] $T' = T + 187(n_1/N' - n/N)$, where T is the initial and T' the final surface tension in dynes. Thus if $(n_1/N' - n/N) = x$,

$$r' = \frac{2\sigma}{p}\frac{T + 187x}{(1 + c(\rho - 1))x}(1 + n/N).$$

This expresses the radius of the droplet in terms of the original and final ratios of the number of molecules of solute and solvent in solution. It does not, however, admit of any simple interpretation, and is, as a rule, liable to considerable or even fatal error, because the nuclear conditions are probably not reached until the solution is too concentrated. In this case the usual laws of physical chemistry lose their meaning. *Cf.* § 48.

46. *Equations for concentrated solutions.*— A statement of the case is better made as follows, supposing the effect of solution in diminishing vapor pressure to be known, particularly in the region of concentrated solutions. Let $\delta p = f(c)$, where δp is the decrement of vapor pressure at the high concentration c, of the solution. Hence

$$f(c) = \delta p = p_x - p'_x = \frac{2T\sigma}{\rho r}$$

nearly. This condition holds when evaporation ceases with the occurrence of a stable nucleus. T and ρ refer to pure water.

If c and c_1 be the original concentrations of two given dilute solutions; if c' and c'_1 be the concentrations after evaporation to the nuclear stage, and if the cor-

---

[1] *Cf.* Winkelmann's *Handbuch*.

responding radii be similarly accentuated $c' = cr^3/r'^3$ and $c'_1 = c_1 r_1^3/r'^3_1$, where r' and r'_1 are the final radii. Hence, after reduction, since $\rho = 1$

$$r' f(cr^3/r'^3) = 2T/\sigma = r'_1 f(c_1 r_1^3/r'^3_1).$$

If the drops in both dilute solutions are initially, *i. e.*, immediately after shaking, of the same average size, $r^3 = r_1^3$, and the equation is thus a relation between r' and r'_1, the radii of the nuclei for the two given solutions. The results accentuate the need of observations on the vapor pressure of concentrated solutions.

47. *The mechanism generalized.* In connection with the simple mechanism of § 44 for producing nuclei of a startling degree of smallness by mere shaking, nuclei which may or may not be without electrical charge, the question naturally arises whether the mechanism may not be sufficient to account for nuclei in the presence of saturated vapor, in general.

Suppose, therefore, that such chemically powerful agencies as the X-rays or Becquerel rays, or ultra-violet light, or the electric glow, etc., on being passed through a saturated vapor, produce in that vapor a new chemical synthesis, in degree however small (since the insignificant vapor pressure of a few hundred nuclei per cub. cm. is alone in question), *soluble* in the liquid from which the vapor arises. Then immediately around the new molecule there will be a region of vanishing vapor pressure. The new molecule, whether it be ionized or not, will therefore grow by condensing vapor, until further growth is arrested by the increment of vapor pressure due to the preponderating surface tension which accompanies continued dilution. In other words, the critical diameter is again reached.

The relations here involved are peculiar and need a more detailed elucidation. If vapor pressure increases with increasing convexity, for capillary reasons, but eventually decreases again as a result of the concentration reached on evaporation, to a value nearly zero or at least below the normal vapor pressure at a flat surface, it follows that as the size of the drop continually decreases the vapor pressure at its surface must pass through a maximum. The accompanying diagram, figure 20, is an attempt to represent the case graphically by making the vapor pressures the ordinates and the radii of the given droplet of solution, the abscissas. The line *ab* indicates the normal vapor pressures. All particles whose sizes correspond to the abscissas between *s* and *b*, therefore, evaporate in the lapse of time, those lying near the maximum *m*, fastest, those lying near *s* or *b* with proportionate slowness, while the latter are also lost by

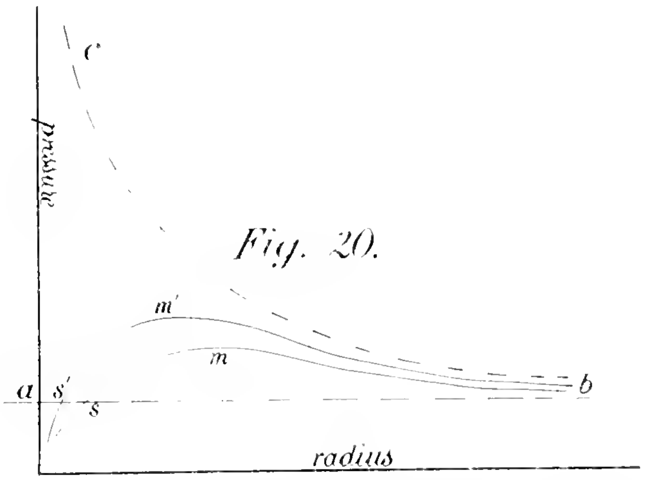


FIG. 20.—DIAGRAM SHOWING THE RELATION OF VAPOR PRESSURE TO THE RADIUS OF THE NUCLEUS FOR DIFFERENT STRENGTHS OF SOLUTION.

subsidence and may be dismissed from consideration. On the other hand, particles whose radius is smaller than the abscissa corresponding to s, will grow so that x_s is the stable radius of the nucleus obtained by shaking the given dilute solution.

If the solution is weaker, the droplet shaken out of it will have to evaporate further to reach the critical density of the stable nuclear state, and the increment of vapor pressure due to surface tension will also be larger or the maximum, m', will be higher. The curve $bm's$ now represents the conditions and is to be similarly interpreted.

If the solvent is pure or contains only a trace of solute, the nucleus will vanish completely, or else the particle left may be too small to serve as a condensation nucleus for a given pressure decrement of exhaustion. The size after the lapse of time depends on the fixed quantity of salt originally entrapped.

If the vapor is not quite saturated, the chances for evaporation will be enhanced. The line ab will be correspondingly lowered, but equilibrium may result for a smaller size of nucleus, until eventually the solid saline residue of the nucleus alone is left. In so far as these concentration nuclei occur in the atmosphere, one is justified in concluding that their size (apart from the effects of temperature and barometric pressure on surface tension and vapor density[1]) will increase under mean atmospheric conditions as they are suspended at higher distances above the earth's surface, until the levels of perpetual saturation are invaded.

There is one outstanding question relating to the time losses which must now be considered. These coefficients, dn/dt, are much smaller in concentrated than in weak solutions. This observation was referred to the diffusion of the nucleus and its absorption at the walls of the vessel with different velocities, k. The diagram, figure 20, shows, however, that near the points s there must be retarded evaporation for all particles, because of the small differences of vapor pressure remaining. Hence the persistence of nuclei shaken out of solutions might be ascribed to this effect. True, no reason is evident why strong solutions should differ from weak solutions in their relative time losses, $d \log n/dt$. See § 19. Special experiments are nevertheless needed to clear up the matter, and they must be so devised as to give direct evidence of the occurrence of diffusion or motion of nuclei, and the value of its amount. If this is large enough to be compatible with the data for k in this chapter, then the hypothesis of retarded evaporation may be dismissed.

It is with this end in view that the experiments of the next chapter are contrived and the results show that the motion of the phosphorus nucleus as actually observed, is considerably faster than the average case computed for the nuclei in the present chapter and consequently the interpretation here accepted is corroborated.

18. *The critical density.* In this place I may again call attention to the fact, that if retarded evaporation were effective in giving the nucleus permanence, if the observed dissipation of the nuclei of solutions were in any way dependent on evaporation and not on the motion of nuclei, then those nuclei which are produced by shaking solutions of hygroscopic solutes like $CaCl_2$, H_2SO_4, etc., which can not

---

[1] Note that temperature and elevation produce opposed effects on T and σ. T increases at the lower temperatures; σ decreases from preponderating pressure.

wholly evaporate their water, should be more stable than other saline nuclei. The results show emphatically that this is not the case.

Nuclei generated from hygroscopic bodies in the above tables, and their rate of evanescence, *i.e.*, their absorption velocity, k, is not exceptional and is no greater in the first case or less in the second than that of saline bodies in general. Hence, as the nucleus is necessarily a solution in case of the former solutes ($CaCl_2$, etc.) it is reasonable to suppose it always to be. It has been shown that the pressure decrement $\delta p < 2$ cm. of mercury (my apparatus in its present form does not allow me to go below this, though the limit is much lower) is more than sufficient to precipitate the nuclei produced by shaking. For such small decrements the equation $.29\, \delta p/p = \delta\theta/(273 + \theta)$, where θ is the temperature in degrees C, may be assumed. Now the decrement of vapor pressure, $\delta\pi$, corresponding to $\delta\theta$, is at 20° about $\delta\pi = .11\delta\theta$; whence $\delta\pi = .25$ cm. for the observed excessive δp. In other words, the vapor depression of a few millimeters is certainly much more than is required to stop the evaporation of the nucleus, so that if this depression is to be due to the solute, the solution need not even be very concentrated. In case of H_2SO_4 at 20° the nucleus would hold more than 75 % of water, and at lower temperatures much greater dilution would suffice.

49. *Temperature and barometric pressure.* Conclusion.—It is obvious from the last paragraph that the temperature and pressure of the medium must play a very important rôle in relation to the constants of the nuclei obtained. In the present research I have made no attempt to determine this, not only because the vapor pressure relations of concentrated solutions must be more fully investigated, but because the method adopted above of producing the nuclei in question, is too crude for the purpose. It will in the first place be necessary to find a limiting value of the nuclei producible by agitation per cubic centim., or at least to make this nucleation a definite function of controllable conditions. The method which I have had under way (though the results cannot be included in the present report) consists in producing comminution by the impact on each other of two independent very fine jets of the same solution under large hydraulic pressure. In this way not only is the nucleating mechanism increased in efficiency but the availability of apparatus wholly of glass is at hand. It follows, then, that the opportunities for retaining the solvents absolutely pure are much enhanced, particularly in case of the hydrocarbon solvents. Finally, the correlative electrical behavior of nuclei is, under these conditions, more definitely open to investigation.

In the present volume, however, direct evidence for the diffusion of nuclei is the final issue.

CHAPTER VI.

THE DIFFUSION OF NUCLEI OF LIKE ORIGIN IN DIFFERENT MEDIA.

1. *Types of diffusion phenomena.* In a survey[1] of the diffusion rates of nuclei derived from the same source and under otherwise like conditions, but suspended in different media (*i. e.*, in air saturated with different vapors), the occurrences may be classified with reference to two extreme types: the first includes vapors derived from such strongly ionizing liquids as have been examined, like water, ethyl alcohol, methyl alcohol, etc. In these cases the coronas obtained from the same initial nucleation, on successive condensations by the exhaustion method, are always regularly annular, or, at most, distorted in color only. With the alcohols the coronas may show the colors of two successive coronas (in the sense defined in Chapter II), in the upper and the lower halves of the same rings, but there is no distortion of form appreciable. With water vapor the coronas do not even show color distortion. Examples of this kind are given in Chapter IV, §§ 27, 28, and need not here be further treated.

The second type of phenomena are observed with vapors derived chiefly from the non-ionizing liquids, like the hydrocarbons, gasolene, benzine, etc., carbon disulphide, benzol, toluol, etc., in which the successive coronas derived from the same original nucleation show gradually increasing distortion of form. If the initial corona is annular and the distribution of nuclei therefore uniform, the following coronas pass through campanulate distortion,[2] and finally become mere color strata. Examples of this kind are also given in abundance in Chapter IV, § 10–26.

The distinction between ionizing and non-ionizing solvents which is here implied, is not, however, a perfectly rigid rule. In treating such a liquid as acetone (Chapter IV, § 29), one is already put at a loss in the manner above specified, and the presence of ionizing power is to be regarded as incidental.

2. *Conditions of homogeneous distribution.* The effect of precipitation is a disturbance of the original homogeneous nucleation. The nuclei, as a whole, are dropped with the fog and their distribution changed. The degree to which the uniform distribution will be kept up depends, therefore, on the rate of diffusion of the nucleus. It follows that the nuclei of the first group must diffuse very rapidly, so that all parts of the receiver continually contain the same number per cub. cm. The effect of removal of nuclei by loading is thus quickly wiped out. On the other hand, the diffusion of nuclei of the second group (non-electrolyzing solvents) is apparently slow by comparison. It is quite possible to observe the air in the

---

[1] *Am. Jour.* (4), XIII, pp. [illegible], 1902.

[2] Chapter IV, §§ 7, 8, 9.

lower half of the receiver full of nuclei, or to bring about other similarly stratified conditions evidenced by semi-coronas, quarter coronas, etc. Indeed, when foreign nuclei are introduced they usually appear, on exhaustion, to be distributed in layers, usually in couches immediately over the surface of the liquid. Chapter IV, §§ 17–20, 23–26. The rates of diffusion are here easily measured, whereas in case of the electrolytic solvents like water, measurement is difficult, not only because diffusion is over 100 times faster, but because the diffusion of nuclei into pure air is a branched design, like the roots of a tree. Finally, unless the vapor tension of the liquid is too small (like petroleum), only the normal coronas of Chapter II, § 6, need be expected to occur in the cases of the vapors of non-electrolytes. For it is not unreasonable to associate large coronal particles with the corresponding large nuclei.

3. *Effect of the medium.*—It follows from this that the nuclei derived from the same source, and under otherwise like conditions, must be relatively small in case of a vapor of the first group of liquids, and relatively large in case of a vapor of the other liquids. The same nucleus, so far as its apparent origin is concerned, differs in size with the medium in which it is suspended or in which it is generated.

[On reading the proofs of this chapter, I observe that a discussion of the diffusion upward of the vapor itself into air has not been inserted. This diffusion is so much slower than would correspond to the data observed for nuclei—it corresponds to a quadratic law, while the order of vapor diffusion is not identical with the orders of k found in this chapter—that I overlooked it. The diffusion line for benzol, for instance (fig. 4, below), is about 40 times in excess of the values which would correspond to the upward motion of an 85 per cent vapor saturation, into air. Again, in the case of carbon disulphide, Chapter IV, § 26, the diffusion of nuclei out of the liquid is tested in terms of the apertures of the coronas. These *increase* in the course of time, showing a gradual increase of nucleation for the same vapor pressure. An increase of vapor pressure for the same nucleation would produce larger fog particles and smaller coronas in the lapse of time, the reverse of what was observed.

Nevertheless, from computations which I have since made at some length, it is necessary to admit, that if what has been interpreted as the diffusion of nuclei at approximately constant vapor pressure, is the diffusion of a definitely undersaturated vapor, at approximately constant nucleation, large diffusion rates are not excluded, and the inferences as to nuclear velocity have been robbed of their force. Thus, for benzol, the observed data would correspond to the diffusion of a vapor at about 1/3 saturation, into homogeneously nucleated air. In fact, by varying the pressure differences on exhaustion, one should be able to test the progress of the diffusion of a vapor into nucleated air throughout the whole extent of the column.

Hence the argument of the present chapter must be read with this alternative explanation in view, and I shall have to return to the subject more specifically elsewhere. In all cases, however, the velocity of the nucleus must be in excess of the velocity of the observed plane of vapor.]

4. *Structure of nuclei.*—The next inference to be drawn is some notion of the chemical composition of these nuclei. For convenience merely, they are usually supplied by introducing into the receiver air which has passed over phosphorus, or burning sulphur, or glowing charcoal, etc. They may be obtained, however, without putting anything material into the receiver, by passing the X-rays or other form of radiation through it. An incidental experiment of this kind among many may be cited here. A thin-walled glass flask, 23 cm. in diameter, containing a small charge of alcohol, was exposed to the X-rays of a focus-tube of mild radiating intensity. Examined by exhaustion (pressure decrement 16 cm.) after 5, 10, and 15 minutes had successively elapsed, no coronas were obtainable. After 30 minutes of exposure, however, a corona was obtained, and several subsequent exhaustions were needed thereafter to remove the nuclei. The production of nuclei in case of weak radiation is thus very gradual. It takes time to make them; but when once produced, they show a degree of persistence identical with that of nuclei of any other origin.

Hence, so far as the behavior of the resulting nucleus is concerned, there is no qualitative difference referable to its origin. One must therefore look upon the gaseous contents of the receiver as containing the stuff out of which the nuclei are made. The inquiry is thus narrowed down to this: which of the gases involved (air or vapor) is made colloidal in the manner specified. If the air is selected, then there is no immediate reason for the apparent difference of size of nuclei of the same origin in electrolytic and non-electrolytic solvents respectively. If the vapor is selected, then the difference in size corresponds to the electrochemical difference of the liquids.

5. *Possible electronic agencies.*—If one adheres to the electrical point of view, the agency which holds the nucleus or molecular cluster together is presumably associated with the electron. One should therefore anticipate greater conductivity in case of the much more mobile nuclei of the first type (vapor of ionizing liquids) than in the sluggishly moving nuclei of the second type (vapor of non-ionizing liquids), though it is not certain that the electron resides permanently with the same nucleus. I am not aware that experiments of this kind have been tried. One may note that the smallest nuclei occur in liquids of greatest, the largest in liquids of least, specific inductive capacity; but all this is tentative.[1]

Finally, the order of condensation here implied should be noticed. The electron, by its mere presence, condenses the nucleus or molecular cluster (whether liquefied or not), the latter being always so small an aggregation of molecules as to remain optically inappreciable. The nucleus for Kelvin's thermodynamic reasons condenses the visible water globules seen as coronas on exhaustion. The diameters of these two groups must be in the ratio of less than 1/1000. The uniformity of nuclei produced by shaking may also be thus accounted for, inasmuch as some sort of charge must accompany the shaking. Their persistence in the presence of electrolytes like HCl or the salts may be plausibly anticipated.

These are some of the advantages of an electronic hypothesis. Nuclei are so

---

[1] It breaks down for acetone.

frequently associated with electrical charges that it seemed expedient to examine the occurrence of the remarkable differences of diffusion from the electrical point of view first. The advantages of the simple mechanical hypothesis already stated in the last chapter,[1] may now be reaffirmed for reference.

6. *Thermodynamic agencies.*—After this general statement of the phenomena in question from the electrical point of view, I may revert to certain advantages of the mechanical theory for the production of nuclei in a medium of saturated vapor. It is here supposed that the increment of vapor pressure at the surface of increasing convexity is finally compensated for by the decreased vapor pressure due to the concentration of an evaporating droplet. It is inferred that a case of equilibrium will eventually result, corresponding to a particular radius and degree of concentration of the nucleus, which is thus merely a concentrated solution. Incidentally, the nucleus may or may not be electrically charged. Hence this theory accounts at the outset for nuclei, whether ionized or not. It accounts for nuclei produced by any kind of radiation in the manner discussed in the preceding chapter (§ 47). Correlative electrical phenomena (§ 21 below) are not wanting.

Nuclei produced spontaneously by certain liquids like concentrated sulphuric acid, in presence of water or other vapor, by carbon disulphide in presence of its own vapor, by dissolved naphthalene in presence of benzol vapor, etc., admit at once of the same explanation, assuming that these bodies emit a slightly volatile constituent, soluble in the liquid from which the vapor arises. A similar explanation holds for the nucleation from phosphorus, flames, glowing bodies, ignited metals, etc. Finally, the nuclei produced by shaking have suggested the present hypothesis. The temperature and hygrometric conditions at which nucleation in case of a phosphorus-source is a maximum differs decidedly by Chapter I from the temperature, etc., at which ionization is a maximum.

EXPERIMENTAL EQUIPMENT.

7. *Method.*—For the reasons stated, the method of determining the rate of diffusion of nuclei is simple and direct. Nuclei are introduced into the bottom of a tall cylindrical receiver containing saturated vapor issuing from a flat pan of liquid, and the height to which they have diffused after a measured length of time is tested by adiabatically cooling the vapor. The height of the fog bank seen immediately after exhaustion shows the limiting altitude which diffusion has reached, and there is usually a sharp plane of demarcation rising regularly in the lapse of time between the nucleated air below and the air free from nuclei above. It is assumed that when diffusion of a sluggish relatively heavy medium takes place against gravity in this way in a room of reasonably constant temperature, the influence of conviction is not a serious factor.

The position of the advanced front of diffusion at the end of a given period of time is thus, as a rule, well determined. The position of the plane of demarcation immediately after the nuclei are introduced (*i. e.*, the fiducial zero) is not determinable with the same degree of certainty. In the case of the slowly diffusing vapors,

---

[1] Chapter V., §§ 44, 47–49.

such as arise from the non-electrolyzing liquids, the initial plane may be definitely lowered by successive exhaustion and its position in this way fairly well determined. A study was made at some length in the case of benzol, the limit or error of which is traced in the following tables. In case of the vapors from the ionizing liquids, like water or the alcohols, this method fails, because the apparatus, after the first exhaustion, is liable to be filled with nuclei. It then becomes necessary to quite remove them by aspirating filtered air through the vessel before the next experiment can be made. So tedious an operation involves much loss of time, but no way of avoiding it was discovered. In these cases, therefore, the position of the plane of demarcation at the beginning of the experiment can only be inferred.

Indeed, this seems to be an insuperable difficulty incident to the present experiments; for, even in the former cases, the successive precipitations remove nuclei which are thereafter lost for diffusion. Hence, a modification of method was later introduced to add fresh nuclei instead of filtered air after each exhaustion. Though in the nature of an interference with the experiment, the consequences, either good or bad, remained of small moment.

8. *Apparatus.*—The diffusion cylinder is shown in its completed form in figure 1. The glass diffusion tower, *AABB*, was about 1 meter high and 13 21 cm. in diameter, slightly tapering toward the top. Both ends were ground flat, the lower standing on a greased plate of ground glass, the upper receiving the flat metallic lid, *BB*, securing the tubes leading to the exhaustion reservoir, *C*, to the filters, *F*, etc. A pan, *P*, of copper at the bottom of the receiver, held the liquid from which issued the vapors to be tested. The lid carries the vacuum gauge, *G*, graduated in cm. of mercury and reading to about 40 cm. A vertical centimeter scale (not shown) is marked with india ink on the outside of the wall of the receiver, and by its aid the height of the fog bank could be read off at once, with the usual precaution for a horizontal line of sight. The illuminating lamp, usually a circular hole in an opaque screen in front of the mantel of a Welsbach burner, was placed at a distance of about 3 meters away in the direction of vision and at the probable height of the fog bank, estimated in advance of the observation.

The main filter *F′*, consisting of a long tube of compressed cotton, communicates with the atmosphere through a $CaCl_2$ desiccator tube, *H′*, so that the air may be both dry and filtered. The tube which conveys this air to the bottom of the receiver, *AABB*, is provided with two stopcocks, *a′*, *b′*, one of which, *b′*, is kept permanently but very slightly open, in order that the current of air through the filter may always be very slow. On removing the filter (rubber joint) this tube serves additionally as a means of introducing phosphorus or other nuclei into the bottom of the receiver. The air in this case should also be dried by an ordinary $CaCl_2$ tube, as shown in figure 2, the phosphorus grid, *P*, being inserted into the upper part of one shank of the tube.

The second filter, *F*, and desiccator, *H* (also to be replaced, if desirable, by a nucleator), has a similar construction to the preceding, but the air in this case is discharged into the top of the receiver.

The exhaustion reservoir *C* communicates with the receiver *AB*, through a wide rubber tube EE', of half inch bore, the ends being secured by ordinary hose couplings to the correspondingly wide stop-cocks, screwed into the lids of AB and C. A spiral spring in EE' keeps it open. The vessel C is a shorter cylinder than the other, but is also provided with a metallic lid. It communicates with the jet pump through the desiccator D, and the filter F'', a stop-cock, c, being interposed. It is well to provide for an additional stop-cock at the jet pump, which, on being closed, prevents the accidental entrance of water into the connecting pipes. A final stop-cock, d, communicates through a filter with the air, and is useful when the exhaustion within C, as shown by the gauge G', is larger than desirable.

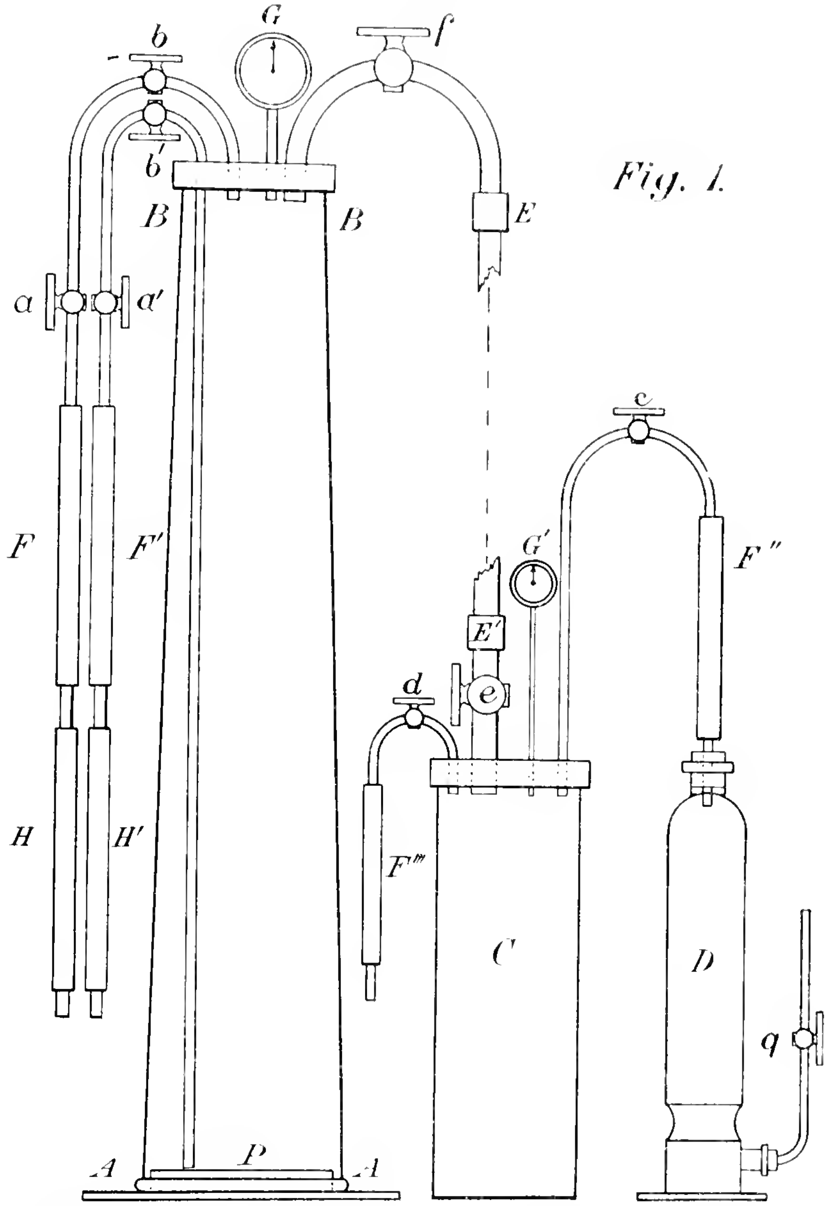


FIG. 1.—DIFFUSION TOWER, AB; EXHAUSTION CHAMBER, C; DESICCATOR, D, AND APPURTENANCES.

The manipulation is as follows: The cocks a, a', c, d, are closed, b and b'

partially so, and c and f open. Then let the jet pump be started and act until the vacuum in C has a predetermined value (pressure decrement usually 50 cm.), after which e is closed. Suddenly opening c exhausts the receiver, AB, as shown by the gauge G (pressure decrement usually about 16 cm.), upon which the observations for diffusion are made at once. The cock c is now closed and e opened for further exhaustion of C, while either filtered air or nucleated air is introduced through F; or nucleated air may be introduced through F' to the bottom and filtered air subsequently through F to the top of the receiver AB; or vice versa. All these adjustments are at times needed. To clean the vessel of nuclei by aspiration, which is by far the most effective method, the cocks a' b' f, c, e, are all left open while the suction proceeds for 10 or 15 minutes.

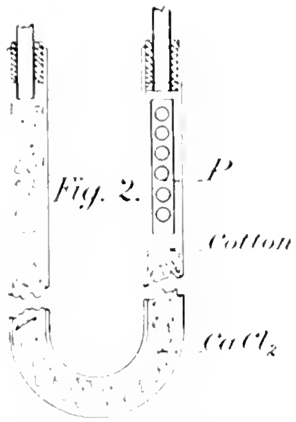


FIG. 2.—DRYING TUBE WITH NUCLEATOR, P.

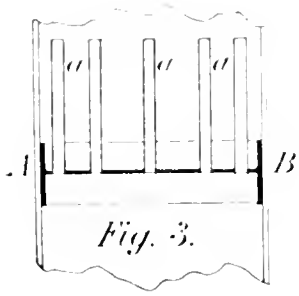


FIG. 3.—TUBULATED PARTITION FOR DIFFUSION OF WATER NUCLEI.

With all reasonable precautions it is often very difficult to entirely exclude water vapor, though its presence is not always a menace. Nuclei of water vapor in the above sense seem to occur simultaneously with the nuclei of hydrocarbon vapor, and they tend in a measure to remain independent of each other. But the former diffuse instantly and fill the vessel, draining the fog bank of nuclei, and soon wiping out the plane of demarcation. It is necessary in all such cases to clean the vessel by aspiration and begin over again. Very slow influx of air is a safeguard both against imperfect filtration and against the danger of errors from convection.

RESULTS.

9. *Benzol.*—The following data show the interval of time elapsed, in minutes, and the height to which the nuclei have risen in this interval. In the case of benzol, in particular, pains were taken to begin with a layer of nuclei as near the bottom of the vessel as possible and then to find the rise in periods of 15, 30, and 60 minutes. Accordingly, in the case of the quarter-hour periods, the rise was first studied as dated from the time when the nucleation was introduced. The height reached by the fog bank is here 25 to 30 cm. The endeavor was then made to adjust the lower level as near zero as possible, by one or two auxiliary exhaustions, made after the nuclei had been introduced. The rise of the fog bank in this case is naturally smaller. It reaches a limit, if time is taken for the fog to subside with each exhaustion, while the nuclei which have escaped precipitation by evaporating their loads are available for further diffusion. There are many of these when the subsidence is slow, and this practice was therefore followed in most of the succeeding experiments. Thus, in the last series of values for quarter-hour periods, the fog on exhausting 2 min. after nucleation (at 0 min.) was 5 cm. high. Filtered air

was then introduced and the second exhaustion made 5 min. after nucleation, showed a fog bank 4 cm. high. Filtered air was again supplied and the receiver left to itself for 15 min. The exhaustion showed the fog bank to have risen to 16 cm.

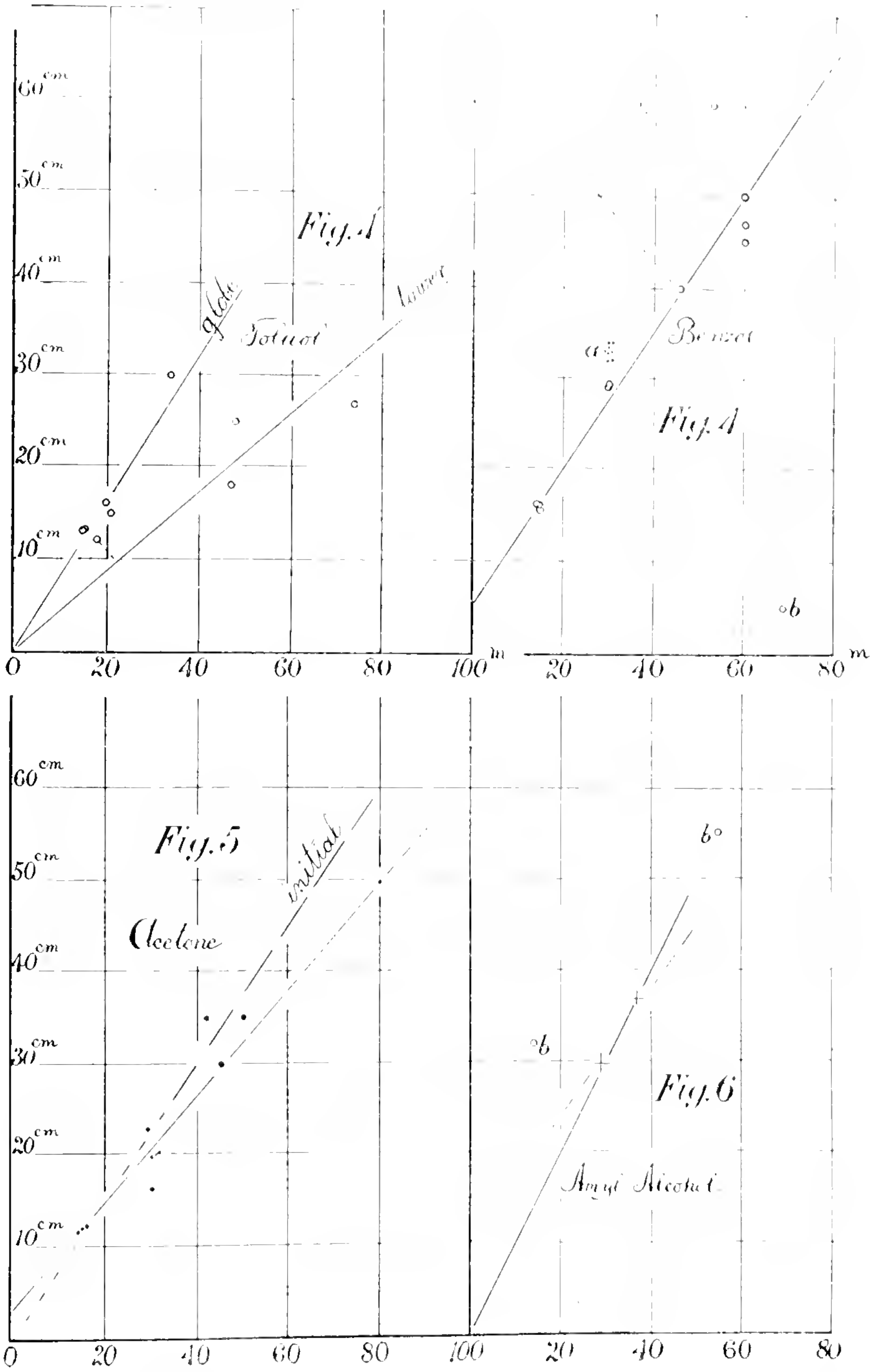


Fig. 4.—Rise of Nucleation in the Lapse of Minutes (Diffusion Upward) in Benzol.
Fig. 4.—Rise of Nucleation in the Lapse of Minutes (Diffusion Upward) in Toluol.
Fig. 5.—Rise of Nucleation in the Lapse of Minutes (Diffusion Upward) in Acetone.
Fig. 6.—Rise of Nucleation in the Lapse of Minutes (Diffusion Upward) in Amyl Alcohol

In constructing the preceding graphs, figure 4 *et seq.*, it will be assumed that the rise in all cases is from the same lower level corresponding to the instant from which time is measured. If the graphs are straight lines the initial level should in a measure be indicated by the graphs themselves. These curves give ample evidence of the difficulties of observation, but nevertheless map out a locus of a sufficiently definite character to prove that more than an incidental result is in question.

What is particularly remarkable is the number of times the nuclei rise after apparently complete precipitation. Thus, in the first part of the table there are nearly 20 exhaustions, but the nuclei retain their rate of motion throughout. The same is true of other parts of the table. In case of the half-hour periods, the plane of demarcation gradually loses definiteness, shading off to nothing at the top, while the motion of the nuclei is eventually faster, their rise higher than at first. These observations are marked *a* in figure 4. The nuclei which finally appear are thus somewhat smaller, and there is a correspondingly slight gradation of size, but the time needed to bring out this gradation shows that it must be almost negligible. Thus the nuclei are all very nearly the same size.

TABLE 1.—DIFFUSION IN BENZOL. EXHAUSTION, 76 cm. TO 62.6 cm. PHOSPHORUS NUCLEI. DIFFUSION TUBE CLEANED BY 5 EXHAUSTIONS.

I. Quarter-hour periods.

No exhaustion between.		One exhaustion between.		Two exhaustions between.		Two exhaustions between. Receiver kept exhausted. (Fog subsides.)	
Time.	Height.	Time.	Height.	Time.	Height.	Time.	Height.
minutes.	cm.	minutes.	cm.	minutes.	cm.	minutes	cm.
15	20–25	0–2	8	0–2	9	0–2	5
16–35	20–25	2–4	3	2–4	6	2–5	4
36–48	20–25	4–19	20	4–6	3	5–20	16
49–64	20–25	19–21	6	6–21	18	20–22	4
65–80	20–27	21–36	18	21–23	6	22–25	3
95	20–30	36–39	7	23–26	3	25–40	16
95–113	20–30[1]	39–54	18	26–43	19	40–43	4
113–128	20–25	54–56	5	43–46	4	43–46	2
128–143	20–27	56–70	23	46–48	2	46–61	15
143–160	20–25[1]			48–63	18	61–64	4
160–176	25–30			63–65	6	64–66	2
176–191	23–28			65–67	3		
192–211	23–28			67–82	17		
211–212	5[2]						
				82–84	2		
				84–86	3		
212–227	20–23			86–101	16		
228–243	20–23			101–103	0		
243–258	17–23			103–118	16		

[1] [illegible] huddled and open. Grading obvious.

[2] Markedly open.

TABLE I. *Continued.*

II. Half-hour periods.

Time.	Height.	Time.	Height.
minutes.	cm.	minutes.	cm.
0–2	0	0–1	7
2–4	3	1–3	3
4–34	29	3–33	29
34–37	8	33–35	7
37–39	7	35–38	3
39–45	5	38–68	33
45–75	32	68–70	7
75–78	7	70–72	3
78–80	3	72–102	34[1]
80–110	33	102–105	7
110–112	7	105–107	4
112–115	3	107–137	30–37
115–145	32	137–139	5
145–148	5	139–142	5
148–152	4	142–172	30–36
152–182	33[2]		

III. Hour periods.

Time.	Height.
minutes.	cm.
0–2	7
2–4	5
4–64	45
64–67	15
67–70	6
70–73	6
73–75	4
75–135	50[3]
0	?
0–60	47
0–2	5
2–47	40

[1] Veil, 30–35 cm. [2] Open coronas, gradually more diffuse above, showing gradation.
[3] Veil, 40–50 cm. high. Frequent breakdown of stable distribution.

10. *Hygrometric discrepancy.*—During the course of this work on the diffusion of nuclei in hydrocarbon vapors, I noticed that on certain days the experiments were apt to break down; the column of air within the tower-like receiver, instead of showing on exhaustion the sharp plane of demarcation between the nucleated

air below and the pure air above, was liable to condense as a whole, almost explosively. This occurred at a definite pressure and after condensation had already begun in the nucleated region. Suspecting that the discrepancy might be due to the hygrometric state of the atmosphere, I made the following tests, which bear out this surmise. The first column shows the pressure decrement on exhaustion, the second the effect produced on the nucleated atmospheric air in the dry receiver. The third column of the table are the corresponding approximate dew points, the fourth and fifth other hygrometric data. In the second and third parts of the table the results of artificially moistening and of drying the air are at once apparent.

TABLE 2. CONDENSATION IN ADIABATICALLY COOLED IONIZED (MOIST) ATMOSPHERIC AIR.

I. Room air.

Pressure decrement.	Effect of exhaustion.	Dew-point of cooled air.	Vapor pressure.	Hygrometric state.
		°C	cm.	
11	Clear	7	[illegible]	
11.5	"	6	.7	
12	"	5.5	.67	
12.7	"	4.7	.64	
13.4	"	3.7	[illegible]	.34
14	Fog	3.0	.57	.33
14	"	3.0	.57	

II. Room air over damp sponge.

Pressure decrement.	Effect of exhaustion.	Dew-point of cooled air.	Vapor pressure.	Hygrometric state.
11	Clear	8	.80	
11.5	" [2]	6	.70	.4
12	Fog	5.5	.68	.39
12	"	5.5	.68	.39
11.5	Clear [2]	6	.70	.40

III. Room air dried over $CaCl_2$.

Pressure decrement.	Effect of exhaustion.	Dew-point of cooled air.	Vapor pressure.	Hygrometric state.
[illegible]	Clear	3.5	[illegible]	[illegible]

It seems to me probable that a method of hygrometry is here suggested which is worth a trial,[1] and for which suitable apparatus could be devised. In other words, artificially nucleated air is suddenly cooled by expansion until a fog just appears. The dew point is computed from the pressure decrement thus determined. If t be the temperature of the air in degrees centigrade and p its pressure, and if the air is cooled from 20° and 76 cm., we may write approximately,

---

[1] Prof. Cleveland Abbe informs me that Espy's nepelometer of 1835 and 1850 is virtually the same as this. See Abbe's *Treatise on Meteorological Apparatus*, 1887, pp. 357–59. "Espy showed that by repeated condensation he precipitated all the nuclei and got an apparently drier air; *i.e.*, it required greater exhaustion to produce the fog."

$dt/(t + 273) = .29\, dp/p$, so that roughly one centim. of pressure decrement will correspond to a little more than one degree of temperature decrement in a dew point apparatus. More than 10 or 15 centims. of pressure difference will rarely be required. Perhaps a fixed exhaustion, together with a measurement of the aperture of the corona produced, is the preferable method in practice. What is particularly remarkable about these air fogs is their enormous rate (say meter/second and more) of instantaneous subsidence. This is, of course, mere evaporation from the finer cloud particles at the top downwards while the air is quickly recovering its original temperature.

With regard to its bearing on the present experiments, it will be seen that the need of the desiccators, *D* and *H*, figure 1, in the above experiments is clearly pointed out. If they are not used half of the experiments are liable to prove failures, while the specific effect of the presence of even unsaturated vapor is yet to be ascertained. Slight heating of the receiver should remove the danger of collapse of the kind here in question in a measure. Experiment bears this out, and shows that the danger of convection encountered in this way is less serious than might be supposed.

11. *Toluol.*—Two sets of experiments were made for this body, one in the spherical receiver (30 cm. in diameter), the other in the diffusion tower. The data of tables 3 and 4 and the graph which follows (figure 4) show the results.

TABLE 3.—DIFFUSION. TOLUOL. GLOBE. PHOSPHORUS NUCLEI, NOT REFILLED. EXHAUSTION, 76–59 cm.

Time.	Height.	Time.	Height.	Time.	Height.
minutes.	cm.	minutes	cm.	minutes.	cm.
0–3	5	24–39	79–82	13	5
3–18	13	39–42	82–102	—	16
18–21	5	42–45	102–105	5	5
21–24	5	45–79	105–126	30	15

TABLE 4.—DIFFUSION. TOLUOL. TOWER. EXHAUSTION, 76–68 cm. PHOSPHORUS NUCLEI. CLEAN VESSEL AND FRESH NUCLEI FOR EACH OBSERVATION.

Time.	Height.	Time.	Height.	Time.	Height.
minutes.	cm.	minutes.	cm.	minutes.	cm.
0–3	0	3–149	40	0–3	5
3–21	12			3–51	25
		0–3	3		
0–3	5	3–156	60	0–3	0
3–77	27			3–139	60
		0–3	0		
0–3	7	3–50	18		

Considered as a whole, these data contain no evidence of a decreasing rate, but rather point to an initial position of the plane of demarcation between 5 and 10 cm. This interpretation will be accepted as there is none more probable.

12. *Acetone.*—The data for this reagent are the most irregular of the whole series of results, if the longer intervals of 100 min. are included. Below 100 min. a graph, figure 5, which points to an initial plane at about 5 cm. may be accepted. The anomalous results marked *b* in figures 4 and 6 are due to acetone.

TABLE 5. DIFFUSION. ACETONE. EXHAUSTION, 76–62.6 cm. PHOSPHORUS NUCLEI. ONE OR MORE EXHAUSTIONS BETWEEN OBSERVATIONS. FRESH NUCLEATION AT EACH INFLUX.

Time.	Height.	Time.	Height.	Time.	Height.
minutes.	cm.	minutes.	cm.	minutes.	cm.
0–3	5	0–3	3	0–3	5
3–18	12	3–18	12	3–171	80
0–3	5				
3–117	32	0–3	5	0–3	5
0–3	7	3–33	16	3–83	50
3–33	25				
		0–3	5	0–3	5
0–3	6	3–6	5	3–45	35
3–32	23[1]	6–161	55[2]		
0–3	7			0–3	5
3–6	5	0–3	5	3–53	35
6–36	20	3–18	30		
0–3	5				
3–18	12				

[1] Veil 20–25 cm. high.

[2] Probably influenced by convection.

13. *Amyl alcohol.*—Much time was spent with this body but only a few trustworthy results were obtained. The presence of mere traces of moisture invariably provoked a collapse of the whole column on exhaustion. It was necessary to introduce the alcohol, after being dehydrated with caustic lime, in a paste of the latter substance. Collapse invariably occurred on second exhaustion, for which reason no attempt was made to depress the initial plane of demarcation. It is possible that the molecules of amyl alcohol are efficient nuclei for water vapor, but at the present stage of research it is difficult to assign a reason for the behavior specified. *Cf.* figure 6.

TABLE 6.—DIFFUSION. AMYL ALCOHOL DRIED OVER LIME. EXHAUSTION, 76-63 cm. FILTERED DRY AIR. FRESH NUCLEI BEFORE EACH EXHAUSTION.

Time.	Height.	Time.	Height.	Time.	Height.
minutes.	cm.	minutes.	cm.	minutes.	cm.
0–91	35[1]	0–29	30	0–37	37[2]

[1] Followed by 9 failures due to collapse. Limed and distilled amyl alcohol.

[2] Followed by 5 failures due to collapse.

14. *Ethyl alcohol.*—Similar care had to be taken with absolute alcohol, though there was less difficulty in avoiding a collapsing column. The initial plane did not admit of depression. Whenever this was tried, the vessel was found to be filled with nuclei on second exhaustion and it was necessary to clean it by aspiration before another experiment could be attempted. Though many measurements were made, the graph, figure 7, is not smooth and points to a high initial plane of demarcation.

TABLE 7.—DIFFUSION. ALCOHOL. EXHAUSTION, 76-62 cm. PHOSPHORUS NUCLEI. FRESH NUCLEATION EACH TIME AND CLEANING THEREAFTER. FILTERED AIR NOT DRIED.

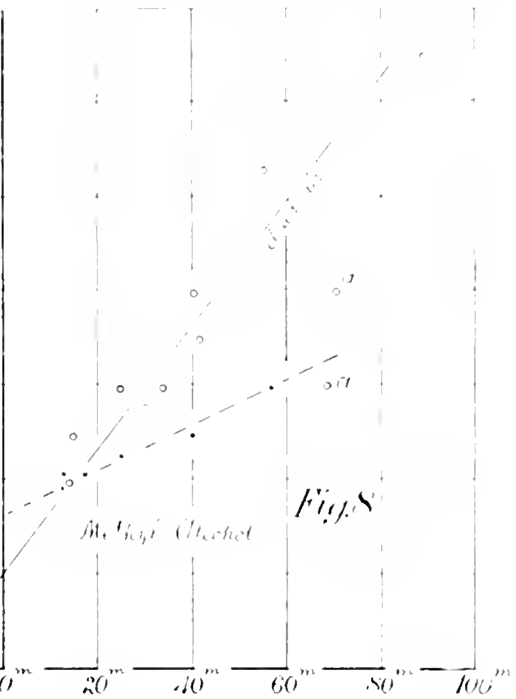
Time.	Height.	Time.	Height.	Time.	Height.
minutes.	cm.	minutes.	cm.	minutes.	cm.
0–3	10	0–15	27	0–70	35
3–6	12				
6–11	20	0–32	45	0–19	28
		0–16	25	0–30	40

TABLE 8.—DIFFUSION. ABSOLUTE ALCOHOL. EXHAUSTION, 76-63 cm. FILTERED DRY AIR. FRESH NUCLEI BEFORE EACH EXHAUSTION. VESSEL CLEANED BY ASPIRATION.

Time.	Height.	Time.	Height.	Time.	Height.
minutes.	cm.	minutes.	cm.	minutes.	cm.
0	0	0	0	0	0
60	40	44	40	11	27
0	0	0	0	0	0
40	38	75	63[1]	25	33
0	0	0	0	0	0
28	33[1]	63	60	120	90+
0	0	0	0		
60	53[1]	18	35		

[1] Veil of 5–10 cm.

15. *Methyl alcohol.*—The first series of results for methyl alcohol, table 9, were obtained without drying the air. Though the initial plane was not depressed for the reason given in the preceding paragraph, tests for its mean position are



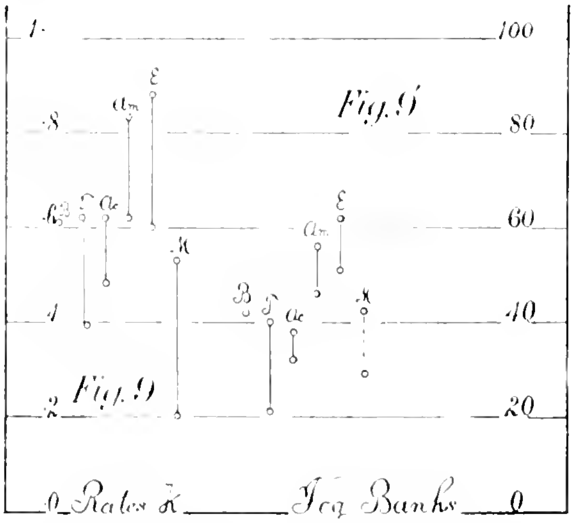


Fig. 7.—Rate of Nucleation in the Lapse of Minutes (Diffusion Upward) in Ethyl Alcohol.
Fig. 8.—Rate of Nucleation in the Lapse of Minutes (Diffusion Upward) in Methyl Alcohol.
Fig. 9.—Velocities of Subsidence of the Nuclei in Different Media.
Fig. 9.—Decay of Nuclei in the Lapse of 30 Min.

given at the beginning of the table. These results differ considerably from table 10 in which the air admitted was first dried in the manner shown in § 8. A high initial plane is again evidenced. *Cf.* figure 8.

TABLE 9.—DIFFUSION. METHYL ALCOHOL. EXHAUSTION, 76.62 cm. PHOSPHORUS NUCLEI. CLEAN VESSEL AND FRESH NUCLEI FOR EACH OBSERVATION. FILTERED AIR NOT DRIED.

Time.	Height.	Time.	Height.	Time.	Height.
minutes.	cm.	minutes.	cm.	minutes.	cm.
0 1	5	0 15	2	0 41	25
Do.	8				
Do.	6	0 16	22	0 14	21
Do.	5				
Do	7	0 18	30	0 26	23
0–15	20				

TABLE 10.—DIFFUSION. METHYL ALCOHOL. EXHAUSTION, 76.63 cm. FILTERED AIR DRIED. FRESH NUCLEI FOR EACH EXHAUSTION.

Time.	Height.	Time.	Height.	Time.	Height.
minutes.	cm.	minutes.	cm.	minutes.	cm.
0 57	5 53[1]	0 103	0 75[1]	0 43	0 35
0 42	0 40	0 70	0 30	0 16	0 25
0 91	0 65	0 72	0 40 ?	0 26	0 30
0 35	0 30	0 77	0 40 ? [2]	0 31 0 15	0 28 0 20

[1] Veil of 5 cm. or more.

[2] Hazy.

16. *Water.* Totally different from all the preceding cases is the behavior of water. The diffusion, in the first place is enormously more rapid, so that the vessel is filled with nuclei and the distribution apparently homogeneous in less than a minute. Furthermore the advancing fog is not compact but stringy in character. It makes no difference whether the nuclei are introduced at the top or at the bottom of the diffusion tower. In either case the advance toward the opposite end is of the same nature. Chemical differences between the nuclei (whether coming from phosphorus, punk, sulphur, etc.) are not accompanied by characteristic differences in the results.

Consequently the rate of diffusion of nuclei in water vapor can not be measured by the present method at all, as there is never a true plane of demarcation apparent for reference. The data given in table 11 are merely intended to indicate the great relative rapidity of the diffusion process in the case of aqueous vapor. Explanatory remarks will be found in the table.

[illegible] ON WATER. EXHAUSTION, 76 [illegible] cm. FOG NOT COMPACT, STRINGS SEPARATED BY CLEAR AIR.

[illegible]	[illegible]	Remarks.
	3	Nuclei put in below for 5^s at δp = 4 [illegible]; exhaustion after waiting [illegible] 15 [illegible]. Ascent of fog strings axial.
	5	
	4	Nuclei put in above, for 5^s at δp = 4
	32	
	7?	
[illegible]		
1	3	Nuclei added above for 5^s at δp = 4^{cm}. Descent of fog strings on outside of column.
15	[illegible]	
15	4	Nuclei added below for 1.5^s at 4 [illegible]; exhaustion 5^m later.
[illegible]		
		Nuclei added below for 1 [illegible] at 4 [illegible], 5^m waiting. Ascent axial.
15	[illegible]	
2	82	Nuclei added above.

After this a variety of experiments were made in which the nuclei were allowed to diffuse through tubes and partitions. Thus sulphur nuclei added below a pasteboard partition, showed on exhaustion a dense fog below, but only filiments above, which on second exhaustion changed to a faint fog above, remaining dense below, etc. Phosphorus nuclei behaved similarly. On successive exhaustion, the fog above gradually grew denser, and eventually coronas of different orders appeared in the two sections. Although filtered air was added above, some nuclei are lifted by the exhaustion which complicates the experiments. Hence the following tests were varied; the diffusion vessel was exhausted at the upper compartment and the nuclei added there, while filtered air was introduced below. In these cases a thin sheet of cotton .5 cm. thick and not even opaque nearly stopped the diffusion of nuclei. Three hours after the nucleation in the upper compartment, the corona seen there was still of the centrally green order, whereas only diminutive normal coronas were in evidence below the partition.

A tubulated partition, figure 3 above, was now installed, consisting of 10 vertical tubes, *a, a,* . . . . in parallel, each 10 cm. long and .6 cm. in diameter, all other communication between the compartments being sealed off with cotton. It was ascertained that the diffusion of aqueous nuclei could be estimated in this way in terms of the sizes of the coronas above and below the partition *AB*, after the lapse of a definite time, dated from the introduction of nuclei above the partition. In measurements made 2, 5, 10, and 60 minutes after nucleation, the coronas still showed colored centers above but were normal and of gradually increasing size below. The results prove the feasibility of experiments of this kind for water vapor; but they were temporarily discontinued because of the difficulty of keeping the walls of the diffusion tower clear of precipitated moisture.

A few special observations were made without partitions. Convective vortices due to the warmer glass walls after exhaustion should be upward on the outside and down in the axis. The initial strands of fog from nuclei in water vapor are apt to run upward in the axis and downward on the outside, according as the nucleation is added below or above, respectively. This peculiar and contradictory behavior is difficult to explain. The whole appearance is something like that of a burning granule of powder throwing off smoke from an advancing center, and it is not impossible that coarse nuclear matter is being disintegrated in some similar way as the nuclei in water vapor are ultimately very small.

Experiments tried with formic acid were all failures from the invariable presence of water vapor.

INFERENCES AND SUMMARY.

17. *Rates of diffusion.*—The irregular distribution of results does not suggest a suitable curve to be passed through them. The heights obtained after the lapse of long intervals of time frequently indicate a retarded rate; but this is to be otherwise expected seeing that after long intervals the number of particles in the plane of diffusion must continually decrease as a result of the losses laterally, and eventually the true plane of diffusion will fade beyond recognition. This will be particularly the case when water vapor is present, for under these circumstances the enormously rapid diffusion of the nuclei associated with water vapor will act as an additional and continued drain on the nuclei associated with the other vapors. It is from this point of view that the abnormally low values in the tables are to be explained.

The effect of temperature, though presumably of marked importance, is beyond recognition in the case of methods of the kind here discussed, and it was therefore ignored.

For the reasons indicated, it will suffice the present purposes to draw mean straight lines through the observations, or, in other words, to consider their average distribution and trend.

In table 12 the results for the absorption velocity, k in cm. per minute, are given in full. The mean rise of the plane of demarcation per minute as at once obtained from the graphs, is entered under k'. This is to be corrected for the instantaneous rise due to the exhaustion by multiplying it by the pressure ratio, p'/p; k is so obtained. All the graphs point to an initial height (time $t = 0$) of the plane of demarcation between 5 and 15 cm., depending on the means available to depress it. There is good reason for this observation, as the nuclei can not be so slowly and carefully introduced as to insure complete freedom from motion. If the initial height were ignored it would be necessary to assume a sharp initial curvature for all the graphs, a condition of things much less warrantable apart from gravitation. Moreover, in the case of benzol, where many observations were made for the same pressure difference, the raised position of the plane of demarcation was directly demonstrated. It was also shown that from the same charge of nuclei, diffusion increases perceptibly in the lapse of time, due to the gradual accumulation of the smaller particles in the front of the advancing column.

TABLE [illegible].—RATES OF DIFFUSION. c FROM GRAPHS. k CORRECTED. PHOSPHORUS NUCLEI.

[illegible]	[illegible]	Remarks			Ordinate at 50'
			[illegible]	in min.	cm.
[illegible]	Benzol	tower	.75	.61	42
[illegible]	Toluol	globe; old	.8	.62	42
[illegible]	"	tower; new	.43	.39	21
3	Acetone	tower	.58	.48	32
		(initial rate)	.75	.62	38
83	Amyl	tower	1.00	.83	51
.83	Alcohol	(initial)			46
		(apparent)	.75	.62	
83	Ethyl		1.06	.88	62
.83	Alcohol	dry air	.72	.60	51
83	Methyl		.24	.20	29
83	Alcohol	dry air	.64	.53	42
83	Water	estimated	100.	83.	—

The table finally contains the ordinate corresponding to a time interval of 50 minutes without reference to the initial ordinate. This is the height of the fog bank, as observed 50 minutes after nucleation. As a whole, the following inferences will apply to it, as well as to the rates k, as may be seen in figure 9, by plotting both for comparison in some suitable way.

18. *Relations to other physical constants.*—A glance at the data found for k, shows that the incidental circumstances of the experiment, the presence or absence of water vapor, the occurrence of impurities in the reagent, etc., are of striking importance. By contrast, those constants which seemed at the outset to be determinating features, do not now appear in the same light. Thus the ionizing properties of the solvent, its electrical conduction, etc., are not the dominating qualities which influence the rate of diffusion. Acetone, for instance, as a moderately good ionizer, has about the same rate as benzol and tolnol, methyl alcohol a smaller rate than all. Aside from the enormous rate for water, ethyl and amyl alcohol have the largest rates obtained, and the latter varies abruptly according as water vapor may or may not be present, or for other reasons.

The ionizing potency of the liquid as a solvent or other similar electrical condition mentioned at the beginning of this chapter, like electric charge, etc., has no immediate influence on the rate of diffusion. A theory like the one given in Chapter V, § 17, seems best adapted to explain the occurrences here observed.

An arrangement with reference to specific inductive capacity would necessitate a distribution of k in the order of water (80), methyl alcohol (33), ethyl alcohol, (27), amyl alcohol (16), benzol (2), toluol (2), acetone (?), which is not the order of k observed. Thus the very low values of benzol and of toluol in the list, have no counterpart in the diffusion rates of these bodies.

If an immediate relation of k to surface tension existed, the distribution of the k values would be in the order of water (80), benzol (28), toluol (28), acetone (25), methyl alcohol (24), ethyl alcohol (23), amyl alcohol (24), which leaves out of account the high value of k for ethyl alcohol and does not adequately account for water. *Cf.* § 20.

19. *Comparison of the present and earlier values of absorption and of diffusion velocity.*—It is finally interesting to resume the comparison of absorption velocities begun in Chapter V, § 9. This is now easily feasible by consulting table 25 and § 43 of that chapter, and table 12 of the present chapter. An introductory reduction, however, is needed, since in table 12 the velocity measured is at once the actual velocity of the nucleus, whereas in the preceding chapters k was computed as if all the nuclei travelled in a single direction. As they necessarily travel in all directions, a rough compensation may be temporarily made by multiplying k by 6, or preferably by the probability factor, $16/\pi$.

The following are the diffusion velocities, n, as found from widely different experiments. From the preceding volume,[1] in which the velocities of phosphorus nuclei in ordinary atmospheric air were studied both by mechanical methods (steam jet and absorption tubes), and by the electrical condenser methods, the mean value of $k = 18$ cm/min. may be taken. Hence $n = 90$ cm/min., nearly. The number of particles was of the order of 10^4 to 10^5 per cub. cm. of air.

In Chapters II and III, by a rough method of comparing coronas of different orders, the value of k for phosphorus and other nuclei present in saturated water vapor to the average extent of 10^4 per cub. cm., the value $k = .1$ cm/min. was ascertained. This is equivalent to $n = .5$ cm/min.

This datum may be compared with the diffusion velocities of table 12 of this chapter, in which fresh phosphorus and other nuclei were used, densely distributed and tested in a variety of vapors, alcoholic, hydrocarbon, etc. The usual values of diffusion velocity lie between $n = .5$ cm/min. and $n = .9$ cm/min., being thus of the order of the preceding case. Water vapor itself did not admit of measurement. The value estimated from the filimentary advance seen immediately after the nuclei enter, $n = 80$ cm/min., agrees more closely with the case for atmospheric air at the beginning of the paragraph. There is much in the behavior of water which is left unexplained. When the nuclei are first introduced into the mixture of air and saturated water vapor, the air contact does not seem to be negligible.

Finally the experiments on the evanescence of the nuclei produced by shaking solutions lead to a series of values of k as follows. A few hundred nuclei per cub. cm. were usually present after shaking the solutions, and less than 50 (usually) after shaking pure water.

For the saline solutions of 1–3 %, $n = .25$; for solutions of .01 %, $n = .40$; for solutions of .0001 %, $n = 10$. For pure water $n = 25$ or even 50.

For aqueous solutions of solid neutral organic solutes of 1 to 3 %, $n = 8$; for solutions of .01 %, $n = 3$. The acid organic solutes, like tartaric acid, seem to behave quite differently. The solutions of this body of 2 %, .02 %, and .0002 %, showed diffusion velocities of $n = .1$, .4, and 1.0, respectively, thus evidencing uniformly greater persistence of nucleation than even the saline bodies.

---

[1] *Experiments with Ionized Air;* Smithsonian Contributions, 1901.

For neutral liquid organic solutes in aqueous solution of 1 to 3 %, $v = 6$; for solutions of .01 %, $v = 12$. Nuclei from these bodies are thus very fleeting.

Finally for hydrocarbon solution of solid hydrocarbons of 1 to 3 %, $v = .10$ or .20, not differing much in persistence, etc., from the salt solutions.

The total range found for the diffusion velocity of nuclei produced by shaking solutions of less than 3 % is thus from $v = .1$ to $v = 50$ cm/min., increasing with the degree of dilution of the solution, the largest value cited (pure water) closely approaching the datum for phosphorus nuclei in atmospheric air, $v = 90$ cm/min.

These variations of the velocity of the nuclei produced by shaking, and its relation to the order of values resulting from the direct experiments with phosphorus nuclei given in table 12, is accounted for by the thermodynamic hypothesis for their occurrence, which makes of them particles of concentrated solution. The size of the nucleus for a given solvent depends essentially on the extremely small mass of solute which it happens to contain. It is larger when shaken from the more concentrated dilute solutions than from the weaker solutions, because the critical density is reached in the former case with less evaporation, and the capillary increment of vapor pressure to be compensated is at the same time smaller.

Thus, it is quite reasonable to suppose that the nuclei obtained from phosphorus or other emanations will be smaller, and, therefore, more mobile than the

TABLE 13.—COMPARISON OF DIFFUSION VELOCITIES.

(1) Nuclei produced by shaking.

Solution.	% of solute.	n	k	v
			cm/min.	cm/min
Alcohol in water	0	55	2.10	11
	1.6	43	.77	4
Naphthalene in benzol (commercial)	2.0	90	.016	.08
	0.2	87	.013	.07
	none	78	.008	.04
	distilled	82	.018	.09
Paraffine in benzol (commercial)	1.0	128	.008	.04
Pure Benzine	--	72	.070	.36

(2) Nuclei introduced from without.

Direct measurements for phosphorus nuclei in benzol vapor				.6
Do. in toluol vapor				.4

(a) Color yellowish. Naphthalene emits nuclei spontaneously nuclei shaken out of the more concentrated dilute solutions, but not so small in general as the nuclei shaken out of pure water or any other pure solvent, in which the amount of solute is an actually vanishing quantity. To carry out this comparison one should eliminate the peculiar features of water and use the same neutral solvent in both cases. Hence, the results for benzol have been brought together in table 13. Water and alcohol have been added because of the greater purity of the solvent. The same inferences follow.

20. *Conclusions.*—A survey of the results obtained as a whole, attests the occurrence of the diffusion beyond a doubt. The consistency with which the fog bank in case of benzol, for instance, is found at a definite height after a definite time under given conditions, no matter how often the exhaustion may be repeated, the obvious tendency of the plane of demarcation to rise regularly in the lapse of time, in every case, etc.,—all these observations can not be the result of chance convections but point to some more definite underlying cause.

But while the occurrence of diffusion and its average rate is thus established by direct observation, the amount of motion in case of any given vapor has not been clearly made out. Water vapor, from its peculiar behavior except in the case of shaken nuclei, would naturally be left aside here for further research; but the other vapors frequently give evidence of very different rates of motion, u, of the nuclei contained, depending on accidental conditions like the presence of moisture, the existing pressure and temperature, etc., not yet made out. Here again, however, the rate for a given charge of vapor is a definite quantity and the observations are consistent among themselves. Witness, for instance, the remarkable results for ethyl and for methyl alcohols, figures 7 and 8, in each of which two definite velocities are given in two independent series of measurements with the same body. Something definite is moving in each case, but that something differs for the same vapor and the same emanation under different accessory conditions.

If the diagram, Chapter V, figure 20, be resumed, in which vapor pressure is represented in terms of the radius of the nucleus, it may again be argued that the curves *bms* and *bm's'* correspond, respectively, to stronger and to weaker solutions, while the curve *bc* shows the vapor pressure of the solvent. With the same mass of solute entrapped in the nucleus, however, the curves will depend on the solutional affinity, as evidenced by the vapor depression of strong solutions. Thus if in the weaker solution *bm's'*, the solute were replaced by the same mass of a body having greater cohesional affinity for the solvent, the conditions expressed by curve *bms* might be regained. As the curves are drawn this corresponds to a stable nucleus of larger size. In other words the nucleus is largest when the affinity is greatest. If we compare the results found in Chapter V, for nuclei shaken out of inorganic saline and of neutral organic solutions, respectively, this result seems to hold good, the latter being much the more fleeting. As it does not follow that the conditions of the figure which is purely qualitative and inferential, hold good, all that need be stated is that in addition to the mass of solute (emanation) entrapped, in each nucleus, the cohesional affinity of the solute and solvent further determines the size of the nucleus.

The question as to the form in which the emanation enters the nucleus in the relation of solute and solvent is beyond the scope of the present inquiry; but in proportion as the emanation consists of fewer molecules, the nucleus will be smaller. A fresh phosphorus nucleation conveyed by dry air may therefore be very different as regards fineness, from a stale nucleation conveyed by dry air.

In the case of different vapors much additional information may be gained from Kelvin's vapor pressure equation which in the above notation is $\delta p \times r = 2T\sigma/\rho = F$, from which it appears that the surface tension (T) actually enters as a single factor among many, to be counterbalanced by the differences of vapor (σ) and liquid (ρ) density. The quantity F roughly computed for the solvents of this chapter shows the following succession of values:

Water,	$F = 1440$
Methyl alcohol,	960
Ethyl "	1323
Amyl "	2545
Acetone,	1813
Benzol,	2427
Toluol,	2862

Hence the factor F, for water is only fifth in the order of size, while the extreme ratios of these factors is smaller than 1 : 3.

Different solvents therefore introduce different relations into the product F, (*i. e.*, the curve *bc* of the figure in question), as well as new chemical conditions, while the occurrence of the factor T in F, renders the presence of traces of water in evaporating nuclei like methyl alcohol, for instance, a serious consideration. The whole subject is therefore, very complicated, and it seems wise to refrain from further inferences until completed series of the experimental constants needed have been investigated for certain typical solvents. It is in pursuance of the work of Chapter V that the nearest approach to definite conditions is to be anticipated.

A final word should be added in relation to gravitation: clearly the rate of diffusion of the nucleus upward will be smaller, the diffusion of the nucleus downward larger, than the diffusion in a horizontal direction. The value found for k is thus too small.

21. *Ionization and nucleation in relation to cloudy condensation.*—Hitherto the only irrefragable evidence showing that condensation is promoted by ionization, or in other words that negative ions are somewhat more active as condensation nuclei than are positive ions, is the brilliant experiment devised by C. T. R. Wilson.[1] Nuclei are here produced by the X-rays in communicating condensation chambers, on the two sides of a vertical earthed metal plate, which receives electrical current normally on one side, through the ionized air, saturated with water vapor, and transmits the current in the same way and through the same medium on the other side. Necessarily there was an excess of negative ions on one side of the plate and an excess of positive ions on the other side. It was found on producing condensation by exhaustion simultaneously on both sides under like conditions, that the

---

[1] *Phil. Trans.*, London, vol. cxciii, pp. 289–308, 1899.

fogs subsided on the positive side many times as rapidly as they did on the negative side, or that the negative ions are in correspondingly greater number. The effect is increasingly marked for smaller supersaturations.

On extending my work with shaken nuclei in the last chapter to solutions of non-conductors in non-conductors, such as naphthalene and of paraffine in benzol, etc., I obtained results leading to the interpretation already summarized for aqueous saline solutions. The purport of the present chapter is the same. The nucleus is to be regarded as an exceedingly small droplet of very concentrated solution, which persists inasmuch as the decreased vapor pressure due to solution, at a certain specific radius is exactly counterbalanced by the increased vapor pressure due to convexity.

If this is true, then it seems doubtful to my mind, whether the experiments of C. T. R. Wilson on the specific condensation effect of ionization can further be regarded as crucial.

If one introduces nuclei or makes nuclei by aid of the X-rays, in what is virtually the acid and the alkaline side of a battery, even if the ionized moist air is the electrolyte, one is conveying nuclei into, or making nuclei out of, different media. The stuff out of which solutes are to be fashioned may be available in different degrees on the two sides. Whatever chemical effect is produced out of O_2, N_2, and H_2O on one side by the rays, need not at all be the same as on the other side, any more than the effect of shaking a very dilute solution need be the same as the effect of shaking a stronger solution, where the results have been shown to be enormously different as to the number, the velocity, and persistence of nuclei produced. Hence from the accumulating evidence which I have brought forward, I am led to infer that the two species of nuclei in Wilson's experiment are for mere chemical reasons liable to be of different degrees of permanence, sizes, and numbers, quite apart from the electric circumstances involved. One can not therefore affirm that the difference (respectively positive and negative) of ionization is the immediate and sole cause of the difference of precipitation rates specified, or briefly that negative ions precipitate more effectively than do positive ions, because both a difference of ionization and a chemical difference is involved.

I refer, of course, to immediate causes. Remotely affinities and cohesions have the well-known electrical relations; but with remote causes I am not here concerned.

Finally, if a marked difference in efficiency as condensation nuclei of positive and negative ions is granted, then any ionized emanation neutral as a whole, like that from phosphorus, should produce two groups of nuclei. On condensation there should be two groups of coronal particles, interpenetrating and subsiding through each other in the way I have frequently instanced in other experiments (Chapter V, § 37). No such effect has been observed. Phosphorus nuclei are rather remarkable for their identity, and the regular coronas observed even after 25 or 50 exhaustions.

While these conclusions as to the origin of the different nuclei involve a theoretical difference from Wilson's deductions, they are not at variance with his practical conclusions; for if through any radiation agency two different emanations are generated (with opposite charges or not), they would in a saturated medium correspond to two different nuclei, and the number of each kind and their diffusion rates in general would also be different. If they should at the same time be opposed in ionization, a separation of charges will result. Indeed if two or more groups of ionized nuclei be generated in any manner whatever, they are liable to have different number and speed constants and lead to a separation of charges, be it only by diffusion. But the case is more definite, as the following paragraphs may indicate.

Inasmuch as the nucleus from my point of view occurs under conditions of potential growth from a few molecules of dry solute to a weak solution (*Cf.* Chapter V, §§ 47, 48), as the air becomes more and more saturated, this growth and diminution must be a common occurrence in nature. The persistent atmospheric nuclei will be more dilute from the surface of the earth upward. The question then occurs whether such growth or change of concentration is accompanied by electric charge, quite apart from what is generally known as ionization (demonstrable presence of non-saturated chemical valencies); in other words whether any change of size of these excessively fine particles is reciprocally accompanied by surface electrification.

In his highly finished investigation published in 1892, Lenard (*l. c.*) showed that in the presence of air, pure water is electropositive, a circumstance which he interprets as a mere Volta contact effect. It needs but a trace of saline solute to reverse the potential. Solutions in the presence of air are electronegative, and more so as a rule as the concentration increases up to a definite value (6.5 % in case of NaCl), for which the negative charge is a maximum. After this, as the concentration increases the potential gradually tends toward zero (attained for a solution stronger than 25 % in case of NaCl). Removal of nuclei by condensation and subsidence is thus virtually a removal of negative electricity, provided the positive air charge is not simultaneously removed. Here then the possibility of a mechanism, in virtue of which growth or increasing dilution is associated with increasing negative charge for the nucleus, is actually at hand; but the difficulty at present rests with the removal of the air charge.

Briefly, the point I wish to make is that the occurrence of charge is incidental and not causal to the existence of the nucleus. What conditions its persistence and condensational activity is purely thermodynamic; what conditions the efficiency of electric transfer is a secondary property, open to investigation though as yet but little understood, and which even in the same nucleus (solution) is present in very variable amount, or may be quite absent. The phenomenon in its electric aspects depends therefore on the critical density at which evaporation ceases (Chapter V, § 48).

In the above paragraphs I have endeavored to indicate how the current lines of argument bearing more or less remotely on atmospheric electricity at present stand; to point out that none of them have as yet been traced to a definite issue, and to show the direction in which I hope myself to contribute.

APPENDIX.

QUADRANT ELECTROMETRY WITH A FREE LIGHT NEEDLE, HIGHLY CHARGED THROUGH A CONDUCTOR OF IONIZED AIR.[1]

1. The principles of construction aimed at in the following paper are: (1) To have the needle swing freely in air, *i. e.*, without liquid contacts; To devise means for suitably charging this needle (2) by induction alone; (3) By transmission of the charge to be measured (potential) by ionized air; (4) Practically, to compensate for the loss of charge of the highly charged needle by conduction through ionized air.

To my knowledge the sensitiveness of Kelvin's original apparatus built upon a Leyden jar has remained unrivalled. Realizing the ingenious use which is made of sulphuric acid which in the instrument is a desiccator, a damper, a conductor, and part of a receptacle for storing large charges, it has nevertheless seemed to me that a useful modification might be attainable if the liquid contact of the needle could be obviated. In relation to such small torques as are successfully applied in galvanometry, it appears that the large capillary and viscous resistances introduced by partial submergence in a liquid, must ultimately, or in other dispositions, prove objectionable. Nobody would, for instance, think of damping an ordinary galvanometer needle in a liquid. It has, therefore, long been my purpose to reduce the torsional conditions of the needle to quartz fiber accuracy.

There is a second point of view: Notwithstanding the sensitiveness of Kelvin's beautiful instruments, they have not found as much favor in general practice as the modification of them devised by Mascart. The troublesome high potentials of Kelvin's instrument are here replaced by a water battery, with advantage and without serious sacrifice, as the sensitiveness of the original instrument was, as a rule, excessive. Mascart, however, retained the liquid damper. If this can also be removed, I think that a markedly increased sensitiveness must be attainable with all the conveniences due to Mascart's modification. Incidentally it appears that inasmuch as the liquid contact means a platinum vane, etc., the heavy parts are needless in a free needle, a further favorable condition.

In the apparatus presently to be described, I have succeeded in installing an air damped light, aperiodic, free needle, and have in this way increased the sensi-

---

[1] *Cf.* Meeting Nat. Acad. Sciences, Philadelphia, November, 1901. Since that day, an instrument made with similar ends in view, but on a different plan, has been described by F. Dolezalek. *Zeits. f. Instrum'k.*, xxi., pp. 345–350, 1901. The capsule attached to my instrument is the feature which I wish to accentuate.

tiveness of Mascart's modification many times without falling below the requirements of a practical instrument.

2. *Original constants.*—The method of work has been direct. I took the well-known Elliott lecture form of quadrant electrometer and after determining the original constants improved on them successively. When the quadrants were permanently charged with a small water battery of about 24 volts (retained throughout), the results were: temporary deflection per volt, 2.5 cm.; permanent

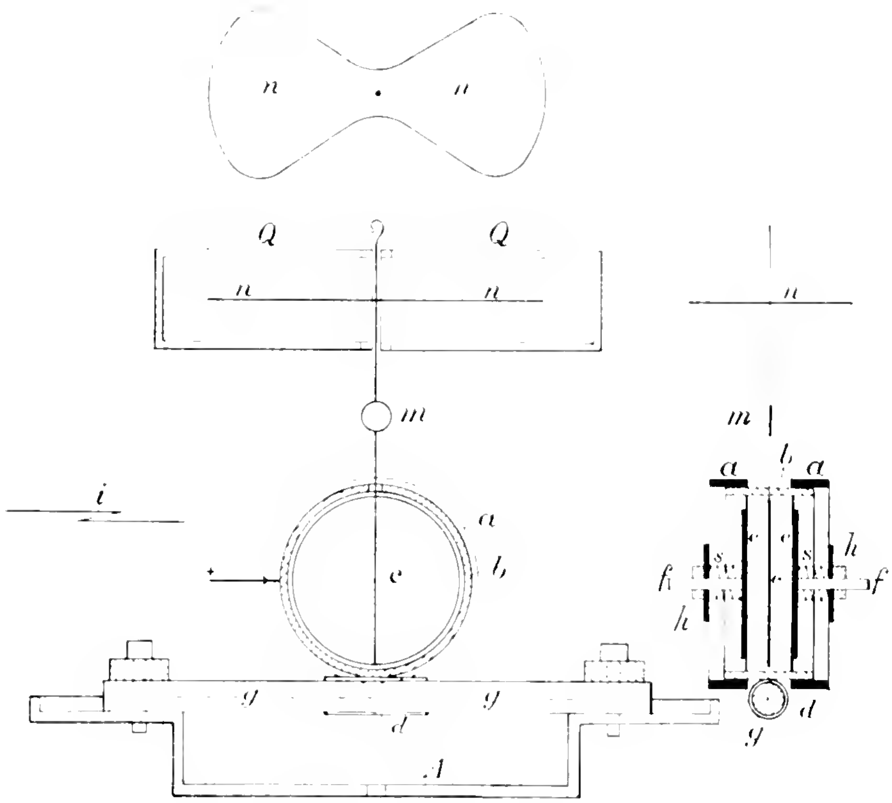


Fig. 1.—Electrometer Showing Capsule, Needle, and Quadrants in Place. Sectional Elevation.
Fig. 2.—Cross Section of Capsule and Ionizer.

deflection per volt, 1.7 cm.; scale distance, 140 cm.; period, 20 seconds; damping ratio, 2/1. The low sensitiveness is due to the large quadrants (12 cm. in diameter, 2.7 cm. high), and the small charging battery, the instrument being adapted to an electrostatically highly charged needle. But as the case of the quadrants is well-known, and the whole improvement aimed at is confined to the needle, the above term of comparison is adequate.

The theory of the electrometer gives us approximately, $\theta = a(V_2 - V_1)(V_3 - (V_2 + V_1)/2)$, where θ is the deflection, a a constant varying as the effective circumferential breadth of the needle directly, and its distance from the quadrants inversely. V_1, V_2, V_3 are the potentials of the quadrants and the needle, respectively. If $-V_1 = V_2$, $\theta = 2aV_1V$, where V_1 is 1/2 the available potential difference. For constant V_1, this is the best adjustment of the water battery. I have found it more convenient, however, to keep $V_1 = 0$, whence $\theta = \alpha V_2 V_3 - \alpha V_2^2/2$ for small deflections.

If the mean deflection be taken (since the constant $\alpha V_2^2/2$ merely determines the zero), $\theta = \alpha V_2 V_3 - \alpha V_2^2/2$ and $-\theta = -\alpha V_2 V_3 - \alpha V_2^2/2$, whence $\theta = \alpha V_2 V_3$, where V_2 is the full potential difference available. In practice the positive and negative deflections are numerically equal, but the scale zero varies with V_2.

Finally, if the instrument is used idiostatically and $V_1 = 0$, $V_2 = V_3$, $\theta = \alpha V_2^2/2$. In this case the instrument gave me $\alpha = .036$.

If $V_1 = V_3 = 0$, the needle and one quadrant being put to earth, $\theta = \alpha V_2(-V_2/2) = -\alpha V_2^2/2$, the same value but opposite in sign.

3. *Apparatus.*—In the figure (sectional elevation) *QQ* will be recognized as the quadrants, *A* as the base plate of an ordinary Elliott lecture pattern of the electrometer. Details are omitted. *A* is to be used as a receptacle for the desiccator and in the definite form of instrument must be deeper and provided with a central hole for convenient discharge. The needle is shown at *nn*, and *m* is the mirror attached to the vertical stem. This carries at its lower end a metallic disc, *c*, all but fitting into the cylindrical cavity of the brass box, *b*. When the needle is at rest, the disc, *c*, lies at right angles to the axis of this box, and the free space between the edge of the disc and the inside of the box is about 1 mm. The hollow cylinder is appropriately closed at both ends, forming a capsule and it is supported by the horizontal glass rod *gg*, fastened down with bolts to the ends of the bed plate, *A*. A sleeve, *d*, serves to join the capsule to the rod.

The needle, *n*, and disc, *c*, are made of very light aluminum foil, .03 thick. In order to secure the necessary longitudinal rigidity in the needle, the foil is folded along the axis as shown at *i*, and rolled down nearly flat. The needle so obtained weighs with mirror less than .7 grams. Its period in the earlier experiments was 30 sec., in the later experiments 60 sec. (remembering that but 1/2 swing is usually needed) and the damping ratios 8:1 and 37:1 respectively. Originally my needles and discs were made of silver-plated mica, but I was unable thus to get the same lightness and rigidity as with aluminum. In the final experiments the disc was even made annular as the damping in case of narrowed quadrants is already excessive.

As a result of this extreme lightness relative to surface, the air damping obtained in disc and capsule may reach aperiodicity, while the torque of the bifilar is correspondingly reduced. The lids of the box, *b*, are adjustable, the ring *aa* carrying a narrow horizontal bar, *h*, centrally perforated so as to admit the screw, *f*, the inner end of which carries the discs, *c*, *c*, by which the capsule is closed. The outer ends of *f*, *f* are provided with a nut, which in view of the springs, *s*, may be used to regulate the distance between *c* and *h* at pleasure. A simple lid, however, was found to suffice equally well, and the discs, *c*, *c*, may be left as much as 2 cm. apart, admitting of ample swing of the needle. In fact so small is the amount of induction transmitted by the discs that they may be made of *glass* through which the edge of the vane *c* may be seen and its freedom tested. The vane, *c*, is received into the box, *b*, through a notch on top parallel to the axis of *b*, sufficiently closed in adjustment by the ring, *a*.

SEPARATION OF THE CHARGE OF THE INSULATED NEEDLE BY INDUCTION.

4. *Method of charging.*—The quadrants are charged directly with the water battery as already explained. To convey the charge to the needle, which is now freely suspended in air and insulated, it was my first endeavor to ionize the air in the capsule, *cc*, by making the discs, *c*, *c*, of wire gauze, and securing pellets of phosphorus to rear discs of mica. Thus the air in the capsule becomes a conductor while the air without insulates in view of the slow diffusion and absorption of phosphorus ions.

Phosphorus was used for experimental purposes. It is not practically suitable since it deliquesces on oxidation. Thorium and uranium preparation placed on *e* would be free from this difficulty. With this plan I succeeded but partially, as the air could not be kept dry enough and the emanating power of the phosphorus is soon extinguished by the moisture of its oxidation. I shall refer to the results below.

It soon appeared that the ionizer was superfluous as the electrostatic induction within the capsule, *b*, is nearly perfect. Thus if a positive charge is imparted to the outside of the capsule as shown, it redistributes itself at once, forming a field within the capsule such that the inside of the capsule is positive throughout its equatorial plane and the edge of the disc, *c*, negative. Nearly the whole field is closed within this equatorial zone, and but little induction is contributed by the lateral discs, *c*, *c*, seeing that the edge of the vane has been brought close up to the inner face of *b* to secure good damping, and *c* is remote. Hence the needle, *n*, *n*, is charged positively by an amount equal to the charge within *b* or on the edge of the vane, *e*.

An instrument is thus obtained which is very similar to the electroscope, only more sensitive and like it of low capacity. The needle of the apparatus being freely suspended, no communication of permanent charge to it is possible for reasonably low potentials if care be taken that no charge escapes by way of the silk fibers of the bifilar suspension. The air within the cover of the apparatus must therefore be kept scrupulously dry, otherwise the zero will shift slightly with each charge.

5. *Observations.*—The needle being free, it was found convenient to take temporary instead of permanent deflections or to use the instrument ballistically, as it were, supposing, however, that the contact is made during the whole swing. The bifilar suspension was about 12 cm. long, .02 cm. below, and .1 cm. above, the needle being charged by a storage battery. Using silk threads of four (glued) fibers each, their individual torsion is already a serious factor.

Withdrawing tabulated statements for brevity, it suffices to indicate that both the temporary and the permanent deflections varied with the potential. The zero changed slightly, showing the undried silk threads to conduct. Since $\theta = a V_2 V_3$

if the mean deflection is taken, it was found that $\alpha = .084$, so that the original sensitiveness has already been increased 2 or 3 times.

6. *Idiostatic data.*—I next discarded the water battery and joined one pair of quadrants with the needle, putting the other pair to earth. The temporary deflections only were taken. The experiments were varied by exchanging the charge of the quadrants and by again earthing the needle (capsule), in which case it was necessary to change the zero manually. The data for the earthed needle happen to be the smoothest. Computing α from the three groups of experiments made, $\alpha = .126$, $\alpha = .090$, $\alpha = .138$ were obtained. These differences as well as the relatively large values of α for the smaller charges (5 volts) indicate a charge in the needle which was not removed, for instance, by touching the needle by an earth wire. Compared with the original value ($\alpha = .036$) the present increase of sensitiveness is 2 to 4 times larger. This is an excess of the increase (2 1/2 times) in § 4. It may be noted again that if the needle carries an independent charge (due to the conduction of the silk fiber), $V_1 = 0$, while V_2 and V_3 are different; whence $\theta = V\alpha_2(V_3 - V_2/2)$, which is a maximum if $V_2 = V_3$. Thus, if the needle carries such a charge the maximum is approached sooner or later than in the normal case of no charge. All this points to the importance of insulated silk fibers.

7. *Miscellaneous tests.*—The use of mica discs at e in figure 2 is apt to be accompanied by hurtful polarization. Approaching these discs too closely to the needle, the damping soon becomes excessive (aperiodic), and the slow moving needle is found to be unstable. Slight gain in sensitiveness in this case is no compensation for the irregular behavior and the narrowed limits of deflection. Paraffined copper discs showed no advantage. All this contrasts strongly with the steadiness of behavior when the discs e, e, are moved far apart.

Before proceeding to test the quartz fiber suspension, I determined to increase the sensitiveness by reducing the bifilar distance further. The results did not show the increase of sensitiveness anticipated, proving that the torque of the silk fibers is now seriously in question and suggesting objections to fibers glued together in multiple. The electrometer held its charge (needle) well, the readings at intervals of 15 sec. being 60, 61, 62, 64, 65, etc., with the zero at 101. This is a drop of about .12 per second, without special desiccation, a favorable value in view of the small capacity. The sensitiveness gained is now $\alpha = .164$, exceeding the original value ($\alpha = .036$), 4 1/2 times.

The effect of the vane c alone, when the quadrants are all metallically connected, was about 1/50 of the deflection due to the quadrants. A similarly interesting question is the relative amount of induction conveyed by the cylinder, b, and by the barriers, e, e, separately. This was found by putting the barriers to earth and charging the cylinder, and vice versa. The results showed the effective charge to reside in the equatorial parts of the capsule, nearest the edge of the disc, c, of the needle. The barriers contribute about 1/6, the cylinder 5/6.

8. *Quartz fiber.*—My next endeavor to increase the sensitiveness consisted in replacing the bifilar suspension by a quartz fiber. The one selected was between

.002 and .003 cm. in diameter. To mount it the end of the fiber was thrust into the mantle of a flame and bent sharply at right angles, then fastened to a suitable rod with cement.

The sensitiveness so obtained was $\alpha = .14$, actually less than the $\alpha = .164$ of the last paragraph. Finding no finer quartz fibers available, I resolved to return to the silk bifilar. The experiment made, however, is sufficient to express the conditions which hold for quartz fibers, as follows: The needles used below weigh less than 1/2 gram. A good quartz fiber, strong enough to hold it, will therefore not be more than .0005 cm. in diameter. Consequently the torque will be reduced over 500 fold, and the sensitiveness of the instrument now be increased to $\alpha = 70$. This is so much in excess of the sensitiveness reached with the silk bifilar that other practical difficulties (excessive damping coefficient), will intervene long before it is reached.

9. *Single-fibered silk.*—These were obtained by splitting the above silk fiber into its four constituents by submerging it in hot water to dissolve the glue. The bifilar obtained in this way was (after desiccation) in every way entirely satisfactory, except with regard to its conduction. The period of the needle increased to 60 sec., its damping coefficient to 37, so that the needle was practically aperiodic. The heterostatic sensitiveness obtained was $\alpha = .33$, over 9 times the original value.

In using the instrument idiostatically the greatest care must be taken to remove all charge from the needle, as otherwise the deflections will vary as the first and second powers of the needle conjointly. Indeed, the second power may often relatively vanish, as will presently be shown. In the experiments the needle was discharged by putting it to earth just before the measurements, but even with this precaution some residual charge is liable to be evidenced by the unsymmetrical deflections.

If the needle carries a charge and if $V_1 = 0$, $\theta = \alpha V_2(V_3 - V_2/2) = \alpha V_2 V - \alpha V_2^2/2$. Hence, if the charge of the quadrants V_2 is reversed, the mean deflection will be $\theta = \alpha V_2^2/2$. The law of squares must hold. If the needle carries a permanent charge equivalent to V_3', this is not reversed on commutation. But in the mean value of $\theta_1 = \alpha V_2(V_2 + V_3') - \alpha V_2^2/2$, and $\theta_2 = (-V_2)(-V_2 + V_3') - V_2^2/2$, viz., $\theta = \alpha V_2^2/2$, the law of squares still holds. If, however, charge runs into and out of the needle during measurement so that the sign of $V_3' = V_3$ is also reversed partially at least, then in the mean $\theta = \alpha V_2^2/2 + \alpha V_2 V_3''$ the simple law of squares will be either accelerated or retarded according as V is positive or negative. In the experiments the latter is usually the case, showing that the needle leaks. The permanent charge of the needle appears in the difference of deflections as $\theta' = 2\alpha V_2 V_3'$, and this may also be made out from the data. Indeed, it has been stated that sometimes the linear law may preponderate.

The sensitiveness reached in these experiments was $\alpha = 2\theta/V_2^2 = .40$, when the needle was charged and $\alpha = .33$ when it was put to earth. This again is, on the average, over 10 times the sensitiveness found in paragraph 2 for like experiments.

10. *New electrometer.*—After finishing this work, I thought it expedient to

make the next step in the direction of greater sensitiveness, by decreasing the distance apart of the upper and lower sectors of the quadrants. In the new instrument the same light needle was used as above, and the new quadrants were about 10 cm. in diameter and 1 cm. high. Though the same capsule was used the damping coefficient was increased by the less roomy quadrants. The needle was quite aperiodic, but its period about 60 seconds.

Again omitting the tabulated results for brevity, let me say that the experiments were made in three sections. In the first the quadrants were charged by a water battery (nominally 48 volts); a diversion, however, was introduced by earthing the middle of the battery. Supposing the two halves equal ($V_2 = - V_1$), $\theta = \alpha (V_2 - V_1)(V_3 - (V_2 - V_1/2) = 2\alpha V_2 V_3$, where V_2 is 1/2 of the electromotive force of the battery. In the first part of the work I found $\alpha = .39$.

In the second part of the work the reason for this low result was investigated. It appears that as the voltage of the quadrants increases from 10, 20 to 40 volts, the deflections pass through a maximum, being actually greater at 20 volts than at 40. The explanation is suggested assuming that the two halves of the storage battery are not equal, so that $V_2 + V_1$ is not zero. As the balance was most nearly maintained for 10 cells the constant becomes $\alpha = .84$, an increase of nearly 24 times.

In the third part of the work one quadrant was earthed, and the other charged with the full number of storage cells. The results were in general corroborative; but here also the sensitiveness failed to increase with the potential difference of the quadrants.

A few idiostatic results were finally tried, showing that on the average $\alpha = .74$.

PRELIMINARY RESULTS WITH A HIGHLY CHARGED NEEDLE.

11. *Charge by induction.*—I now proceeded to take advantage of the observation just made. Accordingly the quadrants were used for measuring the electromotive force of two Clark cells while the needle was permanently charged by a storage battery. My first experiments consisted in seeing in how far an inducing system would suffice. The capsule was charged directly and the needle by induction. The results showed that the sensitiveness soon passes through a maximum, more than ten cells connected with the capsule are scarcely useful. The sensitiveness was low and variable.

12. *Charge by conduction.*—The needle therefore is to be charged by contact. The only loss of charge can then take place through the silk threads or quartz fiber. This method was very successful so far as small equipment with great sensitiveness is concerned. Naturally the needle loses charge in the lapse of time, which, however, can be more than supplied by ionizing the air in the capsule.

The results showed enormously increased sensitiveness. With but 10 storage cells to the needle and capsule the deflection was 50 cm. per volt for a scale distance of 4 meters. Material advantage is secured by charging the capsule. In making these long excursions the period of the needle is increased to almost 2 minutes, which is to be improved by cutting down the damping.

13. *Miscellaneous experiments.*—The occurrence of an insulated needle makes this form of electrometer peculiar, and a special lever is needed to put the needle to earth at will. If the quadrants are charged equally and opposite with the capsule earthed, $\theta = a V_1 V_2$. Hence the deflection is not zero but of a magnitude varying with V_1, the potential of the needle. If the needle is put to earth, $\theta = 0$, and this may be used as a test for symmetry of the quadrants and needle. If V_1 is zero, θ will vanish for all values of V_2. I omit the data.

Holes were differently cut in the vane of the needle, but the effect was always disadvantageous, as might have been expected from theory.

The highest sensitiveness was obtained with a twisted silk bifilar, each thread single-fibered. The constant obtained was $a = .5$. Deflections, however, were too prolonged and creeping to make this result of value even if a quartz fiber had been used.

14. *Summary.*—With the use of a damping capsule in which the air damper or disc of the needle lies symmetrically in the right section of a cylindrical box, with only just space enough at the edge to secure freedom of motion, not only may complete aperiodicity be secured if desirable, but a charge may effectively be imparted to the needle by induction, which is all but equal to the inducing charge. The voltages to be measured are necessarily small.

In view of the light needle, the absence of liquid contacts, the sensitiveness of the apparatus may be made upwards of 10 times greater than is customary where liquid contacts are employed. An advantage of the instrument is its simplicity, its small capacity, its immediate adaptation to quartz fiber suspension, the attainable stability. For the latter purpose the air within the instrument must be dry, and the difficulty of securing this perfect insulation is an objection to the instrument.

The sensitiveness may be enormously increased, however, by charging the needle by contact and using the capsule merely to retain its high potential. As few as ten storage cells will suffice to effect this charging. It is necessary to provide means for the loss of charge of the needle, and this is done in the next section.

TRANSMISSION OF THE CHARGE BY IONIZED AIR.

15. *Phosphorus emanation.*—The ionizer used for experimental purposes was phosphorus. It was attached to the inner faces of the metallic barriers, *i. e.* behind discs of wire gauze. Otherwise the method of experiment was the same as above, except that the reversed deflection (recoil), after the permanent deflection had been reached, was also recorded. As the damping ratio was 8/1, the arc of recoil from the permanent deflection should be 1/9 of its value. The effect is always larger, after which the zero is asymptotically regained. It follows that a charge successively enters upon and vanishes from the needle through the ionized air.

The data showed that both the temporary and the permanent deflections vary as the potential of the needle, but that the recoil increases at an accelerated rate for higher potentials. The sensitiveness varies with the activity of the phosphorus. Again the temporary and the permanent deflections are greatest when the recoil is least.

With regard to the permanent deflection, the question arises whether the positive charge of the capsule leaks into the needle, or whether positive charge leaks out of the needle in other ways, leaving a permanent negative charge. This is determined by the recoil, showing the residual charge of the needle to be opposite in sign to the charge imparted. It follows also that the permanent deflection decreases as the recoil increases.

In the lapse of time the temporary deflections soon reach a maximum, and therefore a nearly constant value; the permanent deflection then steadily decreases while the recoil increases. The fluctuations of the former are reproduced in the latter.

Experiments equally unsatisfactory were made with the idiostatic method.

16. *Highly charged needle.*—I now come to the definite form of apparatus already suggested in § 10. Here the needle is put at high voltage by momentary contact with the capsule, which is kept permanently charged. The potential to be measured communicates with the quadrants, either pair being put to earth alternately. To compensate for any leakage from the needle, the barriers of the capsule are phosphorus grids.

The experiments showed that the sensitiveness remains constant so long as the phosphorus lasts, seeing that the reagent deliquesces in the atmosphere and soon vanishes effectively from the instrument. The damping, moreover, was liable to be excessive, 3 minutes being often necessary to reach a permanent deflection. This was remedied by cutting two nearly semicircular holes in the vane, leaving only the parts near the stem to insure rigidity. The period was thus cut down to 30 sec. The silk bifilar was stretched between hard rubber stems to increase the insulation, and the bifilar distance was made a little larger. The table on page 172 contains an example of the results.

Thus, with the proper needle, a deflection of 5 cm. either side of zero was attained per volt, when the charging potential was but 10 storage cells. The maximum sensitiveness attained was thus $a = 2.5$ about.

17. *Summary.*—From the form given to the damping capsule, it appears that the induction of the preceding section is in excess of the effect of conduction through the ionized air to the insulated needle. Initially both produce like effects, but the permanent deflections are different. The effect of ionization is indirectly or virtually an escape of the charge of the needle, which may go far enough to reverse the sign of the deflection. The result is much like polarization, and increases in the lapse of time. The arrangement is useless for measurement.

If, however, the needle is first charged by contact, and the ionized air is then used as a mere vehicle for supplying the leakage of a highly charged needle, the method becomes practicable for certain purposes. My chief purpose in this appendix was to call attention to the capsule, which, in the manner shown in §§ 5 and 6, has frequently been useful.

TABLE —NEEDLE CHARGED BY MOMENTARY CONTACT WITH CAPSULE; CAPSULE PERM. CHARGED BY STORAGE BATTERY; QUADRANTS WITH 1 CLARK CELL, ONE POLE EARTHED. SCALE DISTANCE, ABOUT 4 M.

[illegible]	Time	Zero	Elongation	Single deflection.
		cm.	cm.	cm.
1[illegible]	[illegible] 45	111 12[illegible] 129	52 103	65
1[illegible]	1[illegible]	106 75 82	16 152	73
10	1[illegible] 40	84 81 87	14 161	74
10	11 15	92 92 92	2[illegible] 172	76
10	12 0	110 110 112	50 179	64

Another needle. Damping vane annular.

30	—	124 122 124	27 247	96 124 > 110
20	—	109 111 113	46 183	64 71 > 68
1[illegible]	30' to 3' 30'	96 96 97	63 132	33 36 > 35
10	4 [illegible]	112 112 113	19 147	33 35 > 34
10	4' 30'	103 103	71 137	32 34 > 33
10	5h [illegible]	1[illegible]5 1[illegible]6	74 139	31 33 > 32
1[illegible]	[illegible] 0'	1[illegible]4 140	111 167	28 28 > 28

8[illegible] Needle. 1 Daniell. Water battery to capsule.

	0' 0'		— —	73 (Initially)
	4		— —	80
	5 30'''		23 } 183 }	80

In more recent experiments, preference was given to a horizontal capsule, the lid of which was a light disc attached to the lower end of the needle and closing the capsule similarly to the disposition in the guard ring electrometer. A pellet of phosphorus was placed in the capsule, and both this and the upper end of the bifilar were connected with the water battery, thus charging the needle from both ends. The leakage in the presence of the phosphorus was but slightly greater than in its absence, being with the quadrants at 10 volts, $.24 \times 10^{-12}$ to $.77 \times 10^{-12}$ amperes in the former case and $.29 \times 10^{-12}$ to $.40 \times 10^{-12}$ amperes in the latter, according as the sign of the charge was the same or opposite to that of the needle. The deflection with phosphorus is here unsymmetrical, but the constancy perfect and the sensitiveness very high. Indeed it was also feasible to charge the quadrants permanently and symmetrically with the water battery and to connect the unknown voltage with the needle either through induction alone in the absence of phosphorus or through the ionized emanation, according as high or low potentials were to be measured.

INDEX.

SMITHSONIAN CONTRIBUTIONS TO KNOWLEDGE

1413

Hodgkins Fund

ON THE ABSORPTION AND EMISSION OF AIR AND ITS INGREDIENTS FOR LIGHT OF WAVE-LENGTHS FROM $250\mu\mu$ TO $100\mu\mu$

BY

VICTOR SCHUMANN

CITY OF WASHINGTON
PUBLISHED BY THE SMITHSONIAN INSTITUTION
1903

The Knickerbocker Press
(G. P. Putnam's Sons)
New York

SMITHSONIAN CONTRIBUTIONS TO KNOWLEDGE

1413

Hodgkins Fund

ON THE ABSORPTION AND EMISSION OF AIR AND ITS INGREDIENTS FOR LIGHT OF WAVE-LENGTHS FROM $250\mu\mu$ TO $100\mu\mu$

BY

VICTOR SCHUMANN

CITY OF WASHINGTON
PUBLISHED BY THE SMITHSONIAN INSTITUTION
1903

Commission to whom this memoir has been referred:

CARL BARUS
C. G. ABBOT

ADVERTISEMENT.

This work forms part of Volume XXIX of the *Smithsonian Contributions to Knowledge*, and gives an account of researches, aided by grants from the Hodgkins Fund, on the emission and absorption of the gases of atmospheric air in the ultra-violet spectrum.

Within the last fifteen years our knowledge of radiation has been greatly increased, and now embraces wide ranges of the spectrum heretofore unknown. Without assigning any place to the numerous kinds of "rays" whose discovery has been associated in the public mind first with the work of Rontgen, and later with that of the Curies, I am speaking here rather of the extensions of the spectrum in wave-lengths which are actually measurable and known. Thus beyond the red the spectrum has now been studied in practical continuity to a wave-length of nearly 100 microns; and at a great remove beyond this is another known region embracing the so-called Hertzian, or electric, waves now employed in wireless telegraphy.

Beyond the violet, progress has been, relatively speaking, less rapid, unless indeed it shall prove that the Röntgen and other radiations fall in this region. But a great step in advance has been made by the unwearied and able investigations of the author of the present work, Doctor Schumann.

The difficulties hindering research in the ultra-violet are great, and consist chiefly in the opacity of the usual optical media to the short wave-length rays. Quartz, for a long time considered best in this part of the spectrum, is found to be too opaque, and has been largely superseded in Doctor Schumann's investigations by fluorspar for prisms and plates. Air even in layers of a few millimeters thickness, is almost wholly opaque, and other gases absorb strongly. It has therefore been necessary to employ a spectroscope from which the air is exhausted to the highest practicable degree; and this and other necessary apparatus Doctor Schumann has designed and constructed with his own hands, though aided by grants from the Hodgkins Fund of the Smithsonian Institution. Commercial photographic plates were found to have films too opaque for the recording of these short wave-lengths, and the author was obliged to devise an improved method of coating the plates used in his investigation.

This memoir contains an account of the special apparatus and method of using it, and continues with a description of the emission and absorption spectra of oxygen, nitrogen, hydrogen, carbon monoxide and dioxide and aqueous vapor for wave-lengths reaching in the case of hydrogen to about 0.10 micron. Illustrations of the apparatus and spectra accompany the text, and it is thought the whole will be a valuable contribution to knowledge, though but preliminary to the researches Doctor Schumann alone is continuing in this spectral region.

In accordance with the rule adopted by the Smithsonian Institution, the work has been submitted for examination to a committee consisting of Doctor Carl Barus of Brown University and Mr. C. G. Abbot of the Smithsonian Astrophysical Observatory.

S. P. Langley,
SECRETARY.

Smithsonian Institution,
Washington, September, 1903

ON THE ABSORPTION AND EMISSION OF AIR AND ITS INGREDIENTS FOR LIGHT OF WAVE-LENGTHS FROM $250\ \mu\mu$ TO $100\ \mu\mu$.

By Victor Schumann, Ph.D.

(Translated from the German Manuscript by Charles S. Peirce.)

The present report describes the most essential results obtained up to the end of the year 1900 in an unfinished investigation which was begun at the end of March of the same year, and was continued without interruption during the interval, this research having had the support of a grant from the Hodgkins Fund of the Smithsonian Institution.

General considerations.—The chief instrument of this investigation was a vacuum-spectrograph with lenses and prism of white fluor-spar.

In a general way, its mechanical arrangement is that of an ordinary spectroscope with collimator and telescope; except that a little photographic camera takes the place of the eye-piece. Its parts, however, have air-tight connections, so that a high vacuum can be produced in it by a mercurial air-pump.

Figs. 1 to 9 are photographic reproductions of the original working drawings in accordance with which the apparatus was constructed by my own hands; so that any instrument-maker who may desire to undertake the execution of such a vacuum-spectrograph may trust implicitly to these figures. The following explanations may be useful.

Figs. 1 and 2 show the photographic plate-holder open. It is adapted to plates 37 x 12.7 mm.

Fig. 3 shows a key by means of which the plate-holder can be shoved into the camera, and by which it can also be withdrawn.

Fig. 4 is the slit with its three micrometers, a'', f'', g''. The first of these, a (1 division = 0.001 mm.), regulates the width of the slit. The second, f'' (1 division = 0.01 mm.), adjusts the length of the slit. The third, g'' (1 division = 0.1 mm.), serves to shift the adjustable diaphragm which regulates the length to any part of the slit that it may be desired to employ. The screw c effects the

the adjustment of the slit to parallelism with the refracting edge of the prism. The three micrometer screws are rendered air-tight by means of the three steel cones, m', s', w'. The slit box d'' is connected with the source of light through a cover shown in Fig. 5, c''.

Fig. 5.—Section of Plate-Holder. Natural Size.

This cover, c'', carries by a flat ground greased joint the Geissler tube, which is centered by the steel pin i'', and after centering is secured against lateral shifting by a slide, h''. It is needless to say that the steel pin is withdrawn when the centering of the tube has been effected. The mode of connection of the tube with the vacuum-spectrograph does not permit the two to be filled independently of one another with such gas as may be under investigation at the time. It will not do to fill both unless the gas is sufficiently transparent. This, however, is not the case with the majority of gases; so that a window has usually to be interposed between the Geissler tube and the cover, c'', so as to diminish the thickness of the stratum of gas to be traversed by the rays. The same arrangement is useful in photographing by sparks and arc-light. In case the observation is not to extend farther to shorter wave-lengths than 155 $\mu\mu$, a sufficiently thin quartz window will answer the purpose. For more refrangible rays it is not transparent enough, and white fluor-spar is the only suitable material.

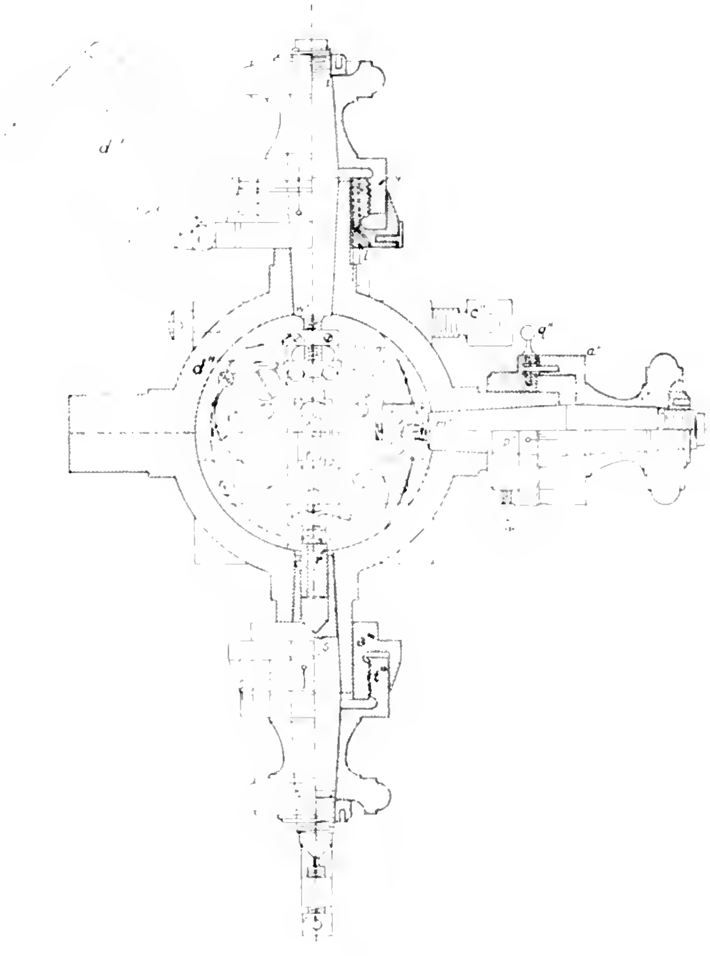


Fig. 4.—Section of the Plate Micrometer. Natural Size.

Fig. 6 shows a section of the part in which the prism (which appears in Fig. 8 as k) is set up. A thick-walled cone, k, is rigidly connected with the collimator.

A hollow cone, d, very accurately ground to fit upon b, is capable of turning round it to the extent of its opening, d_1 d_2, and carries the camera.

Fig. 7 shows the camera in cross-section. The plate-holder, drawn in the cross-section, must be shoved into the inner cone, b', through the slot, l, in dark room light. When the cone is turned, the plate-holder comes before the opening, m', and is exposed to the rays from the prism. A certain amount of air is unavoidably introduced when the plate-holder is shoved in; and in case this interferes, it has to be pumped out before the exposure begins; and it will sometimes even be requisite to wash out the entire interior of the spectrograph with hydrogen.

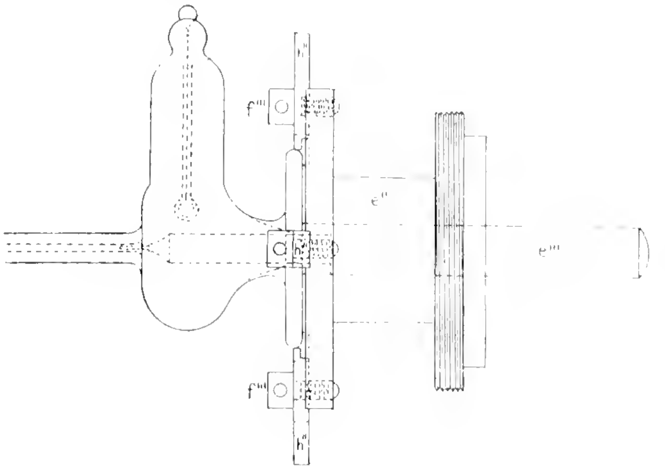


FIG. 5. CONNECTION WITH GEISSLER TUBE. NATURAL SIZE.

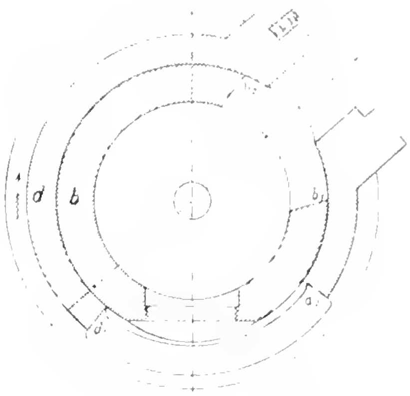


FIG. 6. CROSS-SECTION OF FILM HOLDER. HALF NATURAL SIZE.

Working in dark-room light involves many inconveniences; and I have, therefore, lately provided the plate-holder with a brazen sheath which is shoved into a vertical groove made in k'. In this way, the plate-holder can be introduced into the camera, quite light-tight, in full daylight.

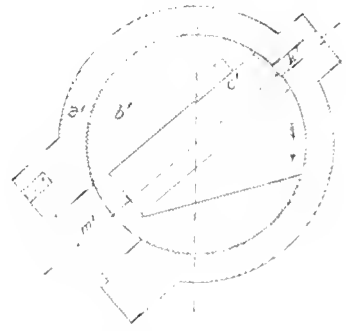


FIG. 7. CROSS-SECTION OF CAMERA. HALF NATURAL SIZE.

Fig. 8 is the elevation of the spectrograph. i is the prism-stand with the prism, k, upon it. It rests, free to turn, upon a conical pivot of the little table, h, which is rigidly connected by a screw-thread with the steel axis, g; and this in turn carries the alidade, l, at the bottom outside the vacuum. The apparatus is connected with the air-pump by means of the ground-glass cock, o. The two thumb-screws, t_1 and t_2, serve to focus the lenses of the collimator and telescope respectively. At the right-hand side of them the camera is seen in section, showing the photographic plate, l, with its plate-holder. The micrometer, s', above it (1 division = 0.1 mm.), serves to move the plate in its own plane parallel to the refracting edge of the prism. This is requisite in case several exposures are to be made successively without changing the plate.

Fig. 9 is the horizontal plan of the spectrograph. The slit is shown at d', with the collimator-tube, c, in which there is a peep-hole, o_1, indispensable for the adjustment of the lens. The telescope has a similar peep-hole, o_2. The telescope carries the camera, which is provided with handles, l, for the purpose of turning its interior cone, b. Upon the outer cone of the camera the drawing shows a divided arc whose divisions are whole degrees. This serves for the adjustment of

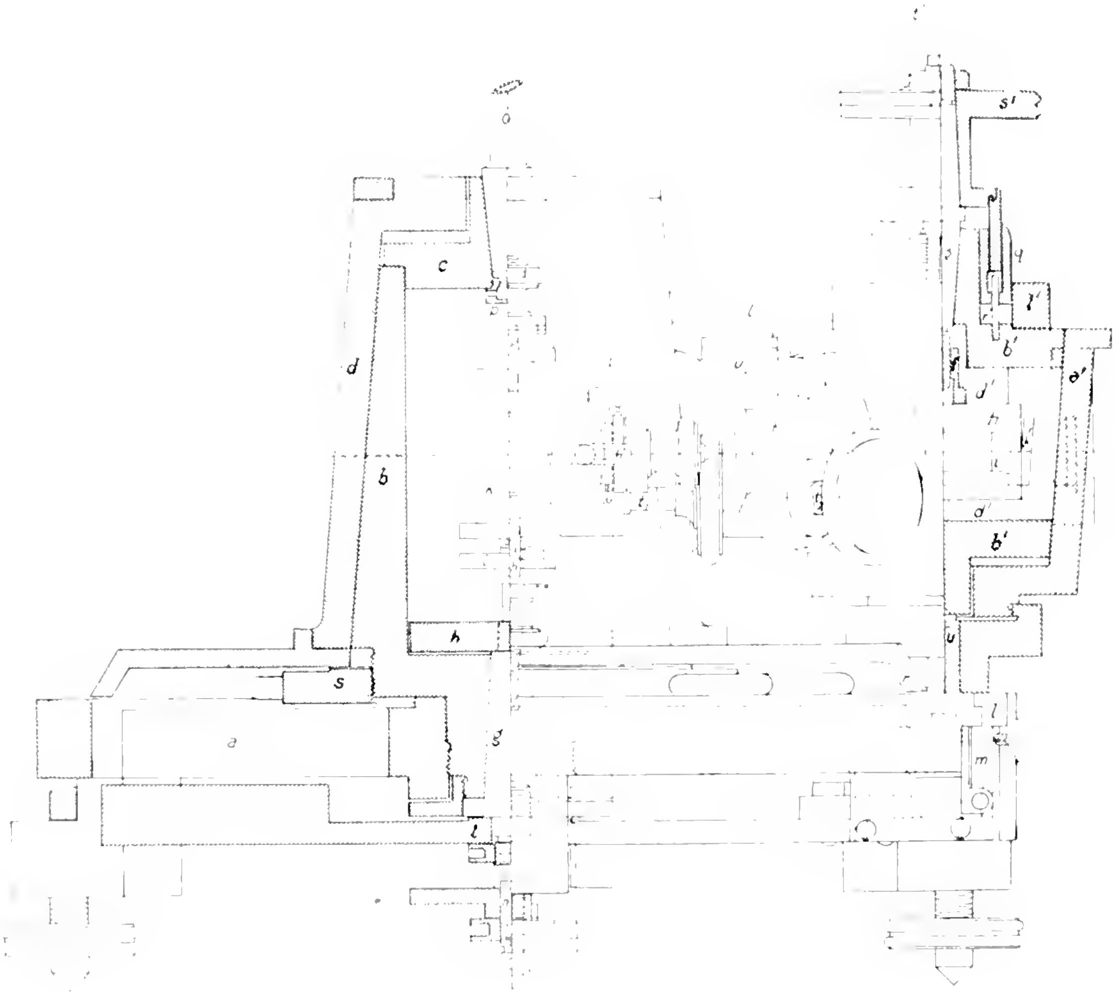


Fig. 8. — Elevation of Spectrograph. Half Natural Size.

the inclination of the photographic plate to the optical axis of the lens; which depends upon the refrangibility of the rays to which exposure is to be made. With a sixty-degree prism of fluor-spar, this angle of incidence is 68° when light of wave-length 185 $\mu\mu$ falls on the middle of the plate. From that point on, it diminishes considerably with the wave-length; so that for the most refrangible region photographed by me it only amounts to 55°. The camera has a counterpoise, q. At r is the index for the setting of the angle between the optical axes of the two lenses in exposures to different portions of the spectrum. At *l* is the vernier for the alidade of the prism; but for a very fine setting this vernier is insufficient, and a

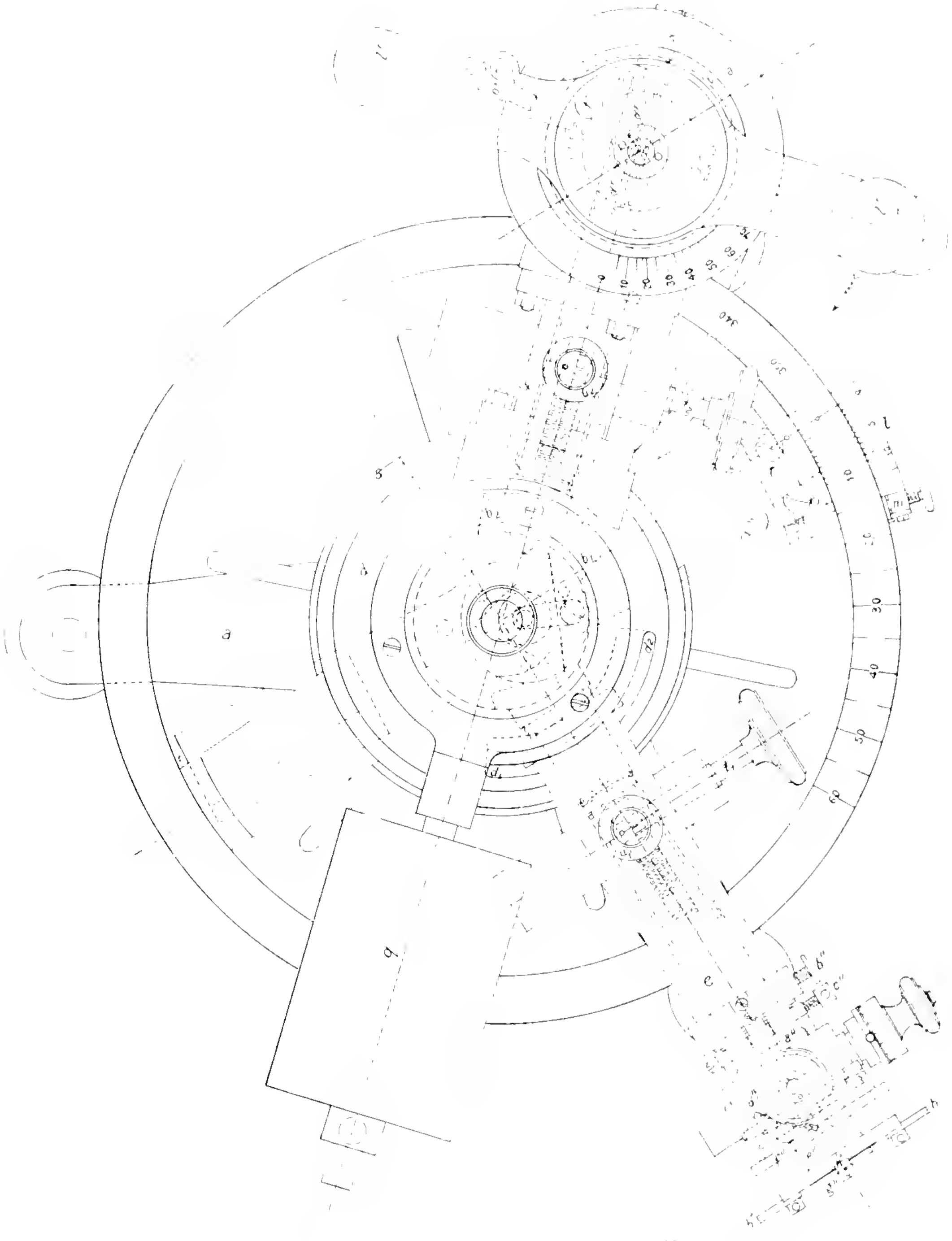


Fig. 9. Horizontal Plan of Spectrograph. Half Natural Size.

micrometer (not shown in the drawing) is connected with it, so that the angle may be read to two seconds of arc. This is used in the measurement of the wave-lengths with a plane grating and lens *in vacuo*. The six rods arranged star-wise about the main cone are handles of a large nut (see *s* in Fig. 9) which serves to loosen the outer cone in case the apparatus is to be taken down to renew the grease or for any other reason. For the greasing causes the two cones to cling together remarkably. The screws, w' (Fig. 8), of the camera and the nut, f'' (Fig. 9), of the slit-carriage serve similar purposes.

The entire spectrograph, with the exception of the main axes, the micrometer-screws, and the slit-jaws is constructed of brass. The air-tightness of the instrument depends no less upon the homogeneity of its material, especially of its castings, than upon the accurate workmanship of its execution.

All the closing surfaces of a chamber from which the air is to be exhausted, no matter how accurately they may be ground together, require, in order to sustain the vacuum, to be lined with a tightening medium. For this purpose, after having tried various kinds of grease, I employ a mixture produced by melting together five parts by weight of white wax with seven parts of the yellow vaseline of Chesebrough & Co. of New York,[1] the mixture being twice filtered through a hot funnel. Care must be taken to have it free from dust, since even small particles of dust, especially filaments, if they get into the grease between the smeared surfaces, may endanger the tightness. In the heats of summer it is advisable to diminish the proportion of vaseline. This grease is sensitive to light, and on exposure shortly turns dark yellow; but this coloration does no harm in the present case. I must warn experimenters against the employment of white vaseline; for (at least, when mixed with white wax) it oxydizes the brass-work quite considerably. The application of the coat of grease to the bearing surfaces is a matter of great importance for the tightness of the apparatus, as well as for its efficiency. Above all, before laying on the grease, the surfaces upon which it is to be laid have to be cleaned with the most scrupulous care. Then, having carefully examined them to see that no little filaments have settled upon them, one should lose no time in proceeding to the application of the grease. In doing this, I make use of a spatula of a thin lancet shape made of instrument-makers' dogwood (*Euonymus europæus*). The grease is to be laid on more or less thickly, according to the size of the surface; but in any case it should be applied as uniformly as possible. In the case of the great cones, I go all over the film so produced with my finger, which I have previously scrupulously cleaned, rubbing the grease in, in two directions. Of course, only one of two surfaces which are to be put together is greased.

When the surfaces are small and are optically plane polished, such as those of the fluorite window, the grease will better be laid on with the finest grade of photographers' retouching pencil, so that the film may be as thin and narrow as possible. If, in doing this, one keeps the line of grease as far as possible from the border of the inner opening, one will easily prevent any grease from getting into the interior of the apparatus when one puts the window into place, a dry strip

---

[1] In another part of this Report I have recommended watch-oil, — a discrepancy due to my only recently having resorted to vaseline, and to the circumstance that this description of the instrument has only been inserted in the report long after the main part of it was submitted.

remaining between the line of grease and the border of the opening. This is a matter of consequence; because any grease exuding into the inside gradually spreads over the entire surface of the window and powerfully absorbs the most refrangible rays. The state of the film of grease has, however, no greater influence upon the duration of the air-tight closure than has the form of the bearing surfaces. We know by the behavior of the glass cocks of the mercurial air-pump that cones without openings close tightly for years, even though they be in frequent motion, like the above-mentioned cones of the micrometers and main axes. Less trustworthy are plane annular and discoid surfaces, particularly if they be subject to frequent movement. Still less secure are rectangular surfaces that are subject to motion of translation. But the air-tightness is diminished in quite a surprising degree by openings through the bearing surfaces such as the passage of light or of the gas to be exhausted may demand. Such openings, as I have found in the case of optically plane surfaces, have a tendency to shove the grease together at the openings, and thus gradually to denude the bearing surfaces, and in this way to form a canal into the exhausted chamber; and this canal, though fine at first, soon increases in cross-section, so that the air, which at first enters only in excessively small amount, soon begins to pour in in larger volume, especially if the closing parts continue to be moved from time to time. When this sort of leakage once sets in, there is no other remedy than that of replacing the spoiled greasing by a fresh one. The circumstances most adverse to tightness are where there are plane slides moving rectilinearly over rectangular openings. Here the denudation of the surfaces from grease at times takes place after but little sliding back and forth; so much so, that, with some kinds of grease, I never could succeed in getting an air-tight closure. For such surfaces Chesebrough's vaseline, without wax, answers best. Slides of this kind ought to be provided with the largest possible bearing surfaces, such surfaces presenting a longer resistance to the tendency of the air to pour in. Here may be mentioned another inconvenience which regularly occurs as soon as the greased parts come to be frequently moved, as for example is the case with all the cones. The initial facile mobility of these parts is of short duration. After some use they begin to run considerably harder, and where the bearing surfaces are subjected to stronger air pressure they begin to oppose no little resistance to motion. This inconvenience is most felt in the cold part of the year when the grease is harder. This can only be remedied by frequent greasing of the surfaces in question. The considerable resistance which the great cones of the camera and of the prism-block offer to turning calls for an installation which shall prevent lateral displacement. Otherwise, the glass tubes leading to the air-pump will be exposed to constant danger of breakage. I have met this need in my spectrograph by bridging over [each of ?] its three levelling-screws with  shackles of the form here shown, so that the screws perfectly permit a vertical, but no lateral, motion of the apparatus. A still more detailed description of this spectrograph is contained in my report to the Imperial Academy of Vienna: *Sitzungsberichte der kaiserlichen Akademie der Wissenschaften in Wien; mathem.-naturw. Classe*, vol. cii, Part IIa, June, 1893, pp. 625–694.

The exhaustion of the spectrograph was effected by a Geissler mercurial air-pump. The source of light was usually a Geissler tube of the "end-on" form, the rays entering and leaving the tube through plates of quartz or fluor-spar. Occasionally, electric sparks from metals were employed. The discharge was furnished by a Ruhmkorff coil giving sparks of 25 cm., the primary current being derived from a number of Grove cells. The electromotive force and the intensity of the primary current were accurately measured. To furnish layers of the different gases for observations of absorption, air-tight brass tubes were interposed lengthwise, coaxially with the collimator, between the source of light and the spectrograph. They could be exhausted and filled with the gas whose absorption was to be studied. The lengths of the tubes therefore correspond to the thickness of the strata of gas which measured 65, 30, 25, 20, 15, 10, 5, 2½ cm. Most gases appear, even in very thin strata, strongly to absorb the rays of the most refrangible parts of the ultraviolet spectrum. Some gases exercise a general absorption, while others give characteristic rising and falling selective absorption-curves. Since these curves interest physicists for various reasons, I have constructed a special apparatus for the exhibition of them in the photographic way. This is shown in Fig. 10 in half its natural size. The principle of it is as follows:

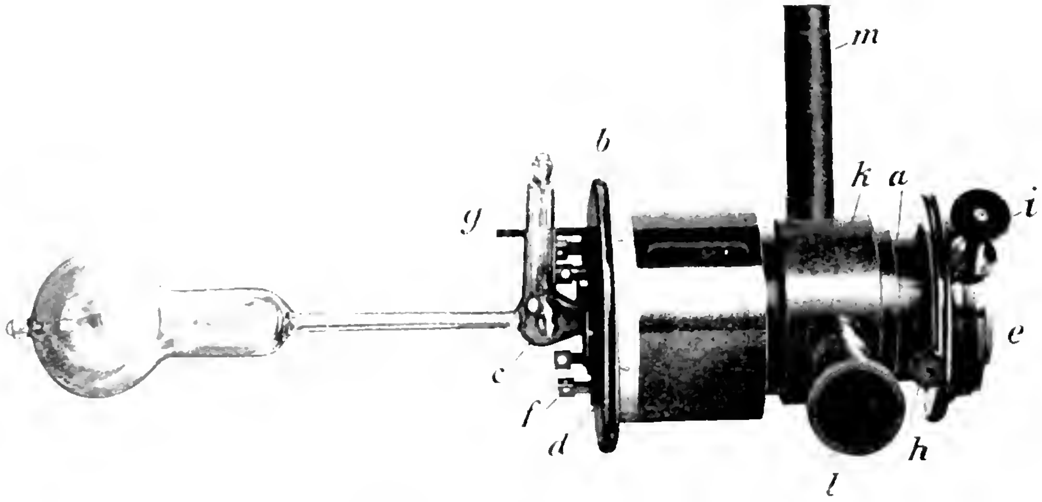


FIG. 10.—ABSORPTION APPARATUS—HALF NATURAL SIZE.

A Geissler tube filled with hydrogen, or other gas, sends its rays to the prism through a chamber of variable depth provided with two opposite and parallel walls of fluor-spar, and filled with the gas to be investigated at atmospheric pressure. One of the windows remains fixed, while the other can be so shifted in the direction of the rays that the distance apart of the two can be continuously varied from 0 to 15 mm. This distance is evidently the thickness of the plane-parallel gas-stratum to be investigated. This whole apparatus is put in the place of the cover of the slit-carriage marked *c′*, in the foregoing description of the vacuum-spectrograph, so that the capillary is in line with the produced geometrical axis of the collimator. The apparatus is constructed in detail as follows: The cover, *c* (Fig. 10).

that fits to the slit-carriage of the spectrograph is connected air-tight with the head of the absorption apparatus; that is, with a thick walled hollow cylinder of brass. In the interior of the hollow cylinder there is a tube of cast-steel which can be displaced along the axis by the aid of a milled-edged disk provided with a female screw-thread within. The measure of the displacement can be read upon the two scales visible in the picture; namely, the whole millimeters upon the longitudinal one, and the tenths of millimeters upon the circumferential one. Upon the face of the steel tube turned toward the cover, *e*, is fixed the fluor-spar window that is moved with the tube, while upon the inner plane surface of the cover, *e*, the other, which is fixed, abuts upon the central light-opening, which leads to the slit. The two windows remain in parallel planes, whatever their distance apart may be. The air-tight connection between the steel tube and the brass cylinder, *a* (Fig. 10), is effected by means of a ring of sole-leather turned upon the lathe and having a cross-section 3 millimeters square, this ring being pressed against tube and cylinder by means of an annular female screw. For the same purpose, the greatest care was taken in preparing the steel tube and its brass guide, to render the cylindrical surfaces precisely circular. To the milled disk, *b*, the Geissler tube, *c*, is fastened by its rim. As the medium of attachment the above-mentioned mixture of wax and vaseline is employed, a small amount being laid upon the rim of the tube. In this case the tube cannot be adjusted by a steel pin as it is adjusted to the cover *e*; and the following process has to be resorted to: The apparatus by the annular shoulder of *e* is stuck into a well-fitting ring, not too light, in which it can be steadily turned about its axis. A suitable pin-hole is now arranged, or better, a short-focussed reading-telescope is directed so as to place the middle of the mouth of the capillary upon the cross-wires. Then, by turning the apparatus round through 180°, and shifting the tube by a suitable amount, it will easily be accurately centered. Lest the centering so attained should be lost, which at first, before the exhaustion, might easily happen, while the tube is only attached by the grease on its rim, four guides, *d*, sliding in the radial grooves of the disk, *b*, are delicately pushed up against the wall of the tube, and are secured there by their screws, *f*. Further, to render the centering quite secure, the support *g* is required. The lateral part of the Geissler tube that carries electrodes should rest against this support throughout the operation of centering, and should continue to do so thereafter. These precautions would, indeed, be needless if the rim of the Geissler tube were precisely on the circumference of the base of a right cone having its vertex at the center of the mouth of the capillary. But this condition is not fulfilled, and could be only at great cost; so that the cheaper arrangement with the support, *g*, is preferable. What is indispensable is that the bearing surface of the rim of the tube should be optically plane and should lie in a plane to which the axis of the capillary is perpendicular; the former condition being required for air-tightness, and the latter for the uniform illumination of the slit.

The filling of the Geissler tube is performed through the spectrograph, which is for this purpose connected with an apparatus for the evolution of the gas wanted. The gas then flows in through the cock, *h*, and through a narrow channel continuous with this, and having its orifice near the Geissler tube. When the cock is closed, the tube continues to hold its gas while the spectrograph is exhausted. Although the gases of the tube and of the absorption-chamber are only separated by the steel tube, I have never found that even hydrogen entered the latter, diffusive as that gas is. The gas whose absorption is to be investigated flows into the absorption-chamber through the tube, *h*, and leaves it through a second tube placed diametrically and having its further end a little below the surface of some mercury. The mercury forms an escape-valve effectually preventing the entrance of atmospheric air, while a very slight over-pressure will cause an outflow.

The circumstance that the steel tube and its bearing are of different materials has the disadvantage that, owing to the different expansibilities of the two metals, the steel tube in the cooler part of the year does not move as readily as it should; and besides, the bearing may be injured. The bearing was originally fitted with great accuracy at the mean temperature of the room. Experiments that were instituted upon the appearance of this inconvenience showed that the reduction of the temperature by only a few degrees Celsius would suffice to damage the bearing and sometimes even the tube itself, if this were moved. Since the whole utility of an apparatus upon the design and construction of which no little pains had been bestowed was thus placed in jeopardy, I provided it with a little heater consisting of a water-jacket, *k*, to enclose the brass cylinder, *a*, at the point of the bearing of the steel tube, which water-jacket, by the aid of a funnel-shaped projection that stands vertical when in use, could be filled with water, and then, by means of the warming-tube, *m*, could be warmed to 27° C. by a little alcohol flame. At this temperature, or even a couple of degrees higher, the apparatus works faultlessly.

It may be thought that it would have been better to construct the whole apparatus of one metal. But there were certain technical objections to this into which it would lead me too far to enter here. It may be added that the apparatus has no pretension to universal applicability, being restricted to the study of such gases or vapors as are chemically indifferent to steel and to fluor-spar. The preparation of the atmospheric gases proceeded throughout in vessels connected by ground-glass fittings. The same thing is true of experiments with the gases which, as will be shown, enter as impurities into the Geissler tubes, such as CO and C_6H_6, whose influence, as appeared in the course of my investigation, required searching attention.

For photographic experiments ultra-violet plates prepared according to my process could alone be thought of, since the gelatine plates have not sufficient sensibility for rays beyond 185 $\mu\mu$. For although the gelatine plates are not completely insensitive for those rays, yet they are so inefficient that nothing more than a barely visible and worthless continuation of the spectrum appears in any case. The cause of this want of sensitiveness is, as I formerly proved, the want of transparency of the gelatine. By keeping this fact in view, I have succeeded, by persistent experimentation, in reducing the proportion of gelatine on my plates until it ceases to do any harm. The thickness of the sensitive layer is, at the same time, thus reduced to but one fifth of what it is upon the ordinary gelatine plates. To this diminution of thickness is due not only their sensitiveness for the most refrangible ultra-violet rays, but also their power of promoting the optical efficiency of the photographic apparatus. What adds to the importance of this fact is that if the spectrum is to be sharply defined over the longest possible portion of it, then the rays will not traverse the sensitive layer perpendicularly, but will, on the contrary, have an angle of incidence of 60° to 69°. The short focal distance (the focus at 589 $\mu\mu$ is 12 cm.) and weak dispersion (with a fluorite prism of 30°) of my spectrograph make the last named property of the ultra-violet plates incomparably more important in the present case than with instruments of stronger dispersion. And it is not the least of the advantages I owe to that property that the very small negatives of the part of the spectrum in question, in consequence of their uncommon capacity for enlargement, nevertheless answer the demands of exact spectroscopy. A numerical example will best show what my spectrograph was in this way able to do. In a part of the hydrogen spectrum about 160 $\mu\mu$ it resolved a length of 13 millimeters into more than 300 clearly marked lines. I need not say that very exact edges and very narrow opening of the collimator-slit were needed for this. My negatives measure 37 by 12.7 mm. The image of the spectrum appears upon them upon a ground as clear as glass. It bears a far greater enlargement than is possible with ordinary gelatine plates.

Filling the absorption and emission tubes.—The absorption-tubes were filled at the atmospheric pressure, at first merely by drawing the gas through them for a long time before the final filling. But it was found that the air was not in this way as completely expelled from the tubes as my experiments required, since even a small residue notably altered the transmissivity of the gas concerned. Consequently in the later work, the tubes were pumped out before the gas was allowed to enter, and were then repeatedly washed out with the gas. The connections of the apparatus for the evolution of the different gases with the absorption-tube would have been much easier manipulated if india-rubber could have been used for them. But my experiments showed that such tubing, because of its exhalations, if for no other reason, may introduce such impurities into the tube as to render it not fit for use, giving the spectrum a totally different appearance. I also ascertained that leakage of air was to be feared even with the thickest india-rubber tubes. For example, through an exhausted Para-rubber tube of 10 centimeters length, 1.15 cm. external diameter, and 0.35 cm. internal diameter, 2.4 $(\text{cm.})^3$ of air passed in fifteen hours. But I attribute only a subordinate prejudicial effect to the air that was carried in through this tube along with the gas, because the washing out and filling of the absorption-tube was at that time done at the ordinary pressure, so that but a very small amount of air would enter, and because there was nothing in the appearance of the spectrum as altered by the influence of the rubber to suggest the influence of air. This opinion was confirmed by the circumstance that when this tube of Para-rubber was replaced by a tube of black rubber, such as is often used to make connections of chemical apparatus, the distribution of energy in the spectrum underwent a new change: namely, while with the former tube the spectrum was weakened generally, the use of the black tube completely annulled the effect of the rays at a wave-length of about 162 $\mu\mu$ through an extended stretch. This behavior of india-rubber led me, in the sequel, to construct the apparatus only with glass tubes and a metallic-screw closing device, which depends upon having optically plane surfaces which are pressed together with great force. I have used this clamp for different purposes and with constant success.

In the preparation of the emission tubes (Geissler tubes), several difficulties arose. The first of these lay in attaching a suitable window; for glass is entirely opaque to such short waves. Quartz is eminently proper for the purpose, and fluor-spar is still more so, since it allows the most refrangible rays to pass freely, which quartz, as is well known, does not. Quartz has the advantage of greater hardness, which is no small consideration owing to the frequency with which the windows have to be taken off and cemented on again. Fluor-spar is relatively soft and in constant use, especially when its surfaces are often cleansed, is hard to preserve from damage. Moreover, there is a circumstance which has narrowly limited its applicability for the windows of Geissler tubes in my experiments. The state of things is this. With Geissler tubes we are led to employ the end-on form for the most refrangible ultra-violet, because it gives a greater emission of light than the cross-wise tubes, and, besides, it is better adapted to the insertion of a plane window. I follow the usual practice of giving such a tube a plane rim at one end upon which the window is readily fastened. But this closure, to be absolutely staunch, is a more difficult matter with the rays here concerned than one would think. The closure must fulfil three conditions, to wit: 1st, it must cut off the photographic energy as little as possible; 2d, it must not soil the purity of the gas in the tube; 3d, it must easily be removed without damage to tube or window. But none of the plans for closing tubes hitherto known satisfy these conditions, not even the grinding out of quartz in the manner published by me in 1886, since, because of its great thickness, it absorbs too much refrangible rays. For my experiments, therefore, a more suitable method of closing had to be invented. Of several processes to which my thorough trials led me, the following has satisfied me best: The rim of the tube and the closing plate, which latter should only be 1 mm. to 2 mm. thick, after being carefully cleaned, are put together and held with a clamp which must not be too large, so that there can be no lateral displacement. Then the joint between the tube and plate around the latter on the outside is to be painted with a thick coat of soluble soda-glass. After two or three hours, when it is dry, a second coat is to be applied. A third would make the tube stauncher, but it is not absolutely necessary. Such a tube will bear the highest exhaustion that a Geissler tube can take, while by scraping away the crust of water-glass with a knife, which is easy, the tube is opened without trouble and readily closed again. The convenient opening and closing is an important point in observations of the ultra-violet, because the inner surface of the quartz window often after a brief use gets a deposit upon it, which partly absorbs the most refrangible rays, and, indeed, sometimes entirely cuts them off, an inconvenience which is the more troublesome because the deposit is generally invisible to the eye. Water-glass proved most useful with quartz, but did not work well with fluor-spar. In this case, the layer of luting loosens itself, usually in a short time, from the fluor-spar and crumbles away. Of course, this throws doubts upon the security of the closure. It is possible that a much thicker coat than that I used would answer better. I have not, however, tried it, but have employed as luting for the fluor-spar a mixture of white wax and clock-maker's oil, which is spread in a very thin layer forming a band half a millimeter broad, in a ring round the end of the tube. Now pressing down the fluor-spar disk a neat and perfect closure is obtained; and it is loosened even easier than the water-glass. It has, however, the inconvenience of soiling the gas in the tube after long illumination, by producing fatty vapors.

The source of light for the absorption experiments.—The best thing for this purpose would be a Geissler tube which should give a continuous spectrum of equal intensity of energy in all parts. Unfortunately, no single tube meets this requirement completely. The hydrogen tube, however, does so in part, giving a continuous spectrum down to 170 $\mu\mu$, where begins a rich line spectrum of tolerably uniform distribution of energy. Such a tube closed with fluor-spar has given me good service in my absorption experiments, particularly by its continuous spectrum. A merit of it not to be undervalued when long exposures are required, as they sometimes are, is that it has an uncommon photographic brightness. For comparison spectra I have employed the spark-spectra of hydrogen, aluminum, and cadmium, which were photographed beside the absorption-spectra.

The source of light for the emission-spectra.—These spectra were given by Geissler tubes of different shapes and arrangements, closed with quartz. Some of these tubes, after being filled, remain in connection with the air-pump, so that they can readily be emptied and refilled. Others are melted off like ordinary Geissler tubes, before they are attached to the spectrograph. For some investigations, however, none of these tubes will answer. In such cases, Paalzow-Vogel tubes of the Paschen-Runge pattern were preferred. In these, the place for the discharge communicates at both ends through liquid valves, of which one consists of sulphuric acid and the other of a solution of bichromate mixed with sulphuric acid, with which the air-pump is so connected that the pumping out of the tubes can go on unhindered, while the vapors from the mercury and from the grease of the pump-cocks are kept away from it. At the same time, the sulphuric-acid valve of such a tube, of which the receptacle is arranged as an apparatus for evolving hydrogen and oxygen electrolytically, serves to produce the oxygen and hydrogen to fill the tube.

The filling of the tubes has hitherto been limited to

Nitrogen
Oxygen
Water
Carbon monoxide
Carbon dioxide
Hydrogen.

These gases have been in part obtained from the atmosphere, and in part have been chemically or electrolytically produced. After being carefully purified, they were dried with phosphorus pentoxide and in some cases with sulphuric acid.

The pressure in the absorption-tubes was equal to the atmospheric pressure at the time. In the emission-tubes, it varied from 0.05 to one centimeter of mercury-pressure.

The electric discharge was effected either by the Ruhmkorff coil alone, or with a Leyden jar, or Leyden jar and spark gap interposed into the circuit, or a Leyden jar and a Hemsalech self-induction coil. The primary current never exceeded 2.5 amperes and 10.5 volts.

Difficulties. Before I touch upon the results thus far obtained, I must allude to a phenomenon which I encountered as soon as I took my first emission-spectrograms. The fact substantially was this. I photographed the spectrum of a Geissler tube filled with air, and obtained a spectrum of considerable photographic effect compounded of numerous thickly successive bands shading off on the red side. Numerous repetitions of the experiment confirmed the result. I concluded from this that I was dealing with the spectrum of air or, at any rate, of one or more of its ingredients. But when I came to examine the latter separately, as I had done the air, I found that the same supposed air-bands dominated every one of them. With carbon monoxide and carbon dioxide, however, they were much stronger; while with water and hydrogen they were weaker. After comparing these photographs with one another, no room for doubt seemed to remain that these bands belonged to a carbon compound which presumably had been derived from the fat of the air-pump cocks and from the occluded and absorbed gases of the inner wall of the tube. However, increased care in cleaning the tubes and in the production of the gases to fill them, from which I promised myself better success, made no difference; the bands remained as strong as before. Now, in order to keep the air-pump vapors of the cock-fat and mercury completely away from the place of discharge, I exchanged the Geissler tubes, which had up to that time been employed, for Paalzow-Vogel tubes. By way of greater precaution, these tubes, before being used, were cleaned for twelve hours with a solution of bichromate of potassium in concentrated sulphuric acid, to destroy any impurities of organic origin which might be present, and were then repeatedly rinsed out with distilled water, and were forthwith closed with a quartz window and water-glass, and dried by the air-pump, though the two sulphuric-acid valves of the tube itself had in the main effected this. In this way, the penetration into the tubes of particles of dust, which might have occasioned the formation of carbon compounds, was as far as possible prevented. By thereupon washing out the place of discharge with oxygen which was evolved from the sulphuric acid of the electrolytic apparatus belonging to the tube, I promised myself, judging by the visible bands of carbon compounds, the sure attainment of my object. Still, these means too proved without effect. Thereupon the suggestion presented itself that occluded gases from the aluminum electrodes might have caused the bands, and the electrodes were laid aside and replaced by glass cylinders covered with tin-foil. But in spite of all, the bands after this alteration remained intact. The tubes were now furnished with new aluminum electrodes obtained from another source, but there was no change in the spectra The bands afterwards, as before, were the regular accompaniments of the photographs of the spectra of hydrogen and of oxygen. As a last attempt in that direction, I shall use a form of Geissler tube which is under construction and which is so arranged that, in the cleaning during exhaustion, a far more energetic heating can be attained than was possible for the tubes previously employed.

It ought not to go unmentioned that all the tubes were observed with a spectroscope both during the cleaning and during the photographing of the spectrum without any impurities making themselves noticeable. This shows how little the visible spectrum can serve as criterion of purity, in filling a tube. The most refrangible ultra-violet is far better adapted to the purpose, and according to my observations, the most sensitive spectral reactions belong to the region of the shortest waves.

Production of the ingredients of air and the spectrographic results. I pass now to the results directly relating to my investigation. Since these results are not complete, notwithstanding my numerous experiments, I can in this preliminary communication only give the most important of them, and not even those without reserve. For it is clear that, as long as the question of the origin of the supposed bands of oxide of carbon is open, a not inconsiderable measure of uncertainty attaches to them all. Besides this, substantially nothing is known of the part of the spectra of gases to which my observations relate, so that at no point did any information come to me from the scientific literature. Finally it ought not to be forgotten how difficult the analysis of the facts relating to spectra in Geissler tubes has, at all times, been found, and how little we really know about the subject to-day, notwithstanding the fact that scarcely any other part of spectroscopy has occupied so much acumen and gift for observation as the exploration of the spectra of electrical discharge-tubes.

I begin with the spectrum of

Nitrogen.—It was prepared in two ways: first, by passing air over potassium pyrogallate; and, secondly, from potassium nitrate and ammonium chloride. It was dried with phosphorus pentoxide, over which the gas remained standing for some time before it was passed into the tube. Nitrogen proved itself very transparent, even beyond 162 $\mu\mu$; yet it absorbed particular wave-lengths very energetically. Its emission-spectrum consists of a number of groups of bands of moderate photographic power shading off toward the shorter wave-lengths and ending below (that is on the less refrangible side of) 185 $\mu\mu$. The observation of this spectrum is uncommonly interfered with by the bands of carbon monoxide overlying it. Beyond 185 $\mu\mu$, I have been unable to prove any nitrogen bands.

Oxygen.—Electrolytically formed oxygen was exclusively employed. The carbon dioxide which was invariably present in small amount at the beginning of the evolution was eliminated by caustic potash; the aqueous vapor, by phosphorus pentoxide or sulphuric acid. In passing to the absorption-tube, the gas was strongly heated in order to destroy the ozone. Oxygen absorbs the rays in the neighborhood of 185 $\mu\mu$ in a series of clearly resolved groups of lines, fourteen in number. These groups, which are of band-like form, constantly approach nearer one another with their deviation, and are shaded off toward the red. Complete absorption is found with the most refrangible of them. It is this which makes the air opaque for all rays beyond 185 $\mu\mu$. The presence of a moderate amount of ozone did not alter the absorption at all.

The emission-spectrum of oxygen is compounded of three continuous maxima, of which the most refrangible is the strongest. It lies at about 185 $\mu\mu$. The observation of these maxima is attended with considerable difficulty, on account of their slight photographic efficiency and because of the bands of oxide of carbon which appear with them. It succeeds best with a Paalzow-Vogel tube and 10 to 16 mm. of mercury pressure. With much smaller pressure even these tubes, though completely guarded against fat and mercury, gave dominating bands of carbonic oxide which hardly allowed the oxygen maxima to appear. It is surprising that I have in this region never obtained lines of oxygen. True, traces of them sometimes emerged upon the maximum near 185 $\mu\mu$, but as soon as I tried to bring them out by longer exposure, the bands of carbonic oxide appeared and covered the supposed lines, so as to make them invisible. Nor was it possible, notwithstanding numerous attempts, to bring out more refrangible rays than those of the maximum at about 185 $\mu\mu$. It may well be assumed that the stratum of oxygen between the capillary opening and the window of the Geissler tube contributed to the ill success of this search by its defective transparency. This stratum might be considerably reduced in thickness, were it not that the deposit on the window would then become worse. Now this inconvenience seems to come on earlier with oxygen than with other gases. For that reason, I have not reduced the thickness of the stratum of this gas below 2 cm., though with others I have not hesitated to go down to 1 cm. The deposit on the window takes place very easily with the Paalzow-Vogel tubes, especially if they have an outer covering, and is a very inconvenient adjunct of them. In this case, in a few hours' use, it often goes so far as to produce complete opacity. The opening and reluting of the window thus necessitated is not only a waste of time, but, on account of the filling with sulphuric acid, a very dubious piece of work.

Carbon dioxide.—This gas was prepared by the action of hydrochloric acid upon calcium carbonate. The gas was twice washed with a solution of sodium bicarbonate in water in order to eliminate the hydrochloric-acid vapor. It was dried with phosphorus pentoxide.

The absorption-spectrum of carbon dioxide is similar to that of oxygen. Here, too, there are indications of a rhythmical series in the shape of inverted groups of lines. But the end of this series is considerably more refrangible than that of oxygen. Accordingly, total absorption begins at a shorter wave-length.

The emission-spectrum is overlaid with the bands of carbon monoxide, the unwelcome attendants of all my spectra. Its photographic action is uncommonly strong, and it extends far beyond 162 $\mu\mu$ into the region of the shortest wave-lengths. I doubt not that, were the tubes sufficiently transparent, it could be photographed as far as the hydrogen spectrum extends. For its wealth of lines it stands unrivalled. I have not been able to make sure whether these bands really belong to carbon monoxide or not. The carbon dioxide itself seems not to participate in the photographic effect. For even the freshly filled tubes gave during the first discharges no other spectrum than the later photographs. Since the dissociation of the carbon dioxide, which according to the general assumption precedes these occurrences, is dependent upon the height of the temperature, I have made preparations to institute experiments in which the heat of discharge shall be far below that of the tubes I have hitherto used. I hope, in this way, to obtain better information than I have hitherto concerning the spectral behavior of carbon dioxide.

Carbon monoxide.—This concerns us here less as an ingredient of the atmosphere, which contains it in very small amount, than as one of those impurities of Geissler tubes which have at all times created the greatest obstacle to the spectroscopic investigation of gases. Carbon monoxide was prepared: 1st, from oxalic and sulphuric acids; 2d, from yellow prussiate of potash and sulphuric acid; 3d, from formic and sulphuric acids; and it was then washed with caustic potash solution to retain the sulphur dioxide or the formic acid, as the case might be, as well as traces of carbon dioxide.

Carbon monoxide absorbs the most refrangible rays somewhat less than carbon dioxide, and gives, like oxygen, a series of rhythmical, inverted groups of lines. The clearness and sharpness of these lines are less than with oxygen, but far more perfect than with carbon dioxide.

The emission-spectrum has already been sufficiently considered in treating of that of carbonic dioxide, so that I have nothing to add here upon the subject.

Aqueous vapor.—The filling of the Geissler tube was effected from a small glass vessel with a faucet containing a few drops of distilled water. This vessel was melted on laterally to the tube connecting the Geissler tube with the air-pump. Aqueous vapor was evolved in the absorption-tube by introducing into it before exhaustion a little cup containing a few drops of water. Then, by pumping out the tube repeatedly, it was at last filled with aqueous vapor free from air. Unfortunately this process has not, thus far, led to certain results, in consequence of the deposit of dew. I must, therefore, reserve a report upon this matter until these experiments have been repeated. What takes place in the tube of aqueous vapor is not clear. The spectrum differs according to the mode of discharge. It consists mainly of hydrogen lines, of the oxygen maximum of 185 $\mu\mu$, and of a great number of other lines, concerning which I have not yet been able to make quite sure whether they belong to aqueous vapor or not. Upon these spectra is laid, in addition, the more or less intense spectrum of carbon monoxide. Finally, by a suitable choice of pressure, form of tube, strength of current, and mode of discharge, all these spectra can be greatly weakened and the spectrum of the electrodes of the tube brought out. My numerous observations indicate a regular dissociation of the aqueous vapor into its elements accompanied by a simultaneous recombination to form water. I have been led to this conclusion more particularly by the study of the spectra of certain Geissler tubes which carried an absorption vessel or drying vessel, as the case might be, which was cut off from the proper place of discharge by a mercury valve, the arrangement being such that the vessel could be opened and closed without trouble by simply turning the tube about its capillary axis. The absorbents used were phosphorus pentoxide, sulphuric acid, and platinum black.

There is a phenomenon which readily comes into play in the Paalzow-Vogel tubes which I regard as affording a more certain proof that oxygen and hydrogen combine under the electric spark even at a pressure of but a few millimeters: namely, if such a tube be filled with a mixture of the two gases, its initial brightness rapidly falls off, and after a short time the tube fluoresces in the highest degree. But the capillary shines forth more or less brightly. The only possible explanation of this phenomenon is that, after oxygen and hydrogen have combined to form water, this is promptly absorbed by the sulphuric acid, which affords a relatively large surface, and that there is consequently a great diminution of pressure, giving rise to the fluorescence. The gases were not mixed by me in equivalent proportions, so that, after the formation of the water, one or other must have remained in excess, and this excess, enjoined with the ineradicable carbon monoxide from the impurities of the tube, would occasion the light in the capillaries. But although I followed these phenomena spectrographically, I have never obtained the lines which, in the other spectra of aqueous vapor, can be regarded as water-lines. Still, a reason for the Paalzow-Vogel tubes not giving these lines may be found in the circumstance that the vapor was too quickly absorbed by the sulphuric acid to give a spectrum for a sufficient time to make an image capable of being photographically developed.

Hydrogen.—Armand Gautier found that this gas in the free state occurs in the air in no negligible proportion. I should, therefore, in any case, have had reason to include it in the list of ingredients of the air here investigated. Besides that, it affords me an admirable comparison spectrum. For none of the spectra with which I have become acquainted beyond 185 $\mu\mu$ has its energy so uniformly distributed and such a wealth of lines as this. Nor is there any that extends so far as that of hydrogen.

The gas was produced from the purest chemicals, sometimes chemically, sometimes electrolytically; and moreover, where it seemed necessary, it was most carefully purified by sodium hydrate, silver sulphate, and potassium hydrate. Particular pains were taken in drying it; for the gas for the final experiments flowed through three successive vessels, filled with phosphorus pentoxide, with stop-cocks in their connections, in such a way as to remain for some time enclosed in each before it was allowed to escape into the next.

The transparency of hydrogen had appeared by my former experiments to be uncommonly great. But my new experience has shown that it is a matter of great difficulty to attain perfect definiteness on this point, since the production of thick strata of pure hydrogen is well-nigh impossible. The walls of the place of absorption will, even with the most scrupulous cleansing, always at last secrete small amounts of gaseous impurities; and these will affect the transparency of hydrogen more proportionately than they would that of other gases, precisely because its transparency is so extraordinarily great. At any rate, it is in that way that I explain the repeated contradictions in the results which I have obtained for the absorption of this gas at different times. I accordingly abstain from making further statements upon this subject.

The spectrum of hydrogen ends, according to my latest results, far beyond the limit which I obtained in 1893 with the apparatus I then used, and which by a merely estimated wave-length I placed at 100 $\mu\mu$. This estimate, as will be later shown, was by no means correct. The number of lines in the photograph, which, magnified 20 times, has a length of 1.4 meters, and of which a portion is shown in Plates I–III, I estimate as at least 1500. Hydrogen develops its highest photographic efficiency at 162 $\mu\mu$. At the supposed wave-length of 100 $\mu\mu$ its effect suddenly diminishes, and this is still more marked if in the path of the light from the tube to the photographic plate, one or more fluor-spar plates are interposed, a thing which the arrangements of the apparatus not infrequently call for. A single such plate 1 mm. thick may weaken the photographic effect at 100 $\mu\mu$ by one half. The thickness of the plate is a secondary matter, for the loss of light depends chiefly upon the number of reflecting surfaces. We may conjecture that the cause of the enfeeblement lies in metallic reflection, possibly aided by absorption of light exercised by gases which these surfaces condense. The weakening is by no means limited to the region mentioned, but with longer waves it is greatly diminished. It may be conjectured that, on the other hand, it increases with shorter waves.

I proceed to give photographic reproductions twenty times enlarged from my photographed spectra. They are the only photographs of the hydrogen spectrum which have been obtained up to this time *in vacuo* or in an atmosphere of hydrogen. In consideration of the not inconsiderable difficulties which had to be overcome in their production, and which still oppose the repetition of the experiments, it may not be deemed superfluous to enter into the details of the taking of this photograph further than, for ordinary photographs of spectra, is either necessary or usual. Vacuum-spectrography can be accomplished even now only under conditions of great difficulty.

The spectrum that is mapped is that of the light of an end-on Geissler tube with a narrow capillary, such as is shown in Spectrum 5, Plate II. This tube was connected with the collimator of the spectrograph. The four originals of the first eight enlarged photographs of this spectral series were obtained with a fluor-spar window interposed between the tube and the collimator. The other four were made without the window, since the spectra that they show would be unduly weakened by the window, and the time of exposure thus rendered extraordinarily long. In the former case, with the window in, the tube and spectrograph could be filled and exhausted independently of one another. But in the latter case, where tube and spectrograph were in communication through the open hole in the slit-cover, both contained hydrogen at such a pressure as the electrical discharge demanded. Since this pressure is only that of some centimeters of mercury, at highest, and since hydrogen is very transparent, since the depth of hydrogen through which the rays had to travel was only 30 cm., since the deviation of the rays by the hydrogen must have been extremely small owing to its small refractivity, and the taking up of any impurities by the hydrogen in the interior of the spectrograph could not seriously be feared, considering the many years during which it has been in use. I do not think that any of these sources of error can be supposed to have affected the correctness and purity of the photographs obtained.

The rays in their passage to the photographic plate traversed a hydrogen atmosphere of moderate density, and not the exhausted interior of the spectrograph only. For the first five photographs, the gas, most scrupulously purified and dried, was led directly into the discharge-tube, and thence into the air-pump. In this way the tube was continuously traversed and eventually filled with gas which must have been either altogether or very nearly free from mercurial vapor. For the other seven photographs the hydrogen, obtained by the action of the purest zinc upon the purest sulphuric acid, and afterward dried, was led through two meters of the air-pump tubing before entering the spectrograph and thence into the Geissler tube. Consequently, it could not, in this case, be so free from mercury as in the other. I have not, however, been able to perceive any particular disadvantage from the presence of the greater amount of mercury.

The induction-current was given by a Ruhmkorff coil, fed by 5 Grove cells and giving sparks 25 cm. long. The effective rays from the tube[1] traversed successively the fluor-spar window, the collimator-slit, the first lens, a 60° prism, and the second lens, over against which was the plate sensitive to ultra-violet light. The lenses and prism are composed of white fluorite. The lenses were plano-convex and had the same focal length, namely, 120 mm. for sodium yellow. The equality of the focal lengths made proper positions of the lenses to be at equal distances, the one from the slit and the other from the mid-plate. Since the refrangibility of the short-wave rays increases very fast in fluor-spar with decreasing wave-length, the focus rapidly shortens with the wave-length. The consequence is that the scale of the image of the line diminishes from the less refrangible to the more refrangible end of a photograph. In photographs patched together to show a long stretch of the spectrum this difference of scale makes itself unpleasantly noticeable, owing to the varying breadth. But on such short photographs as these of the hydrogen spectrum it may be neglected.

When there was no particular reason for placing the prism symmetrically to the course of certain rays, the rule was to give their minimum deviation to the most refrangible lines of the part of the spectrum to be photographed at one exposure; for this is the only way to get a uniformly sharp definition throughout the stretch photographed. If rays are to traverse the prism symmetrically, it will only be necessary, while preserving the equality of the foci of the two lenses and the minimum of deviation, to turn the camera-tube until those rays fall on the middle of the plate. For, as Fig. 9 shows, the camera is so constructed that, whatever may be the angle between the plane of the photographic plate and the axis of the lens, this axis must always cut the mid-vertical of the sensitive side of the plate, which coincides with the geometrical axis of the camera-cone. The considerable obliquity of the plate to the axis of the lens has, along with the advantage of about

---

[1] To protect the window from possible heating, the electrode farther away from the slit was made the cathode.

doubling the image of the spectrum, the disadvantage of rendering the operation of focussing difficult, inasmuch as the image of the slit partakes of the same enlargement; so that, for example, the breadth of lines of about 185 $\mu\mu$ will be somewhat more than double the width of the slit, while lines of about the shortest wave-length hitherto photographed will be somewhat less than double the width of the slit. The edges of such a broadened spectral line correspond accordingly to two different focal distances. This difference becomes proportionately more noticeable the wider the slit and the shorter the focus. Since in my hydrogen photographs foci down to 70 mm. occur and a width of slit of 0,010 mm. corresponds nearly to a difference of focus of 0,02 mm., it might be concluded that under circumstances so unfavorable no spectra good for anything could be produced. Nevertheless photographs of this sort are clearer than might be expected. The reason is that with this relatively wide slit the scattering of the rays by diffraction is of less importance than with narrower slits, although with the latter the disadvantage of the difference of foci of the two edges is not noticeable. I shall return to the subject below. But a more serious difficulty arises from this cause; and an acquaintance with it is desirable in adjusting a vacuum-spectrograph for the different photographic fields within its reach. The state of things is this: Before a vacuum-spectrograph is set to its regular work, it should be calibrated. That is to say, for each photographic field the following constants should be definitively determined: the focal distances, the minimum deviation, the angle between the two optical axes, the angle between the sensitive plate and the optical axis of the telescope. I distinguish, for my apparatus, nine such photographic fields beyond 185 $\mu\mu$. Suppose, now, that the observer has gone through with this arduous task of calibrating his spectrograph for its entire range, and has performed it with a somewhat wide slit; for to save time in the exposures he will naturally prefer to do it so. He will take, let us say, a width of 0,01 mm., and although his slit opens unsymmetrically, he will assume that this same adjustment is applicable for narrower slits. But with these he will find that the greatest sharpness of image has not the focus found for the wider slit, but a somewhat different one; that, moreover, for the attainment of the highest sharpness of images the lenses can now be adjusted incomparably more finely; and finally, that the useful part of the spectrum has materially suffered in length. The principal cause of this phenomenon is the oblique position of the photographic plate with reference to the optical axis; but the unsymmetrical variation of the slit-width, that is, the assumed fact that the slit-carriage has only one movable jaw, aggravates it. It might seem that the difficulty could be obviated by a symmetrical slit. But little could be gained in that way; since the symmetrical motion of the slit-jaws with a slit of a micron's width will present to the instrument-maker insuperable difficulties, as I have sufficiently convinced myself by extensive experiments with slits of the highest precision I could construct.

The reason why, with a plate standing obliquely to the optical axis, the focus depends upon the width of the slit, appears from the following considerations: Suppose the focus for any spectral line has been ascertained with a very narrow slit, say for a slit of width 0.001 mm.; and it is proposed to photograph the same line with unaltered setting, but with a slit of width 0.005 mm.; then undoubtedly that border of the line which corresponds to the stationary edge of the slit would remain in focus, and retain its original sharpness, while the other, since the altered position of the slit-edge corresponds to a different focus, and its image consequently no longer falls within the sensitive film, would become less sharp, and the less so, the more the slit is widened. A good photograph, in short, can now only be obtained after a new focussing has rendered the two edges of the line equally hazy.

Of course, as far as resolution is concerned, photographs taken with a wide slit are greatly inferior to those with fine slits. When the fineness of single lines is desired, as in the measurement of wave-lengths, or the resolution of dense groups of lines, the slit must be narrowed to its utmost. In such cases, I have gone down from several microns to a single micron. Good results of this sort can only be expected with faultlessly linear and sharp-edged slit jaws. Rounded slit-edges and those formed by little planes, such as are found in the majority of spectrometers, are not adapted to the purpose, since the image of the slit is broadened by the light reflected from the sides, and consequently their resolving power is greatly injured. The duration of exposure and that of development must, if the desired fineness and sharpness of the image is to be attained, be scrupulously adapted to this purpose. Otherwise, the line will be too thin or broadened by diffraction to utter worthlessness. But with some painstaking one soon succeeds in photographing lines so fine that they are only formed of one or two rows of grains of silver somewhat coarser than the average and, it must be admitted, not quite regularly distributed. The hydrogen spectrum shown affords some examples of this kind. But let it be expressly noted that the spectrum, with all its lines, can never be successfully photographed with slits of 1 μ or 2 μ, supposing that it contains many thickly crowded lines of very different intensity. The stronger lines, with a time of exposure suited to the weaker ones, acquire great broadening, giving them a washed-out look unadapted to measurement. This is my reason for photographing every one of the fields in the spectrum of hydrogen four times over with increasing time of exposure and sometimes with widened slit. This proceeding is the best adapted for carrying the resolving effect of a vacuum-spectroscope of such slight dispersive power to its highest. If we compare the dispersion of this prism-spectrograph in the most refrangible ultra-violet with that of a grating-spectrograph, the latter will turn out, notwithstanding its considerably longer focus, but moderately superior. A numerical example will best show this. In the vacuum-spectrograph, when the aluminum lines at 1989.90 and 1854.09 Angström units (focal length *in vacuo* 106.75 mm.), with a 60° prism appear at the middle of the plate, they are separated by a distance of 5.8 mm. from one another, while in the spectrum of the first order of a grating-spectroscope belonging to me (having a concave grating of 106 cm. radius and 14,439 lines to the inch), they are separated by 8.2 mm. as measured on Rowland's circle. With increasing refrangibility this ratio varies more and more to the advantage of the prismatic spectrum, so that for the shortest wave-lengths it is superior in dispersion to the grating spectrum of the first order.

In the spectra shown in Plates I–III (spectra 1 to 12) the refrangibility increases from left to right and with the numbering of the strips. It begins, at the least refrangible end, with a continuous spectrum of weak intensity, after which come, first, some faint lines, but then numerous and remarkably strong lines. The continuous spectrum, which is a peculiarity of hydrogen, reaches down without interruption from here to the line 369.9 *μμ* (Ames). The few lines that are found in it probably belong, not to hydrogen, but to slight impurities of it, among which mercurial vapor from the air-pump may well be the chief. Some spectroscopists incline to regard the continuous spectrum itself as a consequence of these impurities, but I am unable to bring myself to this view because of many experiments with very pure gases and with different tubes. It must not, however, be concealed that the intensity of the continuous spectrum is connected with the purity of the filling of the tube. The more scrupulously the gas within the Geissler tube is purified, the weaker becomes the continuous spectrum. But I have never been able to bring about its complete disappearance provided the exposure was long enough.

The numbers in the table on p. 24 will serve as an approximate measure of the photographic activity of these rays on the one hand and of the sensitiveness of the ultra-violet plate on the other.

The first column refers to numbers in my spectroscopic journal.

The "camera-angle" is the angle between the plane of the photographic plate and the optical axis of the camera-lens.

The lines of exposure refer to the taking of the original negatives of the four parts of the plate.

The width of the slit was altered by movement of one jaw only, and the effect of this asymmetry is plainly visible in the photographs.

The values given for the current are merely the values without the coil, when it was short-circuited. These, as well as the times of exposure, are merely given so that differences in the different photographs should not be attributed to variation either of the energy of the rays or of the width of the slit.

The first eight enlargements correspond to only four originals, as each of these originals is twice as long as those of the last four. This is due to the fact that the image for the first two thirds of the spectrum is much flatter than for the last third and so permits photographs twice as long.

The enlargements were performed with a projection-combination with an aperture of 75 mm. by Carl Zeis of Jena. It is the most perfect objective for this purpose in the world.

The dots and little spots are on the originals, being due to slight defects of the coating of the plates which belonged to the method of making them that I still employed in 1895, when these spectra were photographed.[1]

---

[1] V. Schumann: On an improved process for making sensitive plates for the ultra-violet *Annalen der Physik*, vol. v., pp. 349–374, 1901.

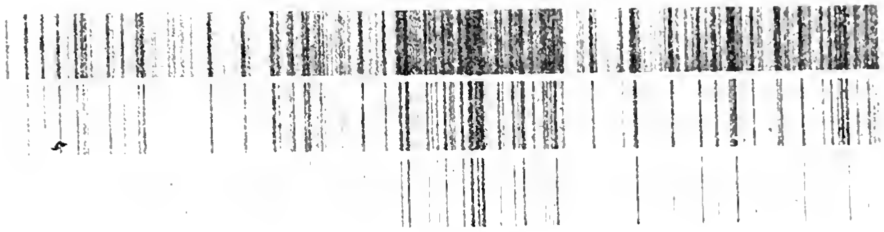
[illegible]	[illegible]	Exposure	Width of slit	Amperes	Volts	No. of the Enlargement
[illegible]	8	1 [illegible] min. 2 [illegible] " 3 [illegible] sec. 4 [illegible] "	[illegible]38 mm. " " " " .0213 "	13.[illegible]	7.7	1 and 2
[illegible]	2[illegible] 75	1 [illegible] min. 2 8 " 3 2 " 4 45 sec.	1.0025 mm. " " " " " "	8.0	7.7	3 and 4
[illegible]	7[illegible]25	1 20 min. 2 6 " 3 2 " 4 1 "	[illegible]038 mm. " " " " " "	21.5	8.1	5 and 6
4138	29.[illegible]	1 50 min. 2 20 " 3 8 " 4 3 "	[illegible]0050 mm. " " " " " "	13.9	7.8	7 and 8
4170	32.5	1 20 min. 2 10 " 3 5 " 4 2 "	" " " " " " " "	25.5	7.6	9
4186	34	1 45 min. 2 16 " 3 8 " 4 4 "	0.0063 mm. " " " " " "	16.0	7.5	10
4194	36	1 35 min. 2 16 " 3 8 " 4 4 "	0.0075 mm. " " " " " "	24.5	7.5	11
4199	3[illegible]	1 60 min. 2 25 " 3 10 " 4 4 "	" " " " " " " "	16.0	7.5	12

OF THE LIMIT OF THE KNOWN HYDROGEN SPECTRUM.

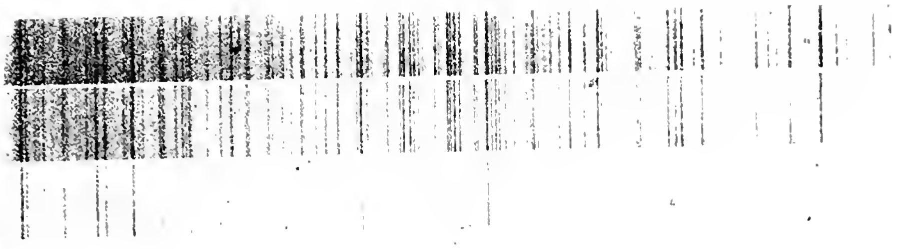
I have been able to follow the hydrogen spectrum for about 6 beyond the last of the spectral series of Plates I-III; but hitherto not with sufficient clearness for reproduction. The most perfect of my photographs of this region (No. 4222) is not clearly enough defined to bear a twenty-fold enlargement. Accordingly, they may here receive a merely verbal treatment. At first, with all my pains, I was able only to secure traces of some blurred lines. It was not until I interchanged the

1

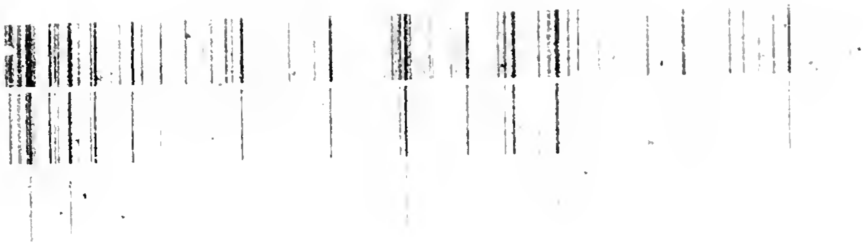
2



3

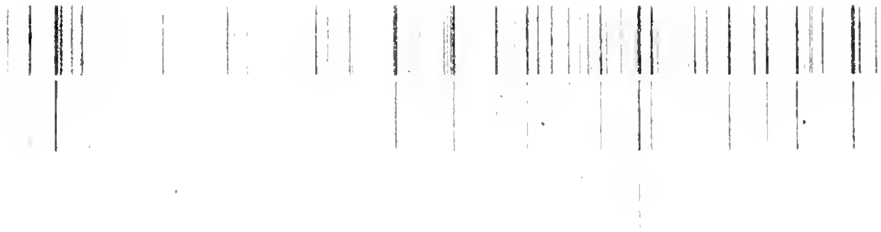


4

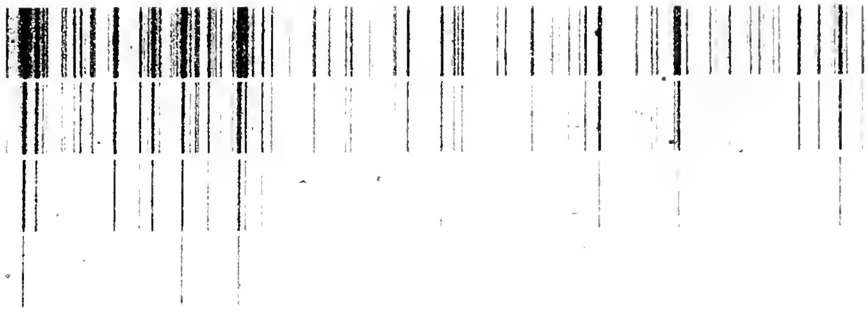


HYDROGEN SPECTRA 1-4.

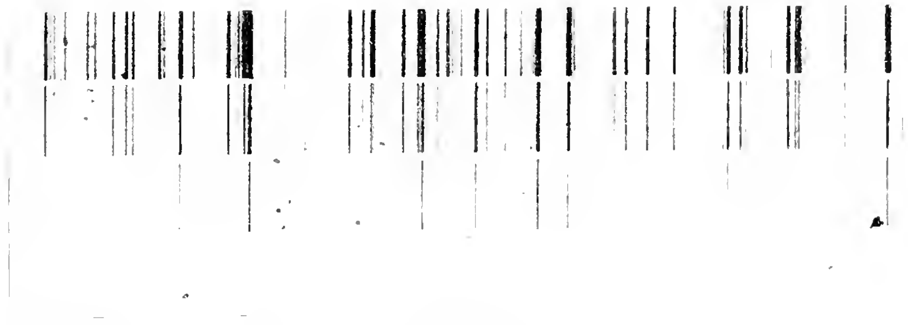
5



6

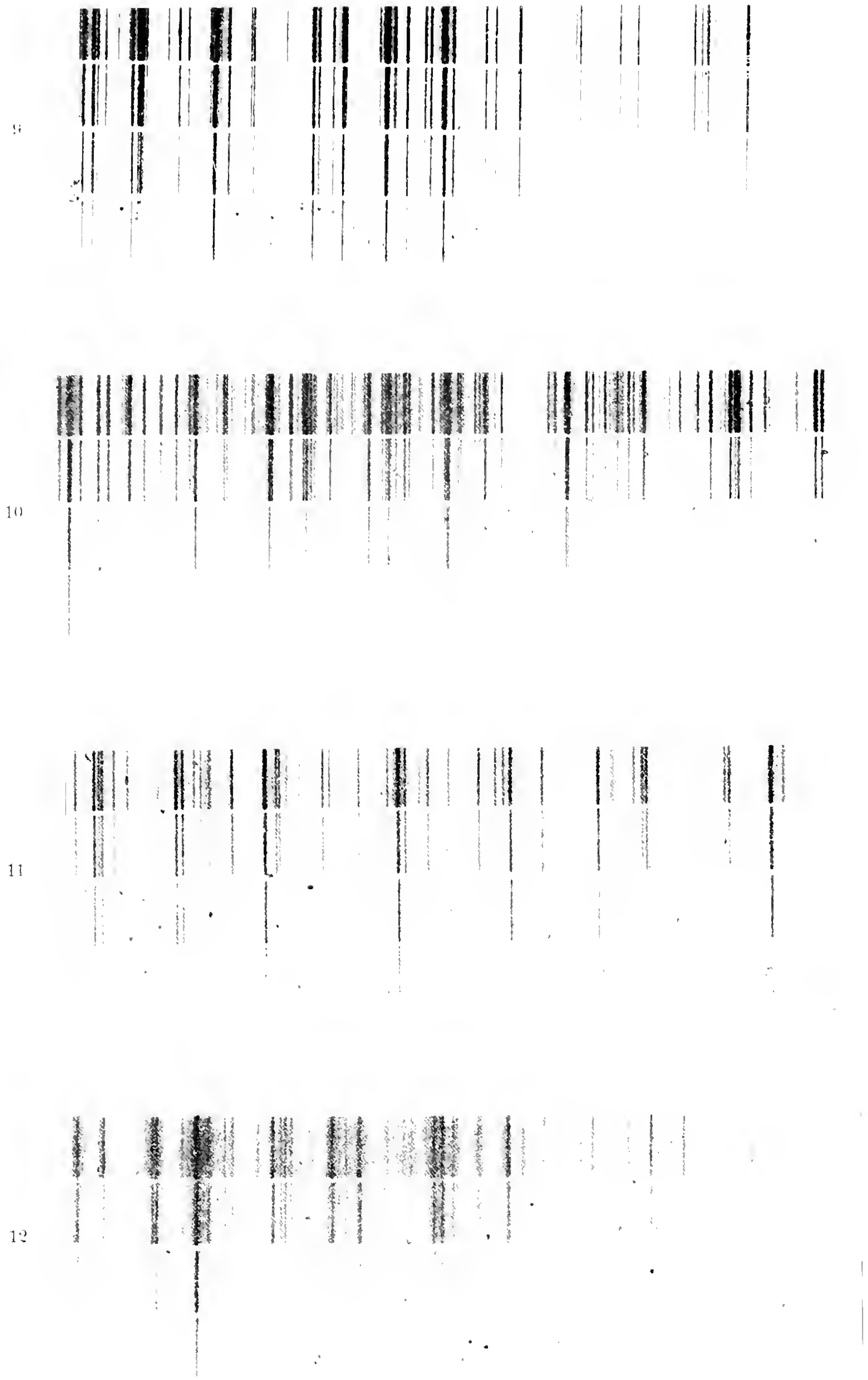


7



8

HYDROGEN SPECTRA 5-8.



HYDROGEN SPECTRA 9–12.

electrodes, taking for the cathode (which with all the other photographs had been at the distant end of the tube) the electrode nearest the slit, that I got any better results. It appears, therefore (and this is confirmed by all repetitions) that the cathode-light of hydrogen, under existing circumstances, contains more refrangible and active rays than the anode-light.

Why do my hydrogen photographs end at this place? For all essays to photograph more refrangible rays with a 60° prism came to naught. I can find the reason for it neither in the want of energy of the rays nor in the insufficient sensitiveness of the ultra-violet plate. Nor can I attribute it to metallic reflection, since this concerns decidedly shorter waves than these with which we have here to do. I suspect rather that this limitation of the effect of my spectroscope is due to the approach to grazing incidence of the rays upon the prism. For I met with a similar reduction of energy with my former 70° prism; yet afterwards when I came to repeat the photographs with a 60° prism I found the spectrum considerably strengthened. It is therefore to be expected that a still further diminution of the refracting angle will lead to the photographing of still shorter rays of hydrogen.

OF THE WAVE-LENGTHS BEYOND 185 μμ.

Information as to the wave-lengths of the new region would be of particular interest. The difficulties of measuring them are, however, so great that neither I nor others have succeeded in overcoming them. The wave-length 162 μμ to which I arrived in 1892[1] was but the result of a first essay; and the apparatus I then had was so far from perfect that this determination is hardly sufficient. Last year, Mr. F. F. Martens[2] took up the question, and resting upon the Ketteler-Helmholtz dispersion-formula deduced from the angle of 21°, which is the difference in deviation between the middle of my most refrangible field and the last aluminum-line at 185.4 μμ, calculated the wave-length of that place in my last photograph to be 125 μμ, but this should probably be 2 μμ higher. It is inaccurate to say, as Mr. Martens does, that this is the wave-length of the most refrangible ray photographed by me; since the deviation of 21° refers to the middle of spectral field in question, and the most refrangible line is deviated about 6° more; which should have been taken into account in the computation. My most refracted line has therefore a wave-length decidedly less than 127 μμ. It must, however, be confessed that my estimate of 1893[3] of 100 μμ was too hasty; since it appears that even now I have not got down quite to that point.

OF THE VACUUM APPARATUS FOR THE MEASUREMENT OF WAVE-LENGTHS.

If, in Nos. 1 and 9, Plates I–III, of the spectrograph, the prism be replaced by a plane reflecting grating and the collimator and camera by two air-tight tubes arranged

---

[1] *Sitzungsberichte d. kaiserl. Akademie d. Wissensch. in Wien; math.-naturw. Classe*, vol. cii, Part IIa, pp. 625–694, 1893.

[2] *Annalen der Physik*, 1901, Heft II, p. 619.

[3] *Sitzungsber. d. kaiserl. Akad. d. Wissensch. in Wien; math.-naturw. Classe*, vol. cii, Part IIa, p. 677, 1893.

for the measurement of wave-lengths, the wave-lengths can be determined by grating and lens, according to the method devised by Cornu and applied by Liveing and Dewar. It is a method of coincidences resting upon the fact that the wave-lengths of two lines which coincide in the axis of the lens are inversely proportional to the numerical orders of the spectra. This method has the advantage of not requiring any ray-filter, such as is required with a concave grating for the separation of mixed spectra. For in my case, the lens not being achromatic, the spectra do not at all coincide, being separated by the considerable difference of their foci. This is an important advantage; for we are acquainted with no suitable filter for these short-wave rays, and a search for such a filter could hardly fail to be a very laborious task indeed. Unfortunately, there is a serious drawback to the advantages of this grating-and-lens method in the circumstance that the one of the two spectra which is sharply focussed is so frequently overlaid with the out-of-focus spectra as to be doubtful. This, of course, will prevent the lines which so suffer from being employed for measurement. The operation, moreover, takes up a great deal of time. Every determination of a wave-length requires a series of photographs which because of numerous particular observations occupies from 5 to 8 hours.

The following remarks relate to the suitable arrangement of the two tubes for measuring wave-lengths *in vacuo*. The slit-jaws are micrometrically movable independently of one another, so that the slit may be symmetrically widened and narrowed. It thus becomes possible, in case the lines to be compared demand very different exposures, to shorten the exposure of the weaker line by symmetrically widening the slit. A rotating shutter is provided for half closing the slit at times. The camera-tube carries the camera with a plate-holder for plates of 12 mm. square. The plate-holder during the photographing is carried by a slide which is vertically movable both micrometrically and by the free hand, and which is also capable of being turned over in the plane of the plate very accurately through 180°, about the optical axis of the camera lens as its axis of rotation. This is requisite in order to ascertain the point at which that optical axis cuts the plane of the plate. Special care has been taken to secure accurate centering of the lenses and their draw-tubes, on which the accuracy of the measures essentially depends.

Whenever the intensity of light is sufficient, the concave grating should be preferred in the determination of wave-lengths. It is important that with it there is but a single surface at which the intensity of the rays is reduced. For the fewer times the light is weakened, the stronger it will be when it reaches the photographic plate, other things being equal. Now the more energetically the extreme ultra-violet light acts upon the photographic plate, the easier it will be to obtain photographs of this light. Nor ought it to be forgotten that these short-wave rays suffer much more by reflection than do long-wave rays. My recommendation of the concave grating stipulates two provisos, viz.: 1st, that the material of the grating should sufficiently reflect these short-wave rays; and 2d, that the grating-spectrum should be sufficiently bright in this part. My photographs with plane grating and lens prove that speculum-metal does in fact sufficiently reflect the short waves. But the second condition relates to an individual character of the grating selected for use. It must be tested by special photographs made for this purpose. For such test a vacuum-spectrograph of suitable dimensions is required. There is no shorter way to the ascertainment of the serviceableness of a diffraction grating for use in the ultra-violet.

The body of the spectrograph should be so constructed as to afford the broadest guarantee for its air-tightness. Moreover, there should be no flexure upon exhaustion. Should there be flexure, however, it is still possible to obtain useful photographs under unaltered pressure, since to this would correspond a constant bending. But should leakage or any other cause alter the pressure fallacious results would be obtained, in consequence of the shifting of lines due to the bending of the apparatus. The exterior best adapted to such a spectrograph would be that of a tube having its walls not too thin and composed of drawn or rolled material. For a tube presents equal resistance to outward pressure, and therefore, supposing its walls to be equally strong, and to be subjected to equal pressure in all directions, will show the smallest bending. A tube drawn of brass or a Mannesmann tube of steel is preferable to a cast tube on account of its greater homogeneity. The open ends must be closed with permanent covers. At one end the concave grating should be set up so as to be capable of rotation about its mid-ruling as an axis, while at the other end should be the slit-carriage, movable in the direction of the rays. To one side of the slit there should be a horizontal slot in the cover of the tube, giving exit to the rays coming back from the grating. Before this slot there should move vertically an air-tight slide containing the plate-holder, so that a series of photographs could be taken one under the other without altering the pressure within. The focussing of the different photographic fields would have to be effected by displacement of the slit-carriage, which to this end must be provided with a sufficiently long air-tight draw-tube.

The most important part of the whole apparatus is the slide carrying the plate-holder. Upon the sufficiency and permanence of its air-tightness depends the minimum pressure obtainable by exhaustion of the apparatus and thus the success and the cost in time of the photographs. But the displacement of the plate and the prevention of the entrance of air when it is taken out are not the only purposes subserved by the plate-holder slide. It has also to make it possible to exhaust the air that comes in with the plate before the latter is exposed to the light. For it is clear that this small quantum of air can be removed much more quickly from the narrow space of the interior of the slide than from an apparatus of many liters' volume. The plate should not be brought before the air-slot until in this way the slide and the plate-holder have been exhausted. Thus when the apparatus has once been exhausted, supposing its other parts to hold, it will only have to be thoroughly pumped out now and then. I must not, however, be understood to assert that in this way the vacuum will hold in the spectrograph for weeks or even for days, as a good mercurial pump, for example, will. Such a degree of tightness is not often met with among vacuum-spectrographs. At best, it will be necessary to pump a little after every change of plate in order to remove gas that has been set free; as, for example, absorbed air. Even when the closing surfaces have been treated with the most scrupulous care and the material is faultlessly tight, small amounts of absorbed gas little by little get set free. In the same way, some air diffuses in through the grease film as soon as it has been for some time in use; and the inflow becomes continually greater the longer the apparatus is left to itself without being pumped out.

All this shows how little any apparatus without such a slide or other equivalent contrivance can be recommended for the investigation of the ultra-violet.

The arrangement of the slide is founded on the supposition that only uncurved plates of moderate length are to be used. It would be desirable, however, for a better general view of the whole region to be photographed as well as for the sake of saving some of the time lost during exposures, to be able to photograph at a single exposure a greater extent of the spectrum, if possible, the entire sensitive region of the plate. In this way, we might perhaps photograph at once the whole spectrum from the cyan blue to wave-length 100 $\mu\mu$ or indeed still farther. The great curvature of the photographic plate which would be requisite could be obtained with ordinary plates, as is well enough known, by means of a film or of mica. Not so with ultra-violet plates, since the preparation of their coating is greatly affected by any unevenness of the surface to be coated, from which films are far from free and even sheets of mica are not sufficiently so; for the coating is deposited thicker in depressions and thinner on elevations of the surface, giving rise to differences of sensitiveness as well as to other defects.[1] Even if one is willing to overlook these inconveniences and to content himself with graphically less perfect spectrograms, or if the process of preparation of ultra-violet plates could be improved in this respect, the inconvenience of the varying activity of the spectrum in different spectral regions will still subsist. Judging by my prismatic photographs this variation is greatest in the ultra-violet, that is, precisely in the part which requires to be photographed *in vacuo*. The consequence would be that the most active regions would be greatly over-exposed before the weaker parts became developable at all, and as a result partial photographs would again have to be reverted to. I cannot therefore advise the employment of long plates, particularly since, for constructive reasons, the advantages of the slide would thus disappear, and at every change of plates the spectrograph would fill with air and would have to be pumped out. In like manner the employment of gratings of long radius is not unhesitatingly to be adopted where the ultra-violet is to be observed to its most refrangible rays. For there is here the unavoidable difficulty of absorption, however far the exhaustion be carried, owing to the small residue of air as well as the vapors from the air-pump; the absorption, of course, being much greater with the long distance which the rays have to traverse owing to the long radius of the grating. This obstacle of absorption is the reason why the shortest wave-lengths are incomparably more easily investigated with short foci than with larger apparatus.

Air. I must pass over my observations of the emission-spectrum of air, on

---

[1] V. Schumann. On an improved method for the preparation of ultra-violet plates. *Annalen der Physik*, vol. [illegible], pp. 349–374, 1901.

account of the bands of carbon monoxide which thus far have made up the whole. Nor is there ground for confident hope that better success will be met with in the sequel. For with low pressure, where success was most confidently to be anticipated, these bands appear irrepressibly in their full force; and with higher pressure the absorption, as I shall presently show, is so marked that the attempt to get an extended air-spectrum in this way promises little. The increased absorption which follows higher pressure might, indeed, be avoided by reducing the thickness of the stratum; but in that case the window of the tube would be so near the capillary orifice that in a very short time the deposit upon it would produce complete opacity.

Information regarding the transparency of air is easier to obtain. All the old investigations upon this subject were limited to strata of considerable thickness, but I have extended my observations to very thin layers. This was suggested by the fact, long ago repeatedly ascertained by me, that the rays beyond 185 $\mu\mu$ were remarkably weakened even by strata less than 1 cm. thick. Since then, notable data concerning the behavior of thin layers of air have come to light, and since I have occupied myself more with this matter than with others, it is proper that I should here confine myself to this.

The above described absorption-apparatus, Fig. 10, was used for the production of the thin strata of air. From the negatives which I obtained with it, I take two and give photographic reproductions of them magnified fourfold.

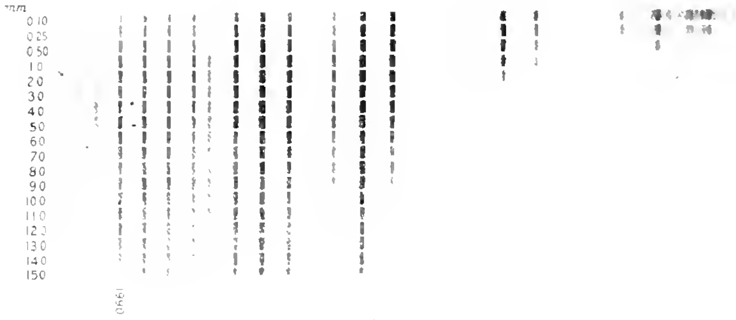
In one plate (No. 5941), *A*, Plate IV, the thickness of the stratum of air was 15 mm., 14 mm., . . . 3 mm., 2 mm., 1 mm., 0.5 mm., 0.25 mm., 0.10 mm.; while the time of exposure was in every case 1 minute, and the width of the slit 0.020 mm. The Geissler tube was filled with dry air at a pressure of $\frac{1}{4}$ mm., and before photographing, electric discharges were passed through it for some time. Without this precaution the source of light would be wanting in the requisite constancy. The first eight spectra, with thicknesses of 15 mm. to 8 mm., end, without any material gain in length, at the wave-length 178 $\mu\mu$. The exposures following extend beyond that wave-length; yet the stratum of thickness 4 mm. first allows the band at 170 $\mu\mu$ to appear. From that point the gain in length of spectrum with diminution of thickness of the stratum is more rapid; and with a stratum of 0.5 mm. the spectrum runs to the end of the plate, corresponding to wave-length 163 $\mu\mu$. The last two strata of the series of thicknesses 0.25 mm. and 0.10 mm. give spectra of considerably increasing intensity, and the inference that the photographed spectra would be longer is confirmed by *C*, Plate IV. These two spectra show more than any of the foregoing how energetically the air absorbs these rays. For better orientation, I add to *A*, Plate IV, a small series of spectra (No. 6066), *B*, of which the uppermost band-spectrum is similar to the uppermost of *A*, while beneath the banded spectra appear the most refrangible lines of the spectrum of aluminum, at 1989.90, 1935.29, 1862.20, and 1854.09 Angström units.

Plainly, a longer exposure would extend the photographic spectra to shorter wave-lengths; and this is confirmed by another plate (No. 5935), *C*, where the exposure was for two minutes, the width of slit 0.020 mm. as before, and the thicknesses of strata of air, 0.05 mm., 0.1 mm., 0.2 mm., 0.4 mm., 0.6 mm., 0.8 mm., 1.0 mm. Unfortunately, the wave-lengths beyond 160 *μμ* being unknown, I am not in condition to state exactly the limits of these spectra. But it will suffice to compare their lengths to show how enormously thin strata of air absorb rays more refrangible than those of wave-length 160 *μμ*. This fact is most evident in the comparison of the effects of strata of thicknesses of 0.1 mm. and 0.2 mm.; for this difference corresponds to a considerable difference in the extension of the spectra. Even the reduction of the thickness from 0.1 mm. to 0.05 mm. results in a very perceptible increase of the energy. It is true that this is not very well shown by C', because the most refrangible lines, for which the increase of energy is most marked, have not sufficient intensity to bear the fourfold magnification, so that they disappear entirely from C'. I believe, however, that I shall not exaggerate if I say that the increase of the thickness of the stratum from 0.05 mm. to 0.1 mm. involves a loss of 50% of the energy.

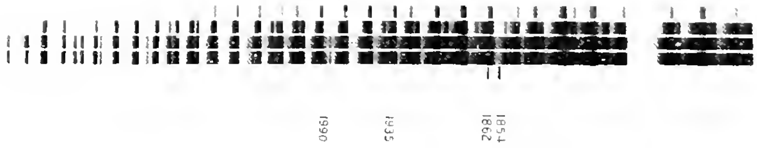
The spectrum of the Geissler tube filled with air, owing to the discontinuity of its spectrum, never shows the absorption-bands near 185 *μμ* due to the oxygen, which appear so clearly when the tube is filled with hydrogen.

Considering the value which an acquaintance with continuous spectra has for absorption-spectroscopy, and in view of the difficulty of searching out suitable sources of light, let me refer to a discharge-tube with which I made many emission-experiments in 1886. It was an end-on tube with an uncommonly narrow capillary — about $\frac{1}{3}$ or $\frac{1}{5}$ mm. wide. If such a tube is exhausted until no discharge will pass through it, or even until it fluoresces strongly, then as soon as a Leyden jar and a spark-gap are inserted in the secondary circuit of a powerful Ruhmkorff coil, it gives an uncommonly bright light of a white color. If the spectrum of this longitudinally emergent light is photographed with correct arrangements, one obtains, instead of a line-spectrum, a continuous spectrum in which, at most, a few traces of washed-out lines are remarked. Sometimes the continuous spectrum enters only as a stripe, several millimeters broad, running the length of the line-spectrum. In both cases this continuous spectrum is well adapted to absorption-experiments in which occur lines and especially groups of lines like those of oxygen. The photographic action of this capillary light is very powerful. Unhappily these tubes are of shorter life than those of the usual caliber. The spark widens the narrow opening by degrees, and with the widening the photographic energy diminishes, and worst of all, it then ceases to be so easy to convert the line-spectrum into a continuous spectrum.

LEIPZIG, January 19, 1901.



A



B

C.

AIR ABSORPTION SPECTRA.